Mine Water
Solutions 2022
June 14-16, 2022 • Vancouver

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of the Fourth
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The Organizing Committee also wishes to thank all of our exhibitors, sponsors, institutional partners and media partners.

Finally, we would like to thank all the delegates who attended the conference to exchange their valuable knowledge and expertise, thus contributing to the great success of the Mine Water Solutions Conference. We look forward to seeing you all again at the next conference in this international series.

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Keynote:
Water in Mine Closure – Let's Reimagine our Legacy

Kate Sommerville, BHP, USA

Abstract

If the mine you are operating was going to be stuck with your company forever – would you do something different with water?

BHP Legacy Assets holds 24 sites in 10 operations. They curate 115 water-and-waste-retaining structures and pits and operate 12 water treatment plants. Our sites meet regulations and are protective of the environment. Re-imagining the legacy of mining will draw on over 25 years of post-closure knowledge to update water strategies and evaluate investment alternatives that improve water-related performance and sustainability in alignment with community self-vision.

The Legacy Assets sites span from coast to coast and from the frozen north to the Sonoran desert. There is a site representing almost every climatic setting, geology, hydrogeology, and geochemical context found in the BHP portfolio. Whether in the arid, water-scarce western US or wet Canadian north, water is the golden thread that connects our tailings, closure, and social value activities and risks. As non-producing sites, our annual operating costs are reflective of the water management, water treatment, as well as maintenance and surveillance of our infrastructure (including tailings dams) required to ensure that our sites remain safe, stable, and non-polluting.

Water risks comprise a quarter of our closure risks. They relate to groundwater, surface water, regulatory, and stakeholder risks with water elements. We have had success in water management and treatment, but also some challenges. We continue to seek more efficient and effective means of meeting our water risk mitigation goals. This includes implementation of short-term risk mitigation (refractory radium treatment modifications, evaporative capacity improvements) to enable evaluation of long-term alternatives (e.g., elimination of evaporation as a remedy to make more water available to the environment, or limiting lime consumption to reduce our carbon footprint). We realize that how we optimized in the past is not necessarily the best when we apply a modern set of optics.

If we can manage the tension between short term demands and long-term outcomes that are realistic, and beneficial to the environment and community, we can promote our industry's licence to operate and personally be prouder of our legacy.

Chapter 1:

Mine Water Management

Hydrometric Monitoring and Effluent Discharge Mixing in Challenging Natural Conditions

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Abstract

River systems prone to backwatering present difficult conditions for collecting reliable hydrometric monitoring data. Furthermore, passive discharge of treated effluent in low-velocity receiving environments may not achieve full mixing without additional measures to promote dilution. Knight Piésold Ltd (KP) designed a hydrometric monitoring network and a treated effluent discharge system for the Rainy River Mine (RRM) in Northwestern Ontario that had both these conditions.

The Pinewood River provides a challenging environment for hydrometric monitoring due to backwatering effects from downstream obstructions, which precluded developing stable stage-discharge relationships to facilitate continuous discharge measurements. Consequently, an alternative to the traditional flow-measurement approach was required. To overcome the difficulties associated with stage-discharge relationships, an acoustic Doppler-type instrument was selected that measures the velocity profile and the water depth continuously. These data are used in combination with a user-specified cross-section to record continuous real-time discharge data.

The treated effluent to be discharged into the local receiving environment must meet strict mixing and water quality standards, as dictated by RRM's Environmental Compliance Approval (ECA). The permitted conditions include constraints on the ratio of instream flow to effluent discharge, in addition to achieving full transverse mixing within a short distance from the discharge point. An analytical mixing model was developed to evaluate the performance of various diffuser options under a wide range of effluent and ambient discharge condition. This data was then used to guide the final diffuser selection and design. The selected design includes a diffuser system with two planar jets using duckbill-type neoprene rubber check valves. This design also provides back-flow and fish-entrance prevention, as the rubber check valves close when the outflow is discontinued. To prevent channel erosion from the discharge jets and prevent utilization

by fish for habitat in the vicinity of the diffusers, grouted gabion boxes, grouted riprap, and interlocked concrete blocks were used to create a protected and stable cross-section.

Introduction

RRM is a gold and silver mine owned by New Gold Inc. that started operations in September of 2017. It is located in the Township of Chapple, approximately 65 kilometers (km) northwest of Fort Frances, Ontario. The mine received Permits to Take Water (PTW) from and discharge treated effluent water to the Pinewood River, both of which are conditional on the actual flows in the river at the time of withdrawal or discharge. To regulate this process, high quality real-time discharge measurements in the Pinewood River are necessary and are required by the mine's ECA and PTW that were issued by the Ministry of the Environment, Conservation and Parks (MECP).

RRM has collected hydrometric data in the Pinewood River since 2015 using a bubbler system and a pressure transducer backup system, both of which rely on an established stage-discharge relationship, or rating curve, to calculate the discharge. There have been ongoing issues with the collection of reliable discharge data along the Pinewood River. During the first few years of operation, the hydraulic control section was impacted several times. This is primarily due to the very low gradient of 0.07% of the Pinewood River, which results in backwatering effects propagating for long distances upstream of obstructions. Ongoing beaver and land use activities, as well as potential ice jams and log jams downstream of the hydrometric monitoring station, have caused backwatering effects that impacted the stage-discharge relationship. To avoid the reliance on stage-discharge relationships for discharge measurements, the hydrometric monitoring network was upgraded to utilize real-time discharge measurements using acoustic Doppler-type instruments, and also expanded to include several monitoring locations. The selected SonTek-IQs are not impacted by backwatering conditions and provide better quality and more reliable discharge data for the mine.

An effluent discharge system consisting of two effluent mixing structures (EMS1 and EMS2) at two different locations was designed and constructed to discharge treated surplus water from the mine to the Pinewood River. Real-time data from the hydrometric monitoring network is used to inform the effluent discharge strategy on a daily basis. The design of EMS1 and EMS2 was informed by the results from an analytical effluent mixing model. After commissioning of the systems, a field-based mixing study was completed to confirm the mixing performance of the systems.

Hydrometric monitoring network

Original hydrometric monitoring network

RRM is committed to collecting continuous hydrometric data in the Pinewood River, and as part of that program, the first hydrometric monitoring station, H1, was commissioned on October 9, 2015. This station is located approximately 800 meters (m) downstream of one of the two effluent mixing structures (EMS1). In addition, Water Survey Canada (WSC) operates their own hydrometric station (05PC023), located approximately 3.8 km downstream of H1. The discharge recorded at this station and at H1 is similar, as there are no tributaries between the two stations. The Pinewood River at this location has a mean annual discharge of approximately 1.6 cubic meters per second (m^3/s), which translates to a relatively low average annual runoff depth of approximately 231 millimeters (mm), based on data from station 05PC023 for the period of record from 2008 to 2015. The mean annual precipitation in this area is 710 mm.

The bubbler and the pressure transducer instruments installed at H1 rely on a rating curve to calculate the discharge, which is subject to changes due to obstructions and resulting backwatering effects in the river. A rating curve is developed by relating the discharge measurements (Q) to water levels or stage (H), where both are measured manually for various flow conditions. Stage-discharge relationships are usually subject to minor fluctuations and typically show some scatter, some of which may be due to the inherent limitations of the measuring equipment and measuring methods. The rating curve for a hydrometric station may change over time if the hydraulic control or the channel characteristics change. Any larger deviations or shifts from the rating curve may indicate a change in the stage-discharge relationship, which could occur due to several reasons, including a change in the cross-section at the onset of overbank flow, channel erosion, sediment deposition or bed shifting, and backwatering due to beaver activity or ice/log jam formation downstream. A change in the rating curve relationship that persists for an extended period indicates that a new rating curve should be developed.

Hydrometric monitoring network upgrade and expansion

In order to improve the ability to discharge the effluent to the Pinewood River within the permitted requirements, three additional hydrometric monitoring stations were established. The monitoring network consists of one station upstream (H2) and one station downstream (H1) of the RRM on the Pinewood River, and two stations in a diversion channel (H3 and H4) within the mine site. All four stations use the same monitoring setup to avoid the challenges experienced at H1, and as such this paper primarily focuses on the H1 discharge monitoring station.

The upgrade of the H1 monitoring station and expansion of the hydrometric monitoring network required several factors to be considered, as discussed below.

Design criteria

The Pinewood River is subject to a wide range of flows, from near zero during the winter and dry summer periods to well over 20 m^3/s during the spring freshet periods and during convective storms in the summer and early fall. The Pinewood River flow data were used in combination with the applicable permit criteria as the basis for establishing the design criteria for the hydrometric network:

- Establish several stations on the Pinewood River and on the mine site to assist with effluent discharge and water-taking operations.
- Provide accurate measurement of flows over the range for which effluent discharge may occur (i.e., 0.1 to 0.6 m^3/s, with maximum measurements up to 2 m^3/s), as specified by permitting requirements. However, it was also desired for the hydrometric stations to provide reasonably accurate measurement for a full range of river flows.
- Designs to limit backwatering and upstream flooding and to be able to withstand high flows without damage.
- Maintain habitat connectivity for species that are resident in or use the Pinewood River for one or more of their life stages (e.g., running, spawning, rearing).

Monitoring network upgrade alternatives

Several alternative discharge collection techniques were reviewed for upgrading the RRM hydrometric network, including using rated discharge structures that provide a hydraulic control, or using continuous discharge data collection instruments. The evaluated alternatives included a natural channel with a rating curve (i.e., the original method that was already in use), rated discharge structures (e.g., flumes or weirs), as well as different acoustic Doppler flow measuring devices. Each alternative was assessed using the design criteria for flow range, fish passage potential, flooding potential, and backwatering susceptibility.

Based on the alternatives review, the options that prevent fish passage, those that increase the risk of upstream flooding, and those that can be impacted by downstream backwatering were considered inappropriate for further consideration. It was concluded that acoustic Doppler instruments, specifically SonTek-IQs (SonTek, 2015a), would constitute the most effective and reliable option for continuous collection of high-quality discharge data.

Selected design and installation

The primary advantage of SonTek-IQ instruments is that they continuously measure the velocity profile and the water depth, which is then used in combination with a user-supplied cross-section data to record continuous discharge in real-time. The discharge measurements are not affected by backwatering conditions (SonTek, 2015b) that may occur due to downstream obstructions in the river. Some of the other advantages of these instruments include the following:

- Accurately measure the flow range of 0.1 m^3/s to 2.0 m^3/s that is required for mine effluent discharge monitoring, but can also measure much higher flows of up to 50 m^3/s.
- Provide continuous discharge record without the need for a rating curve.

- Allow discharge measurements to be collected to an accuracy of ±5 – 10%.
- Cause little environmental disturbance due to their small size with no incremental upstream flooding.
- Allow for uninterrupted fish passage, sediment passage, and the passage of floating debris.
- Have the potential for remote monitoring and can be tied to the existing data logger that has cellular telemetry allowing flow data to be accessed real-time.
- Can operate within a temperature range of –5 to 60°C.
- Have a fixed factory calibration and do not require periodic recalibration.

SonTek instruments have been used and tested by Water Survey of Canada, United States Bureau of Reclamation (USBR, 2016), and the United States Geological Survey (USGS, 2007; USGS, 2015), and have been found to be effective in river conditions similar to the Pinewood River (SonTek, 2012). These systems have also been tested in cold weather conditions in Colorado (USGS, 2007), comparable to those found in Northwestern Ontario, and they were found to perform well.

To increase the measurement accuracy and reduce the requirement for cross-section surveys following larger flow events that may cause changes to channel geometry, a decision was made to install the SonTek-IQ instrument at station H1 in a concrete-lined channel. This would create a stable river cross-section that promotes good flow and velocity profiles across the channel, facilitates discharge measurement accuracy, and provides a stable foundation for the instrument to remain firmly anchored in the channel.

The proposed channel design utilized a concrete canvas, a material comprising a proprietary fiber reinforced concrete mix placed between two membranes that hardens once hydrated (Concrete Canvas, 2018). Prior to the canvas installation, the riverbanks were shaped to a slope of no greater than 1.5H:1V. The SonTek-IQ was mounted on a levelled concrete block embedded in the channel bottom at the centre of the concrete section.

The installation for the other hydrometric stations differed from H1 in that the SonTek-IQs were anchored to the bases of existing culverts on flat concrete platforms. The cross-sections of the culverts were surveyed for input into the internal instrument programming.

Effluent discharge system

KP designed an effluent discharge system consisting of two mixing structures (EMS1 and EMS2) to effectively discharge treated surplus water from the mine to the Pinewood River. Requirements for the design included compliance with the ECA, as follows:

- No discharge is allowed during the winter months from December 1 of each year to the start of the spring melt of the following year, i.e., discharge is allowed only during ice-free periods.

- A minimum Pinewood River flow of 10,000 m^3/day must be sustained in any given day during the permitted release period for effluent discharge to be allowed.
- The effluent discharge to the environment must be submerged and must not exceed a 1:1 ratio with Pinewood River flows.
- Pinewood River water downstream of the effluent discharge locations must meet water quality benchmarks at the surface water sampling locations.
- Effective and rapid mixing of the effluent within the receiving environment must be facilitated, if necessary, by installing effluent mixing structures to improve the overall mixing efficiency.

In addition to the ECA conditions, the discharge effluent is required to mix rapidly with the receiving environment in a manner that does not pose a barrier or physical threat to fish. The effluent mixing structure should minimize formation of visual or auditory barriers that result in a behavioural response in fish that could potentially impede migration or movement patterns.

Design options

Based on the environmental constraints described above, KP completed a preliminary feasibility assessment of effluent mixing options, which is summarized below:

- Natural mixing, where the natural river currents in the Pinewood River disperse the mine effluent.
- Construction of alternating rockfill groyne structures that extend from the opposing river banks partway across the channel and enhance cross-currents and turbulence.
- Aeration with injection of air bubbles along the channel bed that rise to the water surface and generate cross-currents that enhance mixing.
- Installation of a diffuser system on the outlet of the discharge pipe resulting in high velocities and effective dispersion and mixing through entrainment of ambient water.

The use of rockfill groynes as a means of enhancing mixing was rejected as it was determined that these structures could cause backwatering and increase the potential for upstream overbank flooding. Aerator devices would enable substantial mixing of the effluent without causing backwatering effects, but would require ongoing power and maintenance work, with the additional disadvantage that they may have to be removed during winter months, or might pose visual barriers to fish. Natural mixing would be the least intrusive and cost-effective option, but might not achieve adequate mixing under all flow conditions before reaching the compliance points. It was determined that using a diffuser system would result in the highest likelihood of achieving full mixing of the RRM effluent and Pinewood River flows, while meeting all aquatic life water quality criteria and having minimal operational requirements.

Design criteria

Effluent discharge volume and timing requirements from the ECA, in combination with Pinewood River flow data, fish habitat requirements, structure constructability and operational requirements, as well as mixing efficiency, were used as the design basis for assessing the suitability of the various mixing/diffuser options considered in this study. A summary of the design criteria is provided below:

- ***Full transverse mixing*** – governed by the ECA requirement of achieving full transverse mixing by the time the effluent reaches the compliance point approximately 100 m downstream of the discharge point. Full transverse mixing is considered achieved once the concentration everywhere across the channel cross-section is within 5% of its mean concentration (Fischer et al., 1979).
- ***Effluent discharge rate*** – the minimum and maximum effluent discharge rates vary between 5,000 m^3/day and 20,000 m^3/day. A minimum of 1:1 ambient-to-effluent discharge ratio must be achieved. Scenarios investigating mixing of effluent discharges at higher ambient flows in the Pinewood River (e.g., during freshet or large storm events), were also assessed to ensure full transverse mixing is achieved within the required distance.
- ***Effluent water quality*** – the discharged effluent consists of surplus water collected around the mine site that is treated to meet the end-of-pipe water quality criteria set under the ECA.
- ***Effluent temperatures and densities*** – the collected surplus water around the mine site has a similar temperature to the water in the Pinewood River due to having the same atmospheric conditions. The concentration of constituents is sufficiently low (end-of-pipe water quality requirement) and the density of the effluent is equal to the ambient water density. Consequently, buoyancy forces due to small temperature or density differences between the effluent and the receiving environment are negligible considering the large initial momentum forces of the discharged effluent jets.
- ***Effluent pressure*** – hydraulic losses through the effluent delivery pipeline and diffuser system are modelled using the Darcy-Weisbach equation. Modelling results are used to confirm sufficient pressure head conditions at the diffuser inlet to ensure adequate functioning of the system based on ambient water levels and flow characteristics for a range of operating conditions.
- ***Erosion control*** – to prevent erosion along the channel bed and banks due to jet impacts, a combination of grouted gabion boxes, grouted riprap, and interlocked concrete Armortec open cell blocks (Contech, 2020) is used to create a protected cross-section with adequate transition back to the natural riverbed.

Diffuser types

The diffuser design was an iterative process that considered both single and multi-port diffuser systems, with a combination of either round jets or planar jets, where planar jets are typically discharged through a rubber check valve, or a so-called duckbill diffuser. The diffuser design was undertaken in combination with effluent mixing modelling to confirm that the proposed diffuser system would achieve the effluent mixing conditions required by the time the downstream compliance point is reached.

Based on the geometry of the receiving environment, it was determined that duckbill check valves would provide better mixing performance, with the additional advantage of providing backflow and fish-entrance prevention, as the rubber check valves close when outflow is discontinued. In addition, the variable orifice size optimizes jet velocity, improving the mixing process during start-up and shut-down periods, or at lower discharge rates.

Combinations of single or double-port diffuser systems with different types of check valves were analyzed in this study. It was determined through two-dimensional hydrodynamic modelling (HEC-RAS 2D) of the receiving environment that a single-port diffuser system would not remain fully submerged under low-flow conditions due to the larger check valve size requirement, thus not satisfying the design requirement for submerged discharge. This prompted the use of a double-port diffuser system using two 8-inch nominal diameter sleeve-type check valves, which would remain submerged under all effluent discharge conditions, as shown in Figure 1.

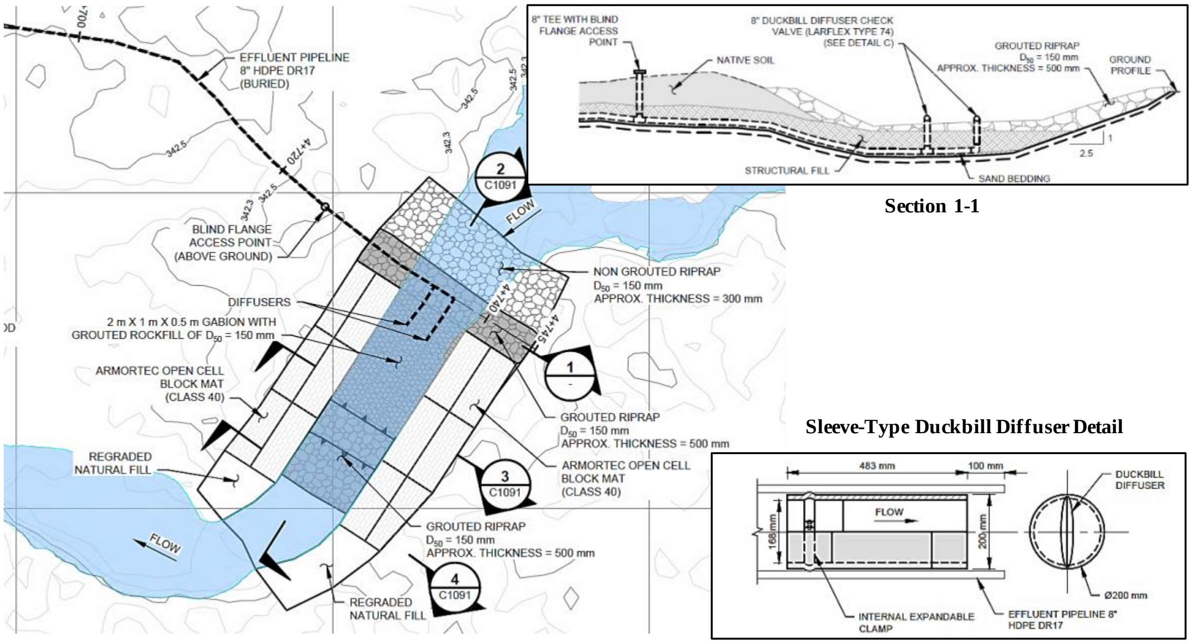


Figure 1: Effluent discharge system design with a double-port sleeve-type duckbill diffuser

Analytical mixing model results

The diffuser design was undertaken in combination with mixing modelling analysis to confirm that full transverse mixing of the discharged effluent is achieved within 100 m from the point of discharge.

Considering that the effluent discharge would be driven by the initial momentum of the fluid exiting the diffuser, the discharge can be characterized as a turbulent jet. As such, the mixing modelling procedure followed the turbulent jet calculations outlined in Fischer et al. (1979).

Analytical mixing modelling results are presented in Figure 2 in terms of effluent concentrations and velocities along the cross-section of the channel at various distances along the point of discharge for the maximum (20,000 m^3/day) effluent discharge rate scenario. Mixing modelling results indicate that the double-port diffuser design system will achieve fully mixed conditions by the time it reaches the compliance point located at 100 m downstream from the point of discharge. In addition, effluent velocities at the jet's centreline dissipate quite rapidly at short distances downstream from the point of discharge.

Effluent concentrations are presented in a non-dimensional form, calculated as a ratio of the predicted effluent concentration (C) at any point to the initial or maximum effluent concentration (C_0), thus representing percentage effluent mixing results in terms of C/C_0. The results shown in Figure 2a indicate that effluent concentrations in the horizontal plane and along each jet's centreline dissipate quite rapidly at short distances downstream from the points of discharge.

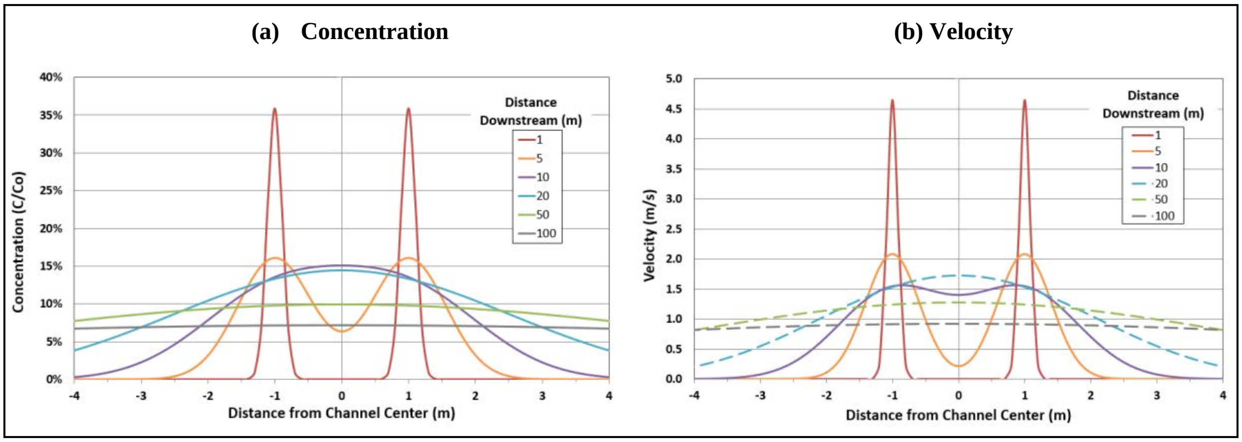


Figure 2: Predicted effluent profile across the double-port jet at various distances from the origin for 20,000 m^3/day discharge rate: (a) Concentration, and (b) Velocity

A different way to visualize the mixing is illustrated in Figure 3, which shows the predicted effluent concentration cloud in plan view. It is predicted that the jets will initially reach the channel banks approximately 15 m downstream from the point of discharge, while the lengths required to achieve full transverse mixing are expected to range from 20 m to 40 m for the required range of discharge rate scenarios.

Effluent velocities were calculated for a number of points across the river at various locations downstream from the point of discharge. Analytical jet equations do not consider physical boundaries in the receiving environment (i.e., channel bed, channel banks, and air-water surface boundaries), resulting in higher modelled jet velocities compared to reality. For this reason, the velocity profiles presented for distances greater than 20 m downstream from the point of discharge are expected to be overestimated and are shown with dashed lines. The analytically modelled effluent jet velocities provide a conservative upper bound that was used in the design of the effluent mixing structure and the associated erosion control measures. The maximum effluent jet velocities at the nozzle exit were predicted to be over 6 m/s, rapidly decreasing to 2 m/s approximately 5 m downstream from the point of discharge (Figure 2b). Velocities were also found to drop rapidly in the horizontal plane laterally from the jet centreline.

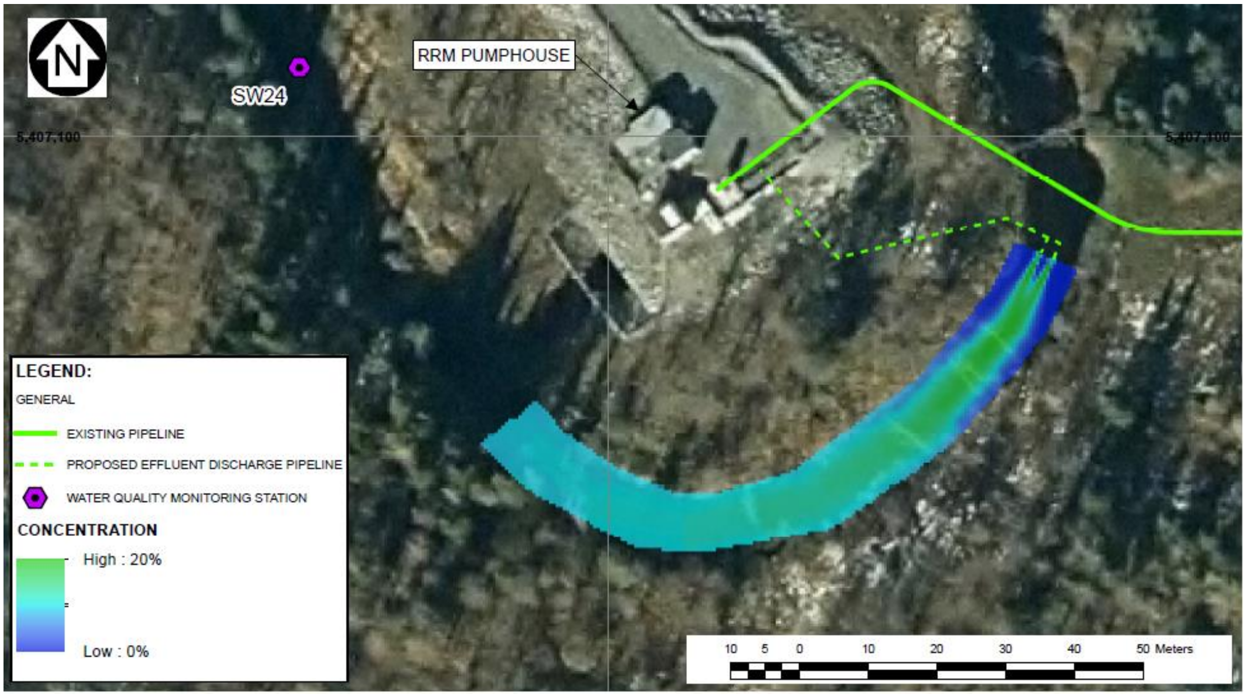


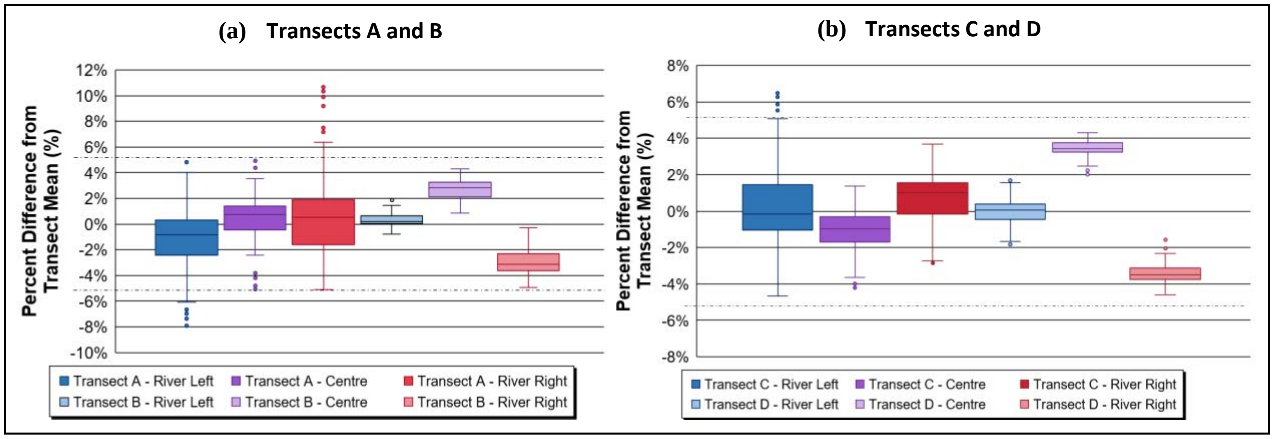
Figure 3: Effluent concentration for the double-port diffuser system at 20,000 m³/day

Effluent mixing evaluation

A mixing study was conducted after commissioning the effluent diffuser system to confirm that there is adequate effluent mixing with the receiving environment by the time the downstream compliance points are reached. The effluent discharge and the discharge in the Pinewood River were both at 10,000 m^3/day at the time the study was conducted. Rhodamine dye was injected into the effluent discharge pipeline at a constant rate. Monitoring of the rhodamine concentrations was conducted at various transects downstream from the discharge location using YSI 600 OMS sondes until it was determined that a steady-state condition in the river had been established and maintained for at least 15 minutes.

The YSI sondes were calibrated to background conditions and were set up to record measurements every two seconds. The YSI sondes were then placed across the river at transects downstream of the effluent discharge system, with one YSI sonde placed at the channel centre, and one placed at each bank within the active flow area, for a total of three YSI sondes per transect. A total of four transects located at 10 m, 20 m, 25 m, and 58 m downstream from the discharge points were assessed, two transects monitored at a time. Transect A (10 m) was the closest to the diffuser, transects C (20 m) and B (25 m) were just upstream and just downstream of a river bend, and transect D (58 m) was located at the water quality sampling dock.

The results are presented using box and whisker plots, with the median represented using a line within the box, and the first and third quartiles of the data set represented by the lower and upper bound of each box, respectively. The size and symmetry of the boxes can provide insights into the typical values, the amount of spread, the symmetry of the dataset, with the "whiskers" and outlier points representing extreme values. The percent differences of each YSI sonde reading from the mean transect concentration over the steady state period, as well as the ±5% envelope indicative of complete transverse mixing, as defined by Fischer et al. (1979), are summarized on the box plot shown in Figure 4a for Transects A and B, and in Figure 4b for Transects C and D (reminding that Transect C is upstream of Transect B).


(a) Transects A and B

(b) Transects C and D

Figure 4: Percent difference from transect mean concentrations at four transects downstream from the point of discharge

The box plots provide a visual representation of the degree of variability, and thus the degree of mixing, within the channel. These results show that the variability in the concentrations across the channel transects decreases progressively from Transects A and C to a low degree of variability by the time the flow reaches Transects B and D. By the time the effluent reaches Transect B located 25 m downstream from the point of discharge, the variability is notably reduced, and all points fall within the 5% envelope, indicating fully mixed conditions. Thus, the results from the field study confirm that the performance of the designed system meets the ECA requirements for adequate effluent mixing.

Conclusions

Hydrometric monitoring has been in place at the H1 hydrometric monitoring station at the Rainy River Mine since 2015. The stage-discharge relationship at this site was frequently affected by backwatering from downstream obstructions and beaver activity, which resulted in periods of poor quality discharge data. The hydrometric monitoring network was upgraded and expanded to help improve the quality of the hydrometric data collection required for effluent discharge from the mine. This was primarily achieved by using SonTek-IQ acoustic Doppler flow measuring devices that measure the discharge in real time without relying on traditional stage-discharge relationships.

An effluent discharge system was designed and constructed to discharge treated surplus water from the mine to the Pinewood River. The design utilized the results from an analytical mixing model, and a double-port duckbill rubber valve diffuser was selected to satisfy the mixing requirements. After commissioning the effluent mixing system, a mixing study was completed to confirm the performance. The mixing study results indicate complete transverse mixing as close as 25 m from the discharge point, suggesting comparable or slightly better mixing results than predicted using analytical methods that estimated a mixing length of about 30 m at the tested low flow rate of 10,000 m^3/day. The differences may be due to better mixing conditions in the field compared to the simplifications and conservative assumptions made in the analytical assessment. This was supported by field observations, which indicated strong mixing conditions close to the duckbill diffusers.

Acknowledgements

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Improving the Performance of Mineral Flotation by Treating Process Water

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Abstract

The drive to recycle process water has obvious benefits in terms of a lower water footprint. However, for some mines, especially those where more than one mineral is simultaneously mined, recycled process water can have a negative effect on mineral recovery by flotation, with a significant economic impact on the operation.

Typically, fresh or makeup water has a low dissolved solids content and does not negatively affect flotation and mineral recovery. However, as the water is recycled, it picks up dissolved solids by leaching the ore, and at some point, the level of dissolved solids may begin to affect recovery. A significant amount of work is being done to identify which species are most detrimental to mineral recovery, how to treat and reduce those species, and how to devise test procedures and models to simulate the interactions of species. We present here some preliminary results showing how water quality affects flotation, and examples of improvement in recovery by changing the type of water used in flotation experiments.

Introduction

Mining requires a steady supply of water resources. However, the availability of water is becoming a significant issue for many mineral processing operations, with the following major trends influencing the use and recycling of water:

- •Mineral ore grade is decreasing, which means that more ore must be processed, and more water must be used to produce the same amount of metal as before.
- •Underground and some surface water resources are becoming scarcer, so less fresh water is available for making up water lost in the mineral processing operation. These losses are mainly

from moisture contained in the mineral concentrate leaving the site and water lost as evaporation. In addition, water is also immobilized with tailings.

- •Pressure is increasing for water resources to be used more efficiently to comply with corporate environmental and social responsibility.

These trends result in a strong drive to increase the recycling of water. To illustrate one way in which this recycling could be achieved, let us consider the following diagrams, the first one being for a typical temperate zone.

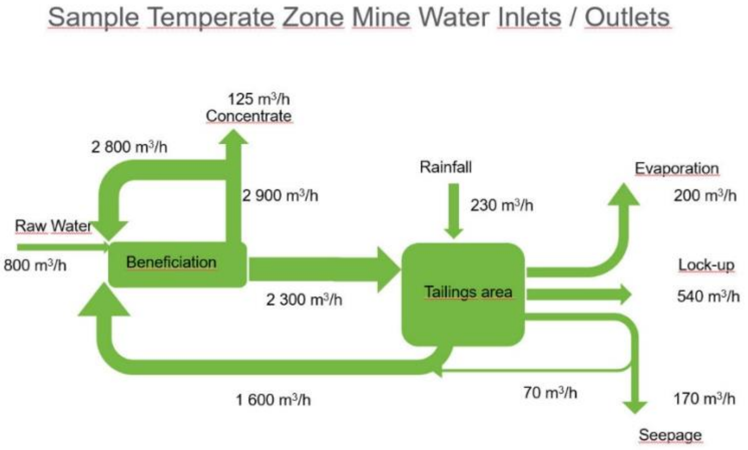

Figure 1: Simple mine water balance for temperate zone

Some temperate region mines even have water surpluses, in which case there are additional issues around effective treatment for water discharge. Now let us look at the situation for an arid zone, which changes the relative flowrates significantly:

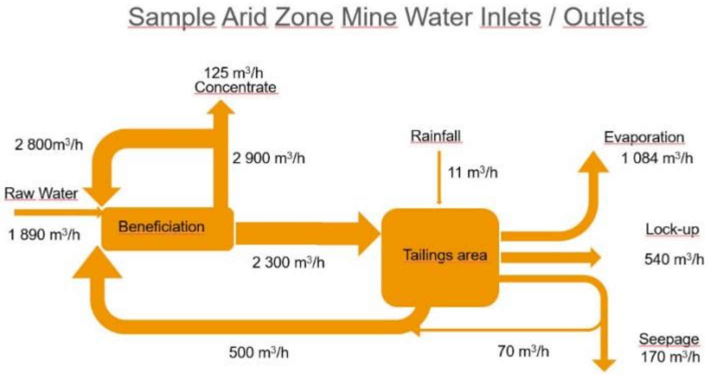

Figure 2: Simple mine water balance for arid zone

Now evaporation is significantly greater, so raw makeup water is therefore greater as well. If the circulating water loop that goes from the concentrator to the tailings storage facility and back is closed, by filtering the tailings and therefore making more water available for recycling, we would have the following:

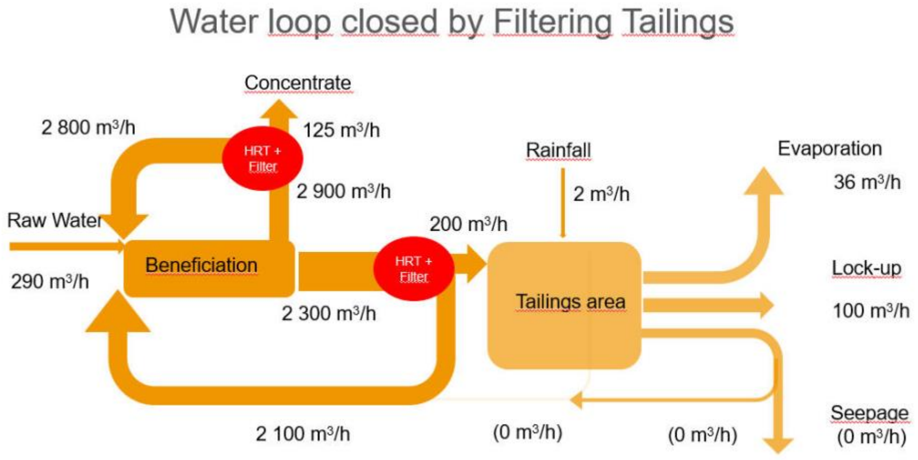

Figure 3: Closing water loop by filtering tailings

Closing the water loop allows for a more efficient use of water with less makeup water needed, and also for a much-reduced need for space to store tailings, with important savings in tailings storage facility (TSF) construction costs. These savings in water cost and TSF construction must be balanced against the capital cost of a tailings filter plant and additional power required for the filtration.

This is just one example, and water can be recirculated at a mineral processing plant in many different ways, from a simple way such as in Figure 2, to a more sophisticated way such as in Figure 3.

Another critical point is that water is in contact with the ore, and depending on the recycling method used, contact with the ore is more or less intense. For example, when tailings filtration is used, water is recycled more often and comes into contact with fresh ore many times more than with conventional tailings handling. As the water comes into contact with the ore, it dissolves species from the ore, a process that can take a long time, or be significantly accelerated when using shorter water loops.

When water is recycled with more intensity, it often accumulates dissolved species because there is more contact time with the ore.

This poses an important question – for a Greenfield site, where we often do not know much about the water quality, what will be the composition of process water quality at equilibrium? Work in this area has led to development of a method to assist in predicting the water quality for projects where the water quality is unknown (Le et al, 2020).

Now we turn to the question of how water quality affects flotation recovery (Liu et al., 2013; Musuku et al., 2016).

For copper sulfides, when water recycled from the effluent of a municipal wastewater plant is used for copper flotation, the organic compounds remaining in the water affect the foam in the flotation cell.

The remaining compounds can cause a loss in the recovery of around 10%. Therefore, the organics must be removed from the municipal wastewater before using it in the copper concentrator plant.

For molybdenite and copper sulfides occurring together, when seawater is used for the flotation process, copper sulfide flotation is acceptable, but molybdenite recovery is decreased significantly by seawater. Therefore, the seawater has to be processed by a reverse osmosis plant to reduce the salinity of the water before using it for molybdenite flotation.

The recovery of copper sulfide on its own is not as sensitive to water quality as other minerals. In particular, nickel pentlandite flotation recovery is very sensitive to changes in water quality. When nickel pentlandite is associated with copper, the sensitivity is increased, as shown in recent work (Kasymova et al. 2021).

We now present some preliminary results of changes in flotation recovery from flotation tests performed with clean water and process water.

Methodology

Flotation tests were run using ores sampled from mining partner companies. Ore samples were taken from concentrator feed, so that no grinding was carried out. The samples were adjusted for pH and conditioned with standard flotation reagents. The pH and other conditions were held constant, while varying only the quality of water used in the flotation runs.

Raw water was taken from the site fresh water supply line, pond water from tailings pond, process water from concentrator thickener overflow, and treated process water was obtained by treating concentrator thickener overflow.

Results and discussion

Table 1 shows preliminary results from flotation tests where different water sources were used as a flotation medium for tests on different commercial ores.

As mentioned previously, some minerals are more sensitive than others toward changes in water quality. In general, it is seen that using either pond or process water (where we know that total dissolved solids are greater for the reasons explained above) shows a detrimental effect on recovery. In particular, iron and copper do not show a very large sensitivity, whereas lithium, gold, and silver show important effects.

Table 1: Preliminary results from flotation tests with treated process water

Source water	Case 1 – Cu	Cases 2 – Au	Case 3 – Ag	Case 4 – Fe	Case 5 – Li
Raw	80.5% Rec. 17.5% Grade	53.0% Rec.	67.5% Rec.	–	88.2% Rec. 31.1 LiO2%
Pond	76.7%	53.1% Rec.	43.1% Rec.	–	67.3% Rec. 5.0 LiO2%
Process	78.9% Rec. 14.0% Grade	73.1% Rec.	62.2% Rec.	85.0% Rec. SiO2 4.7%	59.4% Rec. 4.5 LiO2%
Treated process	85.5% Rec. 19.2% Grade	78.0% Rec.	69.7% Rec.	87.7% Rec. SiO2 1.2%	78.2% Rec. 4.9 LiO2%

If we consider other mining processes, water qualities needed for mineral grinding and conveyance are not important. In contrast, it is known that water quality is critical for electrowinning, which typically requires reverse osmosis quality water with conductivity less than 100 microsiemens and low chloride levels.

Methods of pre-treating the water for use in the flotation runs above include reverse osmosis, sulfate precipitation, dissolved air flotation, oxidation of organics, and filtration. Further details will be given in future publications. In conclusion, a simultaneous deep understanding of water chemistry and mineral processing can result in operational savings.

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Water Treatment Intake and Fish Barrier Design in Mountainous Streams

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Abstract

As part of a new mine water treatment project in the Elk Valley, British Columbia, Canada, Wood Environment and Infrastructure Solutions (Wood) is designing an intake structure and fish barrier in a steep, mountainous creek (the creek). The purpose of the intake is to draw mine-affected water and replace it with treated water, prior to discharging to the environment. A multi-criteria options analysis was conducted to assist with the selection of a design option that is easily constructible, offers ease of operations, is economical, and facilitates environmental enhancement. An options analysis for a fish barrier design was also conducted considering ecologically sensitive fish species, including Westslope Cutthroat Trout (WSCT).

Five different intake options were investigated including infiltration gallery, precast concrete pump well, self-priming pumps, floating barge pump, and new intake downstream of the pond. The treated water is returned immediately downstream of the intake location. An options analysis matrix was compiled to assess each intake/outfall option based on the project criteria. The mining company is in the process of reviewing the options analysis with project stakeholders.

A desktop literature review was completed to understand the mobility of WSCT in order to guide the design of the fish barrier. The following considerations were investigated for fish barrier design: leaping ability; burst speed; minimum water depth requirements; and water turbulence. Due to the remote nature of the site, the following low-maintenance physical fish barriers were considered: drop structure; chute; and pipe. The fish barrier will be constructed downstream of the selected intake location.

This paper will highlight the key considerations for the intake/outfall and fish barrier options appraisal and design. In addition, this paper will discuss key design constraints related to construction and operation in remote settings surrounded by environmentally sensitive habitat. Furthermore, the paper will provide a

summary of sustainability measures, including Indigenous engagement and practices to limit impacts to the environment during the execution of the works.

Introduction

There are several steelmaking coal mines in southeastern British Columbia, Canada, that have been in operation since the 1960s (Ministry of Energy and Mines, 2015). To access the coal, large quantities of rock are mined and placed in piles. Precipitation and surface water runoff transport selenium and other substances from the waste rock piles into the local watershed. This transport mechanism is expected to continue for many more decades (Teck Resources Ltd, 2014). There is strong evidence to suggest that dissolved selenium emissions originating from waste rock piles are deleterious to resident fish populations, particularly the Westslope Cutthroat Trout (WSCT) (Lemly, 2014). Mining activities in this area must adhere to the Elk Valley Water Quality Plan, submitted to the BC Minister of Environment in 2014, which outlines water quality targets including selenium concentrations within the watershed (Teck Resources Ltd, 2014). To achieve the targets set out in the Elk Valley Water Quality Plan, the mining company commissioned a saturated rock fill (SRF) facility for removal of selenium and nitrate from mine-affected water prior to discharge to the environment. An SRF is a mined-out open pit backfilled with waste rock and partially water saturated, which can support a microbial community that is conducive to microbial reduction of selenium and nitrate (Teck Resources Ltd, 2018). As part of the next phase of SRF expansion, the mining company is planning to intake mine-affected water from the creek and to re-supply the creek with treated water from the SRF.

The creek is a braided and steep mountain stream that collects drainage from 8.6 km^2 of mined and natural forested lands. The mining company is planning to expand its mine rock storage facility in the creek's catchment area as the mining operations continue. The braided channels of the creek collect into a sediment pond (the pond) and discharge through a 10 m wide overflow spillway. Figure 1 shows the site location plan, including the creek and the pond. There is accumulation of calcite at the pond overflow spillway, a by-product of mine-affected water that can be detrimental to fish habitats (Teck Resources Ltd, 2014). Figure 2 shows the pond and its spillway. The creek has been identified as a fish-bearing stream through fisheries surveys.

The purpose of the current project is to increase the treatment rate of the SRF. Key components of the project include the construction of an intake to draw mine-affected water from the creek and pump it to treatment facilities (as part of the SRF program) and an outfall structure to return treated water into the creek. A fish barrier will be constructed at the intake/outfall location to inhibit migration of fish species into the intake structure location. Wood Environment and Infrastructure Solutions (Wood) has developed several conceptual options for intake/outfall and the fish barrier. The project is currently at the options analysis phase. This paper describes the aforementioned design options and presents the benefits and drawbacks of each option with regards to environmental effects, cost, operability, and constructability.

Figure 1: Site location plan

Intake/outfall options analysis

The intake treatment design maximum flow rate is 1,500 m^3/day, with planned future expansion to 7,500 m^3/day. Through several stakeholder consultations, Wood analyzed five intake/outfall options at the creek. The first four options draw mine-affected water from the pond, whereas Option 5 is proposed downstream of the pond spillway. In all five options, the treated water pipeline will outlet into the creek downstream of the pond. Riprap armouring will be placed at the outfall location for erosion protection. The five intake/ outfall options are as follows:

- Option 1: Infiltration gallery at pond overflow spillway (see Figure 3) – perforated high-density polyethylene (HDPE) pipes connected to a pump well to draw mine-affected water from the pond, prior to discharging through an overflow spillway. This option will require re-construction of the existing overflow spillway, which will simultaneously address the existing calcification issue (see Figure 2).

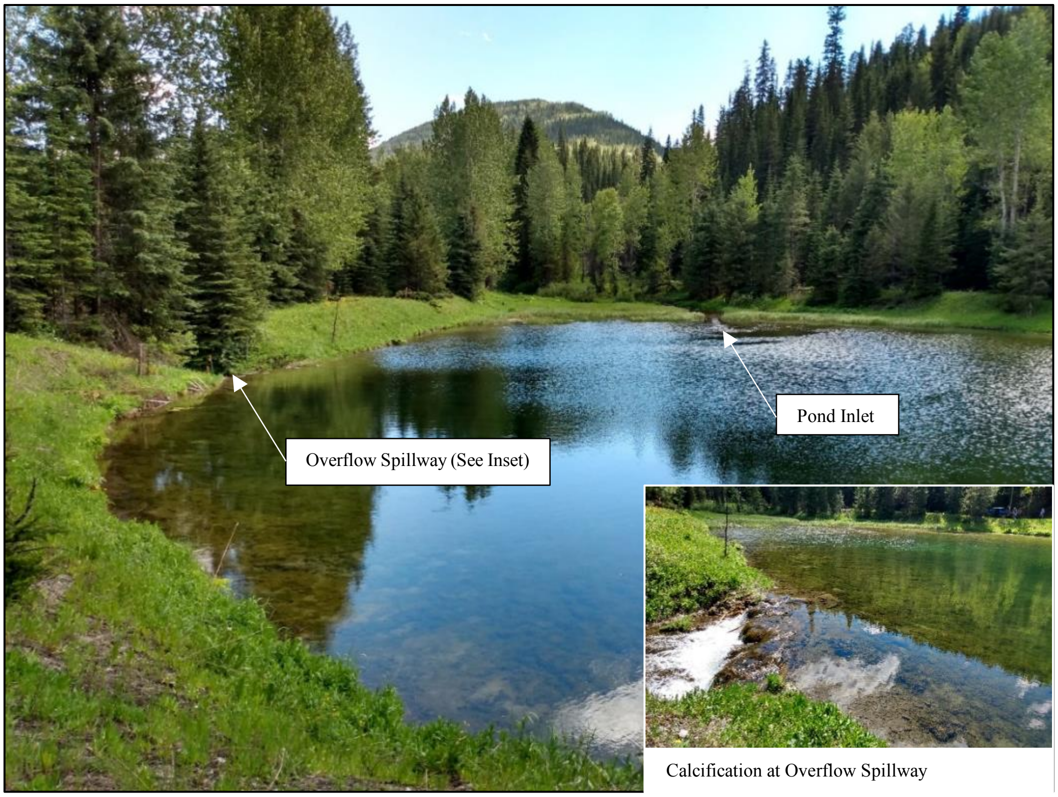

Figure 2: Sediment pond

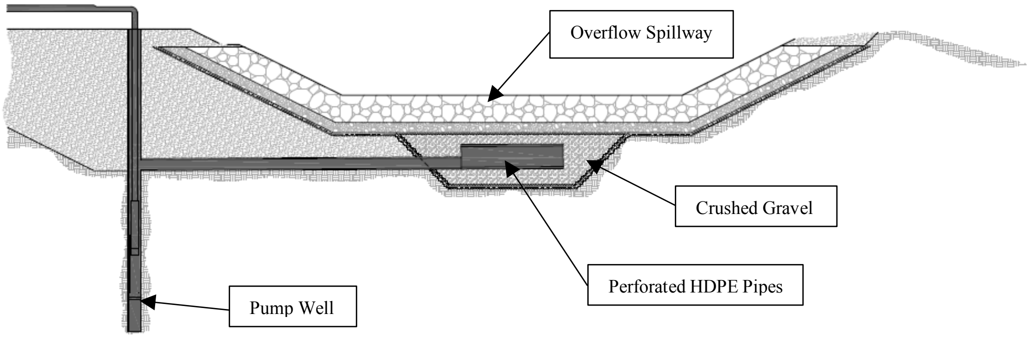

Figure 3: Infiltration gallery at pond overflow spillway

- Option 2: Intake pump well within pond (see Figure 4) – precast concrete pump well-constructed adjacent to the pond spillway. The inlet pipe elevation will be designed below the anticipated maximum ice thickness (0.5 m lower than permanent water level). Provided that a section of the pond berm will be excavated for installation of pump well, Wood proposed that the overflow spillway be reconstructed using concrete lock blocks to address calcification at the pond spillway. The lock block spillway will also offer the flexibility to raise the pond weir, if needed for future expansion.

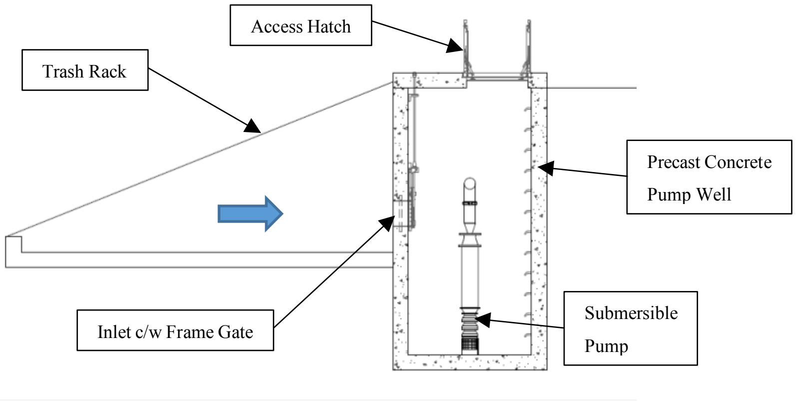

Figure 4: Intake pump well within pond

- Option 3: Self-priming pumps (see Figure 5) – self-priming, end suction pumps will be located on the pond berm with suction hoses extending to the center of the pond. A back-up pump will also be installed for redundancy. Strict monitoring and maintenance of pumps will be required to ensure continual operation. No earthworks are required in the pond to install the self-priming pumps.

Figure 5: Self-priming pumps

- Option 4: Floating barge pump (see Figure 6) – a self-contained unit will be equipped with two pumps (for redundancy) and connected directly to HDPE intake pipeline. A walkway will also be installed for easy access from the pond berm to the barge for maintenance/operations. No earthworks are required in the pond to install the floating barge.

Figure 6: Floating barge pump

- Option 5: Intake downstream of pond spillway (see Figure 7) – a concrete lock block weir wall will be constructed to create a small ponding area. Water from the ponded area will be pumped via a precast concrete pump well intake structure (similar to Option 2). Cut-off walls upstream and downstream of the ponded area may be required to prevent seepage of mine-affected water. This option will be constructed completely outside of the existing pond area.

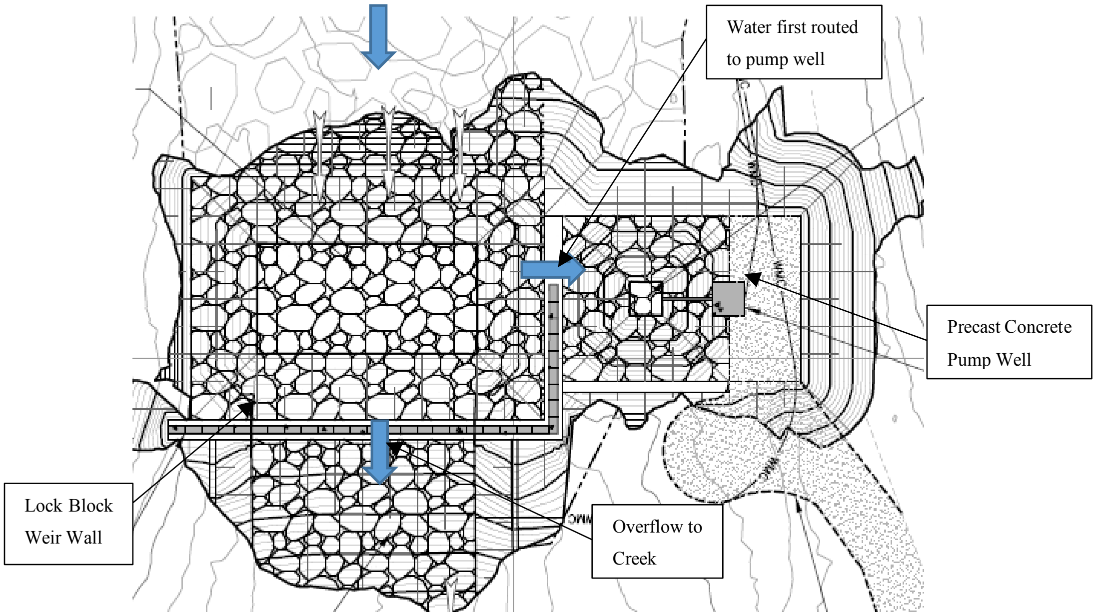

Figure 7: New dam and intake downstream of pond

The five intake/outfall options were evaluated based on key project criteria agreed upon by Wood and project stakeholders. The following list summarizes the project criteria and its key considerations:

- Environmental: impacts to the air, land, vegetation, water, fish, and wildlife directly resulting from implementation of the selected option.
- Constructability: specialized construction equipment, rugged terrain, suitability of underlying soils, and materials sourcing.
- Operation/maintenance: ease of access, ease of equipment replacement, design life and reliability.
- Economic: construction, operational and replacement parts cost.

Table 1 shows the key summary of the options analysis for the intake/outfall options.

Table 1: Intake/outfall options analysis

	Option 1	Option 2	Option 3	Option 4	Option 5
Environmental	+ Removes calcification at existing spillway – Creek upstream of the pond overflow spillway will lose fish habitat	+ Removes calcification at existing spillway – Creek upstream of the pond overflow spillway will lose fish habitat			– Potential for reduction in fish habitat
Constructability	– Disturbance to existing pond berm	+ Opportunity to raise spillway weir for future pond expansion – Disturbance to existing pond berm	+ No pond earthworks required +quick installation	+ No pond earthworks required + Equipment will be shop fabricated and assembled on site	+ No construction near existing pond – New intake location has potential issues including channel erosion and seepage of mine-affected water
Operation / Maintenance	– Potential calcification of perforated pipes – Difficult to replace buried perforated pipes	+ Easy pump replacement – Requires consistent trash rack maintenance	– Requires strict monitoring – Potential freezing of intake pipes – Potential risk of leaks	– Potential to draw sediments from pond bottom – Potential downtime/repairs in case of ice build up	+ Easy pump replacement
Economic	– High construction cost – High replacement cost	– High construction cost	+ Low construction cost – Highest maintenance/ operations cost	+ Low construction cost	– High construction cost

Note 1: Benefits of each option are labeled as "+", whereas drawbacks of each option are labeled as "–" .

The project site is located in a relatively remote area of the overall mine, and vehicular access to the pond is difficult. Therefore, a new access road and pipeline corridor will be built from the intake/outfall location to the SRF. The new access road will allow heavy equipment to be transported to the project site and facilitate hauling operations. Furthermore, the creek will be temporarily diverted around the proposed intake/outfall location to allow for construction in a dry environment. The construction of the access road, any of the above intake/outfall options, and flow diversion will have potentially negative impacts on the environment. Therefore, a strict environmental policy (including erosion and sediment control and care of water plan) will be planned, implemented, and enforced during construction. The erosion control plan will specify use of best management practices (BMPs) such as silt fencing, fibre roll logs, and soil stockpile stabilization to either immobilize sediment or contain site sediment runoff on site. Flow monitoring will also be conducted in downstream watercourses to check for elevated turbidity, which will indicate that additional erosion control measures are required.

Fish barrier selection and design

WSCT is listed as a species of Special Concern in British Columbia due to the "anthropogenic manipulation and degradation of the environment in which it lives" (COSEWIC, 2006). Because of the sensitivities around this species, its habitat, and the management implications for industry, the use of fish barriers can be a powerful tool to maintain regulatory compliance and limit operational risks. There are several types of fish barriers in use around the world, including electrical, hydraulic, and physical barriers. A physical barrier provides a low-cost, low-maintenance solution, and this approach has been proposed for these reasons. To ensure success, an effective physical fish barrier needs to address one or more of the following considerations, in relation to the capabilities of the target species:

- Leaping ability – how high can the fish jump?
- Burst speed – what is the maximum swimming speed of the fish?
- Minimum water depth requirements – is the water deep enough to prevent effective swimming?
- Water turbulence – is the water turbulent enough within the barrier to reduce density and therefore prevent effective swimming?

As with all salmonid species, cutthroat trout are powerful swimmers, with documented burst speeds between 3.55 m/s (Blank et al., 2020) and 4.11 m/s (NRCS, 2007). The mountain rivers and streams they inhabit also require commensurate leaping abilities to traverse natural impediments as they move throughout their habitat. This is demonstrated by the large home ranges for WSCT in the Elk river watershed, reaching a maximum of 23 km in its upper reaches (COSEWIC, 2006), where gradients increase, and the habitat becomes more susceptible to naturally occurring barriers due to limited water depths and channel widths. Adult cutthroat trout have had successful leaps recorded at a maximum height of 0.9 m (NRCS, 2007); however, anecdotal reports from fisheries biologists working in nearby areas have reported successful leaps of ~3.0 m in height by WSCT into hanging culverts. In this instance, it was reported that an area of relatively deep water existed beneath the culvert outfall – providing sufficient "runway" for the fish to initiate a leap.

The natural habitat of WSCT often provides refuge opportunities (e.g., boulders, woody debris, eddies, etc.) amongst obstacles, where fish can rest and recover in an area of reduced water velocity before continuing their movements. In certain instances, waterfalls can create plunge pools to facilitate leaping, and cascade features can present regularly spaced "staging areas" where fish can recover their energy between leaps, as they ascend. Therefore, our approach in the proposed designs for this installation was to use a combination of considerations to increase barrier efficacy – including limiting water depths and increasing water velocity (to prevent effective swimming) and eliminating the presence of a plunge pool (to limit leaping ability).

Due to the remote site location, a low-maintenance fish barrier is preferred. The fish barrier needs to be functional for a wide range of flow conditions, from minimal winter flows to extreme flood events (such as the 1:200-year storm runoff). Therefore, the following three physical barriers were considered for this site:

- Option 1: Drop structure (see Figure 8) – a 2 m high drop structure will prevent fish from leaping into the creek upstream of the fish barrier. The drop structure will be mostly precast concrete with a cast-in-place concrete slab. If regular flow monitoring is required at this location, a steel-plated weir and flow measurement level meter can be installed immediately upstream of the drop structure. Considering that the creek is relatively steep, a 2 m high barrier can be constructed without the need for extensive earthworks.

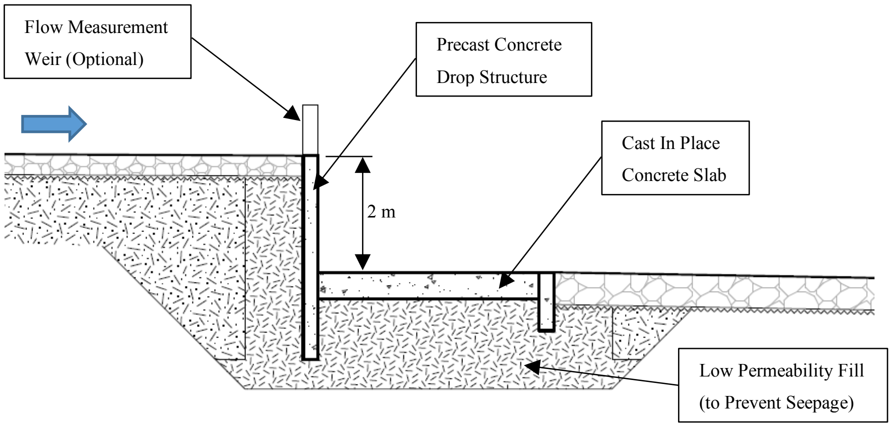

Figure 8: Drop structure fish barrier

- Option 2: Chute (see Figure 9) – Fish barrier will be a cast-in-place concrete chute at a minimum 7H:1V slope. Flow of water over the chute will be fast and shallow, inhibiting fish from migrating upstream of the fish barrier. Concrete blocks can also be placed to reduce flow area and further increase flow velocity.
- Option 3: Pipe – The creek will be conveyed through a 20 m long smooth-wall pipe at a 5% slope. According to BC culvert assessment standards, a 20 m pipe alone would only present a moderate risk to fish passage, but when coupled with the 5% slope, it presents a high risk to fish passage. With the added consideration of smooth walls and lack of internal baffles, this option can be considered as a fish barrier. Designing the pipe with a stream width ratio greater than 1.3 (where

the stream width is ≥1.3× culvert width) would also provide an additive barrier effect due to increased water velocity within the pipe.

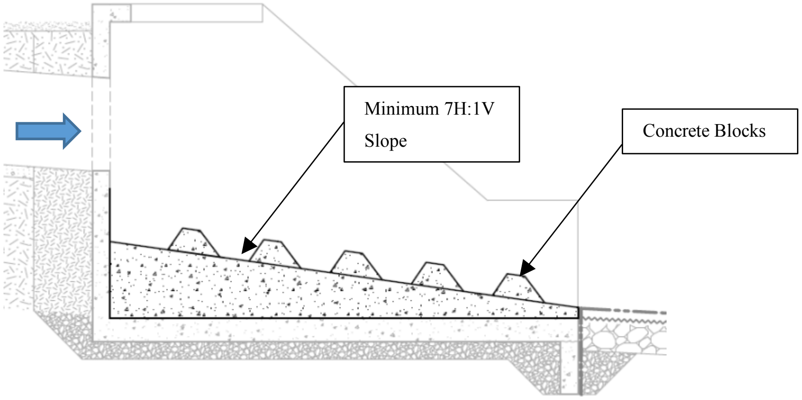

Figure 9: Chute fish barrier

Table 2 summarizes the advantages and disadvantages of each fish barrier option.

Table 2: Fish barrier options advantages and disadvantages

Fish barrier option	Advantages	Disadvantages
Drop Structure	+ Allows for easy and reliable flow monitoring, if needed. + Ease of maintenance.	– Although a 2 m drop should provide an effective barrier to passage, anecdotal reports from nearby areas indicate that WSCT can successfully leap heights ~3.0 m. – During periods of increased flow, the drop height may be reduced and the risk of fish migration above the structure increased if the flow rate is less than the burst speed of WSCT and sufficient water depths are present.
Chute	+ Ease of maintenance. + Outfall drop and slope present an effective barrier to fish passage under normal flow conditions.	– Increased potential for erosion downstream of the chute due to high velocity flow. – Flow velocities and/or limited water depths must be maintained to ensure efficacy of fish barrier. – During periods of increased flow, the drop height may be reduced and the risk of fish migration above the structure increased if the flow rate is less than the burst speed of WSCT and sufficient water depths are present.
Pipe	+ The proposed slope and lack of baffles within the pipe present an effective barrier to fish passage at any flow rate. + Water velocity within the pipe will increase significantly during periods of increased flows, providing an effective barrier to fish passage.	– A large pipe diameter is required to convey the full creek design flow – Potential for seepage around the pipe, eventually undermining structural stability. – Potential for blockage with debris resulting in more challenging maintenance than with open structures.

Conclusions and recommendations

All intake/outfall options analyzed will ultimately serve the purpose of capturing and reducing selenium and nitrate concentrations in downstream receivers and improving water quality for WSCT. The physical fish barrier will be installed downstream of the intake location to keep fish outside of the intake location as well as the pre-treated water. The mining company is in the process of reviewing the options analysis with key stakeholders, Indigenous communities and regulatory bodies. Construction is expected to be completed by October 2023. This project will also be integrated within the mine closure and reclamation plans in which a multitude of values (set by communities of interest, local Indigenous groups and regulators) will be incorporated, in addition to ecological conditions.

Wood will continue with detailed design of the selected intake/outfall and fish barrier options. The following construction and monitoring recommendations are proposed regardless of the selected options:

- An environmental protection work plan will be established and implemented for the duration of construction. The environmental protection work plan should identify critical areas and potentially harmful activities, and steps will be taken to mitigate negative effects to the environment.
- Erosion and sediment control measures will be checked and if needed, repaired or upgraded, on a frequent basis. Regular flow monitoring in downstream water bodies is required to ensure that there is no unintentional sediment-laden runoff from the construction area.
- A strict environmental reporting system should be in place in case any of the following are encountered: spills; invasive plant species; bird nests while clearing; bear dens; badger burrows and fish mortalities.
- Construction activities should be completed in dry conditions, to the greatest extent possible. This may involve diversion of the creek around the work area. In-stream work must be completed within the least-risk fish window.

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Suggested Best Practices for Water Stewardship in Mining

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Abstract

There is increasing stakeholder and societal pressure on mining companies and other large users of water to understand their dependency and impact on water in recognition that water is a shared resource. Potential risks to water security impact both operational performance and the community. These risks will become more visible as competition for water resources increases due to population growth, urbanization, and climate change trends. In response to these conditions, companies are incorporating climate uncertainty in the management of water resources, and are transitioning to proactive water stewardship programs.

All around the world, there are ongoing conflicts between mines and local communities. The high-profile Resolution Copper project in Arizona, USA, has been facing steep opposition from the local Apache tribe due to concerns that the development would destroy sacred land and put the local groundwater supplies at risk for the surrounding communities. In Peru, MMG Limited has announced that they are suspending operations at the Las Bambas copper mine due to protests over numerous social and environmental conflicts, including accusations that dust from the mine is polluting local water sources. In Serbia, the government revoked Rio Tinto’s lithium exploration license for the Jadar project due to environmentalist groups’ concerns over air and water pollution and insufficient communication with local communities. Each of these are examples of current, ongoing issues where mining companies are clashing with local communities over several concerns, not the least of which is water. Often times when communities oppose a mining project, it is due to fear of contamination of the water supply, loss of access to water for the people, or seeing the mine as competing for water resources from established industries such as farming or manufacturing.

A water stewardship program can help companies manage risks related to society, governance, supply, and quality by planning for the unknown in factors such as water management, supply, and resilience. It has become clear that traditional, stationary designs, or solutions that are not adapting to today’s changing world, are no longer effective in water management, and companies must seek solutions that are forward looking. By including potential risks, impacts, and mitigation options in a water stewardship plan, a company can be prepared to handle various situations related to water management and stewardship and its

impact on local communities. There are many protocols and frameworks that provide guidance on water stewardship, such as the Mining Association of Canada (MAC) Water Stewardship Protocol, the International Council on Mining and Metals (ICMM) Water Stewardship Framework, and the Alliance for Water Stewardship (AWS) standard. MAC and ICMM guidance are very prominent in the mining industry, but AWS has gained a lot of traction with some industries such as food and beverage, technology, agriculture and manufacturing. This is because AWS is not industry specific, and the guidance that it offers can easily be applied to a variety of operations. These frameworks have been successful in helping to incrementally guide companies towards initiatives that they need to take in order to understand and plan for the issues that need to be addressed in a water stewardship plan. It is common for members of these organizations to follow their framework; however, smaller non-member companies can still follow and implement guidance without formally joining an organization.

The mining industry is not unique in trying to implement water stewardship solutions to help mitigate community concerns and address water challenges. The food and beverage industry has historically been very active in water stewardship, as water is often directly used in their products. In recent years, water quality and quantity planning has become an increasing concern in the textile, manufacturing, and technology industries as well. There are shared challenges across industries related to water stewardship, and lessons learned from other industries can easily be applied to the mining industry.

Water stewardship programs need to consider the following at a minimum:

- water quality issues on site and surrounding areas;
- water quantity issues on site and surrounding areas;
- stakeholder and community concerns;
- water-related infrastructure on site and surrounding the site;
- site-related water use;
- surrounding water uses in the catchment;
- water governance initiatives in the catchment; and
- water-related legal and regulatory requirements.

Understanding these issues will allow for a site to have adequate knowledge of their water challenges and enable it to set a baseline for creating mitigation programs for identified vulnerabilities. This paper will focus on considerations that, based on experience, are the best practices for water stewardship programs. These concepts include incorporating the effects of climate change in water management (quality and quantity) in planning and design, having strong corporate/site interface in water stewardship training and implementation, and prioritizing collective action mitigation solutions.

Planning for and anticipating the effects of climate change on water management for a site is a key component of any water stewardship program. In addition, it is imperative that criteria and performance expectations are established for a successful program. Due to changes in climate, mines and urban centers are encroaching on each other and competing for resources more and more. Just as population growth, globalization and increasing urbanization are important considerations in water stewardship programs, weather and climate events are key design parameters in water stewardship programs. One way to account for climate change in water-related planning activities is to model climate change scenarios and incorporate them in water balances and other forecasting activities when evaluating future water needs and availability. The local climate system can be affected by human activity such as radiative forcing (where greenhouse gases trap radiation), land and water surface albedo reflecting radiation, and clouds and aerosols reflecting incoming solar radiation. Modelers can simulate key climate variables such as air temperature, water temperature, pressure, density, vapor content, and horizontal and vertical wind velocities to estimate parameters related to water stewardship planning activities.

In many cases, water balances that do not account for climate change may show that there is an adequate amount of water for production needs, but when climate change is accounted for, it may show a completely different story. Climate change projections can infer that a site may face water shortages, or even surpluses, in the near term. By including climate change in water planning, a site may be able to anticipate the challenges of doing business where water is a primary input to the economy. This can include planning engagement activities with local governments and interest groups that have influence over the changing water management landscape. Water stewardship programs extend beyond looking at immediate water needs, and most frameworks demand that companies look at forecasting future needs when creating action plans.

Similar to the implementation of health and safety programs across an organization, the same level of attention must be paid to the rollout of water stewardship initiatives. Corporate-level water-related pledges can be lost when the initiatives are transferred to the site level. A common practice for beverage companies is to implement required training at bottling facilities and/or individual breweries on the importance of water stewardship in day-to-day plant activities. By giving staff active on-site training, rather than issuing a new standard or internal memorandum, this gives staff in charge of implementing water stewardship initiatives a chance to recognize the importance of the programs and take a proactive approach to the initiatives. An additional benefit to having a strong connection between corporate requirements and site implementation is that site personnel often feel very passionate about water in their local communities and understand how to best mitigate community concerns surrounding water. Strong water stewardship programs are not just another “corporate requirement” and are instead fully owned and implemented by the site, with the support of corporate-level initiatives.

Prioritizing collective action can enhance water stewardship mitigation measures. Catchment- or basin-wide solutions are generally seen as more effective than site-specific mitigation measures, especially when dealing with issues such as basin-wide water scarcity or water quality issues. A successful example of collective action is the work being done in the Latin America Water Funds Partnership, which began as a partnership between The Nature Conservancy, the Inter-American Development Bank, the FEMSA Foundation, and the Global Environment Facility. Water funds are organizations that engage with public, private, and civil society stakeholders to assist with water security through solutions that incorporate nature-based infrastructure and sustainable management of watersheds. As of 2021, there are 24 water funds created throughout Latin America, and some water funds have up to 60 private sector members. Some examples include the establishment of water tariffs that require service providers to earmark 1% of revenue to infrastructure projects (Lima, Peru), establish drinking water protection for city residents (Monterrey, Mexico), and establish conservation and reforestation activities upstream (Andean region).

As more companies continue to work towards ensuring they are recognized as responsible water stewards, demand for tactics to deliver stewardship projects will continue to increase. It is important to not only consider the basics of water management, but to also consider best practices for future-ready water stewardship programs. Incorporating climate change in planning measures, building a strong connection between corporate requirements and site implementation, and prioritizing collective action in mitigation measures are concepts that, when considered as part of a water stewardship program, can strengthen the overall initiatives and improve outcomes. Companies in all industries, including mining companies, are increasing commitments to do the right thing by communities and the environment, and water is a great litmus test for the success of these efforts.

Predictive Mine Water Balance Modelling – Does Accurate Mean Reliable?

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Abstract

This work presents considerations that can be used by modellers, mining project proponents, and regulatory reviewers to confirm the reliability of predictive mine water balance models. While examples are from mountainous watersheds of British Columbia, Canada, the findings can be useful for watersheds elsewhere.

Predictive water balance models play a critical role in decision support systems for mine water management by: 1) supporting mine proponents in developing engineering designs with reduced costs and operational risks; and 2) informing the environmental effects assessment of proposed projects. Water resources modellers and reviewers (i.e., the proponents and regulatory agencies) put effort into confirming that the water balance models are sufficiently accurate, so that they can be used to fulfill the abovementioned objectives. Modelling accuracy is normally evaluated through the process of model calibration and validation with past and existing hydrometeorological data. Despite these efforts, accurately calibrated models are not necessarily reliable for prediction of future hydrologic conditions, particularly in mountainous watersheds with complex hydrometeorological processes (e.g., in British Columbia, Canada). This work presents some examples of common causes of unreliable water balance models.

Among these causes, one that can be easily overlooked by the modellers and reviewers, is an over-reliance on model accuracy (i.e., accurate calibration). Hydrometeorological data used for model calibration may be unreliable or may not be pertinent to future conditions. Unreliable data may range from unknown parameters (e.g., evaporation) to inaccurate measurements (e.g., inaccurately measured streamflow), or accurate measurements that are not representative of the entire watershed (e.g., point precipitation).

Even with hydrometeorological data that are accurately measured, the models developed based on such data may not be representative of the future hydrometeorological processes. For example, a model developed and calibrated for an undisturbed catchment, cannot be reliably used for modelling flow pathways from mine components that generate contact water via overland, toe seepage, and groundwater recharge pathways.

Introduction

The authors have developed and peer-reviewed water balance models for several major mine projects, mostly in British Columbia (BC), and observed mining projects' increasing dependence on water balance models to provide reliable information for decision making in the evolving regulatory framework and variable financial markets.

Generally, mining project proponents and regulatory reviewers have different expectations from water balance models. The proponents are most interested in information with major cost or operational implications. For example, whether a project will have a net water deficit (requiring water withdrawals) or surplus (requiring water treatment and discharge), or both (depending on wet or dry climate conditions). On the other hand, the main objective of regulatory reviewers is to confirm whether project-affected flows and water quality will be within acceptable ranges. Given the inevitability of data uncertainty, a water balance model that reliably estimates a range of plausible flows addresses the objectives of both mining project proponents and regulatory reviewers better than a model that predicts an accurate set of values. However, preference of reliability over accuracy can be mis-communicated by the modellers, proponents, and regulators.

This work applies a commonly used modelling approach to three example watersheds with similar hydrologic regimes in BC to highlight potential reliability issues with model results in each case. The study conforms to the provincial recommendation of a minimum of two years of monitored climate and flow data (BC MOE, 2016) and the importance of reliable data collection and analysis (RISC, 2018), and shows that in some cases two years of available data may not sufficiently demonstrate the natural variability of an hydrologic regime. Hydrometric monitoring programs for mining projects are typically not established and maintained by qualified professionals. The collection of proper hydrologic data is critical to water balance modelling and understanding water management at a mine site. Many hydrology monitoring programs are underfunded and understaffed; often, the staff available to run these programs are not adequately trained, and the results are not properly quality reviewed. The ability of any model to be a useful tool for mine operators or regulatory decision maker is dependent upon the data used to develop and maintain it.

Finally, considerations and recommendations are provided for estimating contact water from mine components, which cannot be reliably simulated with models developed for undisturbed catchments, and for incorporating probabilistic approaches to characterize modelling uncertainty.

Runoff modelling approach

Due to modelling complexity, lack of available data, and time and budget limitations, the successful use of physically-based hydrologic models for mining projects has been (and realistically, in the near future, will be) limited in Canada. Instead, lumped conceptual models, which conceptually represent inflow, outflow, and moisture content of a catchment, are commonly used in mining projects. Despite differences in details, most lumped conceptual models that are used for mine water balance models:

- include modules to convert input total precipitation data into rainfall and snowmelt;
- compute evapotranspiration to estimate what portion of rainfall and snowmelt is available for runoff;
- route a portion of available water overland, and store (and release) the remaining portion in (and from) a conceptualized soil water storage reservoir. Overland flow and water released from soil water storage comprise the total runoff from a catchment.

For consistent assessment of example cases in this study, all cases were modelled with the United States Geological Survey (USGS) monthly water balance model, a lumped conceptual runoff model also known as the Thornthwaite monthly water balance (McCabe and Markstrom, 2007). The USGS model was selected for this study because its inputs are normally available in mining projects as part of their hydrometeorological data collection program. Inputs to the model are monthly precipitation, as well as monthly temperature and latitude of the location, which are used for the computation of evapotranspiration. Three sets of parameters control conceptualized processes in the model:

- temperature parameters to segregate total precipitation into rain and snow, and to compute snowmelt rate;
- overland flow coefficients to estimate the portion of precipitation that flows overland;
- coefficients to establish a relationship between soil water storage and release.

Example studies

Three example studies were selected for this study. Two studies, East BC Mine Site and North BC Mine Site, represent watersheds that contained proposed mining projects. Climate and runoff data used for these cases in this study are publicly available via the BC Mine Information website (https://mines.nrs.gov.bc.ca/); however, project names have been removed to allow for an impartial assessment of the data collected for the project. The third example study, Upper Penticton Creek (UPC) watersheds (Moore et al., 2021a and 2021b), is presented to assess the value of having long-term, research-level streamflow and climate data for runoff modelling purposes.

All three example study watersheds are in warm-dry-summer and cold-wet-winter climate conditions. These watersheds demonstrate a nival hydrologic regime with snowmelt-driven high flows during the spring freshet, which generally starts in April and peaks in May or June. After the spring freshet, streamflows decrease in summer and are supplied by groundwater discharge, occasional rainfall events, and water released from lakes and wetlands. Rain-driven streamflows in fall can punctuate the annual hydrograph and create secondary (or in some cases even primary) annual peak flows. Annual low flows occur in winter when precipitation falls in the form of snow and streamflow is limited to groundwater discharge.

Table 1: Summary information of example study watersheds

	East BC Mine Site	North BC Mine Site	UPC watersheds[1]
Catchment area (km^2)	50	50	5
Mean catchment elevation (m)	1,000	1,500	1,750
Concurrent climate and runoff data	36 months	39 months	32 years
Mean annual precipitation[2] (mm/year)	710	800	770
Mean annual runoff[2] (mm/year)	330	530	395

Notes:

[1] Values provided in the table are for each of the 240 Creek and 241 Creek watersheds.

[2] Mean annual observed value during the period of record.

East BC Mine Site watershed

This proposed mining project is in a watershed within the Rocky Mountain foothills, with an approximate catchment area of 50 km^2 and mean elevation of 1,000 metres above sea level (masl).

A hydrometric monitoring station was installed on, and collected continuous streamflow data from, the mouth of this watershed for three water years (i.e., October to September). Installation of the hydrometric station, as well as data collection and analysis, followed the provincial guidelines at the time (RISC, 2009). A climate station, approximately located at an elevation similar to that of the mean elevation of the watershed, collected daily temperature and precipitation data during the same three years.

North BC Mine Site watershed

This proposed mining project is in a watershed within the Omineca Mountains of BC, with an approximate catchment area of 50 km^2 and a mean elevation of 1,500 masl.

Streamflow from the watershed was continuously monitored with a hydrometric monitoring station for three water years (i.e., October to September) and three additional months (i.e., October to December) after the end of the third water year. Streamflow data collection during this period was deemed consistent with the provincial guidelines at the time (RISC, 2009). A climate station, approximately located at an elevation similar to that of the mean elevation of the watershed, collected daily temperature and precipitation data during the same period.

Upper Penticton Creek Study watersheds

The UPC study has been monitoring climate and streamflow data from multiple catchments since the mid-1980s (Moore et al., 2021a). The UPC watersheds are located in the southern interior of BC. For the purpose of this work, two watersheds from the UPC experiment were selected: an undisturbed control catchment (240 Creek) and a treatment catchment (241 Creek) that has been harvested since the mid-1990s. Each watershed has an approximate catchment area of 5 km^2 and a mean elevation of 1,750 masl.

The Water Survey of Canada has had continuous hydrometric monitoring stations on the 240 Creek (ID 08NM240) and 241 Creek (ID 08NM241) since 1984. Daily precipitation and temperature data is available since 1983 via the UPC data repository (Moore et al., 2021b).

Results

East BC Mine Site watershed

During the first year of monthly precipitation, temperature and runoff data were used to calibrate the USGS model. Modelled runoff in the first year has an excellent match with observed runoff, with a Nash Sutcliffe Efficiency (NSE) (Nash and Sutcliffe, 1970) of 0.98 (Figure 1). Generally, an NSE of greater than 0.80 is considered to be a good match in hydrological modelling studies.

However, when the calibrated model was used with the second and third year of data, modelled runoff was unacceptably different from observed runoff, with negative NSE values (Figure 1), which are representative of conditions where the mean annual runoff would be a better predictor than the model.

This discrepancy in model performance is primarily due to unreliable (erroneous) precipitation data during the first year of climate data collection, when the climate station had not been properly equipped with a wind shield and therefore substantially underestimated the precipitation totals. A model accurately calibrated to this one year of erroneous data would be greatly unreliable to predict runoff in the following years.

North BC Mine Site watershed

The first- and second-year data, including reliable climate and streamflow data, were used to calibrate the USGS model. Modelled runoff in the first and second years had an excellent match with observed runoff, with NSEs of 0.94 and 0.98, respectively (Figure 2). However, when the model was run with the remaining 15 months of data (i.e., the third year and three additional months), the NSE decreased to 0.70; the model failed to capture the rainfall-induced high flow in the last month of November (Figure 2).

In this case, although two years of reliable data were used to accurately calibrate the model, the two-year period of modelling calibration happened to lack a distinct feature of nival hydrologic regimes in BC: rain-induced high flows in fall. Therefore, the model was not trained to simulate such high flows.

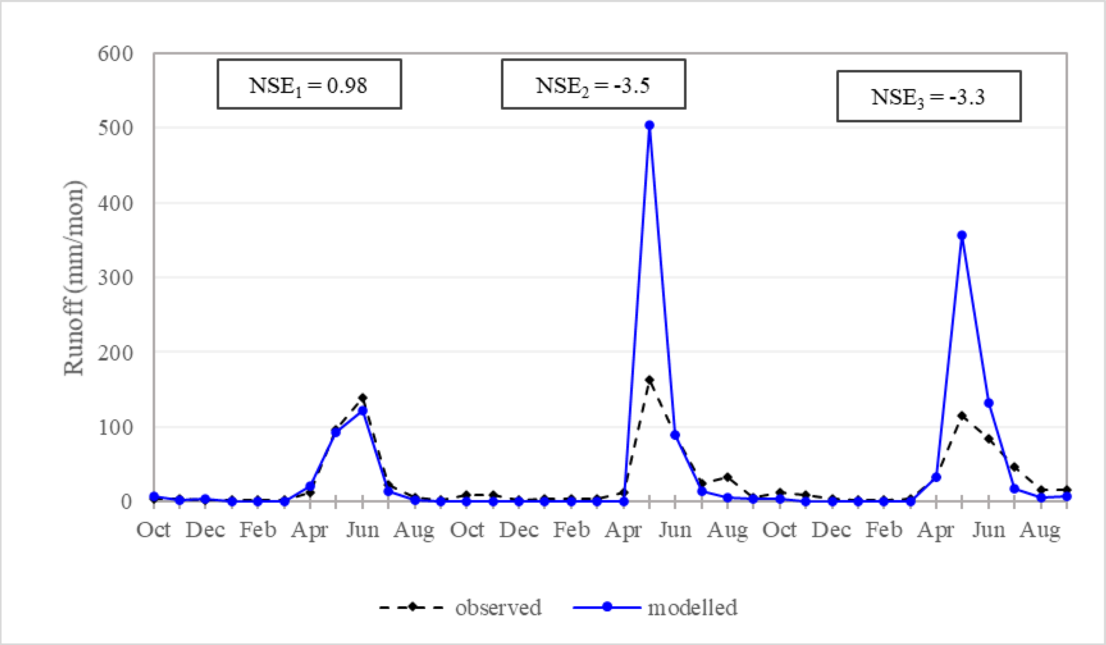

Figure 1: Observed and modelled monthly runoff at East BC Mine Site watershed

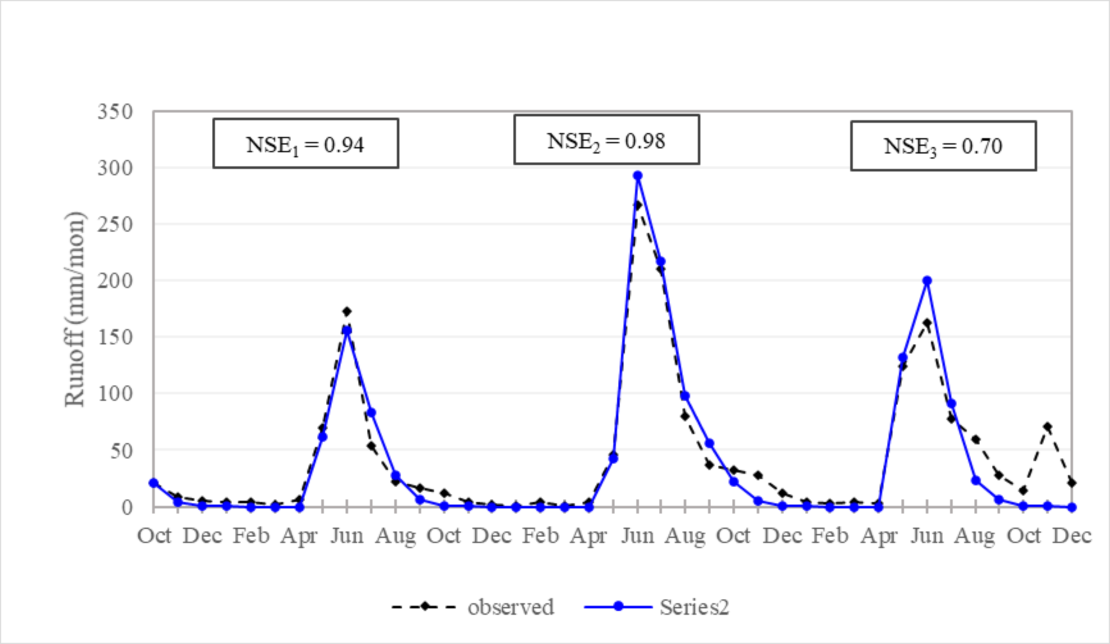

Figure 2: Observed and modelled monthly runoff at North BC Mine Site watershed

Upper Penticton Creek Study watersheds

In this case, 32 years (1984–2015) of reliable climate and streamflow data were available. The USGS model was primarily trained (calibrated) with the first 15 years of data (1984–1999). There was an excellent match between modelled and observed runoff, with NSE of 1.0, for both the 240 Creek and 241 Creek watersheds. Due to the large number of years included in this analysis, as well as the presence of two sets of observed runoff values for the 240 Creek and 241 Creek watersheds, the results are better visualized in a box and whiskers graph (Figure 3).

When the performance of this calibrated model was tested for the 2005 to 2014 period, modelled and observed runoff at the 240 Creek watershed (i.e., undisturbed control catchment) still showed a very good match, with an NSE of 0.90 (Figure 3). However, the 241 Creek watershed (i.e., the catchment with 50% harvested area) showed a weaker match between observed and modelled runoff, with an NSE of 0.81 (Figure 3). Spring freshet high flows (in May) at the 241 Creek watershed are higher than those of the 240 Creek watershed. This flashy high-flow response is an expected outcome when a large portion of a catchment has been harvested. In addition, the reduced vegetation yielded flashier overland runoff in May. The 241 Creek watershed likely has less soil water storage to be released in June than that of the 240 Creek watershed (Figure 3).

A notable observation was made for winter flows in 2005, which were substantially higher than the winter flows of all other years in both the 240 Creek and 241 Creek watershed. An example showing the 240 Creek flows in 2005, as well as the preceding and proceeding years, is provided in Figure 4. As seen in Figure 4, the model was unable to simulate this event of increased winter flow, and confused it with a rain-driven high flow in late fall. Although the main reason for higher-than-normal winter flows in 2005 is not known to the authors, it signifies the fact that the lumped conceptual model that was trained with the 1984–1999 data did not properly conceptualize the physical process responsible for the higher-than-normal winter flows experienced in that year.

Thus, even though the conceptual model performed well for the 1984–1999 period, during which time the processes responsible for flow generation can be assumed to be similar based on model performance, the model performed less well when processes different than those previously modelled occurred. Based on this, prediction of future runoff response under climate change, where flow generation processes are expected to change, will be less reliable.

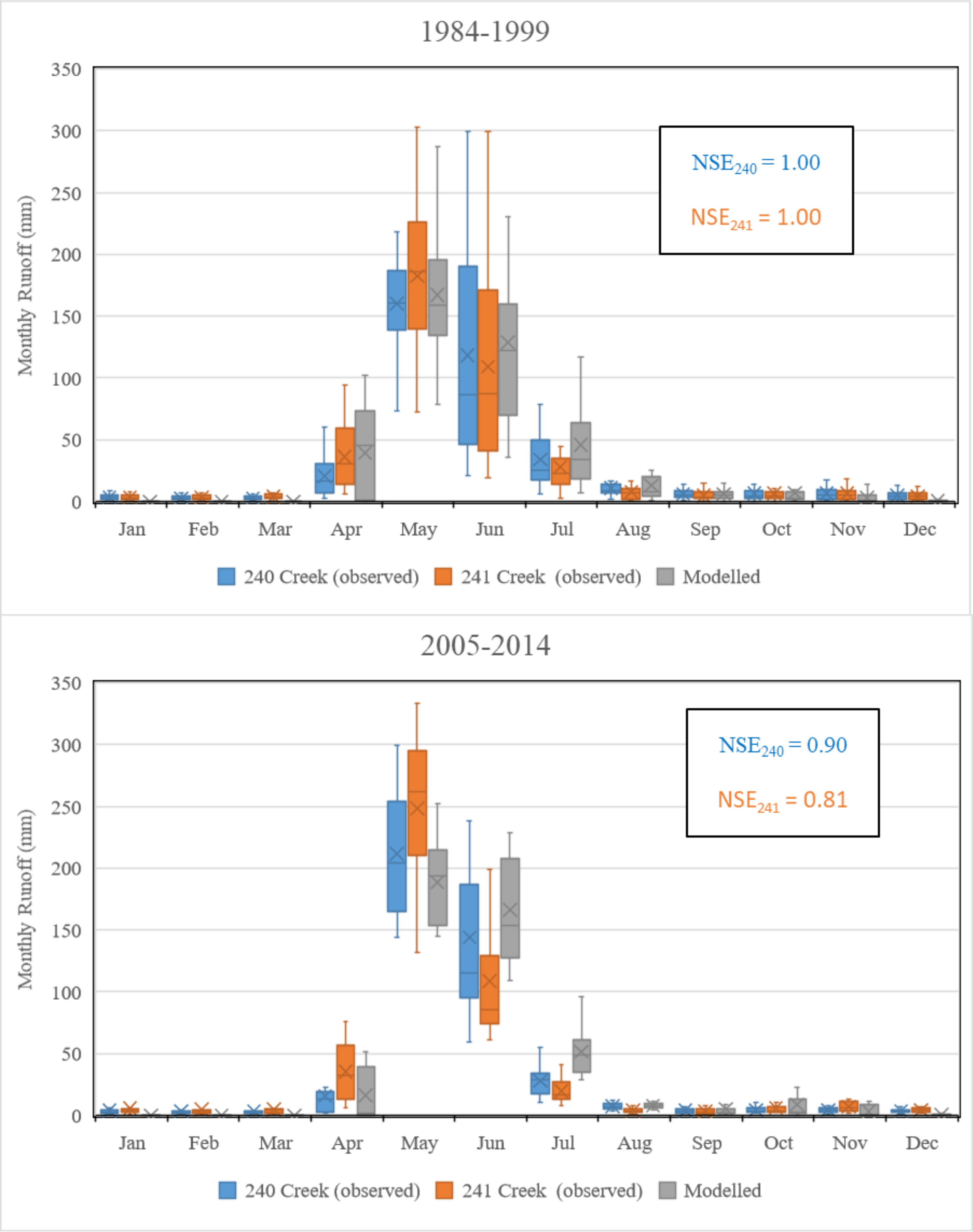

Figure 3: Visual statistical distribution of observed and modelled monthly runoff at upper Penticton Creek watersheds

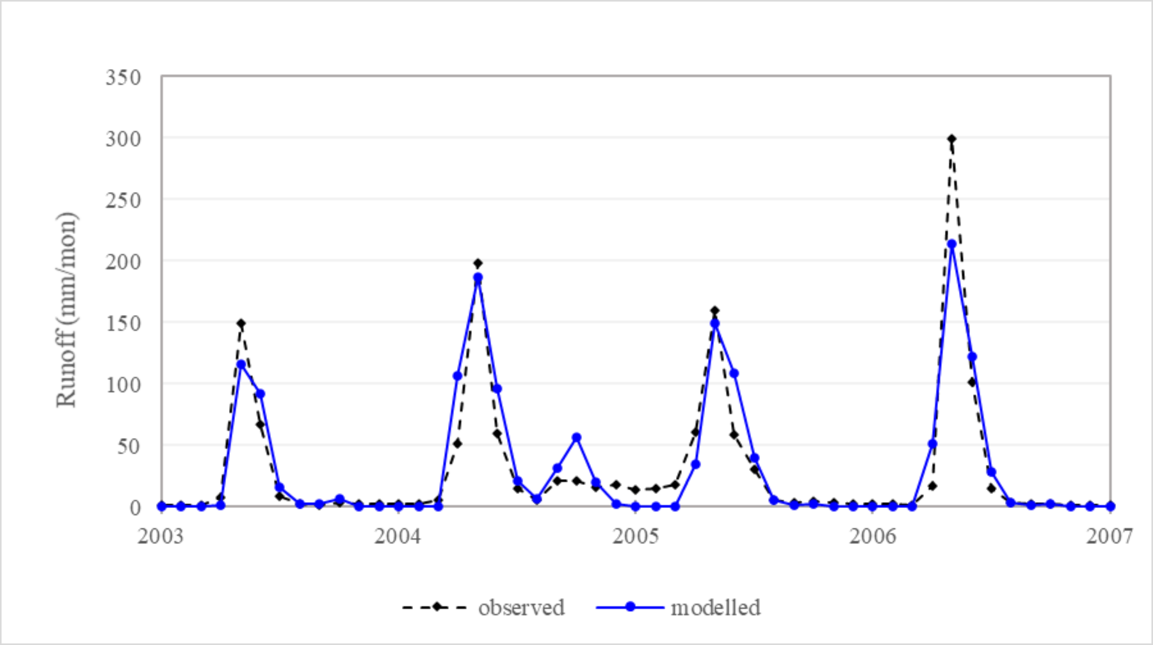

Figure 4: Observed and modelled monthly runoff at 240 Creek watershed, demonstrating high observed winter flows in 2005

Discussion – Runoff from undisturbed catchments vs. contact water from mining components

Combined saturated and unsaturated, physically-based models to simulate these flow pathways are not within the scope of this work. Nor are sufficient data required to reliably calibrate such models available in most mining projects. In the absence of such models, a set of conservative assumptions tailored for the purpose of the study should be made.

Results of the UPC watersheds model showed that a model calibrated to observed runoff from an undisturbed catchment was not reliable for modelling post-disturbance conditions. This illustrates that even when disturbance is as simple as vegetation harvesting, models calibrated to existing conditions do not perform well when conditions change. In the case of mine components (e.g., a waste rock dump), the hydrologic responses are conceptually different from those of undisturbed catchments. For example, the hydrologic response of a waste rock dump to precipitation includes a portion that flows overland, and a portion that infiltrates into the dump. From the infiltrated portion that flows through a combination of macropores and soil matrix, under a combination of unsaturated and saturated flow conditions, a fraction seeps from the toe of the dump and the remainder recharges to groundwater. These three pathways (i.e., overland flow, toe seepage, and groundwater recharge) cannot be reliably simulated with a lumped conceptual model calibrated with undisturbed catchment data.

In the absence of reliable physically-based models, and given the shortfalls of using the undisturbed catchments model as explained above, a simplistic approach typically used for mine site catchments can be incorporated with sufficient, conservative assumptions. In this simplistic approach, coefficients are applied to the annual precipitation to estimate the annual overland flow, toe seepage, and groundwater recharge. The sum of these three coefficients would be equivalent to total runoff coefficient. Resultant annual values for overland flow, toes seepage, and groundwater recharge are then applied to presumed monthly distributions for each of these three pathways to estimate monthly values for each pathway. Assuming that the purpose of an example study is to model the effect of discharging contact water generated from a waste rock dump into a receiving environment waterbody, the following considerations should be taken into account with this simplistic approach:

- Higher coefficients (as explained above) would result in higher modelled contact water values, which would be more conservative than lower modelled contact water values because they would overestimate the effects of contact water effluent discharge into the receiving environment. Observed annual precipitation and runoff values in the UPC watershed show an average annual runoff coefficient of 51% (Table 1; 395/770 =51%). For effluent water quality effects assessment, the overland flow, toe seepage, and groundwater recharge coefficient should be selected in such a way that the sum of them is greater than 51%.
- Toe seepage and groundwater recharge flows pick up more geochemical loads than overland flow. Therefore, it is more conservative to assume more toe seepage and groundwater recharge, and less overland flow.
- Winter low-flow conditions are generally the sensitive months of the receiving environment because they provide the least background flow for mixing with contact water effluent discharge. In such cases, less flashy (i.e., more uniform) hydrographs for contact water, which would assume that contact water store and release is more attenuated than a natural catchment, would be more conservative because they overestimate contact water effluent during winter low-flow conditions.
- The assumptions above would not be conservative if the purpose of the study was, for example, designing the capacity of the contact water collection pond.

If the example study above were to be in the UPC watersheds, the following example assumptions would make a set of plausible contact water estimates:

- Overland flow, toe seepage, and groundwater recharge are 25%, 30%, and 20% of precipitation, respectively. They add up to 75% of precipitation, up from 51% for undisturbed catchments.
- Overland flow can reasonably be assumed to have the same monthly distribution as that of rain and snowmelt. Monthly distribution of toe seepage can be assumed to be the same as total runoff from

undisturbed catchment, and groundwater recharge can conservatively be assumed to be uniform (which means higher contact water during winter low flow conditions).

The results of these assumptions for overland flow, toe seepage, and groundwater recharge, as well as the resultant total contact water, are shown in Figure 5. The figure also shows runoff from undisturbed catchments that is less than the total contact water estimates in all months, especially during the winter low-flow months.

These coefficients and monthly distributions are examples, based on the experience of the authors with similar settings. Uncertainty in such assumptions would be better characterized if such fixed values were replaced with probabilistic values. Figure 6 shows an example where the fixed values used to generate the hydrographs in Figure 5 were replaced with probabilistic values. This probabilistic (box and whiskers) graph provides more information than Figure 5 in terms of the plausible range of contact water generated in each month of the year. This probabilistic approach (i.e., presentation of a range of plausible outcomes) can support both mine planning and regulatory purposes based on the risk perspective of the reviewer.

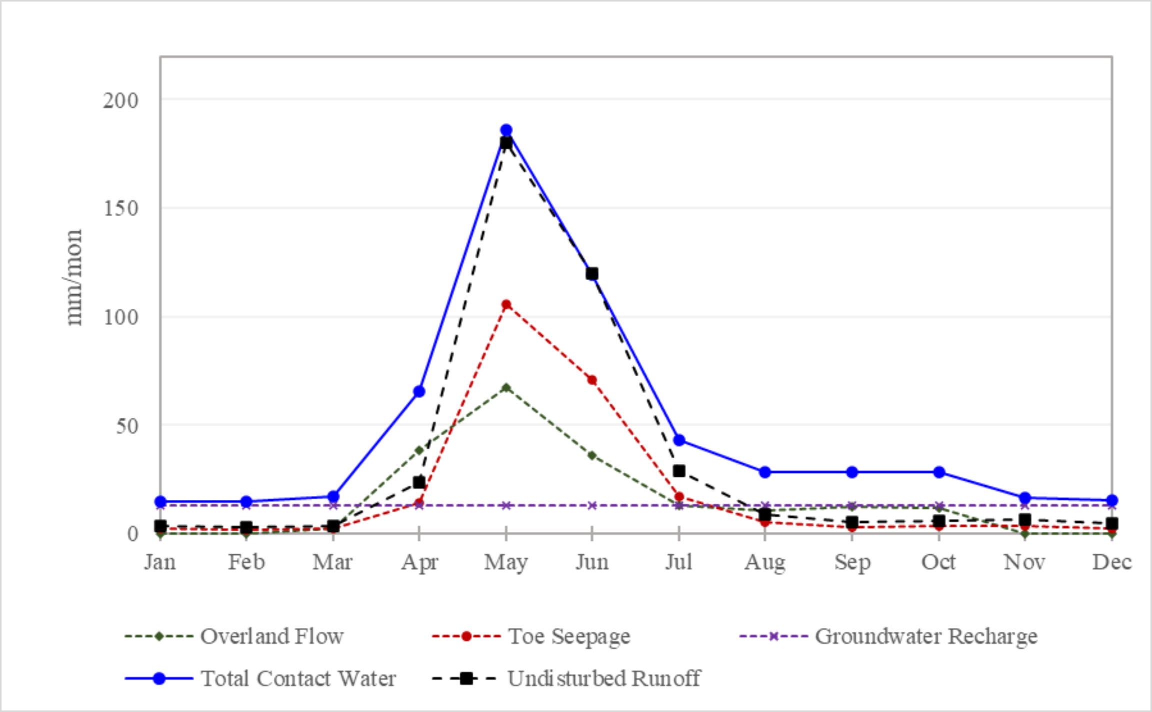

Figure 5: Example comparison of total contact water and undisturbed runoff with data from the UPC watersheds model

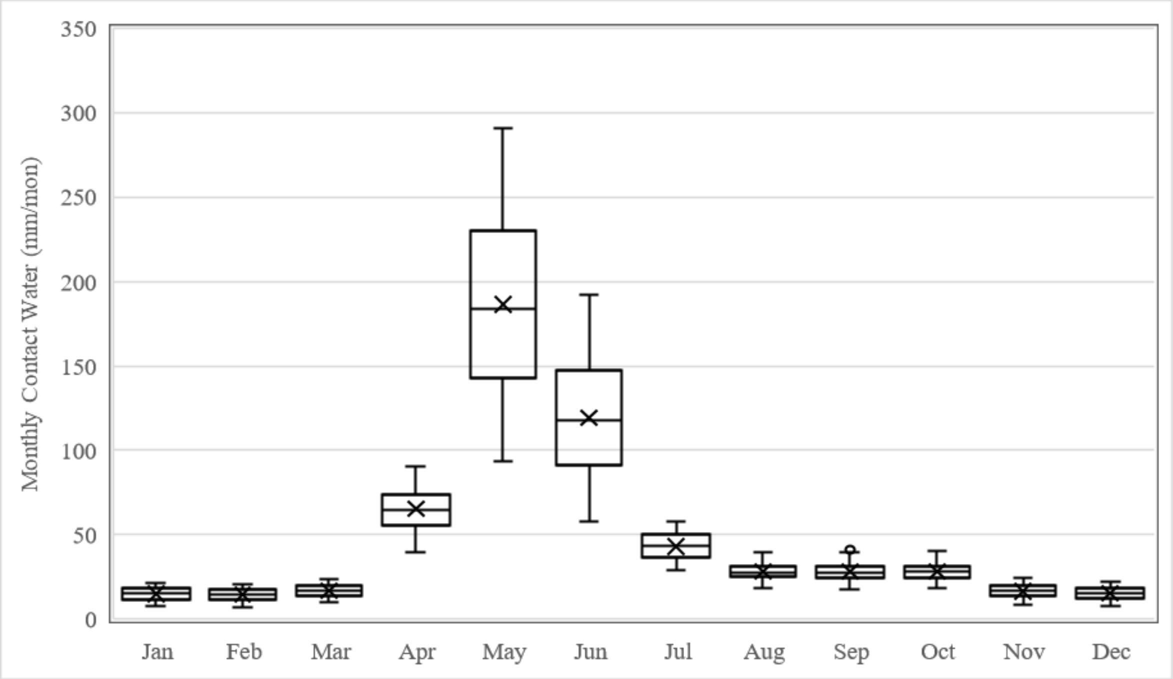

Figure 6: Example for visual statistical distribution of total contact water at upper Penticton Creek watersheds

Conclusions

Reliably monitored climate and flow data are the backbone of reliable modelling results. This study intentionally included one year of unreliable (erroneous) precipitation data in one of the three example studies to demonstrate the implications of such data to model results. Implementation of provincial and federal guidelines in installation of monitoring stations, as well as data collection and analysis, is the most important step of any water balance assessment, and if missed, cannot be compensated with modelling effort.

In development and calibration of runoff models, instead of focusing on an accurate numerical match between the observed and modelled flows, emphasis must be put on confirming that the model reliably generates the known hydrologic responses in a study area. For example, the model must reasonably demonstrate the snowmelt-driven rising limb of the spring freshet, post-freshet recession limb, rain-driven punctuated flows in fall, and winter low flows, given the range of known temperature in the region.

Lumped conceptual models for runoff from undisturbed catchments do not reliably simulate contact water generated from mine components, which are conceptually different from those of undisturbed catchments. Physically-based models capable of simulating contact water from such mine components are data intensive, and even then, they may not provide reliable results. The data required to properly parameterize these models is typically not achievable given the budgets available to mining projects. In the absence of such models, conservative assumptions should be made for contact water generated from mine components.

It is important to bear in mind that a conservative assumption for one study (e.g., effects of contact water discharge into receiving environment) may not be conservative for another study (e.g., estimating the capacity of a contact water collection pond). Likewise, incorporating a probabilistic approach, rather than using fixed-valued assumptions, allows for a better characterization of modelling uncertainty.

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Industrial-Scale Non-Biological Selenate Removal – Examples of Plants and Criteria behind Process Selection

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Abstract

The environmental impacts of selenium are complex and highly dependent on the type of receiving environment. Modern regulations stipulate not only water quality limits but also fish tissue criteria to measure success. Every mineral deposit is different and methods of extraction, tailings management, and waste rock handling vary from project to project. Moreover, the reliance on dilution to meet environmental compliance is often no longer socially acceptable. It follows then that selenium management is not conducive to a "one-size-fits-all" approach. Until recently, all large-scale selenium treatment systems in mining used some form of biological removal, with several hard lessons learned along the way. These include: constant reliance on dilution to meet water quality requirements in the receiving environment; the production of fast accumulating organo-selenium compounds by bacteria; concerns about the long-term stability of selenium in biological treatment residues; and poor treatment performance in situations with variable flow and water quality.

Following a decade of testing and development, non-biological selenate removal is now being applied on a large industrial scale to avoid the shortcomings of biological systems. The first three industrial-scale non-biological systems using electro-reduction of selenium combined with either ion exchange or membrane filtration have been commissioned between 2020 and 2022. As these systems are very new, the operations experience is still limited. However, performance to date matches design expectations, and the experience from these projects can help establish criteria for selecting non-biological over biological treatment options.

Introduction

Selenium released from mining operations is known to produce environmental impacts through chronic toxicity caused by bioaccumulation. Consequently, modern regulations (US EPA, 2016; BC WQG, 2017; Alberta Government, 2018) not only stipulate water quality limits but have also established fish tissue criteria to measure success with selenium management in the long term. At the same time, the mining industry has been under ever-increasing scrutiny by both the public and government regulators for using dilution as part of the management and/or storing of selenium-laden residues onsite in perpetuity. Until recently, all selenate removal systems applied in mining were biological, and the experience collected from these revealed multiple weaknesses and shortcomings, including:

- Constant reliance on dilution to meet water quality objectives in the receiving environment (NAMC SWG, 2013; NAMC SWG, 2020).
- Production of organo-selenium compounds that worsen the impact of selenium due to much faster uptake by aquatic organisms, which accelerates trophic transfer to fish tissue (LeBlanc and Wallschläger, 2016; Sandy, 2016; Phibbs et al., 2011).
- Risk of release of plumes of nutrients leading to low dissolved oxygen in the receiving environment (Teck Coal Limited, 2015).
- Lack of proof of long-term stability of selenium captured from water fixed in biological residue.
- Poor adaptability to variable water flow and quality.

Between 2012 and 2015, BQE Water was approached by several mining companies that recognized that one or more of these shortcomings might prevent them from successfully developing and operating their projects. This provided the impetus for developing a non-biological treatment approach to manage selenate. This started with proof-of-concept laboratory testing, followed by six years of pilot demonstrations on waters with a wide range of quality and an industrial-scale demonstration (Littlejohn et al., 2017; Mohammadi et al., 2016). The effort culminated in the design and construction of three industrial-scale plants. The non-biological selenate removal technology has now been recognized by Environment and Climate Change Canada as a treatment technology for selenium (Environment and Climate Change Canada, 2022).

All three plants were successfully commissioned and entered operations between 2020 and 2022. Experience from developing and implementing non-biological selenate removal helped us establish criteria that can be used by industry to determine whether non-biological treatment presents a good technical fit for individual projects.

Kemess selenium treatment plant in Canada

Project requirements

At this site, surface runoff, waste rock seepage, and underground mine water are collected in the existing open pit that will serve as the new tailings storage facility (TSF) once the new underground mine is developed. When in production, the mine is expected to discharge excess water from the TSF into the environment.

During permitting, representatives of indigenous groups stipulated that mine discharge must report to a specific creek and that the project cannot rely on dilution to achieve the water quality limit of 2 ppb for selenium. This meant that one of the key requirements for the treatment system was the ability to meet the receiving environment objectives at the end-of-pipe. Speciation completed on selenium contained in the open pit confirmed that more than 90% of total selenium was selenate, with the remainder being selenite. The second main requirement was that the solid residue produced by treatment must be stable and suitable for co-disposal with tailings in the TSF. Although the treatment system needs to remove selenium and different heavy metals, this paper will focus only on the removal of selenium. Water quality parameters salient to the design of the selenium removal system are shown in Table 1.

Table 1: Feed water quality for Kemess Selen-IX™ plant

Constituent of concern	Feed concentration (ppm)	End-of-pipe target (ppm)
Sulfate	350 to 2100	None
Selenium	0 to 0.120	<0.002
Nitrate	0 to 25	None

Table 1 shows that no end-of-pipe targets were established for sulfate and nitrate. This was due to the fact that, unlike with selenium, no objection was raised to using dilution for nitrate and sulfate in the creek. This highlights the unique role selenium has as the constituent of concern for local communities who understand the outsized risk of the long-term consequences of selenium – that once released, it could persist in the environment and create multi-generational impacts through bioaccumulation. The Selen-IX™ non-biological process for selenium removal was successfully pilot tested during permitting, and the stability of the solids was evaluated using humidity cells containing blends of tailings with solids simulating conditions in the TSF.

Since the 2 ppb limit has never been achieved by any industrial-scale selenium removal plant, the decision was made to first build the water treatment plant to demonstrate the ability to manage selenium already present in the site water, before developing the new deposit that would release additional selenium.

Description of treatment system

Figure 1 presents a block diagram of the Selen-IX™ process, which consists of two circuits: ion exchange (IX) and electro-reduction circuits (ERC). The purpose of IX is two-fold: 1) use resins to selectively remove selenate from feed water and produce effluent containing less than 2 ppb of residual selenium for discharge to the environment and 2) to concentrate the selenate into a small volume of brine solution. The brine, mostly Na_2SO_4, is processed through the ERC circuit. The purpose of the ERC is also two-fold: first to remove selenate from the brine and fix it in a stable residue; and second, to produce brine sufficiently depleted of selenate to allow for its re-use in resin regeneration in IX.

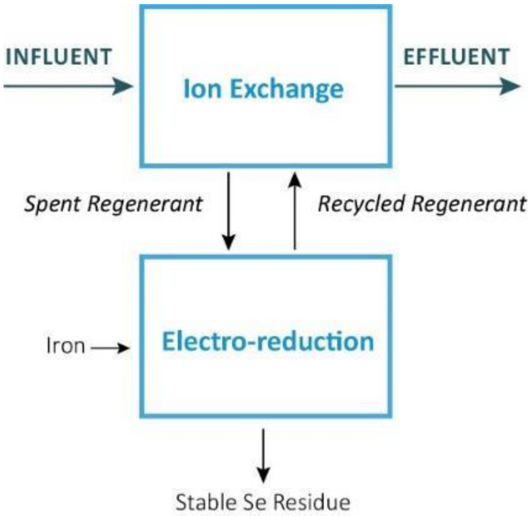

Figure 1: Block diagram of Selen-IX™ process

Any selenite that may be present in the plant feed is removed via ferric iron co-precipitation upstream of Selen-IX™. While this co-precipitation process is part of the treatment plant at Kemess, the focus of this paper is on the removal of selenate, as selenite co-precipitation is a well-established conventional process.

Figure 2: IX and ERC circuits – Kemess Selen-IX™ plant

Figure 2 shows the IX vessels and electrocells installed in the IX and ERC circuits at Kemess used for the selective removal of selenate.

Operating results

The operating results are summarized in Figures 3 and 4. Figure 3 shows the influent and effluent selenium concentrations. Figure 4 shows the concentrations of selenium in the IX regenerant entering and exiting the ERC circuit.

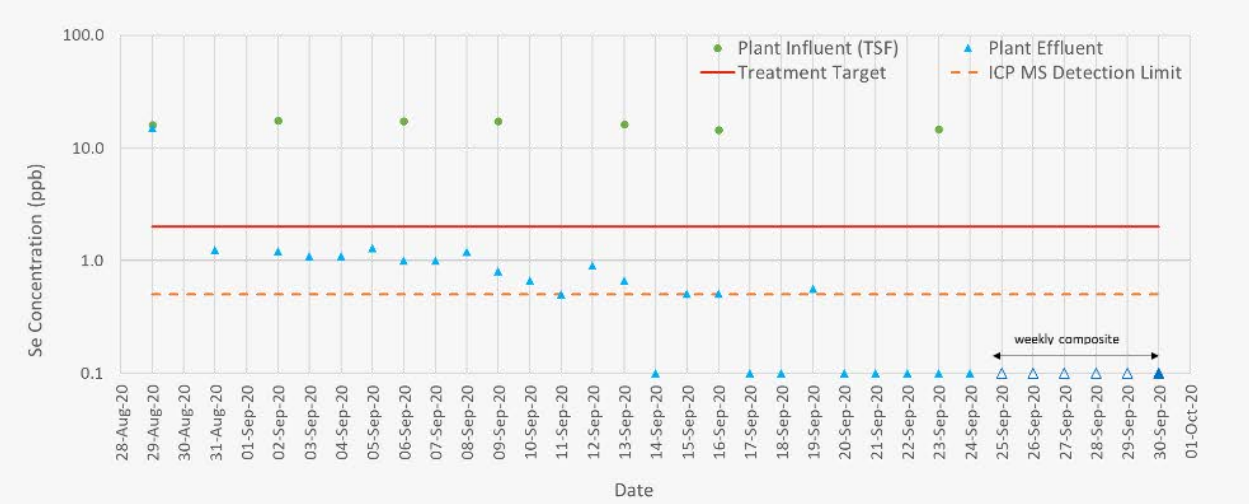

Figure 3: Selenium concentrations in plant feed and end-of-pipe discharge

As shown in Figure 3, the Selen-IX™ process not only achieved a consistent selenium removal to below the target of 2 ppb, but also demonstrated on an industrial scale that selenium levels below the ICP-MS reporting limit of 0.5 ppb are possible.

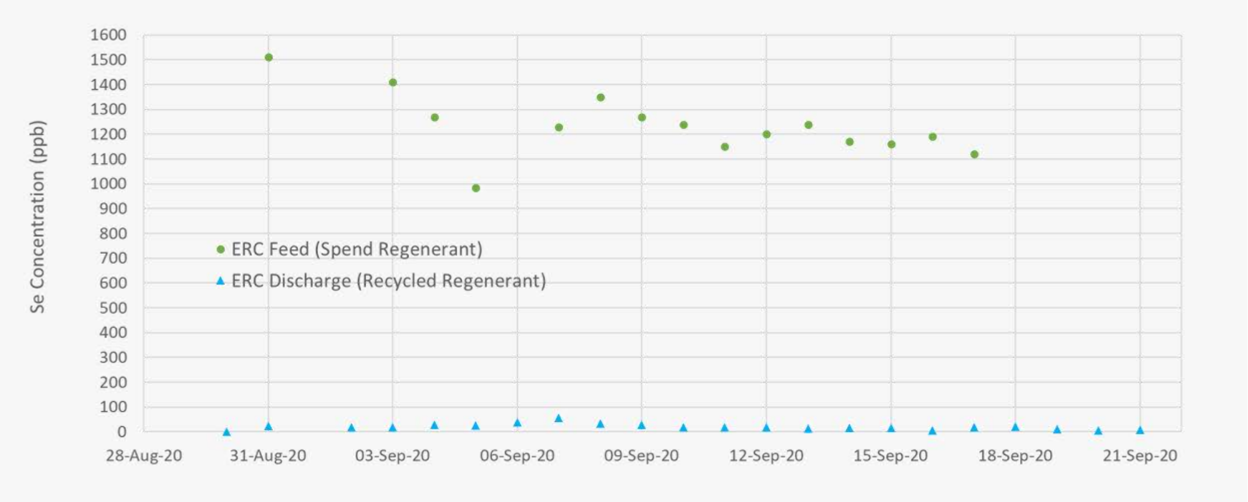

Figure 4: Selenium concentrations in IX regenerating entering and exiting ERC

Figure 4 provides evidence of high-efficiency selenium removal from the IX regenerant into the ERC solids. The concentration in the feed to the ERC circuit of 1.2 to 1.6 ppm shown in Figure 2 provides a direct indication that the IX circuit pre-concentrates selenium by a factor of ~100× compared to selenium contained in the feed. Figure 5 shows a picture of the ERC solids cake that are placed in the TSF. The stability of ERC solids was evaluated during project permitting using humidity cells containing blends of tailings with solids mimicking conditions in the TSF.

Figure 5: De-watered ERC solids to TSF

Following plant commissioning, the plant operated continuously 24/7 for approximately two months. During this period, the IX resin was regenerated and re-used six times, while the entire inventory of regenerant solution was processed and recycled more than 60 times, indicating a steady state was reached. Values for Key Performance Indicators were also validated with all criteria matching design expectations.

Current project status

Following commissioning and operation in the summer and fall, the plant was shut down for the winter in Q4 2020. Subsequently, plans for the construction and development of the new underground mine were put on hold and the water treatment plant was placed in care and maintenance. The permit stipulates that the treatment facility operate only during mine construction and operation. During care and maintenance, waste rock seepage water containing selenium is collected and stored in the existing open pit. And while under care and maintenance, activities are carried out semi-annually to maintain the plant's operational readiness and ensure that the life of the IX resin is preserved.

Coal ash pond dewatering treatment facility in the USA

Project requirements

This project deals with the remediation of an ash pond at a coal-fired power plant. Ash-generated residue from coal combustion has been stored in a pond where water quality indicates contamination from heavy metals and selenium. The project involves treatment of water that has come into contact with ash, discharge of treated water into the environment, and simultaneous relocation of dewatered ash into a new properly engineered facility for permanent disposal. Key project requirements can be summarized as follows:

- Meet an end-of-pipe selenium discharge limit of 7 ppb.
- Operate to a schedule of 50 hours per week Mondays to Fridays.
- Be able to adjust to highly variable feed water flow and quality.

The client selected non-biological treatment, as it is the only treatment option that could meet the key requirements related to intermittent operation.

Description of treatment process

The treatment process for selenate removal for this coal ash pond is the same as that applied at Kemess and described in the previous section. And similar to Kemess, selenite and heavy metals are removed upstream of selenate removal.

Current project status

This plant was commissioned in Q4 of 2021 and is now operational.

Simultaneous selenium and sulfate removal plant in the USA

Project requirements

This site involves active treatment of tailings seepage and underground mine water. In addition to heavy metals, the constituents of concern include sulfate and selenium. One of the main requirements is for the final effluent to pass whole effluent toxicity (WET) tests using *Daphnia magna* and *Ceriodaphnia dubia*. Notably, due to alternating dry and wet seasons, the treatment system is subject to extreme fluctuations in the volume of water reporting to it. This seasonality affects not only the mine site but also the receiving environment, which cannot always provide sufficient dilution to ensure that water quality objectives in the downstream environment are achieved. Consequently, another requirement is for selenium concentration at end-of-pipe to remain below a 1.6 ppb limit.

Selenium speciation assays showed that virtually 100% of the selenium dissolved in the mine-influenced water is selenate. Table 2 summarizes the feed range of concentrations and their respective end-of-pipe targets for the constituents of concern.

Table 2: Feed water quality and effluent targets

Constituent of concern	Feed concentration (ppm)	End-of-pipe target (ppm)
Sulfate	1,850 to 2,550	720 to 950
Selenium	0 to 0.010	<0.0016

The overall project requirements can be summarized as follows:

- Treatment must be capable of fast ramp-up and turn-down to respond to seasonal flows.
- Meet an end-of-pipe selenium discharge limit of 1.6 ppb.
- Treated effluent must pass WET tests with *daphnia* and *ceriodaphnia.*
- Solid residue produced by treatment must be suitable for co-disposal with tailings.

Description of treatment system

The system uses nanofiltration in combination with a gypsum desaturation circuit and selenium electro-reduction circuit. The purpose of nanofiltration is two-fold: 1) to produce clean permeate suitable for discharge and 2) to concentrate both sulfate and selenium in the retentate prior to further processing. A block diagram of the treatment system is shown in Figure 6.

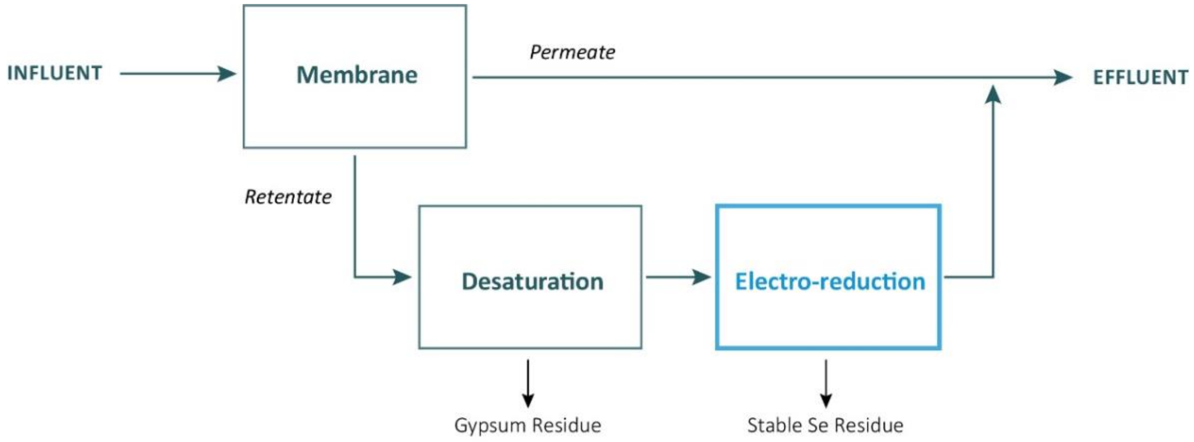

Figure 6: Block diagram of treatment system for simultaneous sulfate and selenium removal

The plant operates at 66% water recovery, which equates to sulfate and selenium concentrations in the retentate approximately 3× greater than in the plant feed. The first step in retentate processing is gypsum desaturation to precipitate solid gypsum. The precipitation is spontaneous and catalyzed by seed gypsum. The discharge from the desaturation stage contains sulfate at gypsum saturation levels of approximately 1,600 ppm. From there the retentate passes through the ERC, where selenium is removed from solution and fixed into a stable and solid residue. The gypsum solids are blended with the ERC solids prior to disposal in the tailings facility.

The ERC design at this plant differs from those utilized in the Selen-IX™ plants. This is due to the retentate produced by nanofiltration having relatively low levels of total dissolved solids (TDS), compared to the IX brine, which reduces the solution electric conductivity. Utilizing the same ERC here would significantly increase power consumption. The unique design feature of the ERC applied to the nanofiltration retentate is that it maintains a constant gap between the cathode and anode in the electrocells – as the anode is consumed, the gap is automatically adjusted continuously. Figure 7 shows the ERC with the constant-gap cells.

Figure 7: ERC with constant-gap electrocells applied to NF retentate

Current project status

The treatment system has been fully commissioned and the plant began operations in April 2022.

Conclusions: Criteria for assessing the technical fit of non-biological selenate removal systems

Selenium management in mining projects is heavily influenced by a large number of site- and project-specific factors. Based on the performance of biological treatment systems and our experience with applying non-biological treatment, the latter represents the only possible option when one or more of the following criteria apply:

- No reliance on dilution to meet receiving environment end-of-pipe limits when the selenium target is at or below 3 ppb.

- Requirement for intermittent or seasonal treatment.
- Proof for the long-term stability of residue containing selenium.
- Project owner preference to ship selenium residue for beneficial re-use off-site.

In addition, a non-biological treatment approach is generally favoured over biological treatment when one or more of the following criteria apply:

- End-of-pipe discharge limit for selenium is below 10 ppb.
- Effluent discharges into a sensitive environment, increasing the risk of impacts caused by constituents introduced into the treated water by biological systems including organo-selenium compounds, nutrients (ammonia and phosphorus), and/or residual BOD and COD.
- Treatment must handle large fluctuations in water flow and quality.

The first three industrial-scale non-biological systems using electro-reduction of selenium combined with either ion exchange or membrane filtration have been commissioned between 2020 and 2022. As these systems are very new, the operations experience is still limited. However, performance to date matches design expectations and the experience from these projects can help to establish criteria for selecting non-biological treatment over biological options.

Acknowledgments

We would like to acknowledge Seabridge Gold, Centerra Gold and IRAP for their respective roles in supporting the development and commercialization of BQE Water's non-biological selenate treatment systems.

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Water in Tailings: A Review of 20 Years of Post-closure Tailings Performance

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Abstract

The mining industry has closed and reclaimed a number of tailings storage facilities, meeting the standards of industry good practice at the time the work was carried out. Subsequent events in the mining world have caused us all to rethink those criteria, and now we see that there are significant subtleties that might escape the caretaker of a closed facility. Many of these are water-related, and this paper serves to point out some things to consider as we update our criteria, modify our practices, and upgrade these facilities in the future.

The fact that these facilities have been in place for many years is encouraging, and one is inclined to take comfort that nothing has gone wrong. But our conceptualization of how tailings storage facilities perform in the long term has been called into question over the past ten years or so. Today's approach is to be more conservative, given that, despite all the improvements in test methods, analyses, etc., dams are still failing. We should perhaps put less faith in chance, and pay more attention to the consequences of a failure, should it occur. When one adopts that approach, the elimination of critical failure modes is an imperative, as is thinking through what would happen should the future not manifest as we predict it to.

This paper discusses seepage and groundwater impacts; freeboard and flooding; and draindown and strength gain.

Introduction

The observations of the authors are based on the review of a number of tailings storage facilities in the past five years leading up to, and in response to, the global industry standard on tailings management (GISTM), which is now being adopted by a majority of mining companies and endorsed by the risk management and finance community. The key finding of note here is the critical role that water plays in the performance of the materials themselves and the structure as a whole.

Conventional tailings disposal involves decantation of a slurry in a large reservoir, recovering the water for re-use, and settling the solids into a stable mass. Some facilities were constructed in valleys, adopting geometries suitable for water dams and impounding runoff from areas upstream of the dam. Without fail, the early facilities discharged impacted water to the aquifer and in some cases to surface waters downstream. The volume of water contributed to the aquifer over the operating life of the facility dwarfed the seepage since operations ceased, making source control now a somewhat token gesture unless the tailings have more recently become more reactive and seep water quality has deteriorated significantly.

A second topic of interest to the design engineer is that of the design basis: how have the set of assumptions made by the designer stood the test of time? We have the benefit of far larger bodies of climate data, so we can refine our estimate of the design storm, for example. At the same time, our collective appetite for risk is lower and some facilities, considered state-of-the art when constructed and later decommissioned, do not meet today's standards.

In the case of dams built using the upstream method, the tailing material itself formed the outer shell of the facility, resulting in a heterogeneous mass. Uncertainty about the material properties in key structural zones has caused many owners to investigate and re-evaluate the dams. One of the more common findings of these investigations of older facilities is that while the assumptions about draindown, consolidation, and strength gain are generally valid, in certain key zones the fine-grained materials may retain enough moisture to behave poorly under seismic loads.

The three broad themes are somewhat related, as will be apparent from the following discussion. The work of the tailings engineer requires an understanding of all these topics: how the materials and water interact, and how the resulting landform will behave under the stresses nature imposes on it. This is interesting.

Chemistry and time

The most significant shift in thinking over the past 20 years has been regarding how we define our timeframe of concern. A common approach was to externalize the potential future impacts because the rules and practices at the time allowed us to do that. We put a limit on our evaluation of what are essentially geologic processes occurring in a geologic timescale, framing the problems in something we could understand: our lifetime. Now we clearly see that the facilities in our care will outlive us and we should think in terms of the lifetime of the tailings storage facility.

The system we interrupted to extract the mineral wealth will recover to some new equilibrium. How fast the system re-equilibrates depends upon how much fuel is in the fire, so to speak, and water is the great diluter and flusher of the products of any chemical reactions. In many cases interventions have been put in place to limit the rate of reaction (covers), limit the flow of water through the reactive material (shaping and covering), and to intercept impacted water to limit impacts to receptors downstream. Now we have evidence as to the effectiveness of these interventions (and they are effective), but we have learned that in some cases they may be required permanently, rather than for the finite time we anticipated. The upshot is that "closure" is not a thing we do once, but rather for a very long post-mining period. As water is the primary vehicle for mobilizing minerals through our environment, managing the influx, reaction with, and egress of water is of primary concern to mining companies.

Groundwater

Environmental and demographic shifts cause us to see the value of groundwater differently now than we did in the past, and miners are held to new standards with respect to quality and availability. The right to contaminate is being challenged, and levels of contamination previously considered innocuous may no longer be acceptable.

Tailings chemistry and water

The chemistry of tailings water is first a function of the process used to extract metals and later a function of the mineralogy of the material itself. When the tailings are first deposited (historically always as a slurry) the water chemistry is dominated by the residue of whatever chemical reactions were employed to separate the metal values from the residual tailings. Later, as that process water drains and is further flushed from the system, the chemical signature shifts towards a function of the mineralogy of the tailings material itself, how available those minerals are to react, and how fast they react.

Water plays a key role as the flushing agent. When the flow is great enough that the tailings approach saturation, water acts as an inhibitor of chemical reaction. This is because most mine drainage needs oxygen.

In arid regions

Where water is scarce (in very dry regions) the reactivity of tailings may be less important as the contribution of mine drainage to the aquifer is small after deposition ceases. However, aquifers in arid regions may be quite sensitive to mine water impacts, and the groundwater resource is prized because it is a scarce resource. So it is incorrect to say that water is less of an issue in arid regions.

A significant volume of water with the process-water fingerprint may be (or may have been) discharged to the environment during operation of the facility, although more modern installations include measures to limit seepage losses and recover seep water for re-use. This plume of impacted water, once sent on its way, cannot be mitigated though source control, the principal source having been shut off when deposition of tailings ceased. The impacts of this body of process water can be seen for many years as the aquifer accommodates the additional water and chemical mass, and mask the impacts of the much smaller flow of mine drainage that follows.

When the tailings drain and (over a long period) the process water is flushed from the system, air (oxygen) will enter the pore spaces and react with the minerals in the tailings. Although the material may be highly reactive and the resulting drainage of unacceptable quality, this can often be managed by limiting the ingress of water so that the products of the reaction are not flushed into the groundwater at an unacceptable rate.

In high rainfall regions

Where there is an adequate supply of water it has sometimes been convenient to use a body of water as a cover for tailings, either by depositing tailings in a natural lake or placing tailings in a reservoir behind a dam designed for the purpose. In such a case there will be a large volume of water in contact with the tailings, but very little oxygen will be available to fuel any mine drainage generating reactions.

These facilities have performed well and are an effective way to limit the impact of reactive tailings. The desired performance depends then on the safety of the dam and the management of the water cover. Together these constitute a very long-term obligation on the part of the owner to maintain the dam, procure the water, and manage the quality of the excess surface water passing through the system.

The common case

Reactivity is limited when water is abundant enough to cut off access to oxygen, resulting in reasonable water quality. Reactivity is favored when water is scarce and oxygen can enter the pore spaces, but the contribution to the environment may be small. Challenging situations arise when there is a periodic pulse of water to flush the products of oxidation into groundwater. Most installations fall somewhere between the extremes and encounter this challenge, with the potential impacts of the smaller periodic flow masked initially by the much greater flow of process-related water. In any event it can be many years before a system achieves some steady state and the effectiveness of the controls can be validated. During that time it is quite possible that the goal posts with respect to groundwater protection move, making this an even more challenging issue.

Surface water

Modern tailings facilities tend to be built so that the upstream catchment area is small and the risk of inundation by a storm limited. That was not always the case in the past. The cost of initial construction is influenced greatly by the size of the dam, and the effort to subsequently raise the dam is a function of the crest length. Placing tailings in an existing valley makes for an efficient storage facility, but potentially with a greater risk of inundation.

Several factors influence our current thinking with respect to surface water management. A quick review of tailings dam failures illustrates that where water was impounded the flow was greater and went further. From a dam safety perspective then, unless the facility is designed to do so it is now considered good practice to avoid storing water in the facility. As discussed above, unless the water cover is permanent it is not advantageous chemically to have fluctuating water levels (in the case of tailings varying extent of the pool), as alternate wetting and drying can lead to poor quality seepage to groundwater. A third consideration is how much water one needs to store to avoid overtopping the dam in an unacceptable way, and our understanding of the design flood has changed.

The design storm

Flood hydrology used to be based on a set of real data manipulated using statistical methods to arrive at an estimate of rainfall duration, intensity, and quantity. The techniques are not flawed, but we continue to be frustrated by new data that tends to challenge how we predicted things would be. The big manifestation of this is the transient nature of the weather patterns we based our predictions on – tomorrow's weather may not follow yesterday's pattern. The only reliable assumption is that we will likely be proven wrong, in the very long term.

The GISTM requires that we manage the tailings facilities, protecting them from the effects of earthquakes, floods, and general weathering. In the past local regulations were considered adequate and a 1:100 year or 1:200 year storm (beyond our lifetime) was considered adequate. Now that we have accepted that these facilities will need to remain intact, to be protective of the environment, for much longer, and that a 1:100 year event can actually occur *in our lifetime*, it is customary to consider the 1:10,000 year event or the probable maximum flood. Calculating the 1:10,000 year event statistically is a challenge, and it is becoming more common to estimate the probable maximum runoff using temperature and humidity and precipitation data compiled globally, making some allowance for the climate trends we are observing.

Runoff

The impact of a precipitation event is a function of the rate at which runoff arrived at the impoundment and either needs to be contained or conveyed through the facility and over the spillway. In colder climates the greatest runoff is experienced when a rain event melts the accumulated snow and the combined mass of water arrives together. As our climate warms we are likely to experience more rain-on-snow events during the spring thaw.

Another climate- or environment-related factor is fire. Storms following shortly after a large burn in the catchment area can result in significantly greater runoff and runoff intensity than anticipated. Under these post-fire conditions the sediment load might be significantly greater than originally considered, causing the hydraulic performance to vary from that anticipated in the design.

The design flood

New approaches and guidance (Canadian Dam Association, for example) as to how the design storms are estimated have led to the re-evaluation of the design of freeboard and spillway capacity. Hydrologists today estimate the inflow design flood (IDF) and environmental design flood (EDF) by determining the combination of duration and frequency, including rain on snowmelt events that produce the greatest volumes, peak flows, and resulting hydrographs. The storm hydrograph is different today as it considers climate change and the available site-specific climate data gathered since closure. We are now faced with the question of whether we upgrade spillways and raise dams to accommodate very low likelihood events, when facilities were closed in good faith according to the criteria of the day. Considering these facilities may exist to perpetuity, one can expect that each generation of engineers will be faced with this question, for marginal reduction in risk.

Passing a greater inflow design flood (IDF) may require a larger spillway or additional backwater capacity. This is influenced less by the total volume of the flood and more by the peak intensity and how fast the flood can pass through the impoundment and over the spillway. This can be limited by the spillway capacity, volume of the impoundment, and in some cases the capacity of the receiving waters downstream.

The environmental design flood (EDF), which is the quantity of water to be stored without treatment (below the spillway invert), is also affected by changes in guidance and approach. EDF storage is required in tailings facilities that have water covers, either for ARD control or radiation protection, and is more common in cooler climates. A greater EDF required additional storage capacity. Where the normal operating level cannot be lowered to make room for larger EDF storage due to other constraints (i.e., such as exposing tailings), facility upgrades such as a raised spillway and crest might be required.

Soil mechanics and water

Water serves as the great lubricant and causes the tailings engineer great concern. In the past it was common practice (and in many cases it remains the practice) to construct paddock dams using the tailings material itself and incrementally raise the tailings storage facility. Classical tailings design presumed that the materials would drain and consolidate after placement. The continued draining and consolidation when operations cease has been relied on to explain how the longer-term design parameters and factors of safety will be accommodated by the structure as it continues to gain strength. The following section relates principally to facilities *built from tailings*, and classic water-retaining structures are a different case.

Hydraulic placement of tailings

Larger (heavier) particles require more energy to be moved, so they tend to settle out first when tailings are discharged at the edge of the impoundment. The finer (smaller and lighter) particles will remain in suspension until the water stills in a pond. Constructing an embankment using hydraulically deposited tailings presumes that the fine and light particles have been carried further from the discharge point, beyond the zone where the strength of the materials influences the slope stability.

Quality control

A tailings storage facility might be constructed over many years, working continuously, day and night, through the range of seasons. The operator must accommodate floods, droughts, stoppages, and changes in material properties as different zones in the ore body are exploited. Today we have video surveillance and satellite-linked instrumentation to aid us, but in the case of some of the older facilities there is a paucity of records indicating how material was placed and what the properties are. What we have found through subsurface investigation and review of available records is that the pond was not always where it was meant to be, was often larger than planned, and the fine material is not always confined to the zones where it would have little influence on slope stability.

Draining, consolidation and strength

Materials placed hydraulically when allowed to drain will experience consolidation and settlement under their own weight and the weight of the materials above them. It is important that they drain so they are not buoyed by the water around them and can come into full contact with the adjoining particles. In a clean sand this is a very effective way of placing and compacting materials so they have a reliable strength.

Fine-grained materials have low permeability and a large surface area, so they tend to let go of entrained water very slowly. At depth there is no evaporation and the capillary forces tend to sustain a state of near saturation: a soil sample will indicate moisture contents near saturation, but a Casagrande-type well will yield no free water. This is not bad in and of itself, but it is inconvenient when this condition is encountered in a zone where this sort of material was not anticipated.

Liquefaction

Our understanding of soil liquefaction continues to expand through laboratory testing and, unfortunately, back-analysis of actual slope failures. Suffice it to say for the purposes of this paper that liquefaction can occur not only when a material is submerged (saturated). Under the right conditions it can occur in soils that are almost saturated – that is, when there is enough water in the pore space to interfere with the stress-strain relationship under rapid loading.

Flux and recharge of fine layers

In dry regions it is common to deploy thin covers that encourage evapo-transpiration. These are highly effective and do prevent most water from percolating into the tailings most of the time. This is generally adequate for the purposes of protecting groundwater, as discussed previously. At issue is how much water can be allowed to pass into the system and pass through the fine layers without leading to local almost-saturation in zones key to the stability of the structure.

Excavations at considerable depth in tailings placed twenty-plus years ago indicate that the fine materials tend to sustain moisture contents close enough to the point of saturation to be of concern to the geotechnical engineer. Whether the subsurface condition might have been different had the surface been shaped or treated differently in an effort to limit infiltration, remains a topic for further study.

The challenge posed by these fine layers then is that they complicate the argument made for consolidation and strength gain. When the fine layers do not drain fast enough they might still be susceptible to liquefaction (unless subject to adequate overburden pressure) and strength loss. The question is whether, with the right surface treatment and given enough time, draining and consolidation might *eventually* result in conditions that are not a concern.

Conclusion

The brief analysis above indicates the key role that water plays in the performance of tailings, and how some fairly simple measures might benefit the long-term performance of a storage facility. It warrants repeating: the tailings engineer (and the mine closure practitioner) must work with the circumstances at the site in question, as not all the potentially advantageous approaches are applicable everywhere. It is evident though that all approaches should be considered as they serve as counterpoints to each other. If, for example, a wet cover seems attractive because limiting the exposure to oxygen would be beneficial, but the climatic setting is not conducive to such a cover, the designer can explore alternative ways of achieving a similar effect. Water will serve as both friend and foe depending upon the particular element of the tailings facility being considered, and it is crucial that designers adopt a multi-disciplinary approach and have a keen understanding of the role water plays in the whole system.

The soil mechanics of mine tailings is being extensively studied presently, and in the coming years we will likely see a valuable body of work arising from that effort. In the meantime we must use our observations of past performance to empirically adopt suitably safe designs in the structures we are building today.

The question of very long-term performance is key in order for the mining industry to meet our commitments to the community. It is becoming clear that the climate is far more variable than we considered likely when many of these tailings management facilities were originally designed and built. Moreover, we continue to adapt our range of concerns as we gain an appreciation of the hazards and learn more. The variability in conditions (and, perhaps, the future material properties) require us to become experts in risk-based decision making and to take the adaptive management approach. It is imperative that we continue to monitor the behaviour of the structures in our care and share what we learn, so that our designs and modes of operation are adequately informed.

Acknowledgements

The authors wish to acknowledge the collaboration of their colleagues at BHP Legacy Assets and the work they are doing to curate, characterize and upgrade the various facilities in their care.

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Climate Change Impact on Water Management Design for the Rehabilitation of the Former Rum Jungle Uranium Mine

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Abstract

The former Rum Jungle uranium mine located approximately 100 km south of Darwin, Northern Territory, Australia, operated between 1954 and 1971 and underwent rehabilitation from 1983 to 1986. The rehabilitation addressed significant environmental impacts caused by acid metalliferous drainage (AMD) and achieved objectives related to aesthetic improvements and reducing public health hazards. Recent studies documented that the original rehabilitation works do not meet modern environmental standards, meaning further rehabilitation work would be required for site closure and relinquishment (Hartnett, 2020).

Since 2009, the Northern Territory and Australian governments have undertaken investigative works to develop an improved rehabilitation strategy that is consistent with the views and interests of stakeholders and that meets contemporary environmental and mined-land rehabilitation standards. The rehabilitation design involves relocation of potentially acid forming (PAF) waste rock to new surface emplacement facilities and a water and tailings filled pit, treatment of contaminated pit and groundwater, and the realignment of the East Branch Finnis River (EBFR) to follow its original course back through the pit (Hartnett, 2020).

There is now general acceptance that human activities are contributing to observed climate change. Continued emissions of greenhouse gases are highly likely to cause further warming and changes in all components of the climate system. Mean, minimum, and maximum temperatures are predicted with very high confidence to keep increasing, as is the frequency of hot spells and droughts. While overall rainfall is predicted to result in both wetter and drier periods depending upon regional geographical influences, climate modelling predicts with high confidence that heavy rainfall events will become more intense. Rising temperatures and prolonged hot spells are predicted to lead to an increase in the frequency and intensity of bush fires. Relevant to the Rum Jungle mine's location, climate change may alter evapotranspiration, soil

moisture, and runoff. The effect of the above climate change-related factors has been studied to ascertain the robustness of the rehabilitation design of the mine. Presented here are some of the key outcomes of the study, in particular the impact of climate change on the pit water level, and the hydrological processes informing the EBFR flow path design.

Introduction

An improved rehabilitation design for the former Rum Jungle mine site was completed in 2020 and involved the design of new waste storage facilities and a backfill strategy for the main pit to accommodate the PAF waste rock that is currently impacting the groundwater and downstream reaches of the EBFR.

The former open cut main pit was 105 m deep and is partially filled with contaminated tailings, resulting in a permanent pit lake depth of ~46 m. The pit is to be backfilled over the tailings with PAF waste rock and then capped with 2 m of inert material, to a maximum level of 2 m below the currently predicted lowest pit water level.

The EBFR is currently diverted to the south around the main pit and the adjacent intermediate pit. Once the main pit is backfilled and capped, the EBFR is to be realigned to follow its original course through the main pit and intermediate pit (which is to remain as a pit lake).

To understand the robustness of the backfill capping layer design thickness and the design of the EBFR realignment, a climate change sensitivity assessment has been undertaken. This has included identification of the relevant climate change influences, and a comparison of the hydraulic and hydrologic modelling results for the main pit, and realignment for the base case under the climate change influences.

Climate change influencers

Australia's NRM clusters and sub-clusters

The Australian Government developed the Regional Natural Resource Management (NRM) Planning for Climate Change Fund, to provide projections of the likely impact of climate change on Australia's natural resources.

Australia has 54 NRM regions (clusters and sub-clusters), defined by catchments and bioregions, which are broadly consistent in terms of history, population, resource base, geography, and climate. The location of the project site is within the Monsoonal North (West) sub-cluster, as shown in Figure 1. The site experiences a hot, humid wet season from November to April and a cooler dry season from May to October.

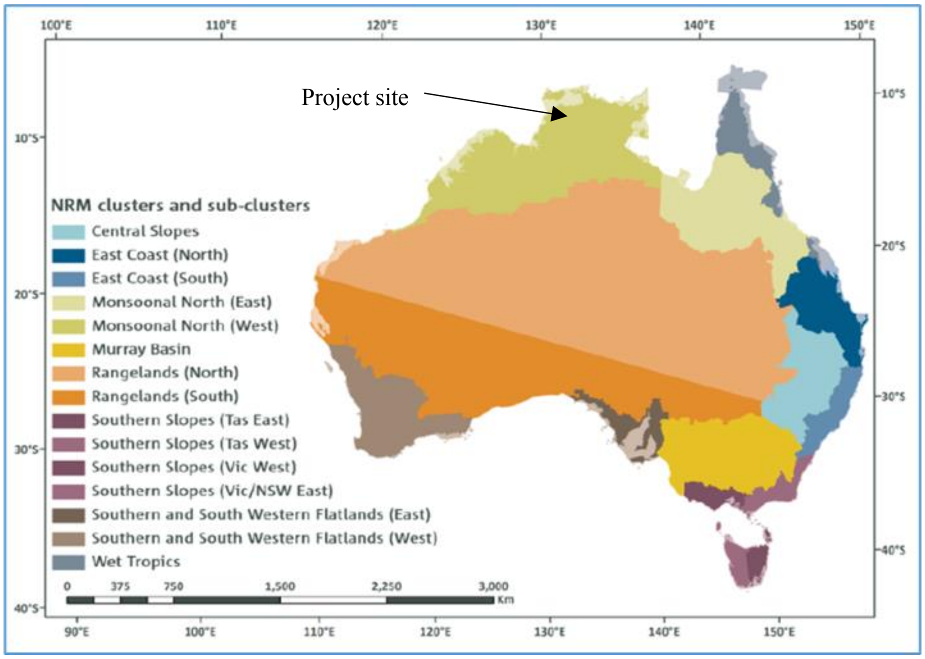

Figure 1: Australia's Natural Resource Management (NRM) clusters and sub-clusters

IPCC AR5 climate change projections

The UN's IPCC (Intergovernmental Panel on Climate Change) *Fifth Assessment Report, AR5* (IPCC, 2014) (note, the more recent AR6 Synthesis Report is due to be released in September 2022), provides climate change projections based on a series of future climate change scenarios encompassing a plausible range of likely outcomes. These climate change scenarios have been developed into Representative Concentration Pathways (RCPs) to explore credible future options, expressed in terms of future carbon emissions and associated radiative forcing. The standard RCPs are as follows:

- RCP8.5 – chosen to represent a future with little curbing of emissions, with CO_2 concentrations continuing to rapidly rise, reaching 940 ppm by 2100.
- RCP6.0 – represents lower emissions, achieved by application of some mitigation strategies and technologies. CO_2 concentrations rise less rapidly than RCP8.5, but still reach 660 ppm by 2100, with total radiative forcing stabilizing shortly after 2100.
- RCP4.5 – concentrations are set slightly above those of RCP6.0 until after mid-century, but emissions peak earlier (around 2040). CO_2 concentrations reach 540 ppm by 2100.
- RCP2.6 – represents the most ambitious mitigation scenario, with emissions peaking rapidly (around 2020), then rapidly declining.

In response to the AR5 Report, Australia's CSIRO and Bureau of Meteorology (BOM) (CSIRO and BOM, 2015) prepared tailored climate change projections for each of Australia's NRM clusters. Regional highlights relevant to the project site include:

- By 2030, warming will range from 0.5°C to 1.2°C (low emissions RCP) to 0.7°C to 1.3°C (high emissions RCP).
- By 2090, warming will range from 0.9°C to 1.6°C (low emissions RCP) to 2.8°C to 5.1°C (high emissions RCP).
- Near-future projections for the dry season range from 35% drier to 29% wetter, depending on RCP scenario. For the west season, projected changes range from 8% wetter to 7% drier.
- By 2090, the projected dry season changes range from 45% drier to 44% wetter, depending on RCP scenario. For the wet season, the projected range is 23% drier to 19% wetter.
- Under all future RCP scenarios, fire weather will become more frequent and harsher.

Climate change influencers on rehabilitation design

Key climate change indicators likely to influence the Rum Jungle rehabilitation design are:

- Climate change induced rainfall: especially peak intensity rainfall events.
- Climate change impacts on fire weather I: considering the potential for a catastrophic fire decimating the vegetation throughout the project site catchment.
- Climate change impacts on fire weather II: considering how the intense heat from an extreme bush fire might change the structure of the soil resulting in hydrophobic conditions.

The above influencers will impact the hydrological and hydraulic behaviour by changing the following inputs to the modelling:

- Rainfall intensity.
- Surface water infiltration parameters, including initial and continuing losses.
- Surface roughness (Manning's 'n').

Climate change and effect on rainfall

Estimating climate change impacts on rainfall intensity

The Australian Rainfall and Runoff Guideline (ARR, 2019) identifies two alternative methods to estimate the impact of climate change on rainfall depths, namely, the simplified method and the detailed assessment method.

Simplified method

This allows for the incorporation of the effects of climate change in the design rainfall used in flood estimation by modelling of the 0.5% (1 in 200) Annual Exceedance Probability (AEP) as a proxy for future estimates of the 1% (1 in 100) AEP event. For the critical duration 30-hour rainfall event, this would represent an increase in rainfall depth and intensity of 15%.

Detailed assessment

The detailed assessment is based on predictive modelling of temperature increases sourced from the Climate Change in Australia website and applying a change in design rainfall from global warming in accordance with the following formula:

$$I_p = I_{ARR} \, . \, 1.05^{Tm} \quad \text{Eq.1.6.1 (ARR, 2019)}$$

where: I_p = Projected rainfall intensity (or depth)

I_{ARR} = Design rainfall intensity (or depth)

Tm = Temperature at the midpoint of the selected class interval

Based on AR5 climate change scenarios for the year 2070 (the minimum period for analysis for long-standing projects, ARR, 2019), a conservative temperature increase for the project site of 2.25°C is considered suitable for estimating future rainfall intensity increases. Using Eq.1.6.1 in (ARR, 2019) this would equate to an 11.6% increase in rainfall intensity.

Table 1 provides a comparison of the resulting rainfall depths. The conservative approach is therefore to adopt the 0.5% AEP rainfall.

Table 1: Comparison of climate change rainfall increases

Duration	Rainfall depth, 30-hour duration	Comment
2019 Rainfall – 1% AEP	318 mm	Baseline
Simplified method	366 mm (+15.0%)	Adopted for sensitivity analysis
Detailed method	355 mm (+11.6%)	Is of similar magnitude

Climate change and effect on infiltration of soils

Physical impact

Catastrophic fire has the potential to destroy the entire contributing catchment relevant to Rum Jungle. The result is exposure of erodible soils via burning of the vegetation on the soil surface. Under intense heat, the following soil changes can occur:

- The predominant sandy clay soil in the upper catchment will crystallize at temperatures of 350°C to 800°C, similar to the firing of clay in a kiln.
- Intensely burning organic material can release a waxy substance that penetrates the soil as a gas and solidifies after cooling, bonding the soil particles together.
- The open pores of a sandy clay soil allow the penetration of heat deep into the soil profile.

These processes result in the top layer of soil becoming hydrophobic, which has the following impacts on hydrologic and hydraulic processes:

- The infiltration rate is reduced or stopped.
- The runoff rate increases.
- Velocities increase.
- Flood depths increase.
- The surface shear stress increases resulting in greater erosion and soils loss.

Impact on modelling parameters

The calibrated infiltration parameters were reassessed to emulate the behaviour of an intense catastrophic fire engulfing the catchment. The results are summarized in Table 2.

Table 2: Climate change impact on infiltration

Parameter	Base case	Climate change influence
Initial loss	38 mm	10 mm
Continuing loss	0.6 mm/hour	0 mm/hour

Climate change and effect on catchment roughness

Physical impact

The contributing catchments are heavily wooded with dense undergrowth and tuff grasses. The effect of a fire denuding the surface is akin to the urbanization of a catchment.

Effect on modelling parameters

- The vegetation in the contributing catchment of Rum Jungle was calibrated with a Manning's roughness coefficient (n) between 0.06 and 0.1.
- In the event of a catastrophic fire the whole catchment would be converted to a Manning's n of 0.04, representing charred stumps and branches with no undergrowth.

The hydrological effects on the runoff calculations included increased runoff rate, increased volume of runoff, and increased flooding.

Hydrological effects of the influencers

Rainfall temporal patterns and the adoption of temporal pattern ensembles

The use of an ensemble of 10 temporal patterns for each storm duration (a total of 290 different storms for each magnitude) is now required by ARR (2019). The temporal patterns have been chosen to represent the variability in observed patterns. The required approach is to select the storm that represents the mean of the ensemble maxima (ARR, 2019).

The baseline 1% AEP discharge

The Rum Jungle rehabilitation hydraulic infrastructure has been designed to safely pass the 1% AEP event. Modelling shows:

- The 30-hour duration 1% AEP storm with temporal pattern no. 6 is the mean of the maximum ensembles and produces a peak flow of 195 m^3/s. This storm is to be used for design purposes and is considered the baseline for climate change influencer effects.
- The critical duration is the 18-hour rainfall event, which produces a maximum flow of 231m^3/s.

Modelling for the climate change influencers has been simulated for the following scenarios:

- Increased rainfall intensity impact.
- Fire weather impact – i.e., change of surface roughness (Manning's n).
- Soil structure impact – hydrophobic conditions leading to reduced initial and continuing losses.
- A combination of all three influencers.

The results are shown in Figure 2, and comparison of the base case results to the results from modelling for the climate change influencers is given in Table 3.

Table 3: Hydrological modelling results

Parameter	Base case	Climate change influence			
		Increased rainfall	Fire weather	Soil structure	Combined
Mean storm duration	30-hour	30-hour	4.5-hour	6-hour	24-hour
Meanflow peak	195m^3/s	230m^3/s	259m^3/s	217m^3/s	340m^3/s
Critical storm duration	18-hour	18-hour	18-hour	18-hour	6-hour
Critical flow peak	231m^3/s	276m^3/s	311m^3/s	257m^3/s	428m^3/s

The results indicate that:

- Catastrophic fire that denudes the catchment of vegetation will have the greatest influence on runoff increases at the site.

- The predicted rainfall increases will have a slightly greater influence than the hydrophobic soil conditions.
- Overall, the peak runoff could increase by approximately 78%, should all influencers occur simultaneously.

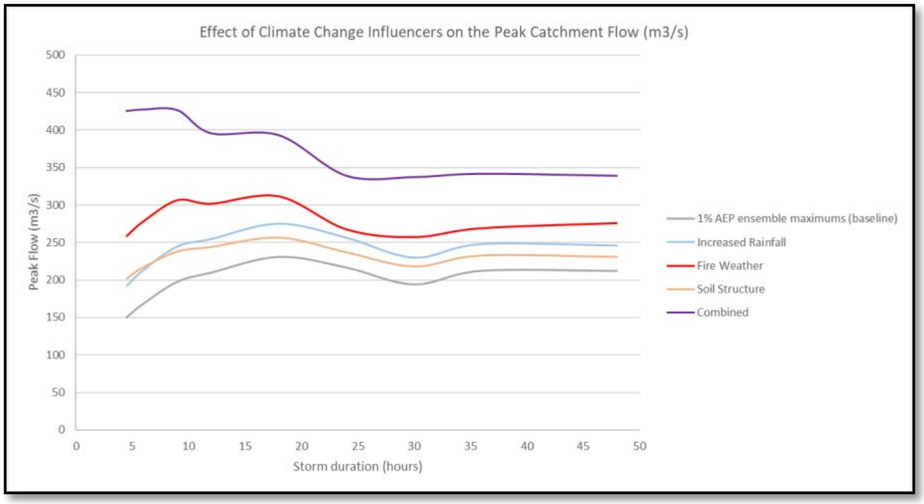

Figure 2: Summary of peak catchment flows for climate change influencers

Impact of influencers on the main pit and EBFR designs

Hydraulic impact

Hydraulic modelling using SWMM-XP 2D software was undertaken for the proposed final rehabilitated topographical surface to understand flow and velocity distribution, water surface elevation, backwater, velocity magnitude and direction, flow depth, and surface shear stress. A comparison has been made between the base case and the combined climate change influences.

The proposed remediated landform

The proposed final landform was developed to address the following minimum requirements:

- The diversion channel is to remain to convey surcharge of the EBFR upstream of the main pit during extreme floods to relieve the hydraulic load of the main pit.
- The existing culverts at the entry and exit of the main pit and the entry of the intermediate pit will be removed to provide a continuous flow path.
- The channel surface would be heavily lined with riprap to prevent erosion. The interstices of the riprap would be covered with a seeded soil mix to promote vegetation and mitigate the engineering appearance. Large boulders and logs placed in a meandering arrangement would provide refuges

for migratory fish during the wet season. The riverbed would have riffles and depressions to retain pools after flows.

- During the dry season the capping of the main pit would be covered by 2 m of water. The permanent groundwater table will ensure the capping remains covered in the dry season. During the wet season the level increases by approximately 2 m, providing a 3 m to 4 m submergence over the capping.
- The main pit has been modelled with the top of the capping surface as level, which is the worst-case condition, only likely to occur immediately after rehabilitation, or should sediment drop out, levelling out the surface over time.

Modelling results

Figure 3 shows the flood extent in the rehabilitated channel for the 1% AEP event with the combination of all three influencers. The contours have been displayed to identify the location of the proposed waste storage facilities. Figure 4 shows the incremental differences between the base case and the worst-case scenario (with vegetation).

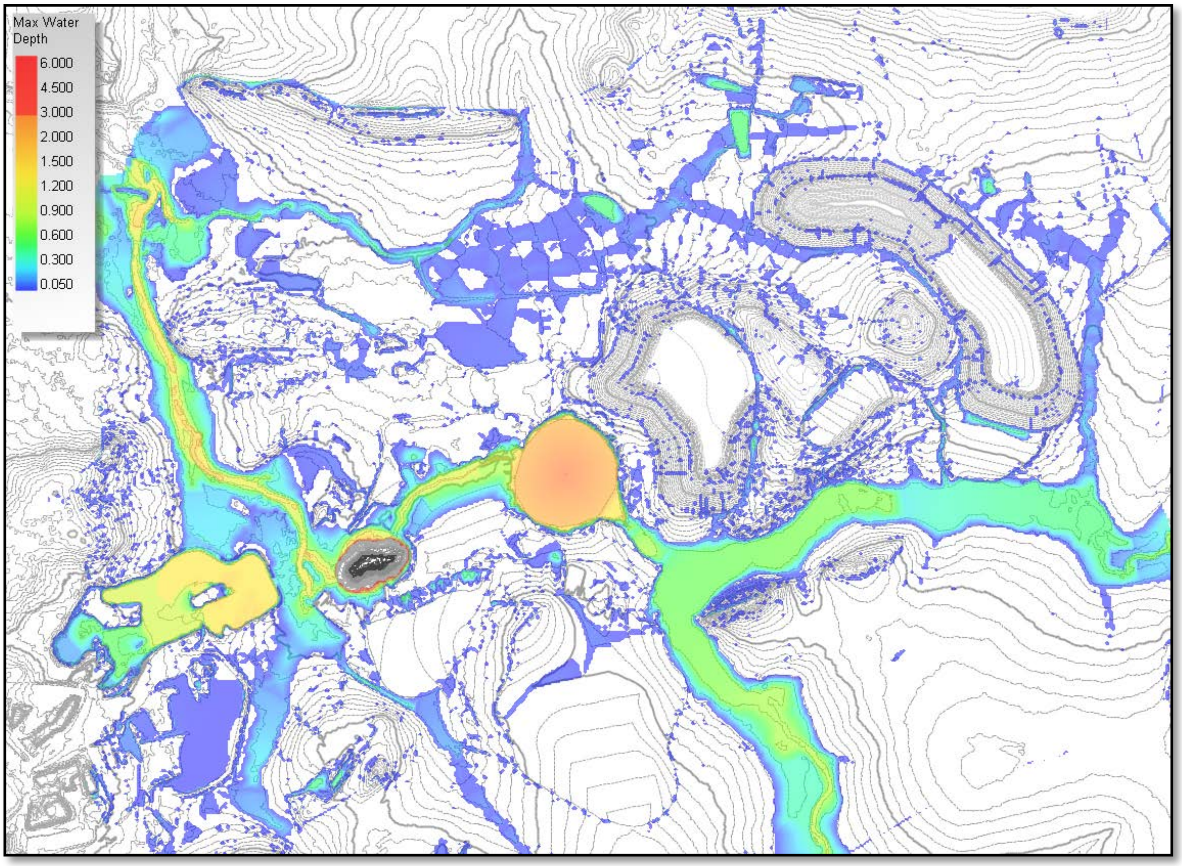

Figure 3: 1% AEP flood depth as a consequence of the climate change influencers

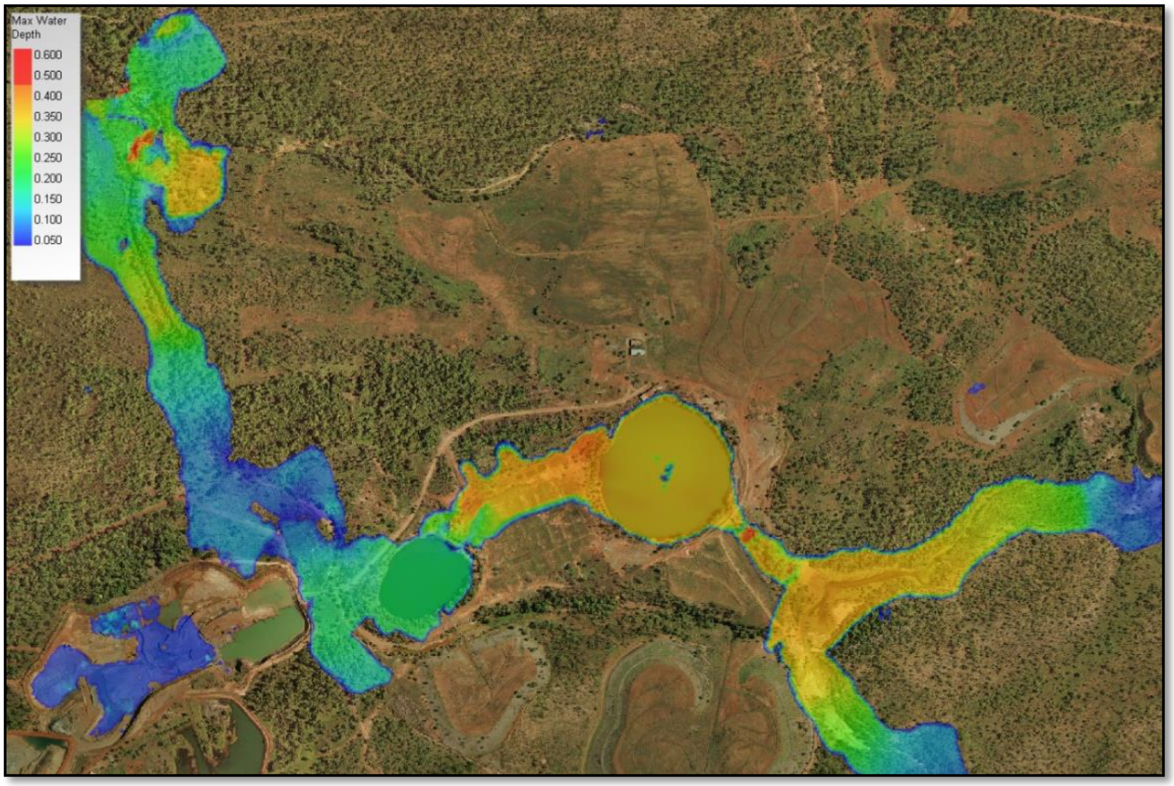

Figure 4: Increase in flood depth as a consequence of the climate change influencers (1% AEP)

The results indicate:

- Climate influencers could increase flood levels within the EBFR between 50 mm and 600 mm, with an average increase of approximately 350 mm.
- The flood level increase would not exceed the defined channel, and hence would not inundate the proposed waste storage facility areas.
- The modified diversion channel will not be activated.

Influence of climate change on velocities

Figure 5 shows the maximum velocity and direction averaged over the depth. Two-dimensional hydraulic modelling cannot stratify the velocity across the full depth. However the research by Ven Te Chow (1959) showed an approximation of the channel bed velocities can be made by halving the average cross-sectional velocity. Modelling indicated that the climate change influencers could:

- Increase channel bed velocities by up to 0.6m/s, which is within the design safety factor of the riprap.
- Increase velocities over the main pit floor by up to 0.2m/s, which could cause mobilization of the sandy bottom.

- Change the flow pattern from a dissipated behaviour to a short circuit between the inlet and outlet of the main pit.

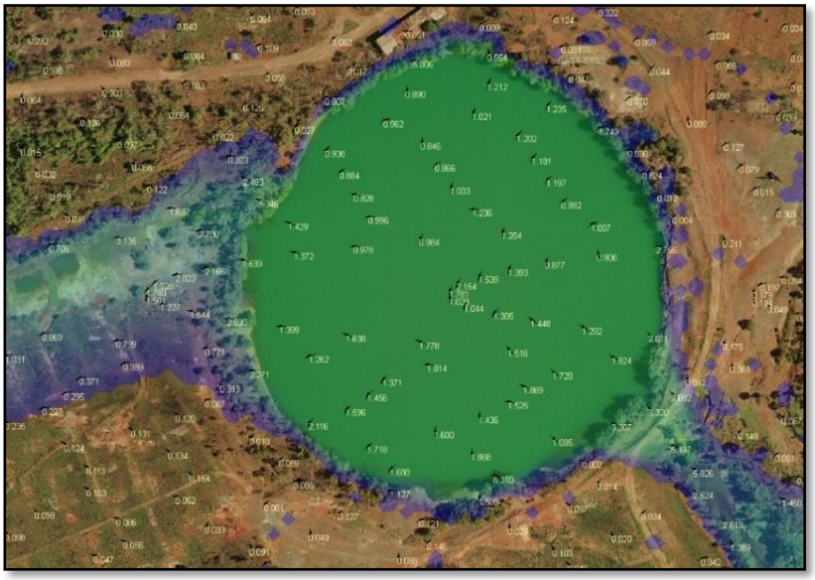

Figure 5: Climate change influencers causing higher velocities and short-circuiting behaviour

Addressing the hydraulic conclusions

The results indicated potential changes in hydraulic behaviour over some areas of the Rum Jungle site due to the influence of the climate change variables assessed. These changes suggest a need for minor enhancements to the erosion protection in strategic locations, including:

- To maintain the design safety factor, it will be necessary to enhance the erosion protection immediately upstream and downstream of the main pit.
- The larger flows are resulting in values within the “line of sight” between the inlet and outlet of the main pit that exceed the mobilization velocity. This can be alleviated by minor modifications (i.e., widening) to the inlet design to ensure flow dissipates as it enters, or is directed north to increase the flow path area and reduce the velocity.
- No other modifications are necessary to the design to mitigate the effects of climate change.

Summary

Evidence (IPCC, 2021) indicates that continued emissions of greenhouse gases are expected to cause further warming and changes in all components of the climate system:

- Mean, minimum, and maximum temperatures are predicted with very high confidence to keep increasing, along with the frequency of hot spells and droughts.

- While overall average rainfall is predicted to result in both wetter and drier periods depending upon regional geographical influences, climate modelling predicts that heavy rainfall events will become more intense.
- Rising temperatures and prolonged hot spells are predicted to lead to an increase in the frequency and intensity of bush fires.
- Climate change may alter evapotranspiration, soil moisture, and runoff.

This report has addressed the potential impact of climate change influencers including:

- Climate change induced rainfall.
- A catastrophic fire decimating the vegetation throughout the catchment.
- The intense heat changing the structure of the soil, resulting in hydrophobic conditions.

The specific design elements to which the requests relate are backfilling of the main pit and realignment of the EBFR to follow its original course back through the main pit. The results indicate:

- Climate influencers could increase flood levels within the EBFR between 50 mm and 600 mm, with an average increase of approximately 350 mm.
- The flood level increase would not exceed the defined channel, and hence would not inundate the proposed waste storage facility areas.
- The modified diversion channel will not be activated.
- Increased surface water velocities mean it will be necessary to enhance the erosion protection immediately upstream and downstream of the main pit.
- The larger flows are resulting in values that exceed the mobilization velocity, hence minor modifications (i.e., widening) to the inlet design will be required.

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PFAS and the Mining Industry: Understanding the Challenges

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Abstract

Per- and poly-fluorinated alkyl substances (PFAS) are a group of man-made chemicals including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). This emerging class of contaminants has been the centre of litigation settlements across various US states. Ubiquitous at very low levels in the environment, PFAS have been measured in water supplies across the US. While the focus on PFAS to date has centred around manufacturing facilities and commonly known aqueous film-forming foam (AFFF) release sites (airports and military bases), international governments have been starting to consider other types of PFAS impacts associated with a broad range of industries.

Although mining has not yet become a key focus area for concerns related to PFAS impacts, mines are beginning to be identified as sources of PFAS. For example, BHP's Mount Whaleback iron ore mine in Western Australia was recently identified as the source of low-level PFAS impacts to groundwater. These impacts have the potential to threaten a nearby drinking water supply, prompting BHP to evaluate PFAS use across its site. The use of PFAS within the mining industry has been long established, for a variety of processes and activities. Consequently, environmental releases of PFAS from mining facilities could occur and require consideration and management.

This paper will provide an overview of the challenges associated with PFAS in the environment, and the implications these challenges may have for the mining industry. It will review PFAS use within the mining industry, site characterization challenges, potentially relevant receptors and exposure pathways, and remedial options, as well as the status of PFAS regulation internationally.

Introduction

Per- and poly-fluorinated alkyl substances (PFAS) are a group of more than 3,000 man-made chemicals including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). This emerging class of contaminants has been the centre of litigation settlements worth over $5.5 billion across the US. Ubiquitous at very low levels in the environment, PFAS have been measured in water supplies across the US. A variety of adverse health effects have been associated with PFAS exposure, including liver damage, decreased fertility, thyroid disease, cancer, decreased immunity, and more.

Mines are beginning to be identified as potential sources of PFAS release to the environment. The use of PFAS within the mining industry has been long established, including use within industrial processes (e.g., use as surfactants to enhance metal recovery, within the ore flotation process, etc.), as well as use of aqueous film-forming foam (AFFF) for firefighting activities. Consequently, environmental releases of PFAS from mining facilities could occur and require consideration and management. As such, this paper will review PFAS use within the mining industry, site characterization challenges, potentially relevant exposure pathways for receptors, and remedial options, as well as the status of PFAS regulation.

PFAS use within the mining industry

As outlined in Gluge et al. (2020), 1.400 individual PFAS substances have been identified for more than 200 uses in 64 different categories, including the mining industry. PFAS substances are widely used due to the many properties that make them invaluable to industry, including:

- the ability to lower the aqueous surface tension
- high hydrophobicity
- high oleophobicity
- high non-flammability
- capacity to dissolve gases
- high stability
- extremely low reactivity
- high dielectric breakdown strength
- good heat conductivity
- low refractive index
- low dielectric constant
- ability to generate strong acids
- operation at a wide temperature range
- low volatility in a vacuum
- impenetrability to radiation

In mining, PFAS uses include ore leaching in copper and gold mines, ore floating, separation of uranium from ore/minerals, concentration of vanadium compounds, acid mist suppressant agent, wetting agents, hydrocarbon foaming agent, and the use of fluoropolymer in pipes, cables, hoses, and conveyor belts (Gluge et al., 2020; Wood Group UK Limited, 2021).

PFAS may also be present at mining sites for uses that are ancillary to the mining operation, such as PFAS-containing AFFF for fire suppression/firefighting activities, cleaning of metal surfaces, and use as a foaming agent in drilling fluids, paints and coatings, and so on. In the case of AFFF, fire suppression systems often need to be tested annually, and traditionally this has involved the discharge of AFFF to the ground surface. As noted by Hunt (2020), mining sites typically have fixed fire suppression/fighting systems that can spray suppressants for long distances from a fixed location, meaning impacts can be widespread.

Site characterization challenges

The characterization of PFAS at any site, including mining sites, should consider PFAS fate and transport in the environment, requirements for adjusted field procedures during sample collection, and the implementation of appropriate laboratory quality assurance and quality control (QA/QC) processes.

PFAS fate and transport

Fate and transport of PFAS in the environment can be highly variable, given that PFAS include many compounds with different physical-chemical characteristics that control their behaviour (ITRC, 2021a). Carbon-fluorine chain length, functional group, charge and degree of fluorination all influence PFAS behaviour. When PFAS are discharged or spilled to a ground surface, the PFAS can adsorb to soil through either hydrophobic or electrostatic interactions and remain close to the source area. PFAS can also show enhanced retention within the vadose zone, given the tendency of PFAS to accumulate at the air-water interface. Alternately, the charged functional group and associated hydrophilic properties can lead to PFAS leaching into groundwater and mobilizing with groundwater flow. Generally, the degree to which PFAS adsorb to solids or mobilize can be approximated by the chain length: longer carbon-fluorine chains tend to adsorb more strongly to solids versus shorter carbon-fluorine chains. Given the high stability of PFAS, once present in groundwater, large plumes can form that remain present for long periods of time. Transformation of commonly assessed PFAS, such as PFOA and PFOS, under typical environmental conditions is limited; however, PFAS precursors or polyfluorinated compounds may transform into more stable PFAS. Uptake of PFAS by plants and animals has been observed, with some PFAS showing bioaccumulation and biomagnification potential. Site-specific considerations cannot be omitted from assessment planning, as they do impact the fate and transport of PFAS, similar to other contaminants (ITRC, 2021a).

PFAS can be found in other media, such as surface water, sediment and air (ITRC, 2021a). Similar mechanisms as discussed for soil and groundwater dictate how PFAS behave in these media as well, including solid-liquid partitioning, and transformation or uptake. Given the surfactant-like properties of many PFAS and accumulation at the air-water interface, PFAS have been observed to form a foam at the top of surface water bodies when present at high concentrations. Many PFAS have low vapour pressures that limit the movement of PFAS from water to air; however, there are some PFAS, such as fluorotelomer alcohols (FTOHs), that show greater volatility. Atmospheric transportation of PFAS can occur through the release of volatile PFAS or PFAS adsorbed to air-borne particulate matter (ITRC, 2021a).

Field sampling procedures and QA/QC

Although standard environmental sampling best practices should be followed, field sampling programs that include PFAS have additional considerations. PFAS are found in many commercial products, which include some of the equipment and supplies typically used to collect environmental samples, creating the potential for sample contamination. Other materials (such as glass) may adsorb PFAS, which would low-bias the collected data. Both cases should be avoided, and this can be facilitated through review of available reference documents regarding PFAS sampling, which notably include the Michigan Department of Environmental Quality's *General PFAS Sampling Guidance* (MDEC, 2018) and the Interstate Technology Regulatory Council's *Sampling Precautions and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances* (ITRC, 2020).

Precautions outlined in MDEC (2018) and ITRC (2020) include avoiding certain clothing, materials, food packaging, and personal hygiene products that may contain PFAS when sampling. Sampling equipment and supplies should not contain Teflon, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), LDPE, polyvinylidene fluoride (PVDF), fluoropolymers, or anything with "fluoro" in the name. Other materials that should be avoided during sampling include Decon-90, post-it notes, waterproof field paper or books, "blue ice" and any type of cooler pack, waterproof markers, sharpies, permanent markers, binders, spiral/hard cover notebooks, plastic clipboards, adhesive paper products, food packaging and containers, and adhesive tapes. Acceptable materials to use during sampling include materials made from high-density polyethylene (HDPE), polypropylene or silicone, decontamination solutions like Alconox/ Liquinox, and field supplies that include loose plain paper, metal clipboards, ball point pens, and ice formed by water.

When executing a PFAS sampling program, PFAS sampling materials should be stored separately from sampling supplies for other parameters. Non-disposable field equipment should be decontaminated between each sample location, and prior to use at a site where PFAS is being assessed. Sample collection should begin at the location where impacts are least expected (i.e., lowest anticipated PFAS concentrations) and move towards locations where impacts are most expected (i.e., highest anticipated PFAS concentrations). Eating or drinking on site during sampling should be avoided to minimize the potential for cross-contamination. Hands should be washed prior to returning to the site following any breaks.

In order to confirm that field procedures have been effective in inhibiting sample contamination, field QA/QC blank samples should be obtained, including equipment blanks, trip blanks, and field blanks. Equipment blanks are collected using laboratory-provided PFAS-free water that is passed through or over equipment used for sampling activities to assess whether the equipment represents a potential source of PFAS to the sample. Field blanks are PFAS-free water samples that are collected in separate laboratory-provided sample containers while conducting sampling in the field to monitor that field activities are not a potential source of PFAS to the sample. Trip blanks are PFAS-free water samples prepared by the laboratory that are transported during the sampling procedure to monitor that PFAS have not been introduced to the samples through laboratory preparation or transportation. The combination of these field QA/QC blank samples will provide confidence that the collected PFAS data are representative of site conditions.

Laboratory QA/QC

Choosing a certified laboratory to complete PFAS analysis is important to maintaining the accuracy and reliability of the data. The laboratory should provide appropriate containers to collect samples (i.e., unlined and made of polypropylene or HDPE); glass containers and certain plastic bags should be avoided, wherever possible. If high PFAS concentration samples are to be submitted for analysis, these samples should be segregated during sampling and shipment, and flagged to the laboratory to support appropriate preparation for analysis. It is noted that there are only a few multi-laboratory validated and published methods for analysis of PFAS, and those released to date have generally been developed for analysis of water samples (drinking water, groundwater, surface water, and wastewater). Draft laboratory methods are available for other media, such as soil, sediment, biosolids and tissue; however, these have not been validated by multiple laboratories (ITRC, 2021b). Following PFAS analysis, it is important to review the laboratory certificates of analysis to confirm the reported laboratory QA/QC procedures, such as method blanks, spiked blanks, and analysis of duplicates, and compare the results to the provided evaluation criteria. This review of laboratory QA/QC may help indicate whether sample matrix interference or laboratory issues could have impacted the reliability of the reported PFAS concentrations.

Relevant exposure pathways

Human and ecological receptors can be exposed to PFAS through various pathways both at a mining site, as well as off-site, due to fate and transport mechanisms (e.g., groundwater migration, wind erosion, deposition). The routes of exposure and the receptors exposed, particularly off-site, can be influenced by the physical location of the mining site. Figure 1 illustrates a potential mining site, the surrounding land use, and the potential routes of exposure and receptors (as indicated by the numbers [#], and explained in the text below). The main expected source of PFAS is the use of AFFF (#1). PFAS may also end up in effluent or tailings ponds through use in processing (#2). These waters are unlikely to be treated for PFAS.

Human health

The most likely potential exposure routes to PFAS for people at a mining site (e.g., workers) are incidental ingestion of soil (#3), potable water ingestion (should the mining site rely on groundwater or nearby surface water as source water) (#4), and, to a lesser extent, direct contact with PFAS-containing products (e.g., AFFF) (#1) and inhalation of PFAS in dust and air (#5). According to ITRC (2021c), exposure via potable water is generally the dominant exposure pathway in comparison to other pathways (e.g., from food), even if PFAS concentrations in the drinking water source are low. If there is an on-site accessible surface water feature, there may also be exposure via incidental ingestion of sediment and surface water (#2).

Figure 1: Potential mining site and surrounding land use (numbers described in text)

Similar routes of exposure to PFAS would also be present for people living near the mining site, including mining workers living in off-site camps, as well as other residential communities, including Indigenous communities. The dominant exposure pathway of concern off-site would still be ingestion of PFAS-impacted potable water (i.e., groundwater or surface water) (#6); however, other routes of exposure could include:

- direct contact with PFAS-impacted soil (due to off-site migration of soil particulates via wind or mining emissions and deposition onto soils) (#7);
- consumption of food exposed to PFAS through watering (e.g., livestock) (#8);
- soil up-take or irrigation (e.g., crops) (#9);
- exposure to PFAS-impacted surface water and sediment (e.g., incidental ingestion of surface water/sediment, ingestion of aquatic biota) (#10);
- and, to a lesser extent, inhalation of PFAS in dust and in air (#11).

Ecological health

The routes of exposure for ecological receptors would be similar both at the mining site and off-site. Plants and soil invertebrates could be exposed to PFAS in soil (#12), although exposure off-site may be limited as impacts would only be transmitted via off-site migration of PFAS through wind (e.g., soil particulate) or mining emissions, followed by deposition onto soils. Aquatic biota could be exposed to PFAS in both surface water and sediment in on-site surface features, if present, and from PFAS migration in mining site groundwater to off-site surface water features (#10). Terrestrial and aquatic mammals and birds could be exposed via impacted surface water (e.g., consumption) (#10) and via food (e.g., plants, invertebrates, mammals, birds and aquatic biota) (#10, 12, 13); however, exposure on-site for mammals and birds may be limited if measures are in place that limit their access to the mining site itself (e.g., fencing).

Remedial options

Remediation depends on the use of treatment technologies that can exploit a contaminant's chemical and physical properties for the purpose of removing or destroying the contaminant from environmental media. PFAS are a challenge to remediate because they are typically found in the environment as mixtures composed of different PFAS with potentially very different properties. The solubility, surfactant properties, stability, and poor adsorption characteristics of different PFAS tend to complicate remediation, as common technologies are ineffective (e.g., air stripping, soil vapor extraction, biostimulation, or bioaugmentation) or have limited effectiveness (e.g., chemical oxidation). There are very few field-demonstrated, cost-effective treatment technologies for PFAS on solids or in water; however, there are proven ex-situ technologies that could be applicable to the situations typically encountered at a mining site and these will be reviewed here. ITRC (2021d) provides an excellent summary of other emerging technologies currently under development.

Mines typically use local groundwater for drinking water, and historical PFAS use may contaminate the drinking water supply to levels above recommended drinking water criteria. Beyond use of AFFF, treatment of process water at most mining sites largely does not address PFAS, meaning PFAS can be discharged to the environment in treated process water and impact drinking water supplies. As the primary concern at mining sites is drinking water, this review will focus primarily on water treatment technologies.

To date, readily available technologies for drinking water treatment have been limited to sorption and ion exchange, whereas treatment of leachates and process waters has included foam fractionation and coagulation (ITRC, 2021d), depending on the composition of the solution. When considering remedial options for mining sites, it is important to note these sites are typically remote and operate under harsh environmental conditions, where power generation can be costly. Consequently, transport of PFAS-impacted treatment media off-site is expensive, sensitive specialized equipment has poor longevity, and onsite disposal of highly soluble and potentially mobile contaminants like PFAS is not practical.

Sorption and ion exchange

Sorption and ion exchange are two removal technologies that bind PFAS using Van der Waals and/or weak ionic forces, resulting in the accumulation of PFAS on the sorptive media. Granular activated carbon (GAC) and ion exchange resins (IX) are the most common sorptive media available used for PFAS adsorption. Various types of GAC have been tested, with most PFAS and manufacturers having developed models to predict mass loading under a variety of solution conditions. Most testing has focused on the efficacy of GAC sorption of long-chain PFAS (Appleman et al., 2013; Ochoa-Herrera and Sierra-Alvarez, 2008) and has demonstrated that GAC treatment can achieve effluent concentrations below detection limits for United States Environmental Protection Agency (USEPA) Method 537.1 (Shoemaker and Tettenhorst, 2018). Although also effective with other organic contaminants such as petroleum hydrocarbons and chlorinated solvents, co-contaminants can displace PFAS from GAC, reducing treatment. Sorption efficiency is dependent on the carbon chain length of the PFAS and the ionic functional group, with shorter chain PFAS and carboxylic acids having lower sorption efficiencies than longer chain and sulfonic acid types (e.g., PFOS adsorbs more effectively than PFOA [McCleaf et al., 2017] and both adsorb more effectively than perfluorobutanesulfonate [PFBS] or perfluorobutanoate [PFBA] [Appleman et al., 2013]).

GAC can be regenerated through solvent (methanol) extraction and the material reused for non-drinking water applications. The solvent extracted PFAS can be distilled to remove the solvent, and the concentrated PFAS can be treated through incineration in a kiln at temperatures >1,000° Centigrade (°C).

Ion exchange has been shown to effectively sorb and treat a broad suite of PFAS at field scale to below analytical detection limits for influent concentrations in the range of several 100 micrograms per liter (µg/L) total PFAS (Kothawala et al., 2017; McCleaf et al., 2017; Woodard et al., 2017). Resins can be designed to target certain PFAS more effectively. But generally, like GAC, perfluorosulfonic acids (PFSAs) have a greater affinity than perfluorocarboxylic acids (PFCAs) for similar chain length, and longer chains have a greater affinity than shorter chain PFAS. IX are also available as single use and regenerable resins, where the solvent extract can be submitted directly for incineration or distilled and the PFAS residue incinerated. Regenerable resins are better suited for removal of higher concentration PFAS (ITRC, 2021d).

IX are highly susceptible to fouling and require pre-treatment for pH, inorganic and organic co-contaminants, and major anions and cations. Low concentrations of dissolved organic matter, iron, or manganese can significantly influence membrane performance and permeability.

Reverse osmosis and nanofiltration

Reverse osmosis (RO) and, to a lesser extent, nanofiltration (NF) are commonly used in mining and many industrial water treatment processes to remove ions from water by forcing impacted water through a semipermeable membrane. Both techniques can concentrate PFAS in the permeate, which can then be treated using a second technology (such as foam fractionation or advanced oxidation) and have been shown to be effective at removing longer chain (>C5) perfluoroalkyl acids (PFAAs) (Loi-Brugger et al., 2008; Tang et al., 2006). In order to preserve the RO/NF membranes for removal of PFAS, pre-treatment is required to remove interfering anions and cations, optimize pH, and remove organic contaminants that might clog the membranes. The effectiveness of RO/NF at removing PFAS has been evaluated extensively in wastewater and drinking water applications where PFAS was not the target contaminant (Tang et al., 2006; Flores et al., 2013; Glover et al., 2018; Dickenson and Higgins, 2016; Merino et al., 2016). Tang et al. (2006 and 2007) studied PFAS from various wastewaters using various RO and NF membranes and achieved >99% removal at PFOS concentrations ranging from 0.5 to 1,500 milligrams per liter. Although RO/NF have high treatment efficiencies at high PFAS concentrations and reliably remove the bulk of PFAS from highly impacted waters (e.g., PFAS-AFFF impacted groundwater where concentrations can be in the high µg/L range), they still require a polishing treatment using GAC or IX to reliably achieve regulatory criteria for effluent limits.

Foam fractionation

As a result of their non-polar tail and polar head, PFAS tend to accumulate at the air-water surface, which facilitates removal via foam fractionation by bubbling air or reactive gases (e.g. ozone) through a water column to form foam. The foam, which is composed predominantly of PFAS and other similar co-contaminants, is then skimmed off the water surface. One application used by the Australian Department of Defence, Army Aviation Centre Oakey (AACO) (base near Toowoomba, Queensland) is referred to as surface activation foam fractionation (SAFF) and uses hundreds of columns to progressively strip PFAS off the top of the water columns (ITRC, 2021d). Various studies have shown that C6 PFAS and greater can be removed effectively with this technology; however, it is less effective on shorter chain PFAS. The treatment rates that can be achieved with foam fractionation depend on the degree of foaming and contaminant load. At high foaming rates, throughput is reduced significantly, but the technology is very useful for removal of longer chain PFAS from concentrated mixed contaminant streams and RO/NF reject.

Developing destructive technologies

There are many destructive technologies in development showing promise for the destruction of short- and long-chain PFAS using oxidation approaches (ITRC, 2021d). Ozonation (in combination with persulfate) activated persulfate, electrochemical oxidation, sonochemical oxidation, supercritical water oxidation, photochemical oxidation (UV-Ox), and other advanced oxidation technologies are in various stages of development. While these technologies are promising, the PFAS concentrations need to be in the range where oxidation is cost effective. At remote sites, like mining sites, where disposal of PFAS can be challenging due to transportation costs, these destructive technologies may be better options for onsite destructive treatment of concentrated waste in combination with a GAC or IX polishing post treatment.

Status of PFAS regulation

To date, internationally, there appear to be no official guidance or guidelines regarding PFAS that are specifically directed to the mining industry; however, many jurisdictions have produced screening values for environmental media that would be potentially applicable to mining sites. Standards and guidelines for surface water, drinking water, groundwater, and soil have been developed for up to 20 PFAS in the jurisdictions of Canada, the United States (US), and internationally. The majority of these standards and guidelines are for PFCAs and PFSAs, with only a few jurisdictions preparing standards and guidelines for select fluorotelomer sulfonic acids (FTSAs) and GenX (a trade name for a group of shorter chain PFAS, e.g., less than six carbons). Some of these values are regulated. Select jurisdictions have also developed criteria for other types of media (e.g., sediment, ambient air, fertilizer, fish tissues, eggs, other food products, etc.); however, these values are often unregulated. Given the primary exposure pathway of concern at mining sites is expected to be ingestion of potable water, this review will focus on standards and guidelines that have been produced for water.

North America

In the US, no federal maximum contaminant level (MCL) has been released by the USEPA for any PFAS. However, the USEPA did define a lifetime health advisory for drinking water concentrations of PFOA and PFOS as 70 nanograms per litre (ng/L) in 2016, which applies to PFOA and PFOS individually and as a sum (USEPA 2019a). The USEPA has also released a screening level of 40 ng/L to determine if PFOA and/or PFOS are present in groundwater and warrant further investigation, but the preliminary remediation goal for contaminated groundwater remains as the USEPA drinking water health advisory (USEPA, 2019b). In 2020, the PFAS Action Act was passed by the House of Representatives to classify certain PFAS as hazardous substances, which is expected to lead to enforceable MCLs in future (Library of Congress, 2020).

In the absence of federal MCLs, pressure from citizens and politicians has caused some states to develop their own standards (Zemba et al., 2019). Many states have developed their own guidelines and criteria, especially for PFOA and PFOS, at a range of values more conservative than the USEPA (ITRC, 2021e). Illinois (2 ng/L PFOA and 14 ng/L PFOS) and California (5.1 ng/L PFOA and 6.5 ng/L PFOS) have some of the most conservative values for drinking water (ITRC, 2021e). Hawaii has set criteria for the largest number of PFAS parameters, with groundwater protective concentration levels for 18 PFAS. The range of guidelines and standards available from the states for the six PFAS for which standards and guidance values are most commonly defined are summarized in **Error! Reference source not found.**1.

Soil guidelines and standards for the protection of drinking water or groundwater have also been released by 12 states for up to 18 PFAS (ITRC, 2021e).

In Canada, Health Canada (HC) has established drinking water guidelines (DWGs) for PFOA and PFOS, as well as drinking water screening values (DWSVs) for nine additional PFAS (HC, 2019). The DWGs and DWSVs for the same six PFAS included in Table 1 are detailed in Table 2. The DWGs and DWSVs were defined to protect human exposure from drinking water sources. The DWGs for PFOA and PFOS are presented as Maximum Acceptable Concentrations (MACs), based on a study that referenced hepatocellular hypertrophy in rats as a result of exposure to PFOA and PFOS (HC 2018a and 2018b).

Table 1: Sample PFAS water guidelines and standards (United States) (ITRC, 2021e)

PFAS analyte	Drinking water (ng/L)	Groundwater (ng/L)	Surface water (ng/L)
PFOA	2 – 667	2 – 40,000,000	70 – 24,000
PFOS	6.5 – 667	2 – 500,000	6 – 300,000
Perfluorononaote (PFNA)	6 – 70	4.4 – 40,000,000	70 – 1,000
PFBS	345 – 667,000	420 – 400,000	400,000
Perfluorohexanesulfonate (PFHxS)	18 – 140	18 – 500,000	700
Perfluoroheptanoate (PFHpA)	20 – 70	2 – 40,000,000	300

Health Canada suggested that an additive approach using the ratio of PFOA and PFOS to their respective DWG should also be considered in cases where PFOA and PFOS occur concurrently in drinking water sources (HC, 2018a and 2018b). In 2021, the Canadian Council of Ministers of the Environment (CCME) produced a federal environmental quality guideline for PFOS in groundwater protective of ecological receptors and human health (CCME, 2021). The CCME value is also summarized in **Error! Reference source not found.**. None of the federal guidelines developed in Canada are currently regulated. The only Canadian province to produce regulated values is British Columbia (BC) (BC, 2019); these values are included in Table 2.

Table 2: Sample PFAS water guidelines and screening values (Canada)

PFAS analyte	DWG (MAC, ng/L) (HC, 2019)	DWSV (ng/L) (HC, 2019)	CCME, groundwater (ng/L) (CCME, 2019)	BC contaminated sites regulation, drinking water (ng/L) (BC, 2019)
PFOA	200			200
PFOS	600		600	300
PFNA		20		
PFBS		15,000		80,000
PFHxS		600		
PFHpA		200		

International

The Australian government completed a literature review for PFAS toxicity and indicated the evidence of human health impacts directly related to PFAS exposure is limited and does not indicate an increase in overall cancer risk (Zemba et al., 2019). However, this government still released health-based PFAS guidelines for drinking water, residential water, and soil for PFOA, PFOS, and PFHxS (ITRC, 2021e).

For other areas known for mining sites, such as South America, Indonesia, Asia, Russia, and the Middle East, country-specific regulatory frameworks for PFAS are unknown. However, many of the countries in these regions are part of the Stockholm Convention (Brennan et al., 2021) which has been regulating select PFAS as Persistent Organic Pollutants since 2009.

Conclusion

PFAS can be found at mining sites both due to their use in industrial processes, as well as in AFFF. The assessment, management, and remediation of environmental releases of PFAS from mining facilities needs to consider the unique receptors and exposure pathways associated with these remote sites, as well as the related logistical challenges for assessment and remedial approaches. As a number of jurisdictions are advancing regulation around the use of PFAS and its presence in environmental media, mining facilities will need to consider the potential impacts and liabilities associated with PFAS use at their operations.

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ECO Score – a New Environmental Standard for Industry and its Applicability in Water Management

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Abstract

Companies have always used quantitative data in decision making as it can be easily communicated, analyzed, tracked, and disclosed to stakeholders. However, environmental performance has not been historically managed in this manner despite being an integral part of business.

Managing a company's environmental footprint can be an intricate process involving many areas of expertise, dealing with qualitative and quantitative matters, in many cases intangible in nature. This has made it, in many cases, complex to deal with and difficult to hold employees accountable for their environmental performance. For Hochschild Mining, this lack of clarity hindered the company's ability to effectively manage their environmental performance.

This is the background against which the ECO Score was conceived in Hochschild Mining back in 2015 and launched in 2017. The ECO Score has allowed the company to express their environmental performance in a numerical fashion, that is, a universal language. It is comprised of environmental indicators representative of the activities performed by the company. A scoring system based on objective and transparent measurements tracks the performance of each business unit within the company. The corporate environmental performance goals based on the ECO Score are established every year and incorporated into the annual performance framework, determining the extent of annual bonus pay-outs to eligible employees.

Due to the ongoing global climate crisis, water is becoming a critical resource. Chronic droughts in some locations or extreme weather conditions in others may result in water shortages and affect operation and drinking water supply for many companies. As such, water management is an integral part of Hochschild's ECO Score, having key performance indicators on water quality, potable water consumption, and implementation of adequate environmental practices. Since the implementation of the ECO Score the

company has been able to reduce its water consumption per person by 53%, saving 1.6 million m^3 of this vital resource.

The ECO Score has proven to be an effective tool to effectively manage environmental matters, including water management. It has allowed Hochschild to hold employees to account and create value for all stakeholders. It also generates revenue through the reduction of the company's footprint, the efficient use of resources, and the mitigation of risks, while strengthening the company's environmental, social and governance culture.

Introduction

With over 100 years of operating experience in the Americas, Hochschild Mining PLC ("Hochschild", "Hochschild Mining" or the "Company") is a leading underground precious metals mining company focusing on the exploration, mining and processing of high-grade silver and gold mineral. Currently, it operates three underground mines, two located in southern Peru and one in southern Argentina. The Company is listed on the Main Market of the London Stock Exchange and is headquartered in Lima, Peru. In addition, the Company has an office in Buenos Aires, Argentina, and a corporate office in London. Its manpower comprises over 3,000 employees.

Guided by its corporate purpose – responsible and innovative mining committed to a better world – the Company endeavours to maintain and reinforce its corporate values, which are: responsibility, innovation, seeking efficiencies, and inspiring and promoting talent. They are the fundamental basis of our sustainability management system for the future, always acting with responsibility and environmental excellence.

Water is vital for humans and the ecosystem, and its distribution and availability due to climate change is one of the main concerns around the world (Rockström et al., 2009). Two-thirds of the world's population currently live in areas that experience water scarcity for at least one month a year (Mekonnen and Hoekstra, 2016). On the other hand, water is used in some form or fashion in most manufacturing processes. Chronic droughts with higher frequencies and intensity, or other extreme weather conditions, may result in water shortages and affect operation and drinking water supply for many companies (Lloyd's, 2010).

As a result, reducing water use and consumption is one of the most important actions for sustainability (Hoekstra, 2017). In this context, the need for water use data has been raised in the last few years by the United Nations Environment Program (UNEP). This data can be a source of valuable information (Pandit, 2015), so there is an ongoing challenge for companies to leverage its utility.

To attend to these matters, industry workforces usually include professionals whose main goal is to manage each company's footprint, such as water used in operations. Managing this footprint is often a complex and intricate process, involving many areas of expertise and dealing with diverse environmental cultural beliefs and values, as well as qualitative and quantitative matters, in many cases intangible in nature (Gallopin, 1981).

It is well known that companies have not been able to express their environmental performance in an objective and precise manner to decision-makers, despite collecting and storing large amounts of environmental data and despite being recognized as a vital tool for decision-makers (Gerrard, 2014). All of this has hindered the effective understanding and management of a company's environmental footprint.

In 2015, Hochschild took on the challenge and developed the ECO Score. This tool has allowed Hochschild to distil the many facets of its environmental performance into a single numerical value.

Methods

The main input used to design the ECO Score is data generated by the Company during its daily operations. In that sense, the tool was developed internally at zero cost and can be replicated in any industrial sector that is already collecting environmental data.

Figure 1: Selene Mine in Peru

The ECO Score is comprised of key performance indicators (KPIs), scored on two levels: at each mining operation and, overall, for the entire Company. The KPIs are based on measurable and transparent environmental metrics. These measurements are closely linked to the environmental footprint of the Company and contribute directly to the sustainability of the business.

The measured environmental metrics are:

- Environmental monitoring: the Company has an extensive network of water quality monitoring stations at all operations to ensure compliance with the maximum permissible limits (MPLs) established by the regulatory authorities. The objective is to have zero deviations from the MPLs.
- Environmental incidents: all activities must be carried out in accordance with best environmental practices to minimize the risk of environmental incidents. The emphasis is placed on establishing preventative measures to avoid such events. The objective is to have zero environmental incidents per year.
- Environmental audits: this element records the number of observations received in each mining operation from the environmental regulator. The objective is to have a maximum of two observations per year for each mining operation.
- Environmental management: the ECO Score also incorporates quantitative indicators directly related to environmental management at each mining operation. These indicators provide the crucial link between mine employees and the Company's environmental performance, since they are directly related to the daily activities performed by the Company. With these indicators, all employees cooperate to reduce the Company's environmental footprint. These indicators include the measurement of:
    - Water consumption per worker: the objective is to keep potable water consumption below 250 litres/person/day.
    - Waste generation per worker: the objective is to generate no more than 1.5 kg/person/day of domestic waste.
    - Percentage of marketable waste: the objective is to market or donate more than 75% of collected industrial waste.
    - Environmental culture: the objective is to achieve compliance of over 95% with respect to critical performance indicators established for each workstation.

The sum of these four environmental management metrics reflects the Company's culture of care for the environment. Good environmental practices, such as responsible water consumption and correct handling of waste are the result of a sound environmental culture.

Figure 2: San Jose Mine in Argentina

The ECO Score for each mine is compared against a scoring table (Table 1). The corporate environmental performance goals based on the ECO Score are established every year and incorporated into the annual performance framework, together with metrics relating to production, profitability, and safety, determining the extent of annual bonus pay-outs to eligible employees.

Table 1: ECO Score standards (2021)

Environmental performance	ECO Score
Maximum	≥5.00
Target	4.80 – 4.99
Threshold	4.50 – 4.79
To be improved	5<4.50

Table 2 shows how the Company calculates the ECO Score for each mining operation.

Table 2: ECO Score calculation matrix

Environmental metric		Range	Score
Environmental monitoring		0	1.00
		1 – 2	0.75
		2 – 5	0.50
		>5	0.00
Environmental incidents		0	2.0
		1	1.0
		2	0.5
		>2	0.0
Environmental audits		0 – 2	1.5
		2 – 4	1.0
		4 – 6	0.5
		>6	0.0
Environmental management	Water consumption per worker	<250 L	1.5
		250 – 350 L	1.0
		350 – 450 L	0.5
		>450 L	0.0
	Waste generation per worker	<1.5 Kg	1.5
		1.5 – 2.0 Kg	1.0
		2.0 – 2.5 Kg	0.5
		>2.5 Kg	0
	Percentage of marketable waste	>75%	1.5
		65% – 75%	1.0
		55% – 65%	0.5
		<55%	0.0
	Environmental culture	>95%	1.5
		90% – 95%	1.0
		85% – 90%	0.5
		<85%	0.0

Note: The maximum ECO Score is 6.0.

ECO Score results are published through the Green Challenge program. The results are tracked and shared with the whole Company on a monthly basis. At the end of every year, the Company rewards the mining operation that achieves the highest score in the ECO Score.

The 2020 and 2021 results have been independently assured following the International Standard on Related Services (ISRS) 4400, validating the calculations obtained by this tool.

Results and discussions

With the ECO Score, the Company has been able to express an intangible concept, such as environmental management, in a universal language, applicable to any industry. The most highlighted results are reported as follows:

In 2021, the ECO Score was 5.24 out of 6, surpassing the maximum objective of 5 points established by the Board. Since 2015, the ECO Score has improved by 59%, reflecting a significantly better level of environmental performance.

In 2021, the Company's overall water consumption was 192.83 litres per person per day (L/p/d), improving significantly against the maximum set for the year (250 L/p/d). Since implementation of the ECO Score, consumption of potable water has been reduced by 53%. In 2021, Hochschild has saved 321,739 cubic meters of potable water[1]. This is equivalent to 2.6 billion bottles of water[2].

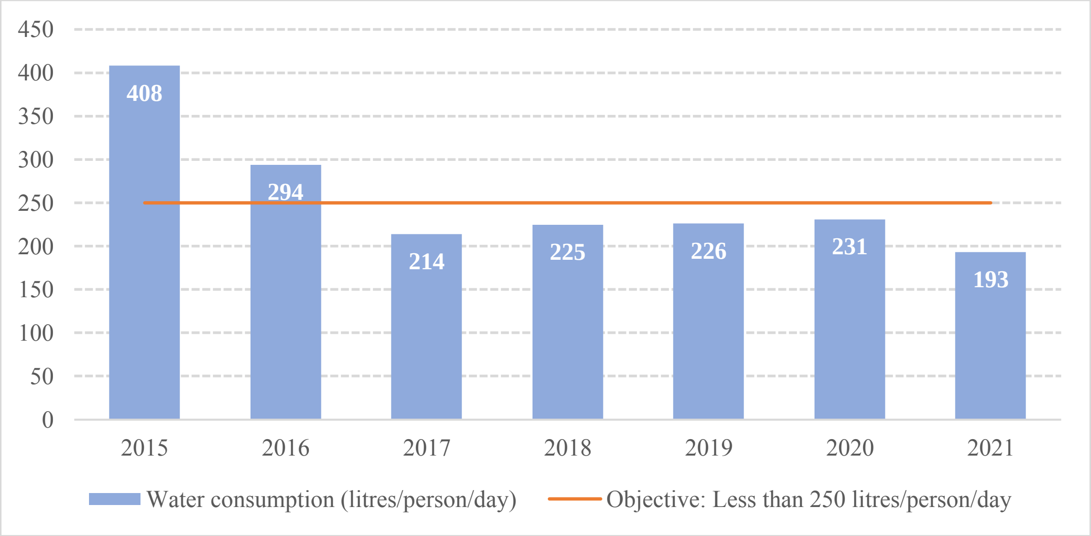

Figure 3: Historical potable water consumption

The strong environmental culture promoted by ECO Score has enabled the Company to identify opportunities to increase the percentage of recirculated water for the processing plants, thus reducing the consumption of fresh water. In 2021, 85.3% of all water used in processing was recycled water, predominantly from water recovery plants at our tailings storage facilities.

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[1] Volume of water saved considering the 2015 water consumption per capita data.

[2] 625 ml bottle.

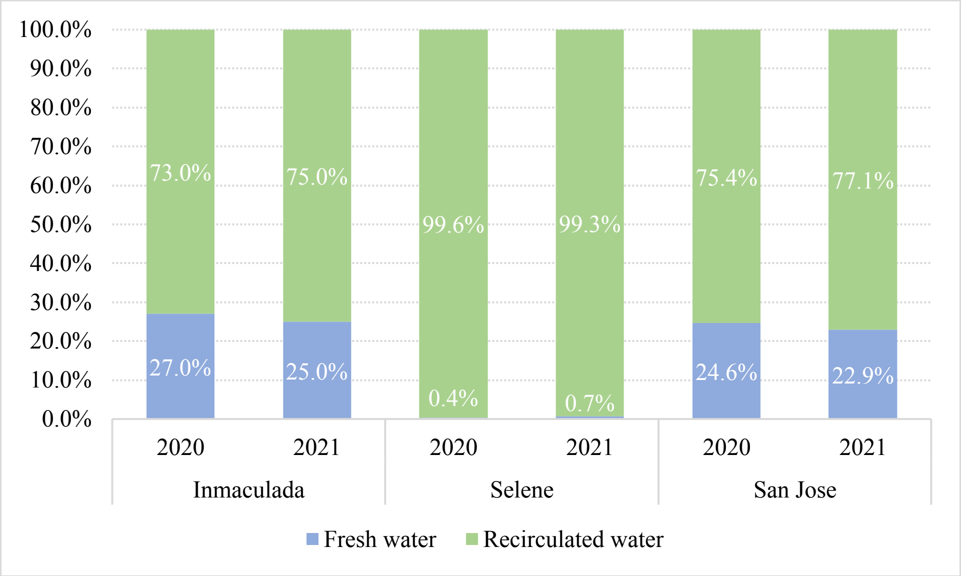

Figure 4: Recirculated water in processing mineral

The following figure shows the volumes of fresh water consumed at the three operating mines.

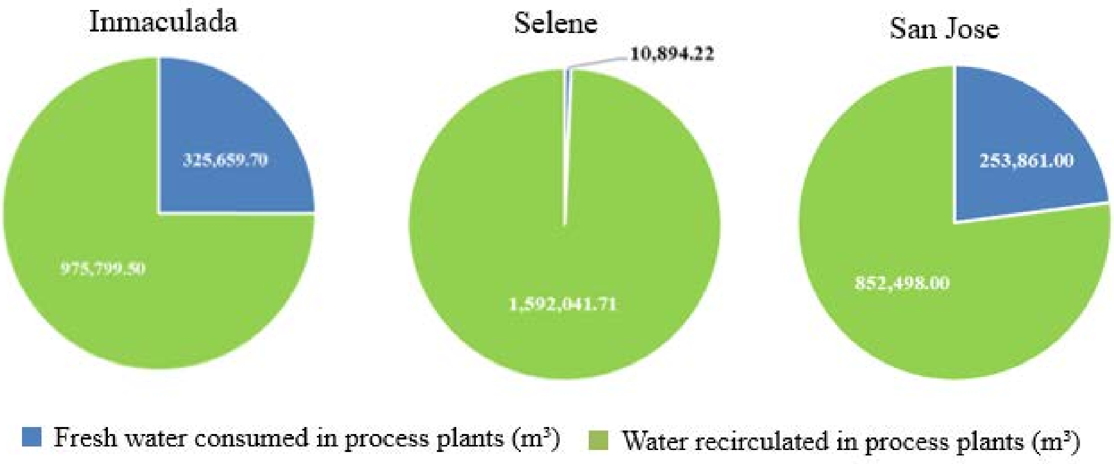

Figure 5: Industrial water consumption in process plants – 2021

Other results achieved through the ECO Score are:

- Between 2015 and 2021 the company reduced the generation of domestic waste from 1.94 kg/person/day to 1.00 kg/person/day, equivalent to more than 7.8 million kilograms of domestic waste.
- Since 2015 the company tripled the marketable waste through improving sorting where only non-reusable or non-recyclable waste is sent to landfill.

- The ratio of observations per visit of our environmental regulator has decreased from 5.2 to 0.1 from 2015 to date[3], equivalent to an improvement of 96%.

This shows that the implementation of the ECO Score has made it possible to achieve a substantial improvement in our environmental performance and water management.

Use in other industries

In 2020, the ECO Score was adopted by Resiter, a regional waste management service provider and strategic partner of Hochschild, in all of its Peru operations. They are trailing different indicators that can best reflect the environmental performance of their activities. During the first year of implementation Resiter was able to reduce water consumption by 18% in one of its operations.

With this, it is clear that the ECO Score can be adopted by any company striving to improve their environmental footprint and contribute to a better world. Our goal is to continue to encourage other suppliers and strategic partners to adopt the use of the ECO Score in their operations.

Conclusion

The ECO Score is an effective and innovative tool used to manage environmental matters, hold employees accountable, and create value for all stakeholders. This tool has allowed Hochschild to quantify its environmental performance and express intangible environmental management into a single numerical value, which can be universally understood.

The healthy competition between mining units generated by the ECO Score, the transparency created around the company's environmental performance, and the integration with the other corporate performance objectives[4] to determine annual bonuses, has allowed the company to encourage its workforce to achieve a common environmental purpose. As a result, the Company is effectively managing its environmental performance, minimizing the Company's water footprint, and reducing risks such as water scarcity. Most importantly, the ECO Score can be seen as a tool that other companies within or beyond the mining industry can adopt to promote a sound environmental culture and effectively manage the water resource.

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Improving Efficiency in Underground Mine Process Water Reticulation Systems

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Abstract

Process water is an integral part of mining operations. Underground machinery requires water to operate, with most sites' usage reaching several hundred gallons per minute. Establishing a reliable supply of process water in underground mines is one of the main challenges affecting mining operations globally. Underground water shortages are far too common, in most cases occurring daily, costing millions annually in lost production. When revenue-generating equipment does not have a reliable supply of water, operations shut down. Most mines have struggled to implement a dependable underground process water-management strategy. Historically when water surges or shortages occur, the solution is to "live with it" and fix the damage caused, or apply a makeshift approach without looking at the root of the problem – the overall system design.

A traditional installation is gravity-fed and allows water to flow through several pressure reducing valve (PRV) stations on its way down the mine ramp or shaft, known as a cascade system. Most PRVs in use today are pressure-regulating valves, which allow for the outlet pressure to be set and adjusted. The issue is that those regulating PRVs often struggle with system pressure changes, sudden flow changes, and increasing water demand. This, combined with valve droop, is the root of almost all underground process water delivery issues.

To avoid costly shutdowns due to poor process water delivery, mine owners have begun to deploy a new approach to system design. This new strategy, which in part involves valves with specialized capabilities, has proven to eliminate fluctuations in water pressure and availability, eliminating costly water shortages or surge situations.

The first step is to separate the main water supply from the underground levels to create a cascading standpipe. This should incorporate ratio PRVs in place of regulating PRVs throughout the cascade system. Unlike regulating valves that have a calculated output pressure, ratio valves operate on a fixed ratio pressure, so there is no set pressure on the outlet side of the valve. This mitigates the issues previously associated with valve hunting within the standpipe system. The next step is to separate the water supply to

each level by employing specialized regulating valves designed to eliminate droop. By creating one system for the shaft piping and another system to supply each level, mines can effectively manage process water.

This paper will review the challenges associated with the current design of most underground process water-management systems, and review a new approach to system design to alleviate the long-term challenges associated with inconsistent water supply. We will discuss system design changes, the real effect of valve droop in gravity-fed systems, and the value of a high-performance underground process water system. Using actual case studies, we will review productivity gains realized within global mining operations that have employed this new approach to process water management.

Introduction

Globally, mines face challenges associated with inadequate water supply on a recurring basis. From water surges to insufficient water delivery, these events result in lost production time and costly repair or cleanup. Instead of looking at the underlying issues with underground gravity-fed reticulation systems, most mines apply a superficial strategy that does not address the root problem. Underground water storage tanks, booster pumps, orifice plates, and control valves are commonly used, but often do not work, or only marginally improve performance.

To truly alleviate the time loss and costs associated with inconsistent process water supply, mine owners cannot look to the impacted system, but instead need to look at the root cause, system design. When a system is properly designed to manage process water flow at all levels, 100% process water uptime is an achievable goal. Yet to meet this goal we must first understand the challenges mines are facing daily. Process water-management issues are rooted in several recurring problems impacting operations. We will walk through these challenges and a design change that has been proven to alleviate these issues and deliver consistent water flow to every level within a mine.

Instability

Instability within underground mining operations is generally seen when the valves installed in a system are designed to regulate on a constant downstream pressure. These valves, traditionally known as pressure regulators, will open more if the supply pressure drops and close when supply pressure rises to maintain downstream pressure. Larger systems with long pipe runs store a significant amount of compression energy. An increase in valve opening after a pressure reduction has been sensed can cause the valve to “make up” for the decompressed volume and react to pressure drops from the increased flow. Though this reaction time is quick in small systems, in larger applications the time between pressure change and valve reaction is delayed, and this slow reaction time results in large pressure surges within the piping system. The closing and opening of a single regulator valve can become out of phase with the system and will cause the subsequent valves to operate erratically. This phenomena is known as valve hunting and is the main cause of instability in underground process water cascade systems.

System design

The root of many process water-management challenges can be traced back to the cascade system design. Traditionally the shaft piping system utilizes the same valves to bring process water down the shaft and feed the levels of the mine. Yet water, which by its nature looks for the flow path of “least resistance”, flows easily down the shaft, bypassing the horizontal levels required to feed a mine. These systems, in turn, typically see water shortages within upper levels and water surges at the base levels of the mine.

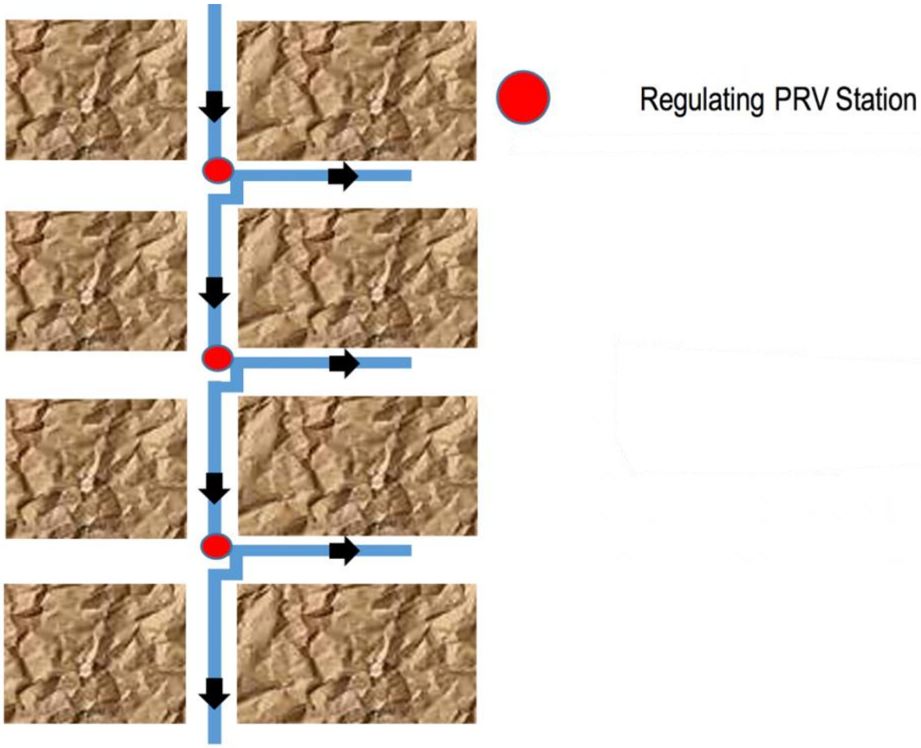

Figure 1: Traditional shaft design incorporating regulating PRVs in a cascade system

This inconsistent flow can cause water starvation on production levels, leading to equipment failures, with surges occurring at the base levels of a mine.

Droop

The two styles of regulating PRVs commonly used in mining operations are pilot-operated globe valves and direct acting pressure reducing valves (DAPRV). All PRVs create a controllable flow restriction that breaks the energy of incoming water and sets the desired downstream pressure. Pilot-operated globe valves use an external pilot that, according to downstream pressure, drains or fills the upper chamber of the valve that controls the flow restriction and thus the outlet pressure. DAPRVs operate differently to a pilot-operated globe valve, employing a spring directly on the flow restriction. As downstream pressure rises or falls, the restriction opens and closes accordingly to allow more or less flow.

Ideally only the restrictor should perform the task of pressure reduction. Pressure-reducing globe valves (pilot-operated or direct acting) used in mining are mostly a “T” pattern, meaning as water flows through the valve it changes direction several times and is constricted through cavities, losing energy uncontrollably. Think of these valve bodies as orifice plates. At low flows the controllable restrictor is doing all the work to reduce pressure; however, as flow increases the valve body effectively becomes an orifice plate, lowering outlet pressure beyond the set point and limiting flow rates. Traditional cascade systems use several regulating type “T” globe valves in series, so this orifice effect is exacerbated.

In underground mining operations these valves commonly experience droop – a decrease in outlet pressure from the set value resulting from an increase in flow rate. Equipment that relies on a specific water volume and pressure cannot function properly and productivity suffers. Valve droop can have dramatic consequences for a mine, amounting to millions of dollars of lost production each year. In Figure 1, the first valve in the cascade system sees all the flow in the mine, causing a significant droop. This droop, combined with frictional losses of long lengths of horizontal pipe, are another cause of water shortages around equipment.

The system design solution

To solve the above issues, mine owners must deploy a different approach to system design. The first step is to separate the cascade system from the system that feeds the mine levels (Figure 2). This change in design will remove the bias for water to flow down and bypass levels, allowing equal access to process water at each operational level. To do this, regulating PRV stations must be removed from the cascade system. In place of the regulating PRVs, a standpipe is created using ratio pressure-reducing valves to control the column pressure, with regulating valves installed off to the side to feed operating levels.

The key is to separate the two systems, one for cascade, and the other for operating levels. Installing regulating PRV stations as a means to feed the levels, rather than within the cascade system, eliminates surges and swings in system pressure, increasing system stability, reliability and safety, as relief valve blowoff and other effects are no longer a concern.

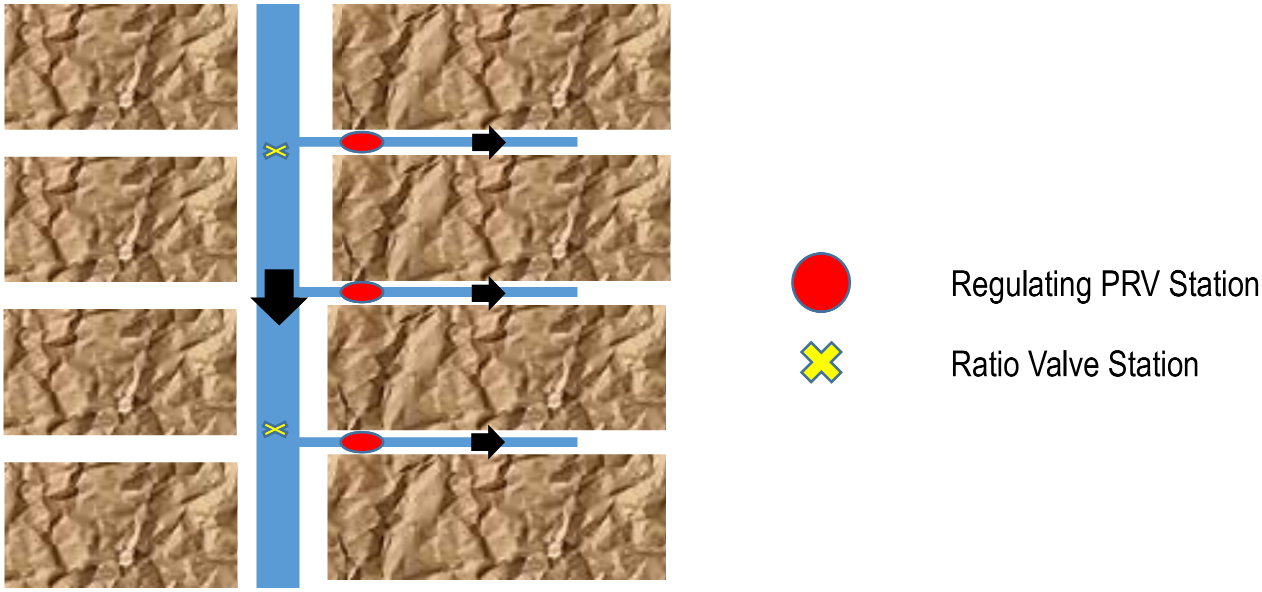

Figure 2: New shaft design with ratio PRV in a cascade system and regulating PRVs feeding levels

To implement this new design, process water-management systems must use ratio valves for cascading, which have been underused in underground mining operations. Unlike regulating valves, the stability of ratio valves is assured because any change in pressure, water supply, or demand, will immediately cause a pressure change in demand or supply proportionate with the set ratio of the valve. Ratio valves installed in series as in deep vertical mine shaft pipelines have proven to show no instability and maintain consistent predictable performance throughout the demanded flow range.

Once the feed piping is stabilized, the next step is ensuring that valve droop and frictional losses in horizontal piping do not cause water shortages around revenue-generating consumers. The solution for this lies in the pressure-reducing valve design. “T” pattern DAPRVs and pilot valves will droop and obstruct consistent water pressure to the levels. Valve droop combined with frictional losses in long runs of horizontal pipe are a key cause of water shortages to the consumers.

To solve this, mines have begun to specify y-pattern valves that provide a nearly unobstructed flow path through the valve, meaning valve droop is removed from calculations. The use of these valves eliminates tampering, as the valve’s outlet pressure can be set based on consumer requirements and the calculated frictional loss on the pipe run with no variation, meaning consistent water supply and pressure.

Conclusion

The design of process water-management systems in underground operations has a substantial impact on the operational productivity of a mine. Reliable water flow is a challenge that mines have grown to see as a day-to-day inconvenience, causing equipment failures and costly shutdowns. Water needs to be balanced to ensure that every area of the mine has equal access to an adequate supply and using a proper design method for the cascade piping and levels has become a trusted solution in mines around the world. With enhanced system designs available, there is no need to continue to live with production losses caused by recurring process water-management issues.

An Overview of Risk Allocation and Delivery Mode for Desalinated Water Supply Projects in Mining

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Extended abstract

Mining requires a significant supply of water. Historically, this water has come from fresh water sourced from underground and surface sources, but that lower cost water has been largely used up. Mining companies have therefore turned to alternative sources of water, such as water recycled from municipal plants, straight seawater, and desalinated seawater.

Future water consumption for mining is expected to increase substantially over the next decade because of the following factors.

- Increased production of metals: Metals production is growing, and part of the increased water demand can be explained by increases in production from the expansion of existing mines and by completely new projects being built.
- Declining grades: In addition to increased production, there is an important increase in demand for water caused by declining mineral grades at existing mines. Historically, the richest deposits were mined first, as they were less costly to mine. As mineral grades decline, more mineral must be processed in order to produce the same amount of metal. The use of water is proportional to the amount of ore, so it follows that more water is needed to produce the same amount of metal. For example, for copper, if the copper grade is 1.5% instead of 3%, it will be necessary to mine twice as much ore and to use twice as much water to produce the same amount of final copper.
- Process changes: processing of oxides versus processing of sulfides (leaching to flotation). As a given ore deposit is mined, sometimes a full process change is required to continue to produce copper. Typically, the portion of a mineral deposit that is located closer to the surface is richer in metal oxides, and the portion of the deposit that is deep down, away from the surface, is richer in metal sulfides. At the beginning of the life cycle of a mine, oxides near the surface are processed first by leaching/solvent extraction/electrowinning, and when the oxides are depleted, the underlying sulfides are processed via milling/flotation.

Unfortunately, the infrastructure used for leaching/solvent extraction/electrowinning and flotation does not have much in common, and the processing of oxides and sulfides requires very different amounts of water. While the processing of oxides in the early stages of a mine typically requires 200 litres of water per ton of mineral or ore, the processing of sulfides requires on the order of 800 litres of water or more per ton of ore. Therefore, when a mine changes in a natural progression from processing of oxides to processing of sulfides, it must increase its water supply, as the water infrastructure that was implemented to process oxides will be inadequate to process sulfides.

As mentioned, this additional demand for water is being satisfied from nonconventional sources, such as straight seawater, desalinated seawater, and municipal effluent plant discharge, all of which often must be conveyed for long distances and to high altitudes.

The last few years have brought major changes in mining water supply strategy, and now include the commissioning of several desalination plants. For these mining desalinated water projects, there have also been important differences over time in the way that mining companies have allocated risk and driven execution. For convenience, we can think of three main phases that have dominated project delivery mode over time:

- Phase 1: The desalinated water supply is only a component of a large EPCM (Engineering, Procurement, and Construction Management) contract, typically encompassing a concentrator plant and other major plant infrastructure.
- Phase 2: The desalinated water supply is an EPCM contract on its own, completely independent of other infrastructure delivery.
- Phase 3: More recently, alternative delivery models are being used, including BOOT (Build, Own, Operate and Transfer) and EPC (Engineering, Procurement and Construction) contracts.

Each of these phases has particular characteristics in terms of risk allocation and the roles of the mining company, the water infrastructure supplier, the engineering partners and finance. These will be discussed further below.

Water related risks are typically classified as physical risk or supply risk when water supply is not enough to meet production plans, regulatory and legal risk when there is a risk of reduced water rights or allocations or the need to prevent or treat contaminated water for discharge, and reputational risk, which arises from water quality problems, i.e. discharging contaminated water. This can cause loss of investment value and extend beyond a site to a whole company.

These have been addressed elsewhere in detail (Morgan and Dobson, 2020). In this article, we are mostly concerned with risks associated with the infrastructure itself, namely, the project execution risk, or risk that the water supply project is not complete in time for the start of a new site, or that the infrastructure does not meet needed water supply targets.

To examine project risk, it is important to understand how mining companies make investment decisions.

Mining companies make their investment decisions based on the results of engineering studies, and often significant sums are spent on projects that never materialize. After a new orebody is discovered, a study is first carried out at a conceptual stage to provide a rough estimate, often with no better than 50% accuracy, of how much capital will be required to develop the orebody. With that information, the mining company determines if it is attractive or not to continue with the project, and then commissions further studies that increase the level of detail for the assumptions made, and the accuracy of the level of investment required. The projects that do not materialize do not provide a high enough return on investment and are abandoned along the way. Sometimes, metal prices change significantly, and studies are brought back to life to continue with further evaluations. At the end of the engineering study process, the mining company ends up with a study, typically at a 90% level of accuracy, and with very detailed assumptions, which is presented to the board of directors for a go/no go decision. When the decision to go is made by the board, the project is often executed immediately. The overall mining project is typically composed of many individual major systems, such as ore mining, crushing and transportation; process plant (concentrator); tailings dam, etc., which can be handled by a single EPCM contractor, but rarely by a single EPC or BOOT contractor.

Similarly, a desalinated water supply infrastructure project has several components, including the seawater intake structure and marine works, the desalination plant and its pretreatment, the pipeline and pumping stations to deliver the water to the mine, and the power supply for the desalination plant and the water delivery system.

Typically, the pipeline and the pumping stations package is the largest cost of the water supply project, because the water must be pumped great distances, often from as much as 200 km away, and to great elevation, often as high as 3,500 m. Straight seawater and desalination projects have been previously compared (Philippe et al., 2010).

It is also unusual for a single company to be able to supply all of these components under an EPC or BOOT contract, and often these contracts are awarded separately. What is more common is that a single EPCM company is charged with coordinating all of the packages and helps the mining company award contracts for each package.

Due to the size and complexity of a full-scale mining project, these projects have historically been carried out as EPCM (Engineering, Procurement, and Construction Management) projects between the mining company and a very large Engineering and Construction firm. In the EPCM contract, the

Engineering firm acts as an advisor and manager for the mining company and makes its money by charging the mining company for the hours it uses to advise and manage the project. The EPCM firm does not carry a lot of risk on infrastructure or hardware because it manages contracts between the mining company and suppliers of individual packages and does not supply infrastructure itself. The individual packages are typically handled as EPC (Engineering, Procurement and Construction) contracts, where the EPC firms deliver physical infrastructure and make their money by taking a margin on the infrastructure and associated engineering.

Because of the size of desalinated water projects, there has been a change from an EPCM firm handling all of the mining project including the water infrastructure, to the water infrastructure being handled as an EPCM contract all on its own. In addition, a recent trend has been for mining companies to avoid tying up a very large investment in water infrastructure, and instead using a BOOT (Build Own Operate Transfer) model, where all the investment is done by a specialist firm that makes money by charging the mining company an amount per unit of water produced, i.e. dollars per cubic meter of desalinated water delivered. Another advantage is that the BOOT contractor will operate the water plant, which has historically been a problem for mining companies lacking desalination operations experts.

Table 1: Risk allocation for several project delivery contract modes

Issue	EPCM	EPC	BOT
Where do funds come from?	Mining company/Bank	Mining company/Bank	BOT developer
Who pays if estimation is wrong?	Mining company/Bank	EPC company or mining company	BOT developer
Who pays if project is delayed?	Mining company/Bank	EPC company / Subcontractors	BOT developer
Who takes technology risk?	Mining company	EPC company / Subcontractors	BOT developer
Who pays subcontractors?	Mining company	EPC company	BOT developer
Who prepares technical specifications?	EPCM company/Mining company	EPCM company/Mining company	BOT developer
Who manages subcontractors?	EPCM company	EPC company	BOT developer
Design changes	Easy	Hard	Very hard
Incentive for quality	High	Low	Low
Contingency costs	Low	High	High
Design responsibility	EPCM company/ Mining company	Mining company	BOT developer
How do they make money?	Charge lots of hours/ add change orders	Pressure subcontractors	Pressure subcontractors
Mining company control over project	High	Low	Very low
Procurement documents	EPCM company	EPC company	BOT developer

This is in essence a transfer of the risk from the mining company to what is in essence a water supply company, much like a utility charges individual customers for their water usage. Table 1 presents many aspects of project execution in terms of risk.

Typical sources of problems in mining water supply projects

We now consider some typical sources of problems in mining water supply projects:

- Lack of mining experience of desalination plant suppliers: The largest market for desalination is municipal, not mining. Therefore, desalination plant suppliers are accustomed to projects where desalination companies supply a municipal desalination project, the desalination plant is the major component of the project, and the desalination supplier is the main supplier. Because of this, the desalination supplier has a strong influence on the timing of the project and often manages the whole project. For a new mining project, the desalination plant is on the order of 5% of the whole project. Therefore, the desalination supplier now finds itself having to accommodate to the way mining companies run projects, with large demands of specifications, drawings, progress reports, formal document management requirements, and a large owners' team controlling everything that the desalination supplier does and demanding top speed of execution.
- Safety standards: Mining companies are very safety conscious and have developed very sophisticated accident prevention and reporting systems. Something as minor as a speeding ticket on the way to a mine site may disqualify a person from working on a project, so it is important that companies starting supply projects with mining companies quickly catch up with the particular philosophy, programs, and reporting requirements for the particular mining company that they are dealing with.
- Speed of execution: As mentioned above, mining projects are typically studied for several years before they are executed, and once the decision is made by the board of directors to go forward, they are typically executed at top speed and with a strong focus on early completion. This typically catches desalination plant suppliers by surprise, as municipal water supply projects do not have these time pressures, at least not as intense as are seen in the mining industry. The reason for this is that mining projects attempt to capture revenue from copper production as soon as possible, and a shortened schedule can mean hundreds of millions of dollars in income, whereas municipal water supply projects are subject to comparably minor penalties for late completion.
- Construction standards: Because of the focus on low downtime in mining, construction standards are very high and redundancy is always a consideration, which is not seen as strongly in municipal projects.

We close with some thoughts on the sharing of infrastructure between neighboring mine sites. While an outside observer may very rightly think that it makes sense to share desalination and water transport infrastructure between neighboring mines, and better yet, between mining companies and municipal water supply utilities, in practice it is quite difficult for this to happen.

As explained above, mining decision making is a long and sophisticated process, and the chances of an investment decision reaching the board of directors at the same time for two different mining companies are practically nil. In addition, mining companies are very concerned about the stability of their water supply and are very sensitive to water supply risk. Therefore, they do not look favourably upon sharing infrastructure with others, as they are worried that issues affecting the other company, for example a strike by the other companies' workers, could affect its water supply and therefore its production. Any downtime by a mining company is typically measured in thousands of dollars per hour, and mining companies are not willing to take much risk on their production.

We still retain some optimism for these infrastructure-sharing projects, but the coordination and timing challenges are significant.

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Groundwater Recharge Estimates in Mine Site Using Integrated Hydrological Model: Review and Critique

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Abstract

Recharge estimation is a fundamental input for water resources management. There are several methods for recharge estimation, although they are normally subjected to large uncertainties. However, the empirical models that are often used in hydrological studies for recharge estimate do not always provide reliable results. For that reason, integrated hydrological models have become a preferred approach for estimating recharge due to the inclusion of major processes of the hydrologic cycle pertaining to surface water and groundwater that are not fully captured in empirical models. In this study, the groundwater recharge was a difficult parameter to estimate because of the complexity of the site's hydrogeological system below a variable peatland and the area's complex snowmelt pattern. The objective of this study was to estimate the temporal and spatial distribution of recharge with MIKE SHE for the study area in order to use it as an input for a complex three-dimensional groundwater model in FEFLOW.

MIKE SHE is a physics-based, deterministic, integrated hydrological framework for hydrological modelling that solves the partial differential equations describing mass flow and momentum transfer. In this study, the MIKE SHE model run incorporated the processes of evapotranspiration, precipitation, snowmelt, overland flow, unsaturated zone, and groundwater flow to simulate recharge. The model was calibrated based on site data for overland flow, hydraulic heads, and snowpack.

This paper presents a summary of the conceptual model for the study site and the various stages of the MIKE SHE model construction, calibration, and analysis of results such as recharge variability in space and time. More importantly, this study highlights some of the challenges associated with the application of the integrated hydrological modelling approach to complex hydrogeological systems and presents some critiques made during the development of the recharge model. Further, it suggests recommendations for improvement in recharge estimates for future integrated hydrological models.

Introduction

Recharge estimation is a fundamental input for water resources management. There are many methods for recharge estimation, although they are all subject to uncertainties (Islam et al., 2016). For instance, empirical models are often used for the estimation of recharge, but do not always provide reliable estimates. For that reason, integrated hydrological models, which help simulate the major processes of the hydrologic cycle including surface water and groundwater, are sometimes used to estimate recharge distribution with less uncertainty. But do integrated hydrological models always provide reliable estimates of recharge?

This paper reviews and outlines some drawbacks associated with using some integrated hydrological models to estimate recharge to a groundwater system in a mine site.

In this study, groundwater recharge was difficult to estimate due to the complexity of the site's hydrogeological system and the complex snowmelt patterns in a spatially variable peatland, hence the use of an integrated hydrological model. The objective of this study was to estimate the temporal and spatial distribution of recharge with MIKE SHE and the result used as an input for a three-dimensional groundwater FEFLOW model to simulate the development of an underground mine and its impacts. The recharge pattern from MIKE SHE was also compared to typical recharge patterns for soils from the Snowmelt Model.

Methodology

The integrated hydrological modelling approach used to estimate groundwater recharge in the study area involved the characterization of the site's geology/hydrogeology, the use of climate data, land use data, overland flow data, unsaturated zone data, and saturated zone data. The utilization of these data in the model was then followed by model calibration.

Study area

The confidential nature of the project does not permit a detailed description of the study site. Hydrogeological information of the site is therefore presented in general terms. The site receives a total precipitation of about 530 mm, with more than 50% accumulating as snow. This snow accumulation on the site's extensive but spatially variable peatland makes characterizing recharge during snowmelt challenging. Recharge is further complicated by the site's complex hydrogeology, which comprises a shallow and a deep groundwater system. The shallow groundwater system is in the high hydraulic conductivity quaternary deposits of glacial, fluvial and aeolian clastic sediments, while the bedrock that forms the deep system is weathered and fractured at the upper part, but unfractured at the base. The bedrock material consists of mafic and ultramafic rocks, quartzite, mica schist and gabbro. Figure 1 shows a map of the study area.

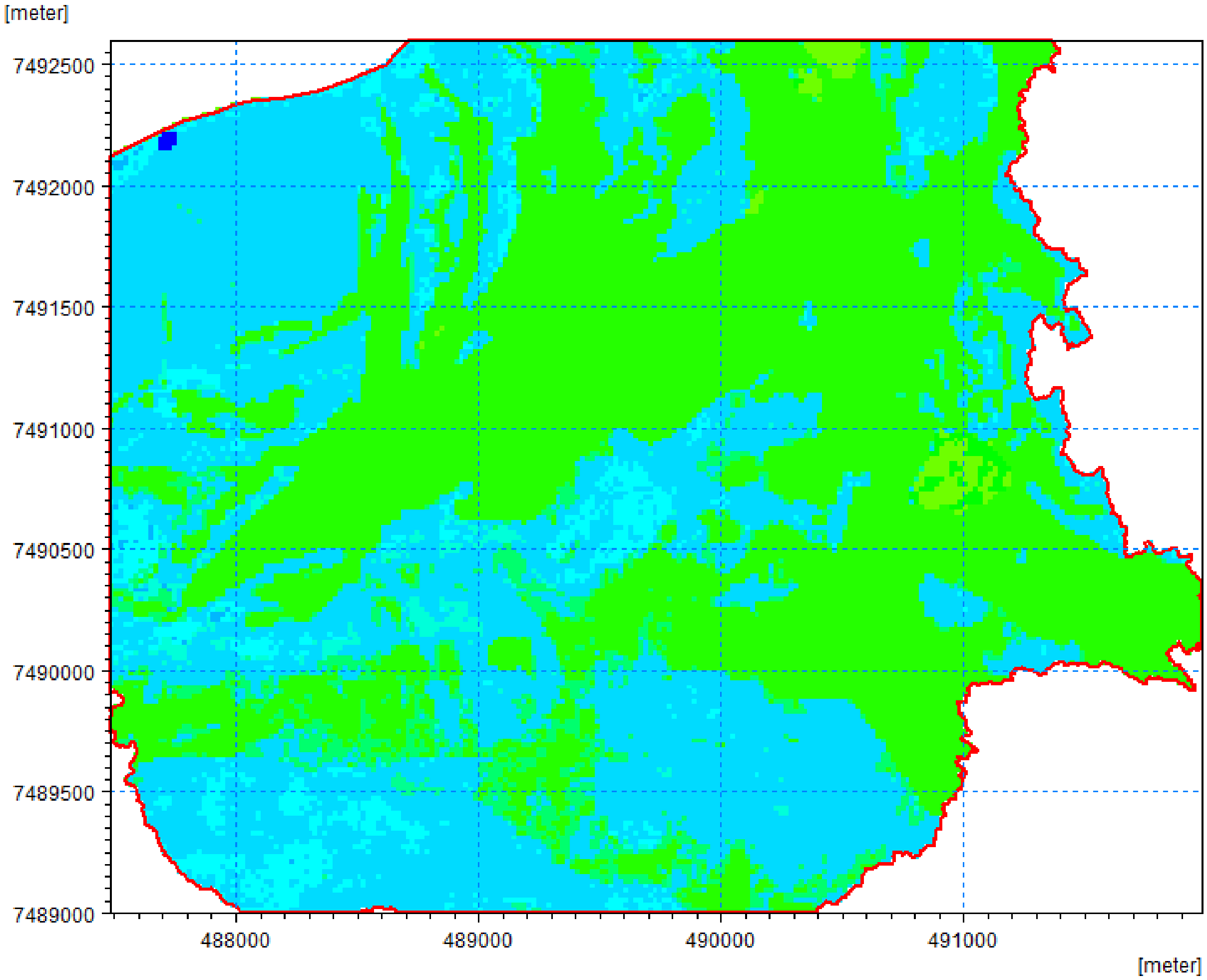

Figure 1: Map of the study area

Structure of the integrated hydrological model as applied to the study area

MIKE SHE is a physics-based, advanced, and flexible framework for hydrological modelling that solves the partial differential equations describing mass flow and momentum transfer (Graham and Butts, 2005). Figure 2 summarizes the structure of the MIKE SHE model in terms of how the various hydrological components are utilized in the estimation of recharge.

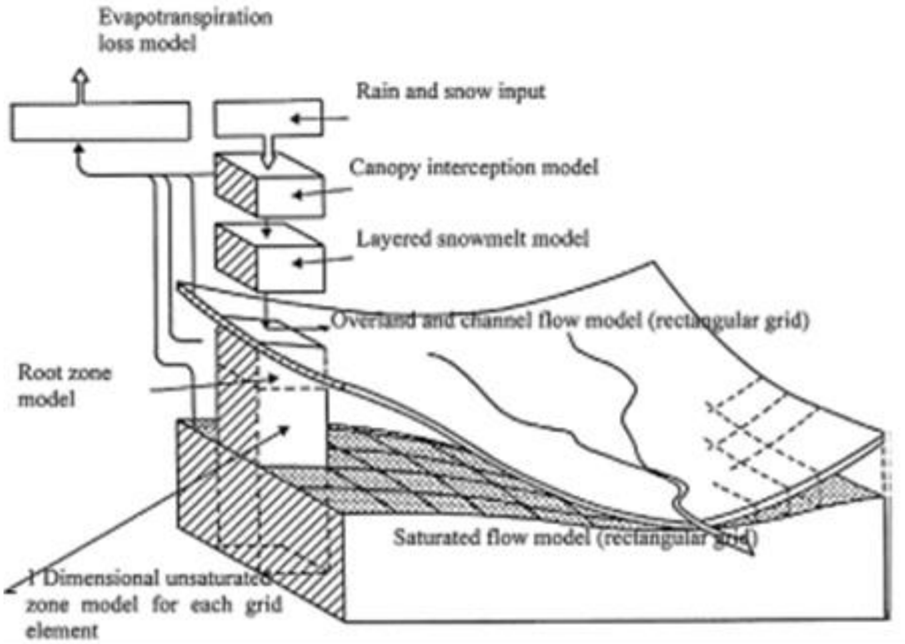

Figure 2: MIKE SHE model structure (Regard et al., 2010)

Data and discussion

MIKE SHE model construction

The model domain (mine site) spanned across three sub-catchments. It was vertically discretized and represented the 15 m depth of the stratigraphical sequence corresponding to the Quaternary deposits. This 15 m thick alluvial deposit that sits atop a deep weathered and fractured bedrock was more significant than the deeper bedrock, because that is the depth where recharge is more important in the model.

The executed MIKE SHE model included the process models of evapotranspiration, precipitation, snowmelt, overland flow, unsaturated flow, groundwater flow, and channel flow and their interactions (Graham and Butts, 2005) to estimate recharge. MIKE SHE describes recharge as “Total recharge” which includes parameters like exchange between unsaturated and saturated zones, recharge from bypass or macropores, direct flow between saturated zone and overland, etc. (DHI MIKE SHE, 2017).

The model was calibrated based on field data from overland flow, hydraulic heads, and snowpack. The input data for the model was based on data measured on site as well as on indirect measures.

Climate data

Precipitation, air temperature, and reference evapotranspiration data were required as climate input data. The first two parameters were obtained from a meteorological weather station close to the study area and were applied to the model daily.

The reference evapotranspiration is the amount of water that is evapotranspirated from a given reference surface (typically of a well-watered grass or crop) (FAO, 1998). This input was obtained from the satellite MODIS.

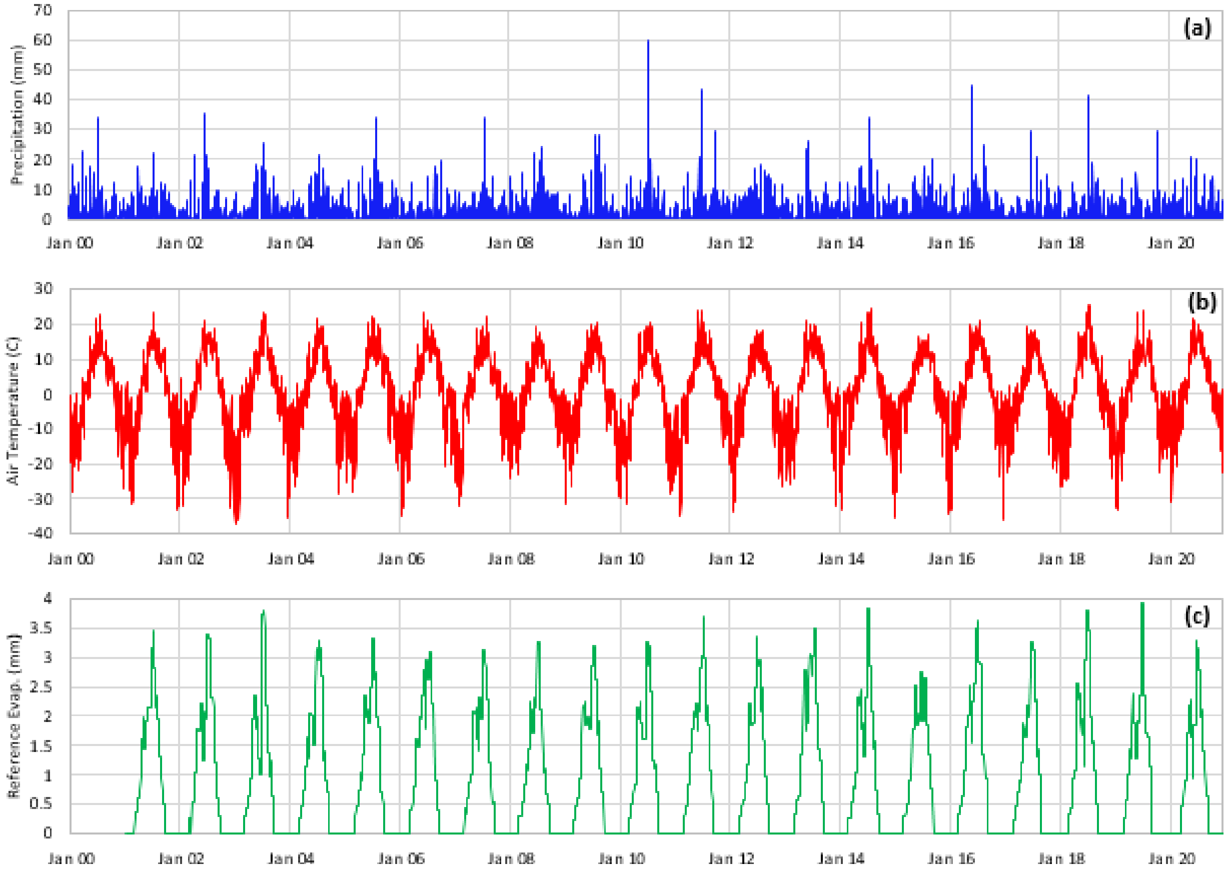

Figure 3: Climatic data input (a) precipitation; (b) air temperature; and (c) reference evapotranspiration

Land use

The study area has different land use areas such as transitional wood, inland marshes, peatbogs, coniferous forest, non-irrigated arable land, mineral, and industrial sites. Evapotranspiration parameters were required by MIKE SHE for each type of crop. The leaf area index (LAI) and root depth for each crop were therefore obtained from FAO's database (Fischer et al., 2008) and used to calculate the real evapotranspiration.

Overland flow

The movement of water over the surface was also simulated by executing the overland flow module, which required parameters such as the Manning's number (M), detention storage, and initial water depth. The Manning's number is the reciprocal of Manning's roughness coefficient (n) and was assigned based on the land use. This parameter varies from around 10 to 100 and a higher value led to faster overland flow, therefore this was a calibration parameter. The detention storage and initial water depth were assumed as zero due to low variability in topography.

Unsaturated zone

As the objective of the model was recharge estimation, the model was built including the unsaturated zone module. Unsaturated soil parameters such as Van Genuchten parameters were taken from literature according to the type of soil, due to the lack of field studies in the area to determine soil properties. In this study, soil parameters were set for gravel, sand, and till, which are the dominant soil types for most recharge.

Saturated zone

The saturated zone required parameters such as hydraulic conductivity and storativity, which were taken from the FEFLOW groundwater model and were subjected to calibration. In the case of the groundwater simulation, boundary conditions such as no-flow and constant head were implemented.

Model calibration and validation

The model was calibrated against observed hydraulic heads measured in the sedimentary deposits, overland flow measured in the three sub-catchments within the model domain, and snow water equivalent calculated based on measured snowpack data.

The calibration determined some model parameters to reach a good match to the measured data.

The model calibration showed that the overland flow was sensitive to the Manning's number, therefore the recharge to the saturated zone was also sensitive to this parameter.

Since the recharge is influenced by processes such as snow accumulation and snowmelt, the parameters of threshold melting temperature and degree-day coefficient were set to 0°C and 2 mm/day/ °C, respectively. For this study, the snow water equivalent calibration did not require much effort in parameter adjusting.

In the case of the groundwater levels, these were calibrated by adjusting hydraulic conductivity and storativity by trial and error. It was noticed that the groundwater table influenced the recharge and evapotranspiration from the saturated zone. Figure 4 shows the calibration of hydraulic heads in two monitoring wells out of tens of them. Simulated groundwater heads at these two wells did not match well against the observed heads. They were even worse in the other remaining wells.

Figure 4: Calibration of the groundwater component. (a) Groundwater table simulated by MIKE SHE; and (b) comparison of the modelled and observed hydraulic heads

Results

After running the MIKE SHE model, an output of daily estimates of recharge to the saturated zone for each cell in the model domain was computed. Recharge varied significantly both spatially and temporally. Different recharge rates were expected due to the spatial heterogeneity of the study site in terms of geology and hydraulic properties of geological materials.

Spatial variations were observed depending on the spatial distribution of geological materials, while temporal variations were more dependent on the seasonal variations of precipitation and temperatures. The central part of the study site, which is covered with gravel, sand, and till had more recharge in comparison to its surrounding regions, which had peat as the main soil cover (Figure 5). According to the MIKE SHE model convention, negative values represent recharge, while positive values represent discharge from the saturated zone.

The estimated daily recharge in the various geological units of the model domain ranged from about 1 mm/d to about 40 mm/d (Figure 6). Average monthly values for recharge ranged from 0.1 mm/d to about 4.6 mm/d, with the highest recharge estimates in the gravel formation and the lowest in the peat (Figure 7). Although recharge trends are captured in the results from MIKE SHE (Figure 6 and Figure 7), recharge estimates did not match so well with typical recharge patterns in till, gravel, and peat from the Snowmelt model (Figure 8).

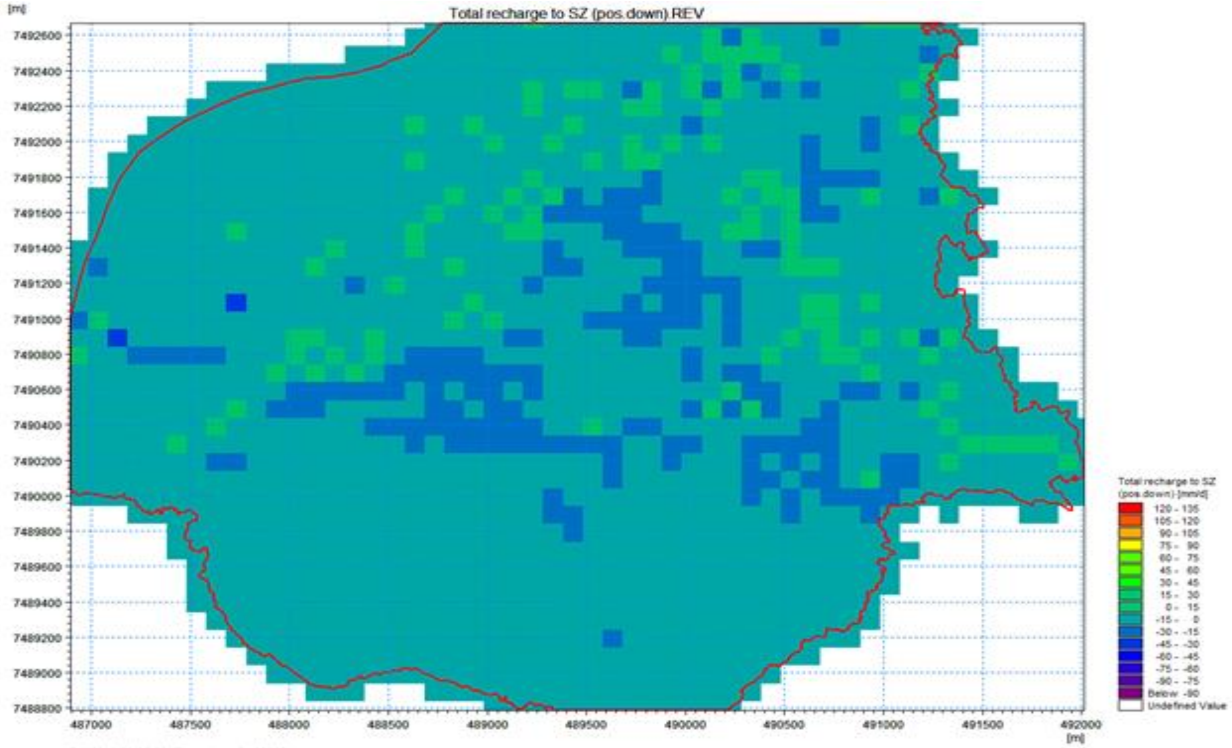

Figure 5: Spatial variation of recharge into the saturated zone

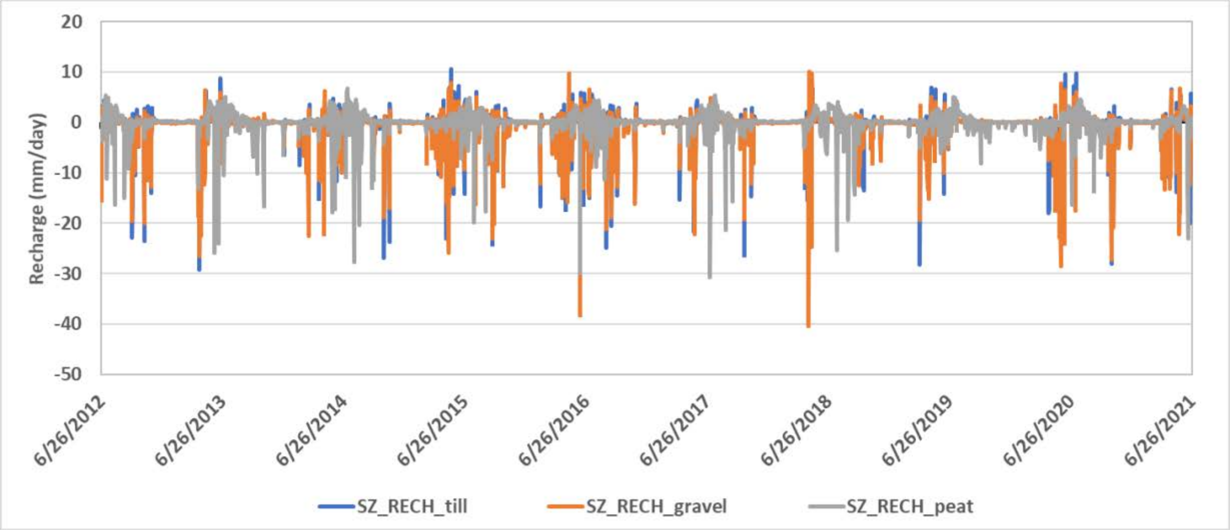

Figure 6: Daily recharge estimates for till, gravel, and peat from the MIKE SHE model

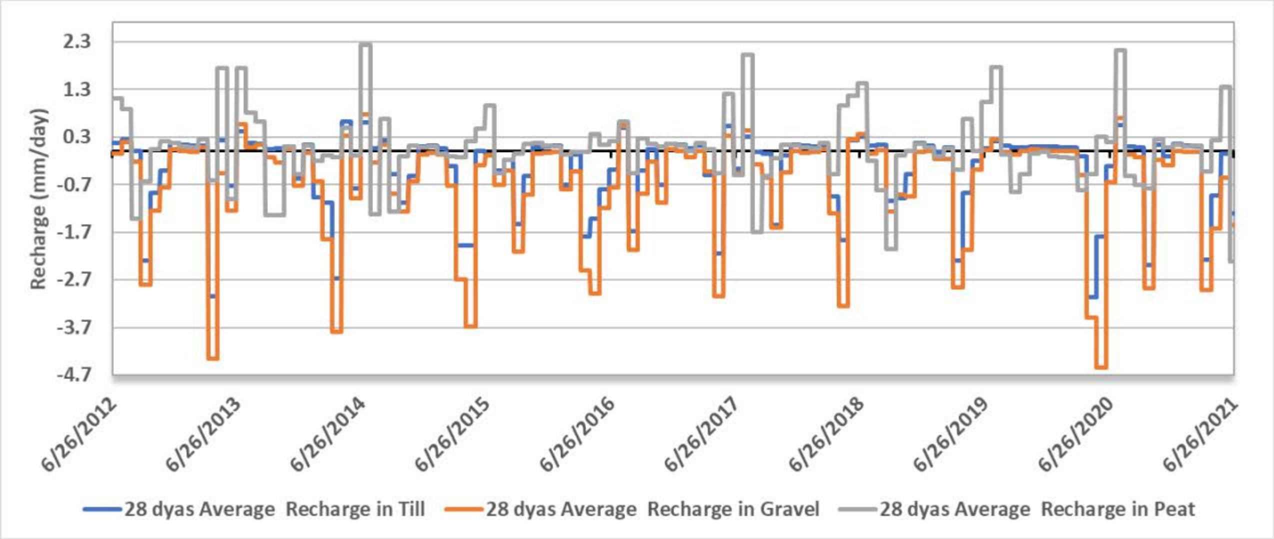

Figure 7: Monthly average recharge estimates for till, gravel, and peat from the MIKE SHE model

Unlike typical recharge patterns for most soils, which indicate zero during sub-zero temperatures, MIKE SHE rather showed a flip-flop trend in daily and monthly average recharge estimates with alternating positive and negative values. These rates are somewhat high in terms of magnitude. For example, a recharge rate of 40 mm/d is relatively high considering a maximum evapotranspiration rate of 3 to 4 mm/d from the surface only. At the same time, daily precipitation is only slightly higher than 40 mm/d.

The plots shown in Figure 6 and Figure 7 each represent recharge estimates from a single cell/pixel of the whole MIKE SHE output. The remaining pixels capture at each time different recharge estimates in the same flip-flop pattern.

Although the developers of the software argue that negative values indicate recharge into the saturated zone and positive values represent discharge from the saturated zone, we think this is not a true representation of recharge on the study site. It was expected that only recharge estimates would be produced in the MIKE SHE model output since the various hydrological processes have already been included in the model.

We identify the inability to deselect some of the components used in the computation of the "Total recharge" by the MIKE SHE model to sufficiently characterize the hydrological response of the study area's saturated zone as the cause of the negative and positive recharge estimates.

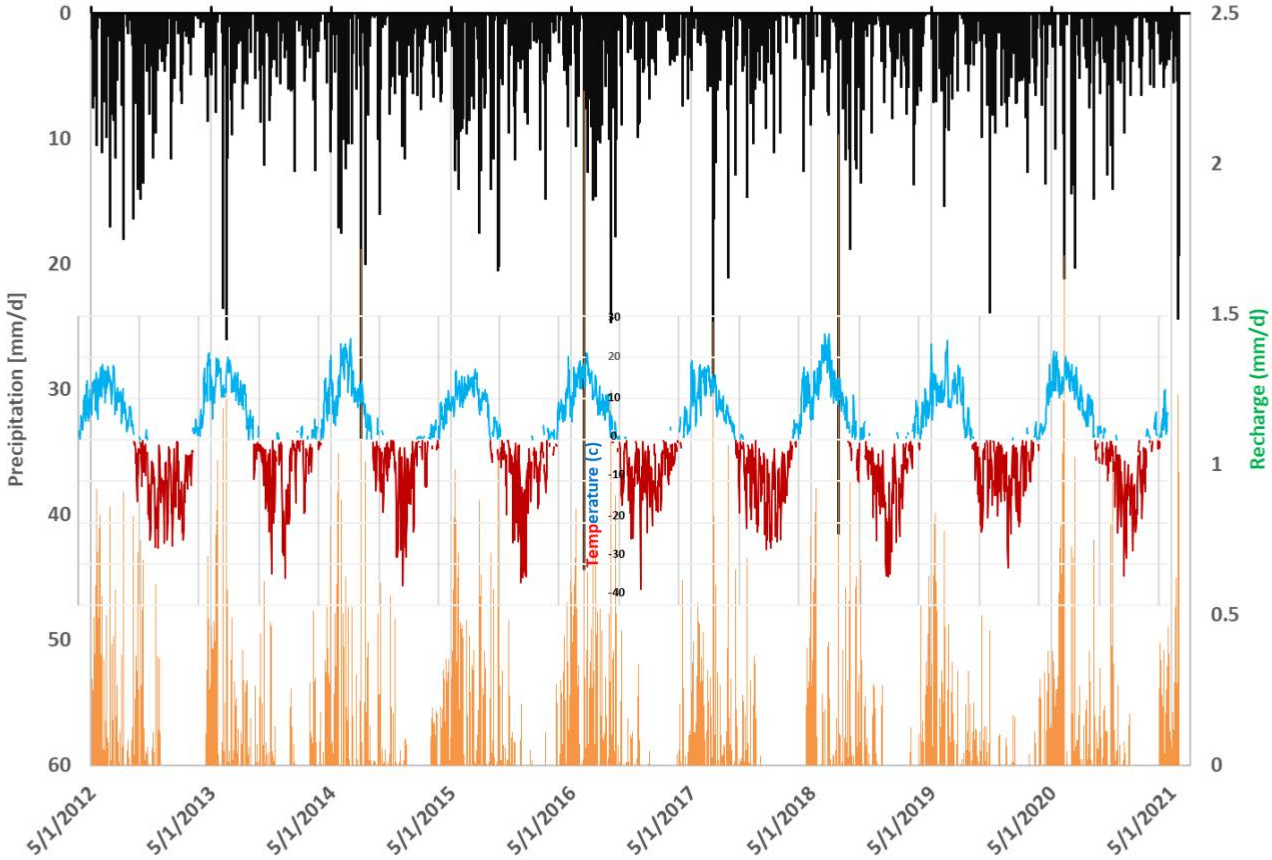

Figure 8: Temporal recharge pattern for geological materials (recharge on lower horizontal axis, temperature in the middle, and precipitation on the upper horizontal axis)

Conclusion

An estimation of the temporal and spatial distribution of recharge to the saturated zone to simulate the development of an underground mine and its impacts was performed with MIKE SHE; a physics-based, fully integrated alternative to the more traditional lumped, conceptual rainfall-runoff models. Results from the model served as an input for a three-dimensional groundwater FEFLOW model. Integrated hydrological models are known to estimate recharge with less uncertainty; however, results from MIKE SHE did not match well with typical recharge patterns in till, gravel, and peat. MIKE SHE results showed a flip-flop trend in recharge estimates (alternating positive and negative values) and high daily rates that are contrary to the typical recharge patterns in geological materials, which are often characterized by zero (no recharge) during sub-zero temperatures or some positive value (indicating recharge).

This study therefore emphasizes that in as much as integrated hydrological models limit large uncertainties in recharge estimates by including components that cannot be assessed with other methods, they should be carefully evaluated before they are used in hydrological analyses. It is also recommended that the developers of the MIKE SHE model provide the flexibility for modellers to select or deselect the various components that are used to estimate recharge to closely characterize different site conditions.

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Managing AMD during Design and Construction of the Expanded Bunker Hill Central Treatment Plant

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Introduction

Mining at the Bunker Hill mine in Kellogg, Idaho, began in 1885 and continued actively into the 1980s. The Bunker Hill mine was one of the largest lead/zinc mines in the world at its peak operation. Tailings produced during mining were disposed of in a tailings impoundment area referred to as the central impoundment area (CIA) located adjacent to the South Fork Coeur d'Alene river (SFCDR). Acid mine drainage (AMD) is collected and conveyed through the Kellogg tunnel (KT) located at the Bunker Hill mine. AMD discharges from the KT at the KT Portal and is collected and conveyed to the Bunker Hill central treatment plant (CTP) for treatment. AMD discharged from the mine is acidic with a pH of ~3.0 standard units (s.u.) and contains elevated levels of metals including manganese, cadmium, lead, and zinc.

The original CTP was built by the Bunker Hill Company and started operation in 1974. At that point it consisted of a lined earthen aeration basin, concrete floc basin, 236-foot (ft) clarifier, lime system, and outfall to Bunker creek (a tributary to the SFCDR). A seven-million-gallon emergency lined storage pond and pump station were completed in 1996 and new mine water pipelines directing AMD to the CTP or the lined pond were completed in 2002. A new hydrated lime slaking and metering system was completed in 2004 to replace the original lime system. The CTP operated at a nominal rate of 1,380 gallons per minute (gpm) prior to being expanded in 2020. The original CTP was labour intensive and had difficulty managing periods of flow variability without resulting in CTP callouts or plant shutdown events. A process flow diagram of the original CTP is provided in Figure 2 of the Appendix to this paper.

Expansion of the CTP for mine water management was started in 2017 and was required based on the Record of Decisions Amendment (RODA) from the U.S. Environmental Protection Agency's (EPA) Bunker Hill Operable Unit 2 preferred remedial alternative and the CTP Discharge Requirements Technical Memorandum (EPA, 2015) that established discharge requirements for the upgraded/expanded CTP to the SFCDR. Discharge limits for the existing CTP and the updated discharge limits for the expanded CTP are shown in Table 1.

Table 1: Existing and expanded CTP average discharge limits

Parameter	Existing CTP limits	Expanded CTP limits
Cadmium (µg/L)	50	2.76
Copper (µg/L)	150	57
Lead (µg/L)	300	16
Mercury (µg/L)	1.0	0.022
Zinc (µg/L)	730	244
pH (std units)	6.0–10.0	6.5–10.0
TSS (mg/L)	20	20

The existing CTP expansion was required to chemically treat and manage sludge for 8,000 gpm of AMD and mine tailings impacted groundwater with a 5,000-gpm filtration process using multimedia filters. The process had to be modified to meet lower discharge standards required for a new outfall in the SFCDR and was transitioned from producing a low-density sludge of ~8% solids by weight to producing high-density sludge (HDS) of greater than 25% solids by weight to increase life of sludge ponds. The expansion of the CTP included several modifications and additions to the existing CTP including the following:

- Two new 125,000-gallon capacity concrete reactors to replace the existing aeration basin.
- Seven new 12-ft diameter multimedia pressure filters.
- New effluent piping to the SFCDR with a new outfall to replace the Bunker creek outfall.
- Upgrades to the existing clarifier and sludge management system to improve reliability.
- One new 105-ft diameter sludge thickener.
- New electrical motor control center and programmable logic controllers (PLCs) to control the expanded CTP and the existing CTP components.

A new groundwater collection system (GWCS) with nine wells and a nominal capacity of 2,000 gpm and a 7,500-ft soil bentonite cut-off wall downgradient of the CIA were also installed to prevent tailings-impacted groundwater from flowing into the SFCDR. A 110,000-cubic yard sludge impoundment area was installed on the CIA for HDS disposal produced in the upgraded/expanded CTP. A process flow diagram of the expanded CTP is provided in Figure 3 of the Appendix to this paper.

Methodology

The CTP expansion project required reliable treatment of AMD during upgrades, necessitating a temporary treatment system (TTS) and sequential system commissioning and start-up using existing infrastructure. Below is a summary of the approach used to treat AMD during the demolition of the existing CTP:

- To replace the aeration basin, a 2,000-gpm TTS, consisting of three 20,000-gallon frac tanks with mixers and process blowers, was used to treat AMD.
- The existing lined pond and existing pumping system were used with a tie-in from the lined pond line to the TTS. To replace/reconnect piping to the influent of the new CTP, a tie-in with valving was installed on the lined pond line to allow for isolation to the existing CTP and connection to the TTS with provisions to allow for future connection to the upgraded CTP.
- A new local PLC for the TTS was used and integrated into the existing CTP system to allow for transition of process control from the existing to the new system in a controlled environment.
- To replace the existing outfall, a temporary discharge pipe to Bunker creek was installed to direct flow to a new filter building or the existing outfall during commissioning of the expanded CTP.
- To demolish and upgrade the clarifier underflow system, temporary piping and valving were tied into the existing system to allow for sludge to be diverted to the old aeration basin or the TTS.
- To install new lime slurry loop piping and tie into the existing system, valving and piping were run to the TTS to allow for diversion of lime slurry to the existing aeration basin and the upgraded CTP, or to a 20,000-gallon frac tank with mixers allocated adjacent to the TTS.

A process flow diagram of the TTS is provided in Figure 3 of Attachment 1. With the configuration described above, a sequencing and commissioning approach was used with onsite operators using operation of the existing CTP and the TTS in parallel during system testing and commissioning to mitigate risk during demolishing the existing CTP and constructing the expanded CTP.

Discussion

Using the approach described above, the facility discharge during start-up of the expanded CTP was maintained with limited CTP shutdowns. Key tie-ins utilized in the existing CTP for the TTS with plans for future connection with the expanded CTP were used to manage the transition of systems as they were brought online. Integration of a separate PLC at the TTS allowed for parallel operations between the TTS, the existing CTP, and the expanded CTP. Once the upgraded CTP was commissioned, the TTS was isolated, removed, and the lined pond pipeline connected to the new reactors. Figure 1 shows the TTS at the CTP.

The expansion of the existing CTP project capital cost was approximately US$40 million (M) or approximately $5,000 per gallon of system capacity. This cost includes design, procurement, construction, start-up, and commissioning. The cost of annual operations for the upgraded CTP is in the range of approximately US$3M to US$4M per year depending on the influent flow rate and chemical consumption. This operating cost range equates to an operating cost of approximately $1.50 to $2.50 per 1,000 gallons of mine water and ground water treated. The upgraded CTP requires four full-time operators.

For comparison, the TTS installation cost was on the order of US$1.3M or approximately US$650 per gallon of system capacity. The cost of the TTS relied on using existing infrastructure as discussed above including the clarifier, sludge management system, and existing outfall. This cost included design, procurement, construction and tie-ins, start-up, and commissioning of the TTS. The cost of operations of both the TTS and the existing CTP were both approximately US$2M per year or US$2.50 per 1,000 gallons of mine water treated (not including rental costs). The existing CTP/TTS required three full-time operators.

Figure 1: TTS layout

Conclusion

Water management for older operations that require upgrades and renovation to replace existing equipment or to update an existing process to meet more stringent discharge limits is a common challenge. The incorporation of modular systems to treat and allow for transitioning from outdated water management systems to newer systems may be a viable and cost-effective option. In the example of Bunker Hill, The TTS was less than 1:20th of the cost of the expanded CTP and during operation, the TTS was able to meet discharge standards for the new expanded CTP. In some cases, these modular systems may even be integrated into a more permanent configuration depending on project objectives, project requirements, and project durations. The transitioning between an existing system and a new system requires strategic planning and commissioning approaches to maintain reliability and continued operation.

References

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Appendix

- Figure 2: Process flow diagram original CTP
- Figure 3A: Process flow diagram expanded CTP (1 of 2)
- Figure 3B: Process flow diagram expanded CTP (2 of 2)
- Figure 4: Process flow diagram TTS

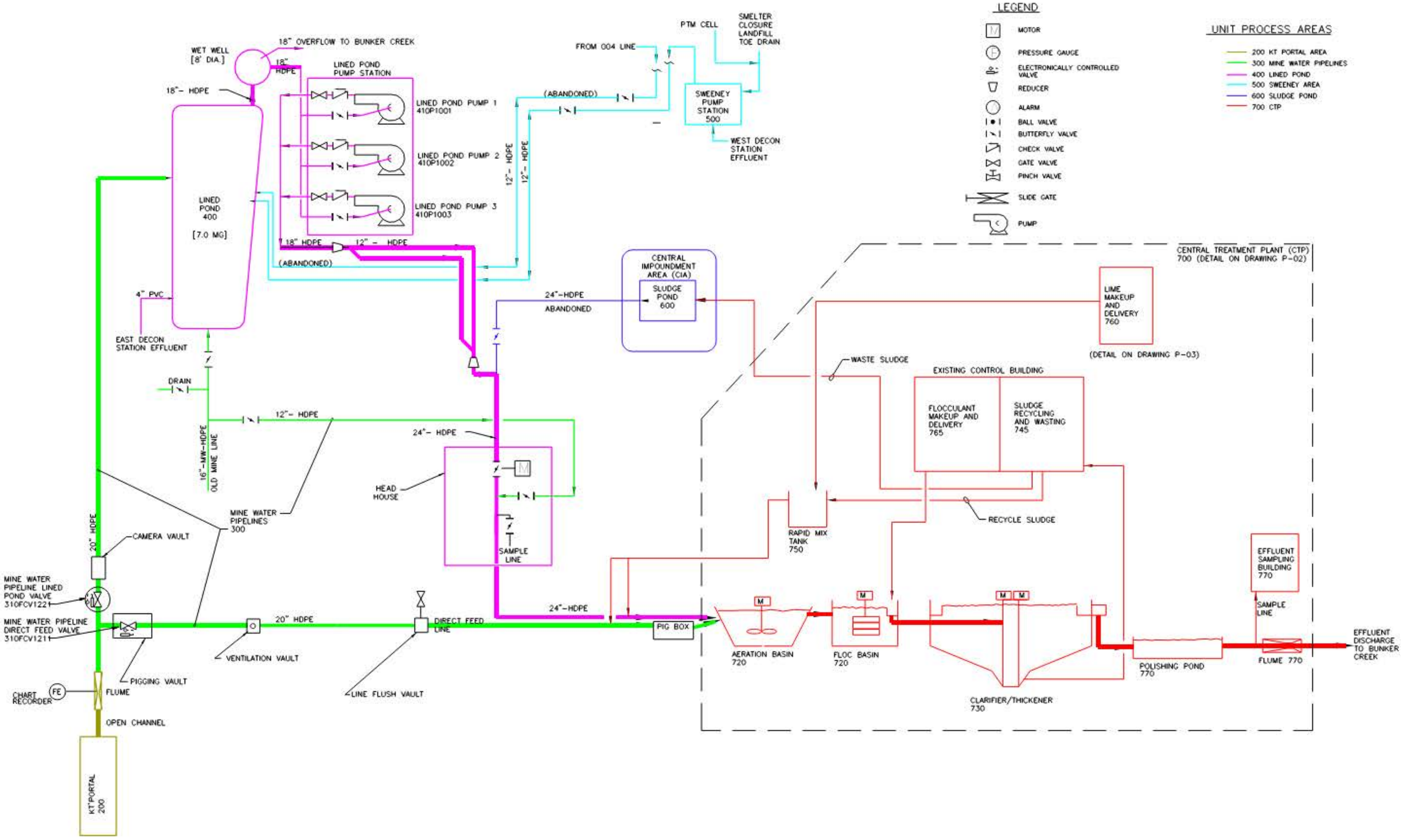

Figure 2: Process flow diagram of the original Bunker Hill central treatment plant (CTP)

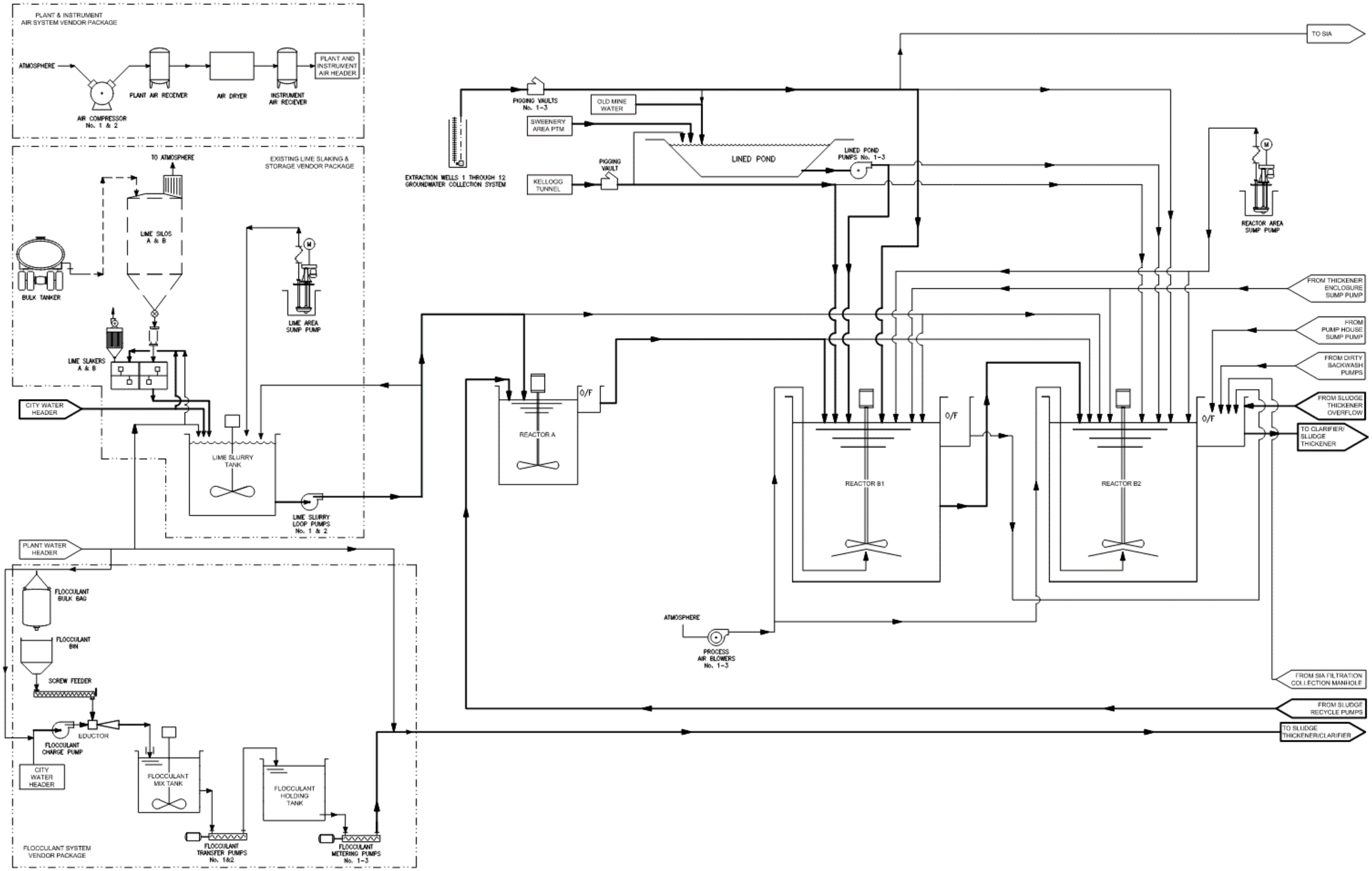

Figure 3A: Process flow diagram of the expanded Bunker Hill central treatment plant (1 of 2)

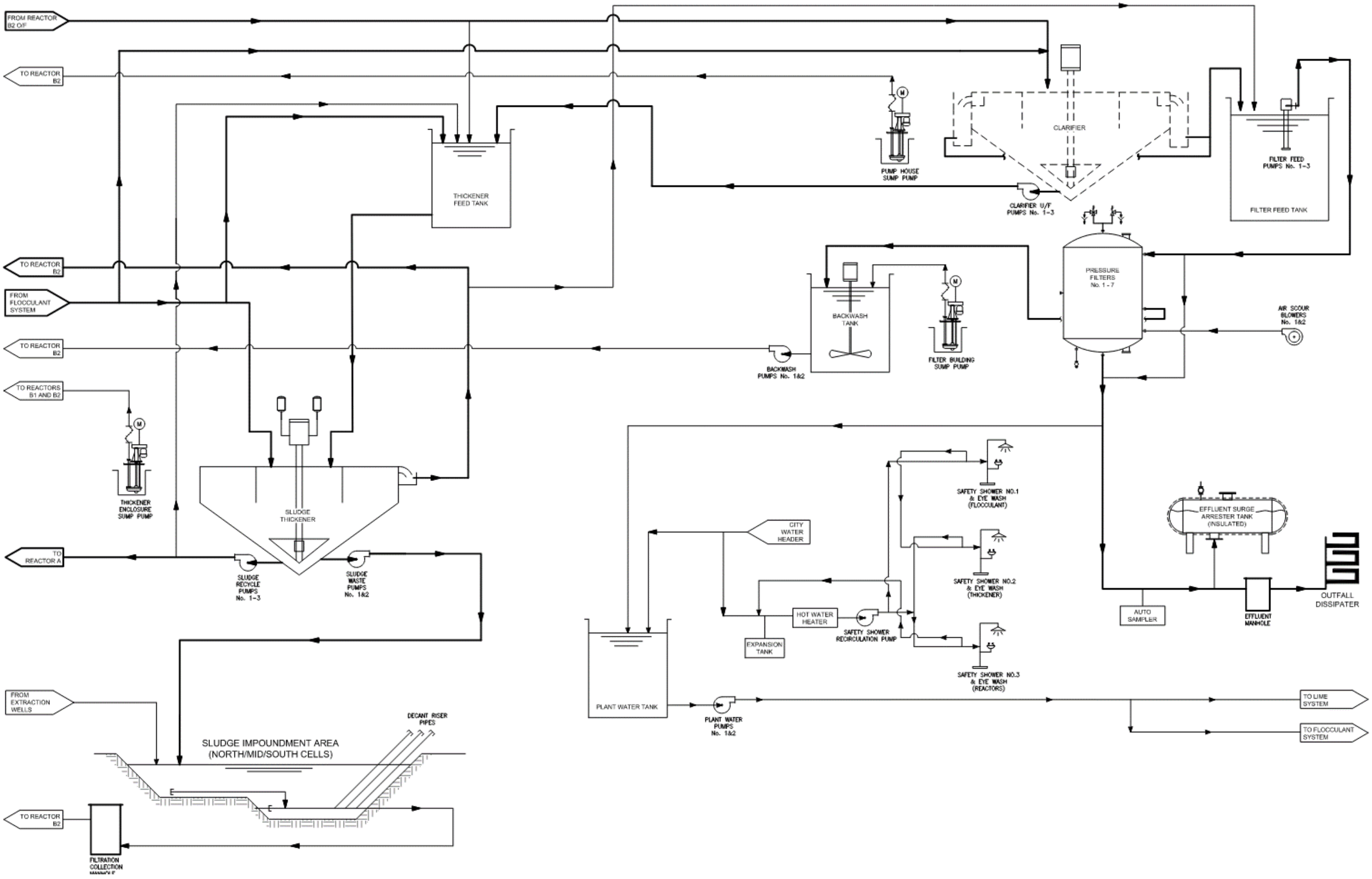

Figure 3B: Process flow diagram of the expanded Bunker Hill central treatment plant (2 of 2)

ATTACHMENT 1

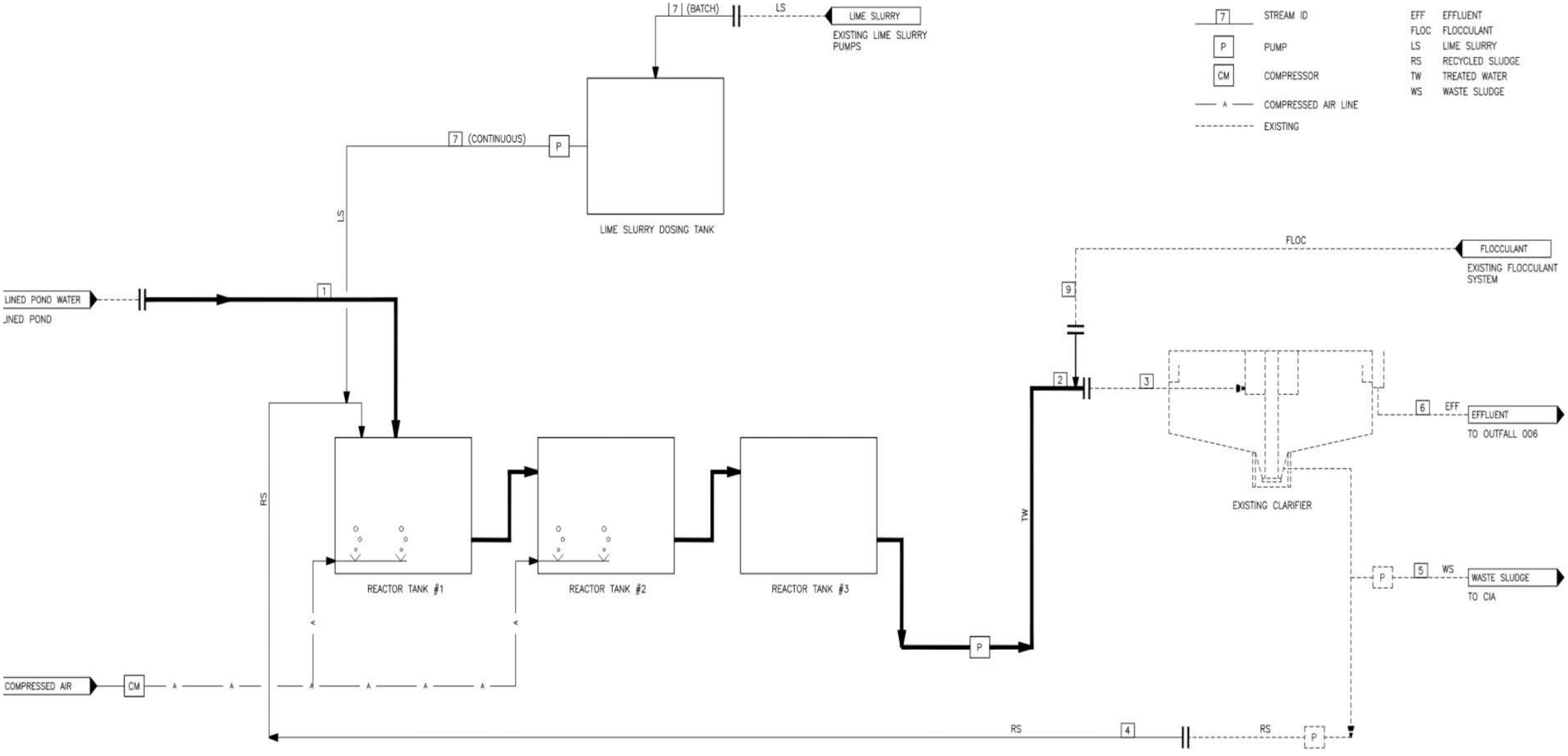

Figure 4: Process flow diagram of the temporary treatment system

Restoring Performance of RO Membranes with Severe Scaling from Contaminated Tailing Pond Water Source Using Specialty Cleaners

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Abstract

Tailings are residues left over after treatment of minerals to clean them of their valuable fraction of an ore. Tailings from mines are discharged as a slurry, which is a mixture of ore particles and water, to a tailings storage facility where water is subsequently recovered and recycled or disposed of (Bascetin et al., 2016).

The use of membranes at mining sites has exploded in the last five years. Mine waters are complex, featuring extremes of pH and high levels of calcium sulfate, metals, and leaching agents. These characteristics lead to challenging scaling and fouling of reverse-osmosis (RO) membranes. Membrane plants for mining are used for various applications, including: enhancing metal recovery, improving purification of water for reuse, reducing tailing storage, and recovering leaching solution. This paper discusses a RO water treatment process used to recover and purify tailings water contaminated with mining waste to make it safer for return to the environment. Part of this treated water is recycled for subsequent use in the mill, significantly reducing the volume of water needed to be withdrawn from the environment for mill activities.

This paper focuses on an upgraded system that treats up to 1,000 m^3/hr of tailings water, producing high quality water that is well below the applicable environmental quality guidelines. This RO system was experiencing several performance issues, mostly fouling and scaling related, that would result in low normalized permeate flow and the need for cleaning every one to two weeks with generic cleaning solutions. The variable water quality, and also the lack of antiscalant pre-treatment, meant that the scale control in the third stage was especially difficult. A membrane autopsy was performed to understand the foulant composition. This paper will discuss the autopsy results in detail, and will also address the selection process of an appropriate specialty cleaner based on the foulant composition, foulant location, and plant design. The performance recovery after cleaning with specialty high, low and silica-specific cleaners will be

discussed and compared to historic data of the system when cleaned with generic cleaners (White et al., 2010).

For remote locations, such as the case at this site, specialty cleaner selection is often influenced by several factors. Ergonomics, safety, ease of use, extreme storage conditions, and transportation are not frequently used as a criterion for chemical selection, but were considered in this specific case during the chemical selection process. Finally, savings by reducing system downtime through more effective and less frequent clean-in-place (CIP) operations will be emphasized. Although fouling is often an unavoidable part of RO water treatment, the benefits and advantages of specialty cleaners for this specific case study are highlighted in this paper.

Project description

The focus of the work covered by this paper is one of the uranium milling operations. The tailings generated from uranium milling activities are stored in in-pit storage facilities. The overall dewatering system that treats the tailings from the in-pits is divided into two parts: contaminated water system that is collected and transported to the mill for reuse; and clean water system that discharges to the environment. A RO plant was installed specifically to reduce contaminants in the dewatering effluent clean water that is returned to the environment.

The RO unit feed water source is tailings water from the nearby holding in-pits, which are high in transition metals and silica. The feed water quality is summarized below.

Table 1: Feed water quality

Parameter	mg/L	Parameter	mg/L
Sr	0.3	Cl	6.8
pH	7.8	Nitrate	3.21
Ammonia	0.1	SiO_2	15
Iron	0.56	F	0.17
Ca	93.19	Na	17.3
Mg	8.99	TDS	496
Al	<0.005	K	5.4
Mn	0.64	P	<0.01
Ba	0.015	Turbidity (NTU)	0.1
SO4	298.5	HCO3	15.8

The well water is pre-treated with a filter system to oxidize and remove iron and manganese. The RO plant technical specifications are summarized in Table 2.

Table 2: RO plant technical specifications

Type	Single pass
Configuration	3 stage 12:5:2
Elements/Vessel	8" × 6 M
Feed water	Well water at ~300 mg/L TDS
Typical RO feed	TDS at ~500 mg/L
RO recovery	90%
Typical salt rejection	95–98%
Feed capacity per unit	5,000 GPM

Any RO plant will begin to foul the moment it is put in operation. Performance losses in RO systems from fouling will occur and the severity of fouling depends on several factors broadly based on feed water quality and plant operating parameters, as well as the pre-treatment system. Clean-in-place (CIP) operations for cleaning membranes are necessary to remove foulants and restore membrane performance. The mechanism of the CIP consists of introducing the chemicals to the membranes, recirculation and soaking times, then flushing the chemicals from the system. In addition, maintaining proper operation of the plant helps the water treatment plant operations team meet water quality goals for successful mining operations.

Cleaning is also recommended before system shutdown, and as part of a preventive maintenance program. A general rule of thumb for CIP is when one of the following occurs:

- The normalized permeate flow drops by 10%.
- The normalized salt passage increases by 5 to 10%.
- The pressure drop across the membrane increases by 10 to 15%.

The three parameters above are considered to be key performance indicators (KPIs) for monitoring system performance and initiating CIP protocols. For the mining site in particular, two KPIs were identified and monitored daily in order to optimize the performance of the RO plant and associated operating costs: *the permeate flow and differential pressure*. Monitoring permeate water quality is important since it is discharged to the environment if it is within acceptable discharge limits.

- *Permeate flow:* Changes in permeate flow rate could be either due to the accumulation of foulants on the membrane surface, or due to changes in the operating conditions (feed water temperature, feed pressure, water quality etc.). In order to differentiate between these two phenomena, permeate flow was normalized to correct for any variations.
- *Differential pressure:* Also called pressure drop or the hydraulic differential pressure, and represented by ΔP, this is the difference between the inlet pressure to the lead membrane element and the reject stream pressure coming off the tail elements. Changes in ΔP are commonly attributed to foulants accumulating on the membrane surface and brine spacer vexar, restricting the water passage through the membrane leaves inside the element. The ΔP is stable as long as the feed and concentrate flows and temperatures are constant.

Both KPIs indicate the fouling potential and extent of scaling, which are the main causes of longer system downtime, frequent CIPs, ineffective membrane cleans, and premature membrane replacements. These KPIs will be used to compare the cleaning efficiencies at the mining site of specialty cleaners against generic cleaners, by evaluating current and historic normalized performance data of the system.

Membrane autopsy and foulant analyses

Fouling has been an issue with the main foulants being silica, barium sulfate, iron and/or filter media from the greensand filters. An independent autopsy was performed to analyze and identify the foulant types on the membrane surface.

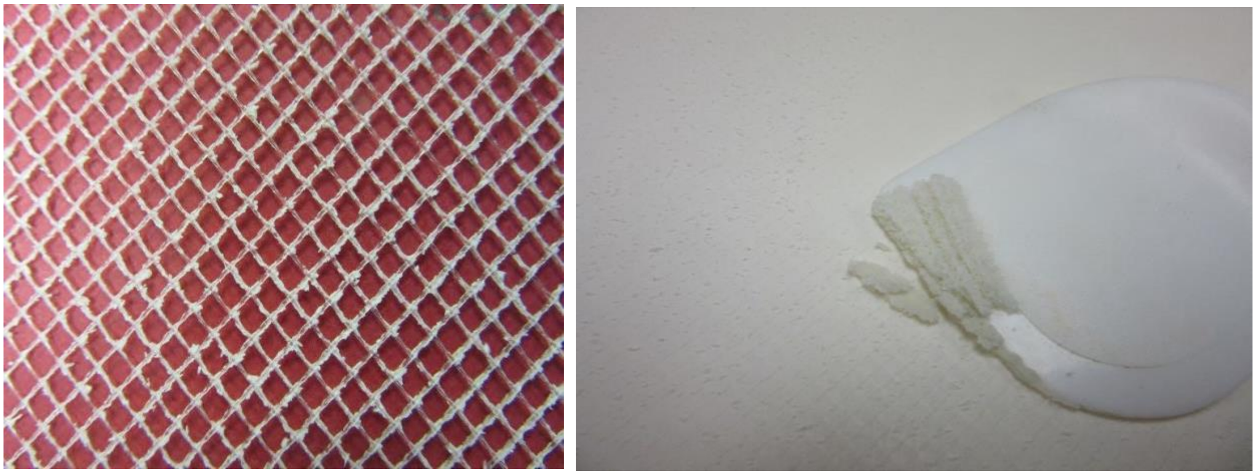

Figure 1: White foulant present on feed spacer and membrane surface

Loss on ignition done on the sample scrapped from the surface showed that the foulant was 94% inorganic scale and about 6% organic material. SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy) done on the white residue from the membrane surface showed the foulant composition to be mostly Si (92%) and Al (3%) .

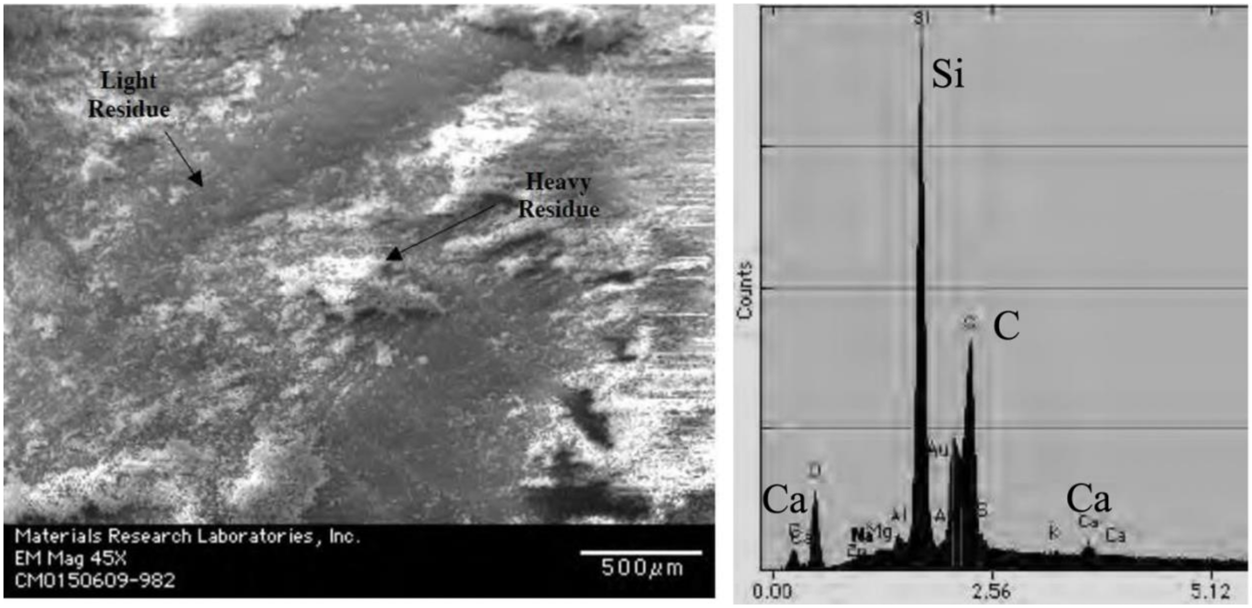

Figure 2: SEM-EDS of white foulant powder shows presence of Si

The Fourier transform infrared (FTIR) signatures indicate that the foulant/scalant consisted primarily of silica and water. The element also showed signs of physical damage from permeate back pressure, which was noticed through blistering on the membrane surface.

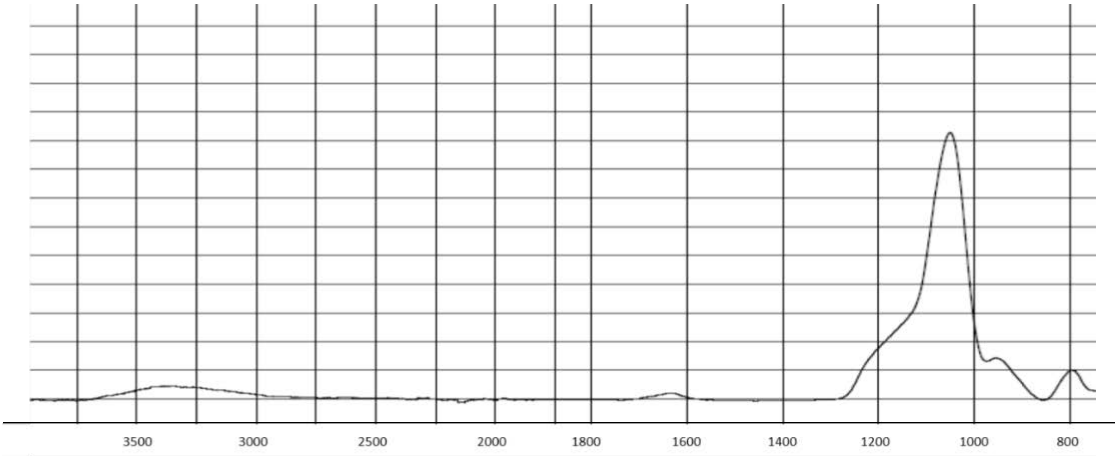

Figure 3: FTIR spectrum confirms the presence of Si

The system was subjected to high temperature cleanings with generic high-pH cleaners such as NaOH solutions, but the system struggled to run at peak performance and had to be cleaned frequently. A case of using PWT specialty cleaners is presented and the corresponding performance improvements are discussed in the results section.

Safety and ergonomics

Chemical cleanings subject the water treatment operator performing the CIP to various risks. The risk factors are ergonomic, such as lifting heavy bags of chemicals, and safety related, including the need for protection against fumes and chemical dust. These considerations were also evaluated during specialty cleaner selection process. Liquid specialty cleaners were selected because they could be pumped into the CIP tank, eliminating the need for heavy lifting of chemicals. Since the liquid specialty cleaners are buffered, they maintain pH throughout the cleaning cycle, reducing the chemical handling required for continued pH adjustment during the CIP. The specialty cleaners used do not release any fumes, and the buffered cleaners eliminate the need for pH adjustment with acid and alkali powders, limiting exposure to respiratory danger.

A 2% CIP solution concentration is recommended for most liquid specialty cleaners to produce effective cleanings. Switching to specialty liquid cleaners provided more effective cleans and a less rigorous CIP regime, ultimately lowering cleaning frequency. This equates to less specialty cleaner storage space, which is especially important for sites, such as mining operations, that are located in remote areas with limited space and subject to high transportation costs associated with shipping chemicals to cold weather climates where temperatures can drop to below freezing.

Results and discussion

One of the trains was chosen to run pilot studies on, to check the effectiveness of specialty cleaners. Train X was deemed the best performing train with the best performance efficiency, producing the longest run times. It was important to select a train that was not impacted by irreversible fouling, otherwise the results from the CIP would not be representative.

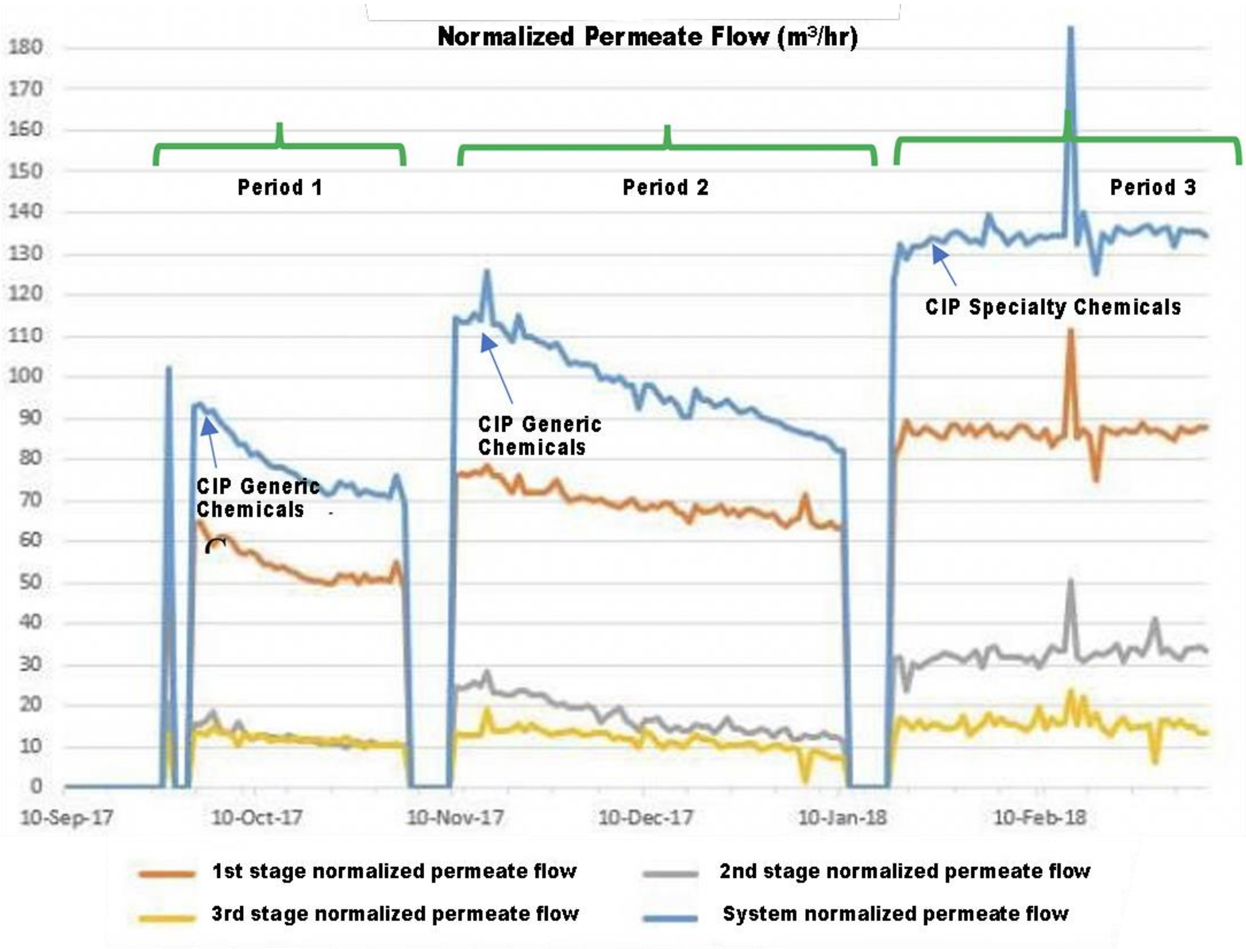

Figure 4: Normalized permeate flow split into three time periods: Train X

Figure 4 shows the normalized permeate flow of Train X with three CIPs done within a six-month period (October to March). The first two CIPs were done using generic cleaners, and the third CIP was done using the specialty liquid cleaner products provided by PWT Chemicals. RO elements were not replaced during the six-month pilot period.

The normalized flow trends during Periods 1 and 2 on Train X are representative of what is observed on the primary skids of all trains, after performing a CIP with generic chemicals. Normalized flow shows an exponential drop after generic cleanings in Period 1 and Period 2 cycles. This is a clear indication that the elements are fouling/scaling rapidly and that the cleans are not fully removing the foulant/scale. With generic cleaners, the average runtime before a skid technically requires a cleaning is about one to two weeks, although this was seldom conducted on time.

Figures 5 and 6 look at the Periods 1 and 2 individually. A closer inspection shows an average flow loss of 0.58 m^3/hr/day during Period 1 (Figure 5). In Figure 6, we observe an average flow loss of 0.53 m^3/hr/day during Period 2.

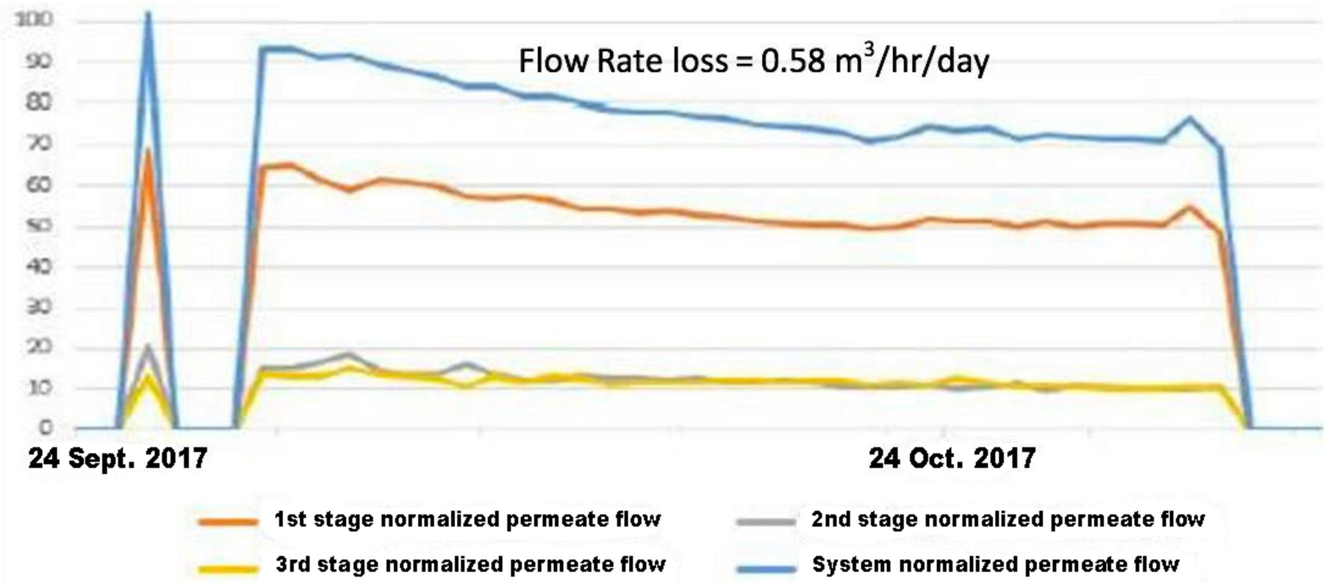

Figure 5: Train X Period 1 – Normalized permeate flow (m^3/hr)

The system normalized flow dropped from 93.1 m^3/hr to about 81.3 m^3/hr, which is greater than a 10% drop in flow in 10 days. This triggers the need to clean to maintain system performance. Period 2 represents the system performance after initial clean.

During Period 2, the system normalized flow dropped from 115 m^3/hr to about 92.4 m^3/hr, which is a ~20% drop in flow in 25 days. This again triggers the need to clean to maintain system performance.

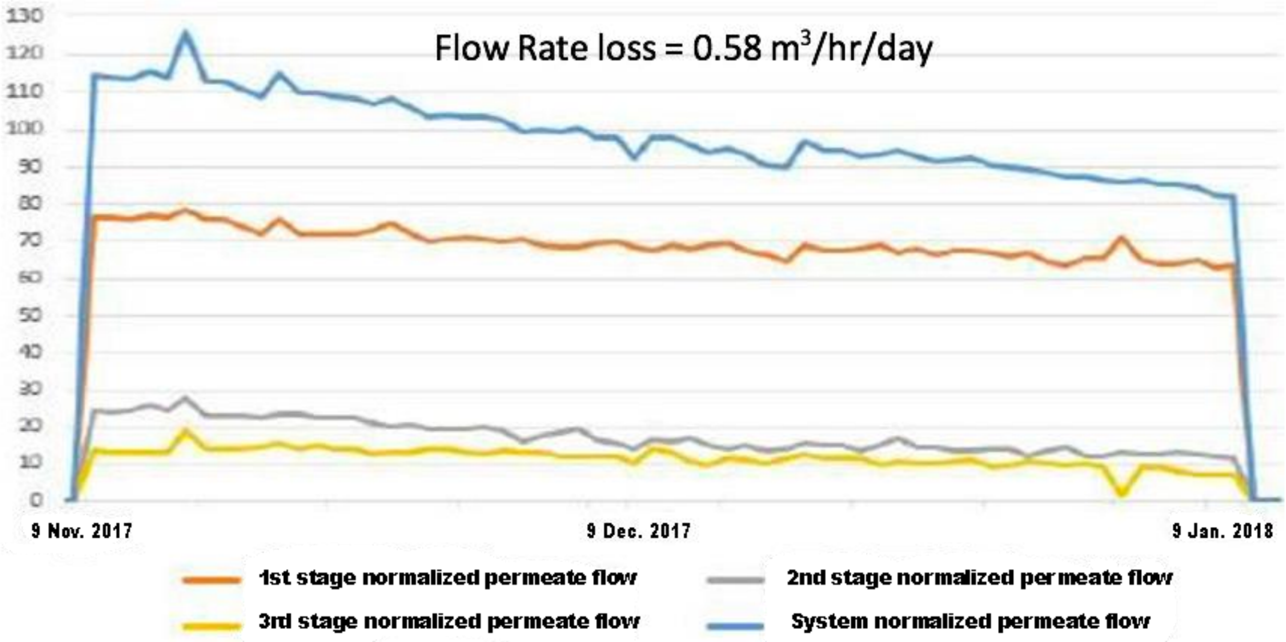

Figure 6: Train X period 2 – Normalized permeate flow (m^3/hr)

Due to the nature of foulant (silica) and its location, the drop in permeate flow was more apparent for stage 2 (grey curve) and stage 3 (yellow curve) compared to stage 1 (see Figure 6). From the autopsy done on the RO element taken from stage 3 described above, energy dispersive x-ray spectroscopy (EDS) elemental analyses identified the white residue as silicon-based, and as the primary foulant/scalant. Furthermore, the FTIR analysis indicated that the foulant/scalant consisted primarily of silica and water.

Generally speaking, when silica scaling occurs, it can be rapid and is commonly detected by a loss of flow in the second or third stages. Silica can exist in a wide variety of structures, ranging from a simple colloidal silicate to a more complex polymeric material. Cleaning strategies differ based on the form of silica. Normally, high pH NaOH-based cleaners are recommended for cleaning polymerized silica. PWT's silica specific cleaner was used in conjunction with other specialty cleaners for cleaning silica scale from the membrane surface.

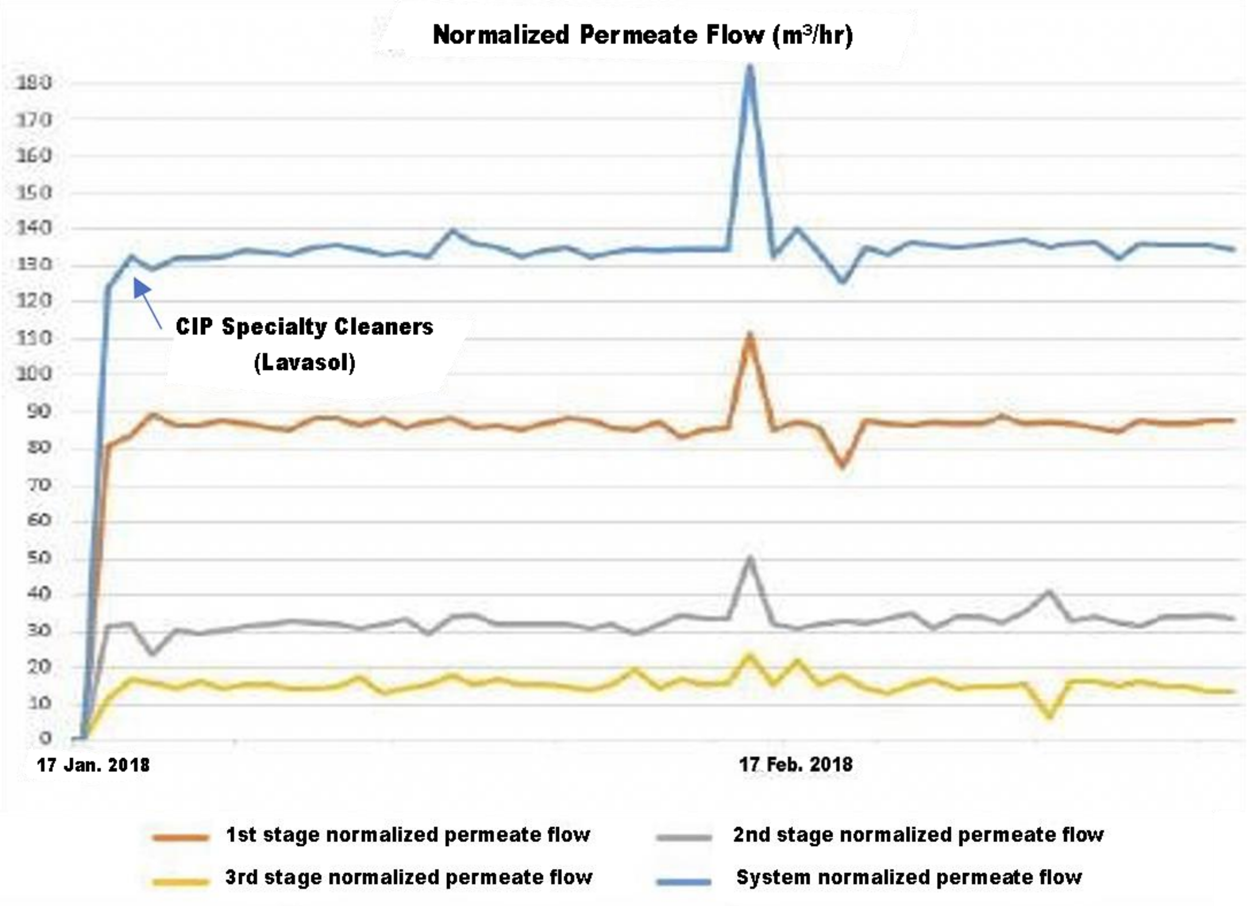

Figure 7: Train C period 3: Normalized permeate flow

Figure 7 shows the performance of Train X after the onsite trial with the cleaners. The normalized permeate flow remained stable with a minimal drop in flow. The average flow loss during this period was 0.037 m^3/hr/day. This flow loss is minimal (94% lower) as compared to the average loss in flow rates of Periods 1 and 2.

There was also a considerable gain in the normalized permeate flow after using the specialty cleaners during the CIP in Period 3. The permeate flow in Period 3 (134 m^3/hr) increased by 16% compared to the flow at the beginning of Period 2 (115 m^3/hr) and was 45% higher than the permeate flow at the beginning of Period 1 (92 m^3/hr). Even after 50 days, Train X showed stable performance with no loss in normalized flow rates. This is significant as the system was able to produce permeate water consistently without having to stop for a cleaning cycle.

In addition to monitoring the normalized permeate flows, differential pressure trends also indicate the health of a skid. Train X particularly excelled in having lower differential pressure and overall lower inlet pressures, which indicates better overall performance.

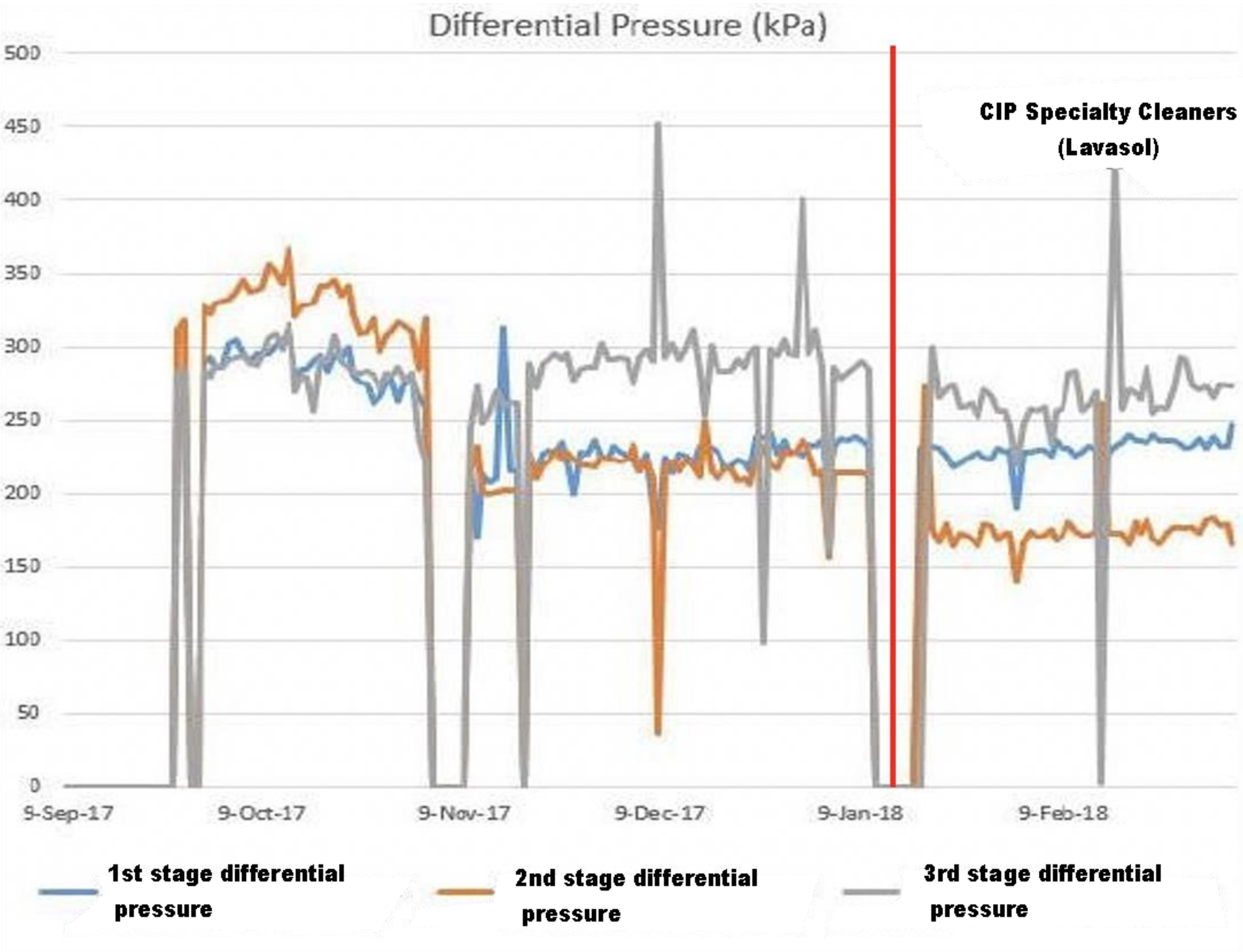

Figure 8: Train X: Normalized differential pressure variations of the system

There is a noticeable drop in differential pressure across the 2nd (orange line) and 3rd (grey line) stages. This is a clear indication that the specialty cleaner was effective.

The average runtime before a train would require a clean (normalized permeate flow drops 10%) was about one to two weeks with generic cleaners. Unfortunately, trains were operated past this early indicator and were cleaned on rotation or when badly needed, when normalized permeate flow dropped close to ~25%, as seen in Figure 9 below. In Period 1, the normalized permeate flow dropped by 25% before a cleaning was performed. In Period 2, the normalized permeate flow dropped by 26% before a cleaning was performed. This is not recommended, as any delay in performing a clean can result in the foulant becoming more compressed on the surface of the membrane and becoming much more difficult to clean and remove.

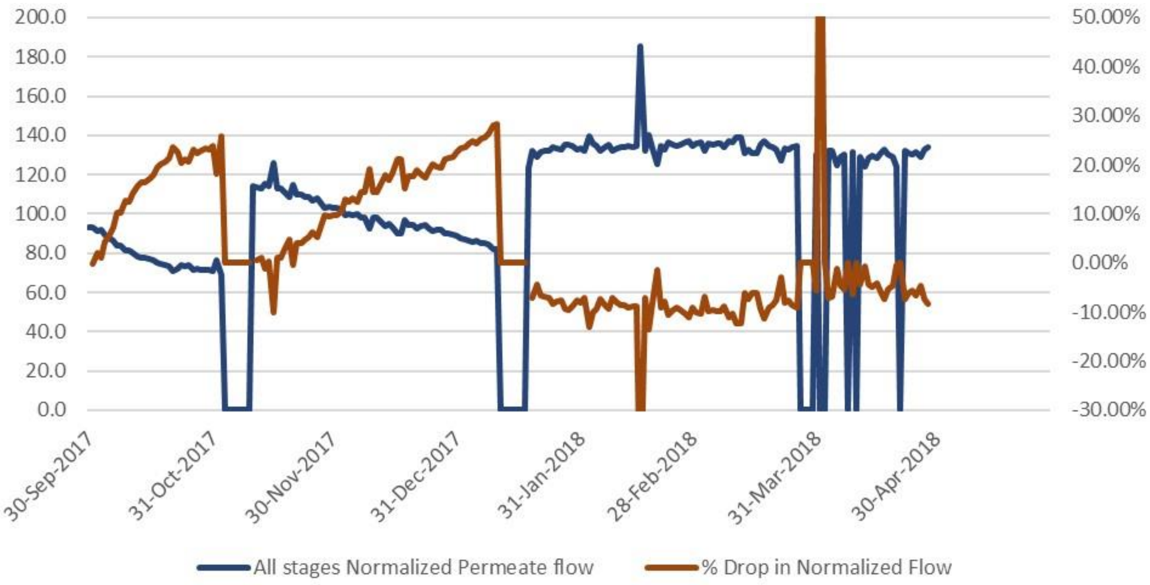

Figure 9: Percentage drop in normalized permeate flow

A Pareto chart was created to track all the instances for system downtime. Figure 10 shows the percentage split between factors for system shutdowns. To date, an accumulated 10,000 hours (417 days) of downtime have been contributed to cleans and membrane changes. That is roughly 1.25 million m^3 of brackish water that was untreated in the 20-month period due to downtime from system cleanings.

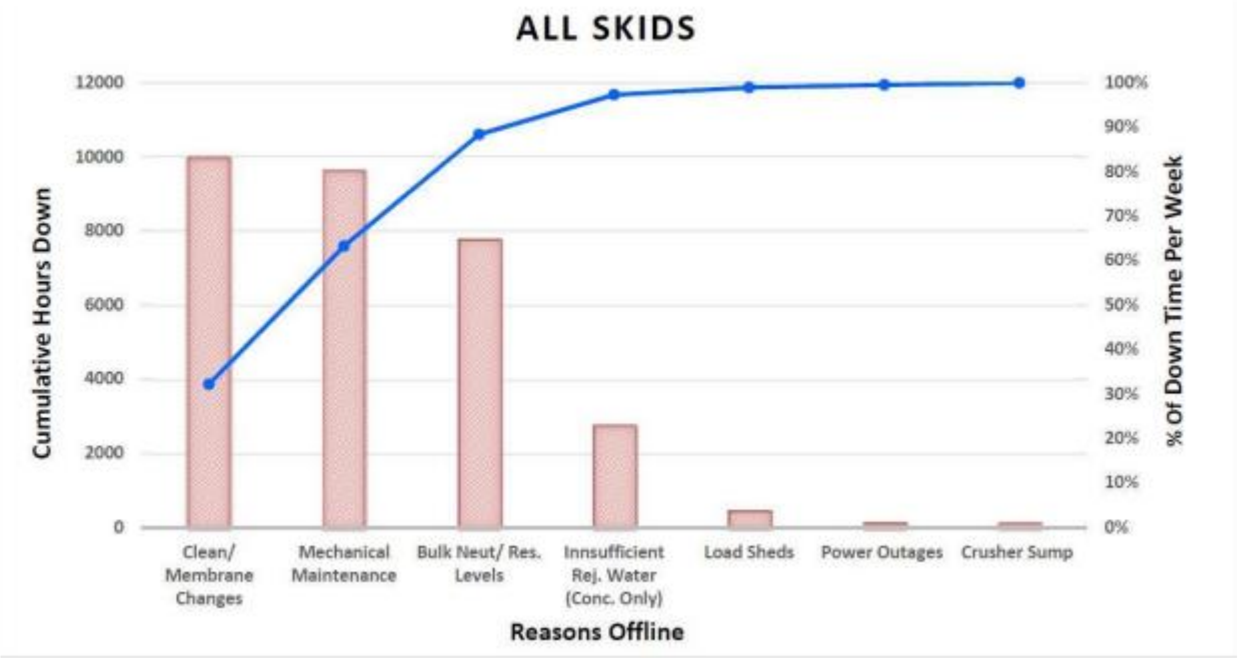

Figure 10: Chart to track downtime factors for the RO system at the mining facility

The use of specialty chemical cleaners to selectively clean foulants from the RO system at this mining site showed obvious benefits over generic cleaners. In a short time of eight weeks, the trial with specialty cleaners more than doubled the run time for Train X, effectively increasing clean water production and also lowering the chemical consumption of cleaners, which in turn lowers operational cost. After the success of cleanings on Train X, the same cleaning procedure was adopted for the other trains at this site.

The operations team spent nearly 30% of their time per week doing ineffective CIPs. Highly skilled human capital resources are very scarce and inimitable in mining operations. A huge portion of the human capital resource was needed for a secondary activity, to perform a CIP, considering the fact that this is not a complicated task but rather a time-consuming one.

Using more effective specialty cleaning chemicals equates to lower frequency of cleaning, decreasing the system downtime and associated time spent on secondary tasks. This means that the operations team can free up and allocate its human capital resource for more important and strategic activities. These are important considerations that are often ignored during chemical cleaner selection process.

Summary

Preliminary results from a trial clean using specialty cleaners from PWT Chemicals on one Train X showed a very positive response. The specialty products PWT recommended effectively removed foulants and restored system production capacity and efficiency. The specialty cleaners were selected based on the autopsy analyses and were chemically designed to specifically treat and maintain RO membrane elements fouled with Si and $BaSO_4$ scale and organic materials. Along with improving KPIs, the specialty cleaners offered safer, more ergonomically appropriate chemicals to handle.

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Engineered Controls to Mitigate Nitrate Leaching from Explosives in Blast Holes

Johan Hawinkel, MTi Group, Australia

Abstract

The principal rock fragmentation methodology in both open pit and underground mining is blasting using commercial bulk explosives. Bulk explosives used in most modern mining operations contain between 70% and 94% of ammonium nitrate. When loaded into the blasthole and in contact with the groundwater, these explosives leach nitrogen species into the groundwater. Different factors such as water inflow and outflow, explosive composition, and sleep times, affect the quantities of nitrogen species effectively leaching into the environment. While the most common bulk explosive, ammonium nitrate-fuel oil (ANFO), readily dissolves in water, explosive manufacturers have designed more water-resistant explosive emulsions for better performance in damp and wet conditions. However, issues remain around water contaminating explosives, affecting their performance, and explosives leaching nitrogen species in the groundwater, with adverse effects on local ecosystems.

While in many jurisdictions agriculture is the main source of nitrogen species leaching into the groundwater and the environment, the contribution of mining, and blasting in particular, is increasingly becoming a point of focus for external stakeholders, as well as a likely target for regulatory bodies. Current control measures range from improved, more water-resistant formulations of bulk explosives, through better blast designs, to best operational practices to avoid spillage and leakage while also minimizing sleep times, thereby vastly decreasing the time between loading and initiation. These controls, however, do not entirely eliminate leaching, which is also exacerbated by the sleep time and large groundwater flows. To completely eliminate the presence of nitrogen species in the groundwater caused by blasting, an impermeable barrier needs to be installed between the explosive and the borehole. Traditionally, liners have provided this impermeable barrier, eliminating any leakage of explosives in cracks and voids and avoiding the explosive-water contact as the conduit for nitrogen species leaching. Liners have the added benefits of improved explosive performance, increased sleep times, and elimination of blast fumes. Even though lining blastholes is an engineered control to the environmental problem, it is not a common practice in most mining operations due to the inefficient installation process, the operational burden, the added costs, and the risks

introduced to the charging process. This paper discusses some of the barriers to routinely adopting this groundwater control technique, suggests possible solutions, and explores a relevant case study.

Introduction

The discussion around explosives in wet environments has traditionally focused on explosive performance, with suppliers continuously developing explosive formulations and delivery methods to increase the explosive's water resistance. However, since the 1980s the role of explosive associated nitrogen species in groundwater and waterway contamination has gradually gained attention.

In the last decade, several mining projects have been subject to increased scrutiny on the nitrogen content of their effluent mine water. In some jurisdictions with particularly sensitive waterways and a high societal expectation of water quality and eco-system protection, mine operators need to consider the potential of upcoming regulation of leaching of explosive related nitrogen species, including nitrate, nitrite, and ammonia. Probably the most advanced jurisdiction is British Columbia (BC) in Canada, where the Ministry of Environment and Climate Change Strategy has developed a document called *Guidance on Preparing Nitrogen Management Plans for Mines using Ammonium Nitrate Fuel Oil Products for Blasting* (Environmental Protection Division, 2018). This guidance document can be used on a voluntary, preventative basis, or as part of the submission for an Environmental Management Act (EMA) permit.

One of the most effective controls against leaching of nitrogen species from explosives post-delivery down the blasthole, a contact point inherent to the blasting operation, is the use of liners. While traditional polyethylene (PE) liners often introduce more issues than they provide solutions, engineered multi-composite polymer liners can deliver a solution, while being cost effective and operationally practicable. In addition to mitigating nitrogen compound release, other benefits, often interlinked, can be achieved.

The role of explosives in nitrogen leaching

Nitrogen species leaching into the groundwater and surrounding ecosystem is often associated with agriculture and livestock. However, lately more attention has been directed to the leaching of nitrogen species from blasting in mining operations.

Commercial explosives all contain nitrogen compounds because of the high energy release in their decomposition and formation of N_2, as well as the formation of large volumes of gas enabling the rock-fragmenting process. However, it is precisely these nitrogen compounds that are a key contributor to nitrogen species leaching into mine water, including nitrates, nitrites, and ammonia.

While environmental studies and modelling often predict the contaminating impact of metallic components contained in the rock mass, nitrogen species leaching into the water is often overlooked in preliminary studies. Morin and Hutt (2009) suggest that due to the low concentration of nitrogen species in rock, pre-mining tests often produce low aqueous concentrations of nitrogen species and are not accounted for in predictions. Only after mining production starts and blasting commences, does the true extent of nitrogen species leaching become evident and as such, case studies on existing operations become an important source of information.

One of the earlier and often cited sources is a study of nitrogen and phosphorus nutrients entering the aquatic environment around British Columbian coal mines (Ferguson and Leask, 1988), providing a prediction methodology to calculate nutrient release. The study states that between 0.2% to 5.1% of the nitrogen in the explosive will be lost to the water, depending on the type of explosive. However, other studies suggest that between 12% and 28% of mass nitrogen used in explosives (Morin and Hutt, 2009) and between 4.7% to 32.2% of mass nitrogen used in explosives (Sedenko, 2018) respectively was leached by the groundwater.

While the wide range of values, from 0.2% to 32.2%, could raise questions around the value of using case studies as a predictor, a wide variety of factors come into play including explosive type, hydrogeology, sleep times, operational discipline, and whether the leaching occurs pre- or post-detonation.

Sources of explosive related nitrogen species

All commercial explosives whether ANFO, watergels, or emulsions are ammonium nitrate (AN) based with additions of fuel oil, waxes, salts, and other additives. The release of nitrogen species into the groundwater stems from the dissolution of the AN in water, releasing ammonia and nitrate, or from its chemical reaction products.

Explosive manufacturers design and commercialize explosives with different degrees of water resistance, such as ANFO, which dissolves 25% in six minutes, and emulsions which dissolve 1.2% after six days (Revey, 1996). However, all explosives have contact points along their life cycle, some of which are unintended such as during storage, transport and on-bench handling, while others are inherent to the blasting activity. At any point where there is contact with water, there is a potential for nitrogen species leaching to occur at their respective rates.

Spillage in storage and transport

AN is often delivered to larger mine sites in bulker bags and is then stored in sheds or silos. Explosive emulsions are either transported as desensitized matrixes and later sensitized, or manufactured on the mine site from AN solution. Both the AN and the explosive emulsions are then loaded in delivery units or mobile processing units (MPUs) using pumps, gravity feed, or loaders. In both products and processes there are multiple transfers that can result in spillage and subsequent contact with water.

Spillage in delivery

On larger mine sites, bulk trucks or MPUs deliver the explosives to the blastholes, using augers for ANFO and Heavy ANFO, and pumps and hoses for emulsions and high emulsion content Heavy ANFO. Spillage can result from simply delivering explosives aside the hole, from drippage while moving from hole to hole, or from flushing hoses and auger prior to returning to the workshop or between changing product types.

Spillage in the hole

The ideal blast hole is cylindrical and in competent rock, but many blast holes are in weathered and fractured ground, intersect large cavities, or even drill into past underground workings. While drilled versus designed hole depth is often verified prior to loading, fractures and cavities are hard to detect until the explosives start running away in the cracks and voids (if at all detected). Continuously measuring the explosive charge height while loading can signal runaway explosives, but often many kilograms of explosives disappear in these voids prior to detection. If discontinuities in the explosive column occur, explosives might fail to detonate.

Damp holes

In deciding whether to load ANFO (dry product) or water-resistant emulsion (wet product), holes are often "dipped" and marked prior to loading. If no water is detected the hole is loaded with dry product. However, even if no water is present, the hole walls can still be damp, and the highly hygroscopic AN prill will absorb moisture from the environment, potentially leading to nitrogen species leaching. This effect increases with sleep time, that is the time between loading and blasting, which can often be days, but sometimes can be weeks.

Wet toes

Often water accumulates in the bottom or toe of the blasthole, and emulsions are preferred because of their higher water resistance. However, small quantities of stagnant water in the bottom of the hole are often neglected where the preferred choice of explosive is ANFO, either because of the lower cost of ANFO or for simplicity when most holes are considered dry. A simple calculation suggests that in a 311 mm diameter drill hole with 1 m of water in the toe, over five kilograms of the contained nitrogen will have leached into the water within six minutes (62.29 kg/m × 94% AN × 35% contained N × 25% leaching).

Dynamic water

In underground and open-pit mining below the groundwater table, when a blasthole intersects an area with high hydraulic conductivity and significant water inflow, the water can simply wash the explosives out of the holes, regardless of the solubility. These explosives carried with the water will not detonate and will eventually dissolve in the water, either in-situ or downstream.

Misfires

Misfires occur when the explosive charge, or part thereof, does not detonate. This can be caused by, for example, discontinuities in the explosive column, poor timing sequence design, failure of the initiation system, desensitization by pressure transmission between holes, etc. Due to stringent misfire prevention practices in most jurisdictions and better and safer initiation technology, misfires occur less frequently nowadays, and probably make a limited contribution to nitrate leaching.

Non-ideal detonation

Explosives are designed and manufactured to be stoichiometrically balanced and to produce an ideal detonation whereby the explosive ingredients decompose to steam, carbon dioxide, nitrogen gas, and heat. However, when the explosives have a positive oxygen balance, a non-ideal detonation occurs, leading to poor explosive performance. The reaction products contain NO_2 and NO_3 gases, which produce orange blast fumes. As part of the rock fragmenting mechanism, these gases also expand in cracks and microcracks of the blasted rock, and are then transported to processing facilities or waste dumps, with the potential of being leached into processing water, tailings, or effluent water.

Methodologies to mitigate nitrogen leaching from explosive sources

Because the explosive-water contact occurs throughout the entire lifecycle of the explosive, not a single solution to mitigate nitrogen species leaching exists. However, even a combination of current practices and methodologies leaves several of the contact sources without an effective control.

Operational discipline

Because most explosives are stored separately from initiation systems, are transported in desensitized form, and are not readily initiated through ignition or a spark, spillage is probably not regarded as critical from a safety point of view, as for example hydrocarbons or fuels. However, careful management and deployment of bulk explosives through controlled transfer of materials, use of overflow recipients and safety valves, spill kits, spillage procedures, and rigorous on-bench practices does reduce wastage, thereby minimizing nitrogen species leaching as well as costs.

Use of water-resistant explosives

Due to the high solubility of ANFO in water, any damp or wet blasthole should use an emulsion or a water-resistant blend of emulsion and ANFO, whereby the emulsion coats the ANFO. Although most explosive suppliers have emulsions with excellent water-resistant capabilities, some issues remain while other challenges are introduced.

First, emulsions usually come at a higher cost per tonne and have a higher density (0.9–1.4 g/cm^3) than ANFO (0.8 g/cm^3), increasing the overall explosive cost per blasted tonne. In addition, due to the higher density and higher volumetric energy content, emulsion often provides too much explosive energy for the required blast result, causing overblasting of softer rock, excessive vibration, highwall damage, etc. Desired blasting outcomes would require a lower density ANFO, but water presence dictates a higher density, higher energy emulsion not ideally suited to the rock.

While emulsions have a drastically reduced solubility in water, nitrogen leaching from emulsions still occurs (Revey, 1996). Increased sleep times increase the total amount of nitrogen species entering the groundwater and eventually also degrade explosive performance, resulting in reduced fragmenting power and in non-ideal detonation. This generates NO_2 and NO_3 blast fumes, and is another contributor of nitrogen species to the rock and groundwater.

Finally, while the additives and the intimate contact between fuel phase and oxygen phase in the explosive emulsion provide significant protection against dissolution in stagnant water, dynamic waterflows can wash away emulsions into voids and cracks, or even out of the blasthole in underground vertical upholes. The washed-out emulsion remains without detonation, disperses in the environment, and could leach into the environment at almost the same rate as ANFO in some circumstances (Sedenko, 2018).

Use of blasthole liners

While several nitrogen species leaching points are due to error or negligence, or at least are not by design, the explosive-blasthole contact point is inherent to the blasting process. Blasthole liners are a comprehensive engineered control to protect explosives from water in this intentional point of contact. Liners or sleeves are usually made from synthetic materials and provide an impermeable barrier between the explosives and the environment. In addition, they take a cylindrical shape the size of the blasthole diameter when deployed, and contain the explosives in a consistent explosive column.

Blasthole liners have been around for decades, but their uptake has been limited despite the multiple benefits. While inexpensive, these traditional polyethylene liners have several issues, limiting their use as a solution against nitrogen leaching.

First, the polyethylene material is usually too weak to be a reliable solution in often abrasive and broken ground. Liners will rip and tear, water will ingress, and explosives will leak out, defeating the main purpose of the liner. Making these liners more resistant and thus more suitable to the environment, comes at the cost of increased weight, with significant trade-offs in ease of use and manual handling.

Second, deployment of liners adds another step and another visit to the blasthole in an already labour-intensive blasting process. Deployment is often slow and difficult with liners twisting, folding, and blocking holes, thus further delaying the process. These difficulties are exacerbated in underground environments with long, vertical upholes and difficult and confined working conditions. Another consideration, particularly when using traditional liners in combination with ANFO, is the risk of build-up of static electricity on the synthetic liner and the, albeit low, risk of initiation due to the creation of sparks.

Finally, the tendency to prescribe emulsions over engineered barrier controls has limited the adoption of liners with more significant premiums attainable in the sale of emulsions. Even if other factors, such as rock mass competence or highwall conditions, favour the use of lower density ANFO, mining operations are often directed to higher density, water-resistant emulsions by the suppliers.

Blasthole liners do provide a comprehensive solution to mitigate the leaching of nitrogen species from explosives into the groundwater, particularly at the post-downhole delivery contact points, where explosive-environment contact is inherent to the blasting process. However, material properties, operational inefficiencies, and commercial interests have resulted in a very limited uptake. Blasthole liners do not provide solutions outside the blastholes in other key points, such as transfer between recipients or on-bench spillage.

Solutions to common lining challenges

Liners are often considered a cheap, commodity-like accessory to the blasting process manufactured by bulk plastic manufacturers. Dedicated R&D and engineering, however, has addressed most of the challenges commonly encountered with traditional lining. By eliminating the flaws and inefficiencies of traditional liners, blasthole lining again becomes a compelling solution to nitrogen species leaching, while addressing other blasting concerns at the same time.

Material competency

Traditional polyethylene liners are extruded in bulk volumes emphasizing lower costs, as opposed to greater performance. Reconsidering material requirements and using the latest polymer manufacturing technologies has enabled the development of multi-composite, high-tensile strength, conductive liners with impermeable, heat-sealing and ripstop properties at a fraction of the weight. Industrial production can achieve costs that make them a feasible solution, while providing a highly resistant water barrier.

Ease of use in deployment

Currently, automated liner deployment is a remote prospect, but ease of use and process flow of blasthole charging can be addressed through targeted modifications in the liner design. Gusseting[1] during manufacturing for instance, provides a liner with a lay-flat width smaller than the hole diameter. Once

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[1] Gusseting of blasthole liners is protected by MTI-PAT-028 (exp).

deployed down the hole and charged with explosives, the liner expands to take on the hole diameter. The gusseting allows for easy downhole deployment eliminating twisting, folding, and choking of the blastholes, avoiding delays and process losses.

Blasthole liners with heat-sealing properties can be easily provided with an impermeable seal at the bottom of the hole when using semi-automated feeder mechanisms. These machines, which can be mounted on the back of a utility vehicle or mobile processing unit, allow for fast and consistent deployment.

While lining deployment is an additional process, it can be done post-drilling but independent of the charging process, either in advance or immediately prior to charging. If done prior to charging and the same explosive and charging methodology is used, the lining process will add time to the overall blasting process. However, if the liner enables the use of an alternative explosive better suited to overall conditions rather than a highly water-resistant pumpable emulsion, significant time savings can be achieved. A time-and-motion study in a large New South Wales (Australia) coal mine showed that by pre-lining and switching to an augered Heavy ANFO, charging time of a blast pattern could be reduced by more than half.

Table 1: Time-and-motion study on a large Australian coal mine, comparing use of 30/70 pumpable emulsion and augered HANFO in 229 mm non-lined and lined blastholes

	Charging with pumpable emulsion	Lining and loading with HANFO	Pre-lining and later loading with HANFO
Time to line	0 sec	2 min 24 sec	2 min 24 sec
Time to load	4 min 37 sec	1 min 44 sec	1 min 44 sec
Total charging time	4 min 37 sec	4 min 8 sec	2 min 24 sec

Static buildup

The build-up of static electricity while loading lined holes with ANFO can be addressed by integrating a carbon yarn in the woven polymer. This patented carbon yarn will eliminate the safety risk and ensure compliance with local regulations on antistatic materials and the use of ANFO. However, integration of the antistatic yarn is only possible in woven materials and not in bulk, multi-purpose extruded polyethylene.

Engineered liners: a solution to nitrogen species leaching and more

The use of engineered liners deals with the legacy problems of traditional liners, while providing the most effective, wide-spectrum solution to nitrogen species leaching in the explosive-blasthole contact point.

Avoid blasthole leakage

Deploying a highly resistant liner in blastholes eliminates all contact with water in the toe of holes, damp walls, or potentially rainwater or surface water inflow post loading, in turn eliminating any leaching of nitrogen species into the environment. Even in holes intersecting very active hydrogeological layers, both in open pit and underground operations, the explosives are protected within the impermeable barrier. This avoids the explosives being washed out of the hole into the environment or being disintegrated, washed away, and eventually dissolved.

In highly fractured ground, rock mass with cavities or areas with pre-existing underground workings, ripstop and high-tensile strength liners contain the explosives within the drilled diameter of the blasthole and can span large intersection of cavities. The liner contains the explosive in a single, continuous column, avoiding any spillage into the fractures and voids. At the same time, it eliminates discontinuities in the explosive's column, ensuring full column initiation and avoiding post-blast partial misfires and explosive residues. Even if the blastholes are initially dry, spillages and residues from voids and fractures can eventually end in processing circuits or waste dumps and continue to leach nitrogen species in processing or run-off water. This occurrence is eliminated by lining the blastholes.

Ensure ideal detonation

One of the root causes of non-ideal detonation is contamination of compliant, well-designed explosives with water, drill cuttings and fallback. When a blasthole is lined, ingress of foreign material into the explosives, be it dynamic water or drill cuttings from the surface, is eliminated, providing the proper conditions for ideal detonation. Positive oxygen-balanced, non-ideal detonation produces NO_2 and NO_3 gases and injects these into the rock mass. Ensuring ideal detonation through lining produces inert nitrogen instead, ultimately eliminating another source of leachable nitrogen species.

Further benefits

While there is a strong and sensible argument to line blastholes with engineered liners from a nitrogen species leaching perspective, additional benefits, although some mutually interdependent, exist.

Explosive performance

Leaching of nitrogen into the environment also means leaching energy-rich nitrogen bonds into the environment. These nitrogen bonds are the key explosive energy and gas providers for rock fragmentation, and their leaching has a detrimental effect on the explosive's rock-breaking performance. Eliminating nitrogen species leaching allows the explosive to perform to its full potential and consume the explosive energy the mine has ultimately purchased. Given the liner material does not degrade in the timescale of blasting, sleep times can be greatly extended, allowing blasting when production, not explosive integrity, dictates.

The same nitrogen deficiency, caused by nitrogen species leaching, leads to a positive oxygen balance and generation of blast fumes that has potentially significant health, safety, and regulatory impacts.

Ensuring ideal detonation by maintaining the designed oxygen balance will ensure no NO_2 and NO_3 gases are released.

Other contaminants

In addition to ammonium nitrate, commercial bulk explosives contain fuel oils, hydrocarbons, salts, emulsifiers, waxes, etc. By providing an impermeable barrier, liners also protect the environment from contamination with these other explosive additives.

Explosive selection

Blasthole lining provides an additional degree of freedom in explosive selection by eliminating the water resistance constraint in many instances. This allows mining operations to match the explosive type with the rock mass to achieve the desired blast outcome. At the same time, premium emulsions can be substituted by less expensive but fit-for-purpose ANFO. This substitution most probably offsets the liner cost and, on many occasions, provides a net cost saving.

Improved recovery

Finally, in areas with very high waterflows, particularly in underground vertical upholes, lining can simply enable blasthole loading to the full drill hole depth where previously impossible. Apart from eliminating wastage and spillage, this allows better stope and ore recovery by blasting to design.

Case study: UG gold mine

An underground gold mine in the Bibiani gold belt in West Africa experiences severe issues when loading vertical production upholes in their ore-producing stopes due to large amounts of water flushing out of the holes. Some of these holes would intersect underground waterflows. The situation deteriorates significantly during the wet season from April to June.

The mine uses a watergel explosive with high water-resistance. The product is recognized in the industry as a “sticky” product that would hold up well in vertical upholes. However, even this high-performing explosive would require up to three attempts per hole for the explosive to stick, prior to the installation of retention plugs. The holes of up to 25 m in length could lose up to 100 kg of explosives when completely flushed out after loading. While not the key focus of the mining operation at that moment, the large quantities of flushed explosives would eventually find their way to the groundwater.

The mine decided to trial engineered lining in a stope blasting ring at a production level at 1,575 m depth with several holes intersecting waterflows. The wettest hole as well as the two adjacent holes were selected for lining. A highly resistant liner was deployed using the charging equipment and secured in the hole with inflatable plugs. The three holes were then charged with watergel. During the charging operation no explosives leaked from the holes and the holes were loaded in a single pass. Better rock breakage and stope height was most likely achieved due to a fully loaded column and a continuous charge.

The application of the engineered liner in this operation with extreme flows of dynamic water shows that explosives can be contained and protected from the environment even in harsh conditions. If the explosives can be contained, then nitrogen species leaching from the blasthole can be mitigated. It is worth highlighting that similar results could be achieved using packaged explosives, a product the liner effectively emulates. However, packaged explosives come at a significant cost premium compared to bulk explosives.

While conditions in this case study are not commonplace, they illustrate lining performance in a worst-case scenario. Additionally, multiple examples exist of mines struggling to contain explosives in underground blastholes due to waterflow. In some regions, such as West Africa, this is seasonal due to the wet and dry cycle. In other countries with wet climates and high water tables this is mostly subject to the geology and permeability, with similar examples found in Ireland, New Zealand, and the Nordic countries.

Conclusion

Blasthole lining has been around for decades but due to the various operational and material issues with liners and the lining process, the use of water-resistant explosives has been the preferred solution for mining operations operating in humid or wet environments. This solution has been strongly promoted by the explosive suppliers fetching premium prices for these water-resistant explosives in the absence of a compelling alternative until recently. However, with nitrogen leaching from explosives becoming an increasing focal point of the impact of mining on the environment and waterways, it is becoming evident that water-resistant explosives can reduce, but cannot eliminate, nitrogen species leaching.

Applying material and process engineering expertise to the multi-purpose, commoditized polyethylene liners can overcome the traditional lining flaws. Multi-layered and composite polymers address material performance. Interwoven carbon yarns eliminate the buildup of static on the liner in the explosive delivery process. Gusseting and semi-automated feeder mechanisms introduce new efficiencies in the lining deployment process.

The installation of an impermeable barrier of engineered material eliminates many of the contact sources between the explosive and the groundwater, providing the best possible solution to mitigate nitrogen leaching post-delivery of the explosives down the hole. The migration of nitrogen species into the environment also implies the loss of high-energy content nitrogen bridges from the explosives with reduced explosive performance and blasting outcomes as a necessary consequence. New material and process technologies make lining again a compelling control in the mitigation of nitrogen leaching species, at the same time allowing procured explosives to perform at their full potential for the intended rock fragmentation.

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Chapter 2:

Mine Water Characterization and Prediction

Transient Simulation of Dewatering to Estimate Potential Effects on Water Resources for an Open Pit Lithium Mine in North Carolina

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Abstract

Piedmont Lithium Carolinas, Inc. (PLL) is proposing to construct an open-pit mine in the Carolina Tin-Spodumene Belt (TSB) of North Carolina where lithium-bearing spodumene pegmatites occur. PLL intends to extract lithium-bearing spodumene for refinement to battery-grade lithium hydroxide, to support manufacturing of lithium-ion batteries. The approximately 1,548-acre site is in an unincorporated area of Gaston County, near Cherryville, North Carolina. On behalf of PLL, HDR Engineering, Inc. of the Carolinas (HDR) performed groundwater modelling to estimate water withdrawal rates for pit dewatering, and evaluate the possible effects pit dewatering might have on local water resources.

The mine will be comprised of four 600-feet deep mine pits excavated at different rates and times over 20 years. Rock quality designation from 288 rock cores was evaluated as a surrogate for hydraulic conductivity; 10 monitoring wells were installed; stream flows were monitored; and an aquifer test was conducted in support of the model. A geologic model based on the rock core was used as the stratigraphic basis of the groundwater model. Because the bulk hydraulic conductivity is low, dewatering will be done in-pit by sumps. The mined rock is spodumene pegmatites in a deformed massive granite with almost no intrinsic and limited secondary permeability, so deep rock hydraulic conductivities is very low. Simulating the material changes and competing dewatering in multiple changing pit shells over the mine’s life is a complex task. A series of transient models were undertaken to simulate mine pit excavation and backfilling over time. This complex model was conceptually challenging, and mathematical instabilities occurred during some simulations.

The groundwater flow model was constructed with six hydrostratigraphic layers. The model domain encompassed the area that potentially contributes water to the mine pits during dewatering, or that could be

affected by dewatering. Mine pit shell extents were represented in the transient models through a change of aquifer materials. MODFLOW drain cells are varied in elevation over the modelled period to reflect changing dewatering conditions as pit extents expanded. The series of transient groundwater models that simulated dewatering through the 20-year anticipated life of the mine were used to estimate water withdrawal necessary to dewater the mine pits as they are excavated and associated drawdown in the adjacent aquifer. Each change in mine pit configuration and dewatering operations altered groundwater flow paths and resulted in re-evaluation of the site conceptual model.

Model results indicated that withdrawals would range between 575 and 2,300 gallons per minute, and drawdown greater than one foot would be limited to areas near the pits (within less than a half mile) as they are excavated. Discharge of pumped water through permitted National Pollutant Discharge Elimination System (NPDES) outfalls to streams and wetlands was found to reduce impacts to baseflow conditions. Additional site characterization studies in support of the model and additional modelling are under way. Moving forward, the model will be used to site sentinel monitoring wells, size dewatering pumps, make decisions regarding the mine process water budget, and evaluate potential mitigation measures for impacts to surface water bodies and nearby private water supply wells.

Introduction

Piedmont Lithium Carolinas, Inc. (PLL) is proposing to construct an open-pit mine in the Carolina Tin-Spodumene Belt (TSB) of North Carolina where lithium-bearing spodumene pegmatites occur. PLL intends to extract lithium-bearing spodumene for refinement to battery grade lithium hydroxide, to support the manufacturing of electric vehicle (EV) lithium-ion batteries. The approximately 1,548-acre site is in an unincorporated area of Gaston County, approximately one mile east of Cherryville, North Carolina. The mine will be comprised of four pits that are excavated at different rates to approximately 600 feet over a 20-year period. On behalf of PLL, HDR performed groundwater modelling to estimate the rate of water withdrawal during pit dewatering operations, and evaluate possible effects pit dewatering may have on local water resources and water users. The model was also used to site sentinel wells around the permitted boundary to provide early detection of drawdown prior to drawdown in private supply wells. Post-mining recovery will be the subject of future modelling.

Conceptual model

The groundwater flow model domain includes the southern portion of Indian Creek watershed, Beaverdam Creek watershed, and a reach of the South Fork Catawba River. The 32.5 square mile (mi^2) model domain and site boundary are shown in Figure 1. PLL plans to mine resource from four 600-feet deep mine pits (North, South, East, and West pits) within the permitted mine boundary. Mine pits are separated by existing streams and wetlands that will largely remain intact during and after mining.

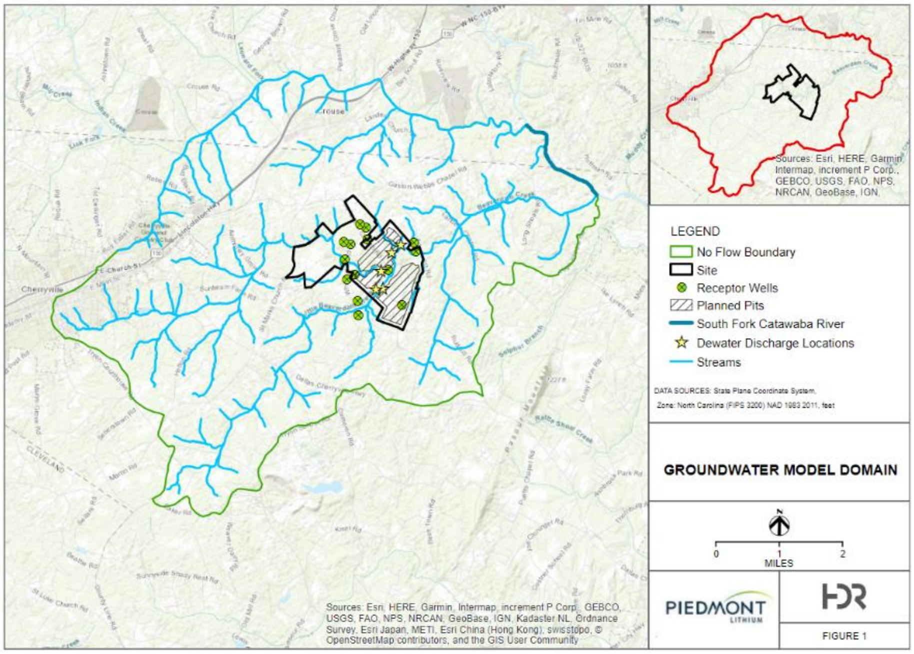

Figure 1: Groundwater model domain

Hydrostratigraphy

The site is located within the TSB, which is comprised of metamorphic and igneous rocks overlain by weathered by-products of the rock and residuum (Kessler, 1942; Schaeffer, 2019). These materials can be divided into the following hydrostratigraphy:

1. *Overburden* is generally residuum consisting of alluvial and regolith deposits composed of silt from weathered bedrock, with some rock fragments as gravel and sand.
2. *Saprolite* is derived from weathering of bedrock in-situ where some of the original rock texture and structure remain, yet the minerals have been altered to the consistency of soil.
3. *Transition zone* is a thin zone between the saprolite and the underlying bedrock where there is less weathering, but the rock is highly fractured, weathered, and not competent.
4. *Bedrock* is generally metavolcanic amphibolite intruded by pegmatites (some of which are spodumene bearing). The amphibolite exhibits little foliation or other structures. Other areas within the model domain are comprised of foliated metasedimentary rocks, which in some places, have relict bedding. Neither the metavolcanics nor the metasedimentary rocks have significant primary porosity, so almost all the water in these units exists in joints and fractures. At some locations, Triassic diabase dikes have intruded the crystalline bedrock and may be responsible for some of the lineations described below. As reported by Daniel et al. (1997), groundwater flow in the bedrock aquifers is

controlled by fracturing. And further, it is likely that erosion results along fractures so that streams and rivers are associated with areas of higher fracturing and hence more transmissive fractured bedrock.

5. *Lineations,* including valleys and linear topographic expressions visible in aerial photographs and topographic maps, are likely due to weaknesses in the bedrock such as faults and fractures and more easily eroded folded rock units, and may indicate zones of higher hydraulic conductivity. These lineations can be simulated as higher-hydraulic conductivity material. However, their attitude in the subsurface is uncertain. Daniel et al. (1997) found that valley floors had higher hydraulic conductivity than hill tops, and that the valley walls transition between the two. This variation in hydraulic conductivity is consistent with valleys being coincident with subsurface fractures.
6. *Mine pits* become open holes that are dried by dewatering. Mine pits that were dried during dewatering either will rewet as pit lakes after dewatering, or will be filled with low hydraulic conductivity fill consisting of native waste rock material and non-hazardous mine tailings.

Boundary conditions

Groundwater flows are generally from inflow to storage to discharge; boundary conditions describe the specific features that make up these processes. Inflow to the model domain is generally from recharge due to precipitation, although under stress, water may be diverted from adjacent systems or captured from surface water. Storage is the quantity of water occupying space in the system and from compressibility of the aquifer matrix. Discharge under natural conditions is usually to surface water bodies (streams, wetlands, rivers, and lakes) and evapotranspiration. At the site, discharge is to streams (e.g., Beaverdam creek), wetlands (which typically feed streams), the South Fork Catawba river, and evapotranspiration where groundwater is near the ground surface. Also, water is withdrawn from the system by water supply wells, reducing discharge to surface water (no large water supply wells are documented in the model domain). These boundary conditions are accounted for in a groundwater model to ensure the appropriate water budget is simulated and are shown in general on Figure 1 (more detailed wetlands were simulated than shown).

Temporal constraints

The calibrated steady state model of natural state conditions described below provided the initial conditions for the transient modelling. Pit dewatering was simulated with a series of transient models to account for the changing pit geometries and locations of dewatering. The transient models represent annual mine pit extents with portions of different pits open at the same time. The pit dewatering sequence simulated is shown in Table 1. Drawdown due to dewatering is greatest when the mine pits have been excavated to the designed terminal depth. After completion of mining, pits either fill with water or are filled with low hydraulic conductivity material. Multiple stress periods were simulated in the multi-year phases to account for changing pit geometries when the same set of pits were mined over multiple years.

Table 1: Transient model sequence of mine pits

	Pits with dewatering			
Model year	**South pit**	**East pit**	**West pit**	**North pit**
1	Mining			
2	Mining	Mining		
3	Mining	Mining		
4	Filling	Mining		
5	Filling	Mining		
6–10	Filling	Mining		
11	Filling	Mining		
12	Filling	Mining	Mining	
13	Filling	Filling	Mining	Mining
14–20	Filling	Filling	Pits merged mining	

Dewatering and water handling

Water was assumed to passively seep into the mine pit and then be pumped from the lowest levels of the mine pit into settling basins prior to being discharged to adjacent streams or wetlands. Dewatering was simulated by MODFLOW drain return cells (DRT), which estimate the amount of water removal necessary to dewater the mine pits. Drain elevations were set equal to the bottom of the pit. The water removed by drain cells was returned to the model at the planned discharge locations. Water from mine pit dewatering returns to the model infiltrates to groundwater, or flows out of the model domain through streams and wetlands. Using the DRT cells to return water from dewatering operations to the model allowed the evaluation of water handling effects on water balances for wetlands and streams, drawdown at nearby wells, and recovery of water levels in adjacent idle mine pits.

Model development and calibration

Modelling software

Groundwater modelling was performed using the USGS groundwater model software, MODFLOW-NWT (Niswonger et al., 2011), which allowed a variable spaced grid that focused on areas of interest, while staying generalized in remote areas. Aquaveo's model pre- and post-processing software, GMS (Aquaveo, 2021), was used to develop the groundwater flow model.

Discretization

The model grid was refined both horizontally and vertically so that features of the CSM and the focus area near the site could be simulated with greater detail than remote areas that are generalized. Cells in the model range between 50 feet on a side where the grid is focused around the mine pits, to 500 feet on a side where the model is generalized further away from the site.

Model layers

The model was constructed using the following six layers to represent hydrostratigraphy within the model domain.

Table 2: Layer description

Layer	Hydraulic conductivity (ft/d)	Vertical anisotropy (ft/d)	Specific storage (1/ft)	Specific yield	Description
1	1.5	2	0.01	0.2	Overburden: regolith and fluvial deposits
2	1	2	0.001	0.15	Saprolite: bedrock eroded to soil
3	2	2	0.001	0.2	Transition zone: highly fractured and weathered rock beneath the saprolite
4 / 5 Hard rock	0.0075	1	0.0004	0.01	Bedrock: Hard rock found between streams
4 / 5 Soft rock	0.25	1	0.0004	0.1	Bedrock: Soft rock found near streams
6	0.0075	1	0.0004	0.01	Deep bedrock: Hard rock with closed fractures
Pits	5,000	1	0.001	0.1	Mine pits: Simulated as high hydraulic conductivity material as pits were excavated, once dried, cells representing mine pits are represented by dry-cells. After dewatering, the pits are simulated as either rewetted high hydraulic conductivity (mine pit lakes) or with rewetted low hydraulic conductivity material (backfill)

Boundary conditions

Recharge was based on studies done in the adjoining Indian creek watershed by Daniel et al. (1997), who estimated recharge at 10 inches per year within the model domain. Recharge was simulated using constant flux in the MODFLOW Recharge package.

Streams were based on the USGS National Hydrographic Dataset (NHD) flow lines shapefile (USGS, 2019) for generalized model areas and the detailed digitized stream map shapefile (HDR, 2018) at the site. Streams were simulated using the MODFLOW Stream package, which allows individual stream segments to gain or lose water and connects flow between reaches. Each node along the streams was referenced to the surface elevation from a digital elevation model (DEM) (USGS, 2013). The bottom conductance, roughness, width, and connection to incoming upstream flow were added to each stream segment. Beaverdam creek, the largest stream in the domain, was simulated as 25 feet wide and Little Beaverdam creek was simulated as 15 feet wide. Smaller tributaries were simulated to be 5 feet wide. Stream bottom conductance was set to 1(ft^2/d)/ft.

Ponds in the model domain are generally created by small dams on streams and creeks. Although they may affect groundwater flow locally, the effect is similar to that of the stream at the same location. For that reason, changes in simulated base flow in streams were used to assess impacts on ponds.

South Fork Catawba river is the down-gradient model boundary and was simulated using the MODFLOW river package. This package uses the riverbed elevation based on the DEM (USGS, 2013) along the stretch of the river and an estimated conductance value for the riverbed.

No-flow cells are inactive model grid cells (water can pass through vertically as recharge). Since the domain is larger than the effects of dewatering, the domain is bounded by no-flow cells (inactive cells in the grid beyond the domain). Also, no-flow cells are used to simulate the empty space of dewatered pits.

Steady-state calibration

Once constructed, the groundwater model results were compared to mean water levels from 10 monitoring wells at the site, base flow estimates for streams in the Indian creek watershed as documented by Daniel et al. (1997), and stream flows measured in May 2019 within the site boundary. An aquifer test conducted was influenced by a recharge event (i.e., hurricane) making it unusable as a transient calibration target; however, estimates for storativity and hydraulic conductivity from the test were used to guide the modelling. A second aquifer test is planned for the second quarter of 2022.

The means and ranges of variability in groundwater levels measured in 10 monitoring wells over a one-year monitoring period were calculated and compared to simulated water levels. Simulated levels at 9 of 10 wells were within the range of observed levels within two standard deviations of the mean water level and within one standard deviation of the mean in four of these wells. The root mean squared error for the base simulation is 3.6 feet, while the mean square of the observed standard deviation is 4.3 feet, showing the water levels simulated are within the variability of the observed water levels. Water levels in one well on a hillside were off by 28 feet. This water level variation could be due to a nearby fracture, spring, or other condition not simulated by the model. Adjusting the model to match the one well would cause loss of calibration at the other wells. Hydraulic conductivity simulated by the calibrated model was at the low end of the values observed during the aquifer test. However, the pumping test was hampered by a recharge event and likely overestimated hydraulic conductivity.

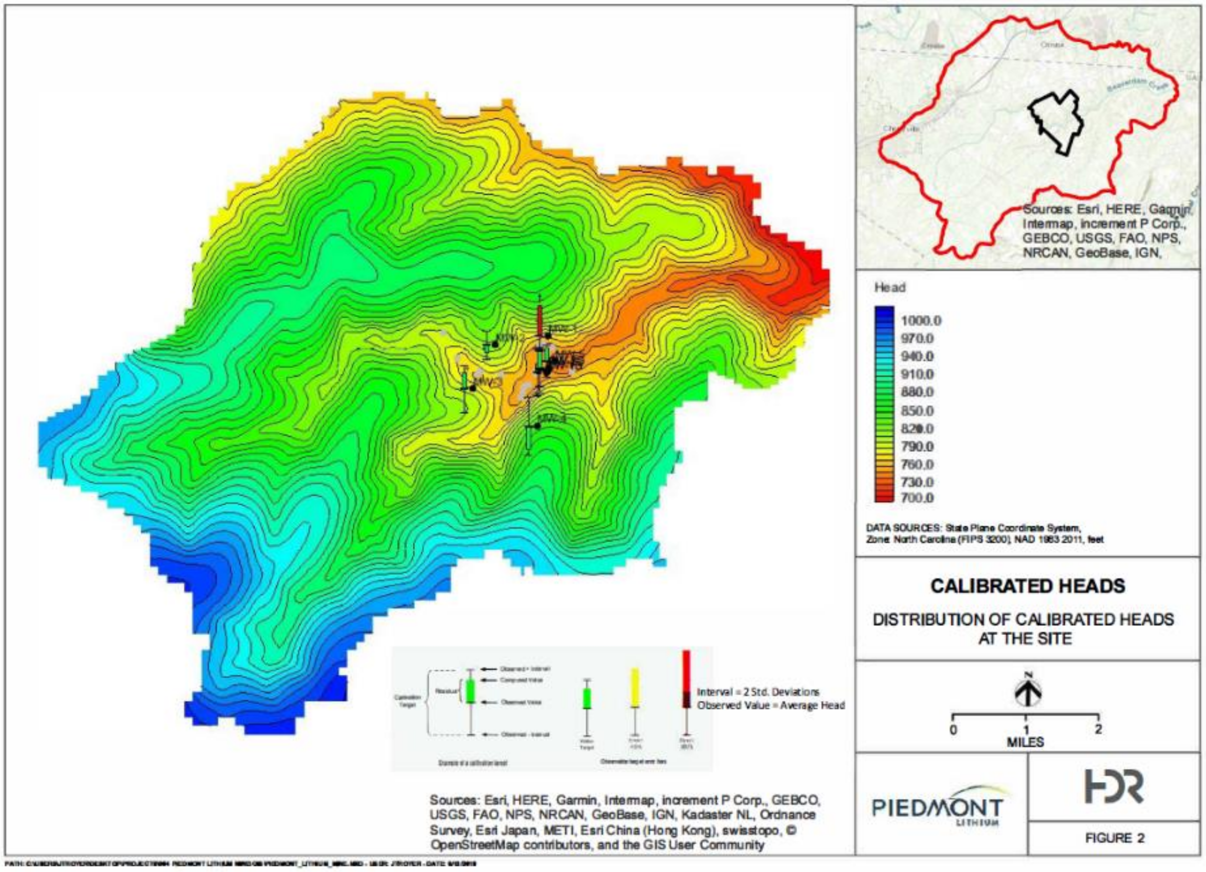

Figure 2: Calibrated heads

Total flow in a stream includes runoff into the streams, lateral flow from the soil, and base flow. Baseflow is the portion of stream flow which is discharged from the groundwater. Baseflows were estimated by Daniel et al. (1997) at four locations on Indian Creek within the model domain. The baseflow simulated by the base model was compared to these locations (Table 3). Stream flow (specifically baseflow) measurement locations that were compared to the calibrated model are shown in Figure 3.

Table 3: Simulated baseflow and baseflow reported by Daniel et al. (1997)

Measurement location (see Figure 3)	Reported flow (ft3/s) (1997)	Modelled flow (ft^3/s)	Percent difference
81	0.16	0.17	5.6
79	0.75	0.69	7.3
82	1.79	1.77	1.4
75	0.28	0.26	6.5

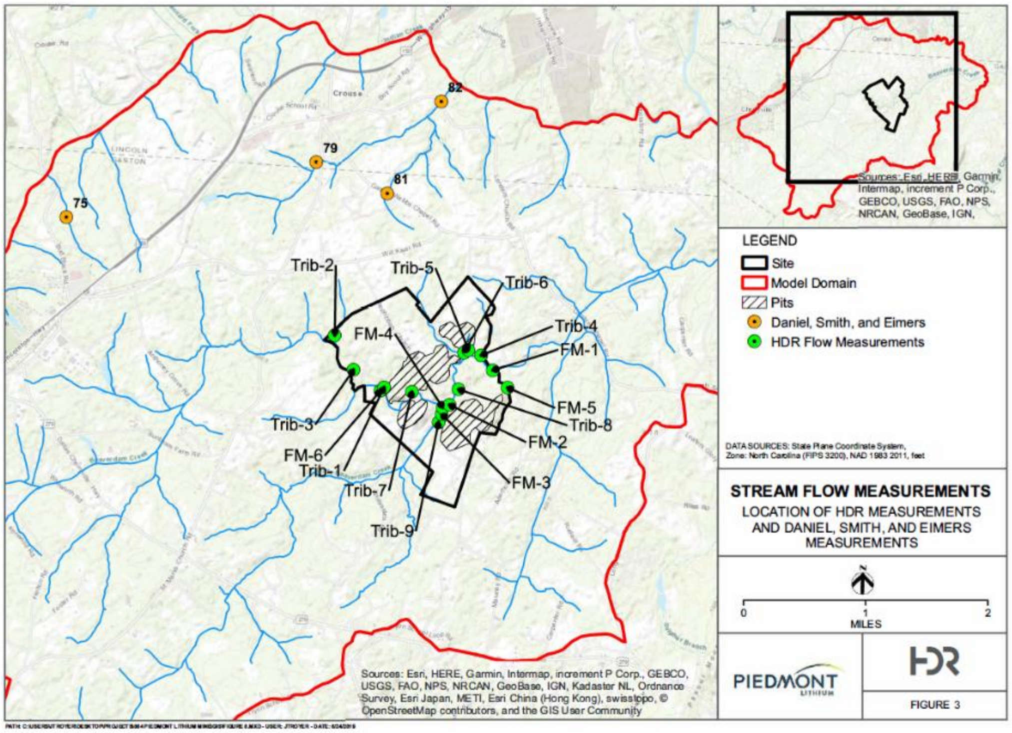

Figure 3: Stream flow measurements

Stream flows within the site were measured on May 13 and 15, 2019. The USGS stream gauge on Indian creek (the adjacent watershed) was at the 95th percentile and 85th percentile daily flows for those two days, meaning elevated total flow was measured and not baseflow. When these stream flows are compared to model output (baseflow, so likely less than 50th percentile), all simulated flows were less than measured and most were at about 50% of observed. While this is a qualitative comparison, the model-predicted base flows are within observed flows and likely approaching actual baseflow values.

Determining mine pit shells through time

PLL's most recent estimate of resource extent was used to establish the potential extents of pit excavation used in the transient model (see Figure 1). Annual mine pit geometries were estimated by the mining engineer, Marshall Miller & Associates (MMA), in 2021 and provided as 3-dimensional shapefiles of surface topography. MMA used MiningMath SimSched software to optimize pit geometries and Maptek's Vulcan Evolution software to establish the mine operations schedule (MMA, 2021).

The mine pit topography was subtracted from the modelled ground surface topography for each annual change in mine pit geometry. Mine pit extents for model layers were based on contours from the pit excavation geometries that coincide with model layers. Pit excavation depths did not always coincide with established model layering, so a layer was considered excavated where the pit shell was deeper than 50% of the modelled layer thickness and the material was changed to open pit.

Simulating mine dewatering over time

The complexity of the model required the model approach and solution method to be re-evaluated with each change in mine pit and dewatering geometry. A series of transient models simulated annual configuration of each pit over a 20-year anticipated mine life (Table 1). Model cells within mine footprints were represented with water-filled, high-conductivity cells that are allowed to go dry when water levels drop beneath them. Additionally, drains placed in the model to collect simulated groundwater seepage through the face of the pit or flow through a lower layer were reconfigured to fit each new mine pit footprint. The model runs were more successful when each footprint change and drain configuration was conducted with an independent transient simulation. Often, the solver scheme used in one phase of mining needed adjustment to accommodate the next phase of mining. Final heads generated from a simulation became the starting heads for the next simulation in the sequence. Final drawdown at the end of the 20 years of simulated dewatering is shown in Figure 4.

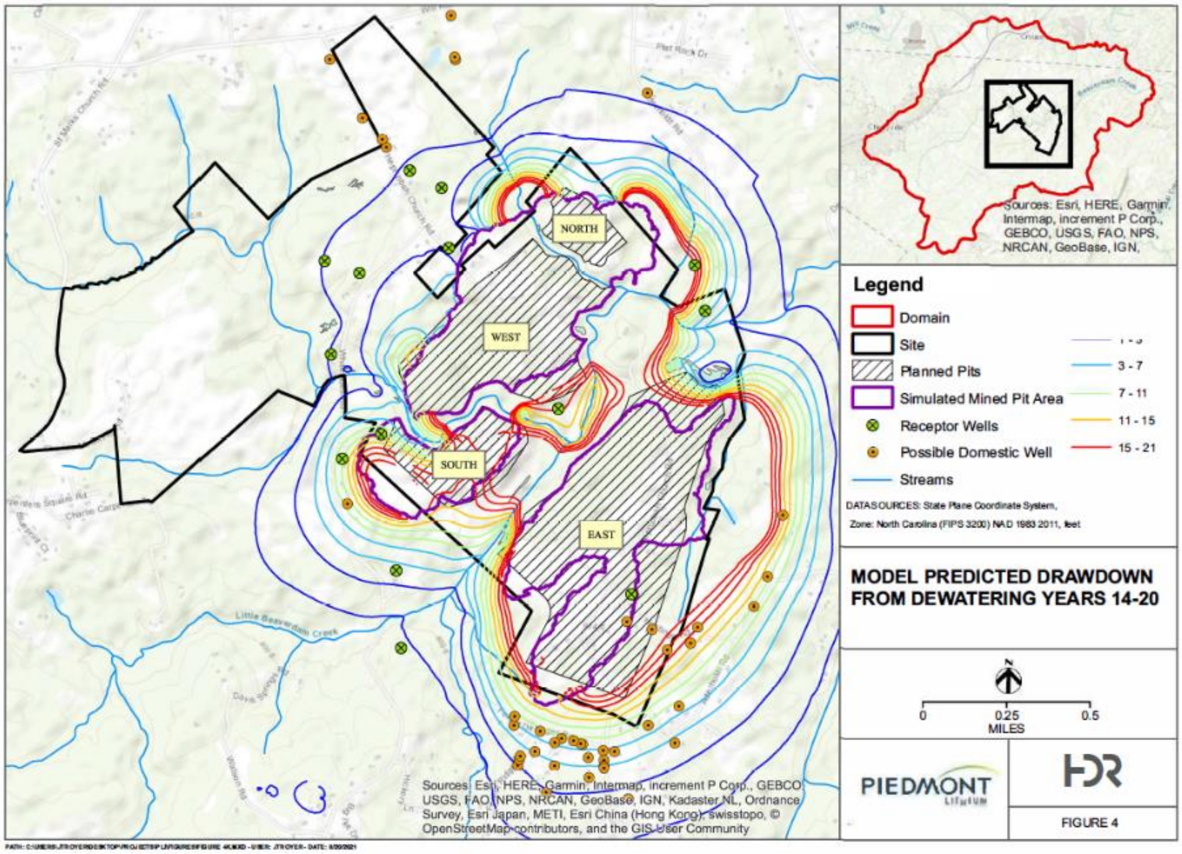

Figure 4: Model predicted drawdown at the end of the 20 years of simulated dewatering

A volumetric water budget analysis for each transient model was performed. Dewatering rates at various stages of mine pit operations were estimated based on the volume of water removed by the drains and the time period of the simulation. Estimated dewatering rates ranged from 575 gallons per minute (gpm) to 2,300 gpm for the largest mine pit footprint, as presented in Table 4.

Table 4: Model predicted dewatering withdrawal rates

	Pumping rate (gpm)				
Model year	**South pit**	**East pit**	**West pit**	**North pit**	**Total**
1	525	50			575
2	975	1,225			2,300
3	725	775			1,500
4	25[1]	1,025			1,050
5	75[1]	950			1,025
6–10	N/A[2]	1,250			1,250
11	N/A[2]	1,575			1,575
12	N/A[2]	1,050	950		2,000
13	N/A[2]	0	500	850	1,350
14–20	N/A[2]	N/A[2]	1,075[3]		

[1] Pumping to maintain drawdown while filling pit with excavated material.

[2] Pit complete, no dewatering modelled.

[3] West and North pits are merged.

Simulated drawdowns at two wells located off the mine property resulted in significant loss of water in the well column. PLL plans to place sentinel wells at strategic locations along the site boundary to provide early detection of excessive drawdowns. Mitigation for wells that experience water column loss will be addressed case by case.

The potential changes of discharge to wetlands and stream baseflow due to dewatering were assessed for each variation of the mine pit footprint and drain configuration by comparing water budgets for each wetland or stream reach with the base simulation (no mine pits or dewatering). Several wetlands were predicted to go dry during dewatering, and baseflow to three streams crossing the site is expected to be significantly reduced. PLL plans to return groundwater collected during dewatering to stream locations downstream of the mine pit near the site boundaries to reduce downstream effects of dewatering. These processes were explicitly simulated in the model. Discharge to streams will comply with NPDES requirements. Some discharge water may be released to the most potentially impacted wetlands.

Subsurface conditions are varied and complex with fractured bedrock being simulated with a porous media model. Sensitivity analyses were not conducted due to the long run times associated with each model step, but may have shown which parameters model results were sensitive to and are planned for the future.

Identifying sensitive parameters may improve model performance and reduce run times, as well as enable the estimation of potential variability in the modelled outcome.

Conclusion

Dewatering for the planned mine life at a multiple-pit lithium mine in the Carolina TSB, including the complexities of overlapping mine pit excavation schedules, was successfully modelled using a series of linked transient models based on a well-calibrated steady state model and storativity values from aquifer testing. Each phase model outcome was used as the starting point for the next step, which was modified to include the new pit geometry. Model results indicated that impactful drawdown would be limited to the areas near the pits as they are excavated. Withdrawal rates needed to dewater the pits ranged from 575 to 2,300 gpm. Discharge of pumped water through permitted NPDES outfalls to streams and wetlands was found to reduce impacts to baseflow conditions. Mitigation of impacts to wetlands may include discharging portions of the dewatering water directly to potentially wetlands during dry periods. Moving forward, this complex model will be used to site sentinel groundwater monitoring wells, size pumps necessary to dewater the pits, make decisions regarding the mine process water budget, and evaluate potential mitigation measures for affected surface water bodies and nearby private water supply wells. Additional aquifer testing is being conducted at a location within a planned mine pit to verify and update the model parameters used and inform needed adjustments to the current model and transient calibration.

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Seamlessly Integrated Modelling Approach: From Conceptual Geological to Numerical Models

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Abstract

Three-dimensional conceptual geological models (CGMs) of complex hydrogeological systems are often simplified in numerical groundwater models to analyze groundwater flow regimes. Although CGMs are accurately developed in most cases, the oversimplification of critical geological features in numerical models does not reflect CGMs to simulate the groundwater flow system. This leads to simulated results often not comparing well with observed data. The objective of this study is to address this problem through a seamlessly integrated modeling approach that retains key geological/ hydrogeological features from CGMs in numerical groundwater models. This eliminates the disconnect between CGMs and numerical groundwater flow models. This paper applied the approach in the development of a groundwater flow model for a mine site. The three-dimensional CGM was developed in Leapfrog Works and integrated into FEFLOW using Leapfrog's hydrogeology module as an input file. Results from the numerical groundwater flow model showed no reduction of geological features from the CGM. Simulated well data also closely matched observed well data, highlighting the success of this approach in improving the groundwater modelling process.

Introduction

An understanding of geology is fundamental to numerical groundwater modeling. Hydraulic heads, flow directions, residence times, and other hydrogeological properties are strongly controlled by geological features. Therefore, an accurate conceptualization of geological models is a fundamental and crucial step for understanding geological controls on groundwater hydrodynamics.

Conceptual geological modelling involves the analysis and 3D visualization of geological data and geological information collected from borehole logs, geological maps, geophysical data, and basin analysis.

These conceptual geological models (CGMs) often provide information about geological processes, rock type, age, thickness, discontinuities like folds, faults, and other petrophysical properties such as porosity and permeability. Groundwater numerical models, on the other hand, provide information about groundwater flow directions, flow velocity, travel time, permeability, storativity, dispersivity, concentration, initial and boundary conditions, etc., all of which are dependent on CGMs. The development of a numerical model involves the discretization of the model domain using Finite Differences Method (FDM) or Finite Element Method (FEM). These FDM or FEM packages then use numerical codes to solve the groundwater flow equations with respect to time.

Significant advances in computing technology in recent years have made the complex tasks of geological modelling and groundwater modelling less cumbersome through the development of robust modelling tools like Leapfrog Works (Seequent, 2017) and FEFLOW (DHI Group, 2022). These have helped to narrow the gap that exists between geological modellers and groundwater modellers, who often work independently and for different objectives. For example, whereas geological modellers place strong emphasis on rocks (stratigraphy) and geological processes, groundwater modellers are more focused on groundwater flow mechanisms and aquifer parameters, resulting in huge gaps between these two fields. Apart from this huge gap, frequent simplifications of critical geological features in numerical groundwater models may impact actual flow systems. This means that the performance of a particular numerical groundwater model solely depends on the initial subjective discretion of the modeller.

This paper addresses the disconnect between CGMs and numerical groundwater models through a seamless integrated modelling approach that retains key geological features from CGMs for effective numerical groundwater modelling. This integrated modelling approach is not a substitute for superior quality field data that is always required for the development of CGMs, nor is it an automatic guarantee of good numerical groundwater results. It only serves to limit the often-oversimplified assumptions regarding geological features in numerical groundwater modelling.

Methodology

The study commenced with the development of simple CGMs and numerical groundwater models using Leapfrog Works (Seequent, 2017) and FEFLOW (DHI Group, 2022) respectively.

Leapfrog uses data and parameters such as lithological codes, Digital Elevation Models (DEMs) and drawn polylines, to implicitly construct surfaces based on spatial interpolation of the point attributes using radial basis functions (RBF), and kriging techniques to construct CGMs (Seequent, 2017).

FEFLOW on the other hand, discretizes the model domain using the Finite Element Method (FEM) to solve the groundwater flow equations using built-in numerical codes.

Data and discussion

Different CGMs were first developed for simple geological formations before applying the integrated modelling approach to a more complex geology. Conceptual geological models were developed from stratigraphic data obtained from borehole logs, mapped fault lines, and fractures. These geological data and information were compiled, modelled, and visualized with Leapfrog Works. The left side of Figure 1 shows a simple CGM developed with Leapfrog Works. From the same data, several other simple CGMs depicting different geological scenarios (not shown here) were also developed. These included cases of simple formations with vertical faults and no shifted stratigraphy, as well as cases with inclined faults with no shifted stratigraphy.

In all the geological scenarios, the Leapfrog model's interpretation of field data closely matched what the geologist had conceptualized. With Leapfrog's hydrogeology module as an input file, the CGM developed for each geological scenario was integrated into FEFLOW seamlessly, while retaining the integrity of these geological features.

An example of such seamless integration is shown in Figure 1. This integrated modelling approach was then applied to a more complex geological formation (mine site) after its success on simple cases. The site data included long records of observed data from hundreds of wells, stratigraphic data depicting different geological formations, hydrological data, and hydrogeological data. The shallow well data depicted the hydrogeological conditions of the upper alluvial aquifer, while the deeper well data described the conditions of the weathered and fresh bedrocks. The vertically declined hydraulic conductivity of the bedrock was implemented in the model. After the interpretation of field data by the developed Leapfrog CGM had closely matched what the geologists had conceptualized for the site, the CGM was then seamlessly integrated into FEFLOW.

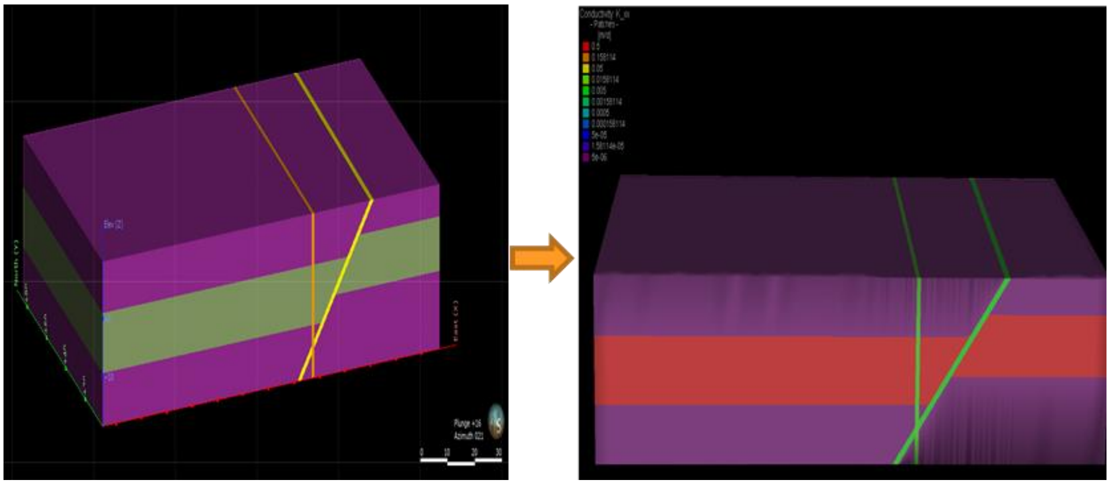

Figure 1: Conceptual Geological Model developed in Leapfrog Works (left) integrated seamlessly into a numerical groundwater model (right) using Leapfrog's hydrogeology module

In FEFLOW, two groundwater flow modelling scenarios were implemented. The first was based on the retained geological features from Leapfrog's CGM, while the second scenario was based on the case where geological details of the mine site were modified according to the groundwater modeller's discretion. For instance, multilayered alluvial sediments were assumed to be a single material and assigned a single hydraulic conductivity value.

Similarly, the bedrock was assumed to be impermeable and assigned a lower hydraulic conductivity, instead of assigning higher hydraulic conductivity values for the weathered and fractured parts. Results from these two scenarios were later compared.

Results

After applying the integrated modelling approach to the developed Leapfrog CGM of the mine site (Figure 2), features such as layered alluvial deposits, and deep highly fractured and faulted zones around ore bodies, which would have usually been oversimplified in most groundwater models, were retained in the FEFLOW model. Similarly, pinching layers and bedding layers were retained in the numerical FEFLOW model without any simplifications or modifications (Figure 3).

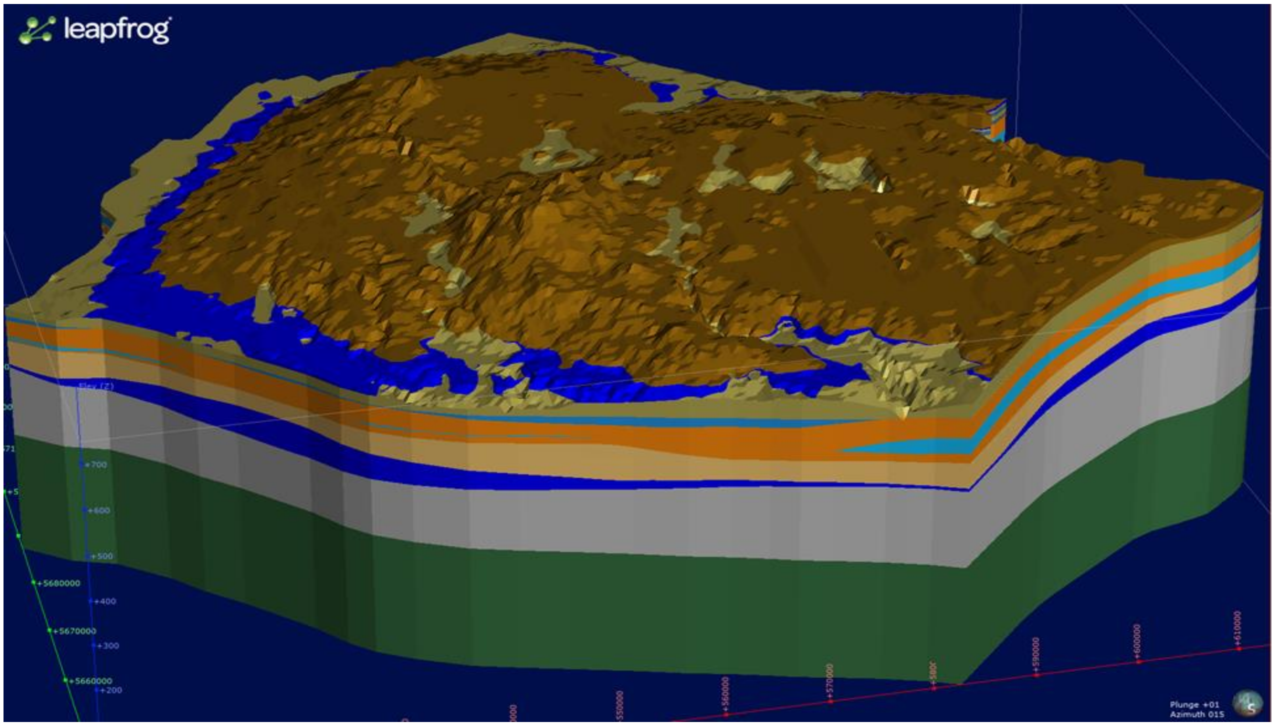

Figure 2: Three-dimensional representation of the conceptual geological model (CGM) of mine site

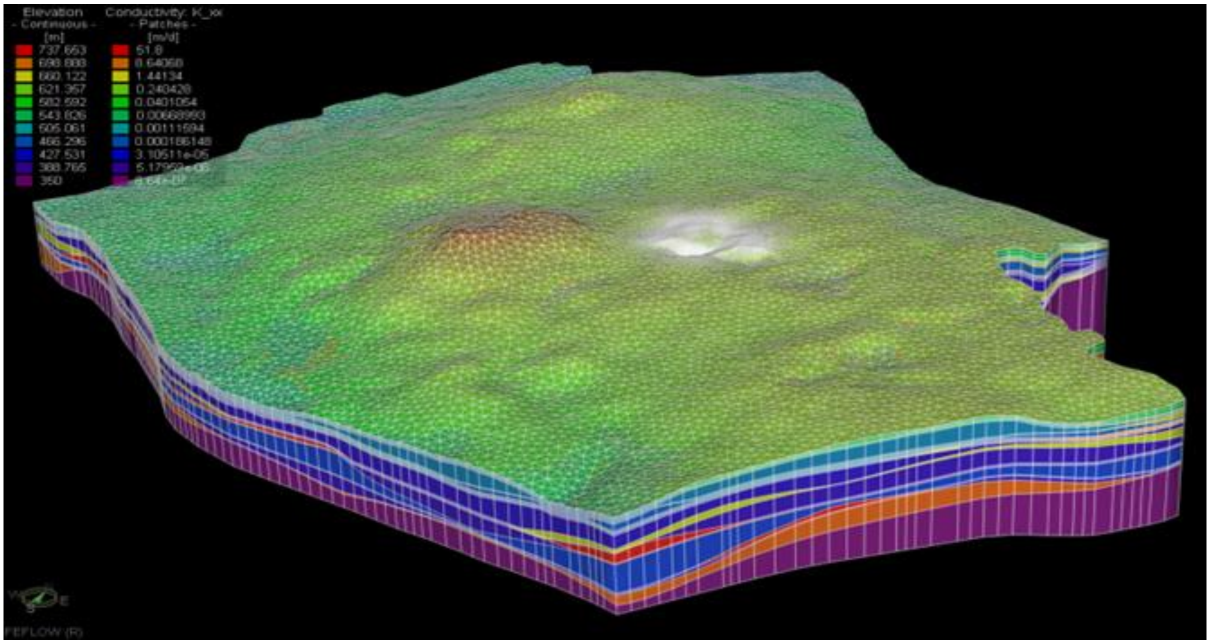

Figure 3: Geometry of the 3-D finite element groundwater flow model seamlessly transferred from the CGM in Figure 2

The two numerical FEFLOW groundwater modelling scenarios tested on the mine site provided different results. The model calibration performed in the scenario with averaged stratigraphic units, smoothed pinching layer, and other modifications made to geological features on the site resulted in simulated groundwater results not matching well with observed data (Figure 4).

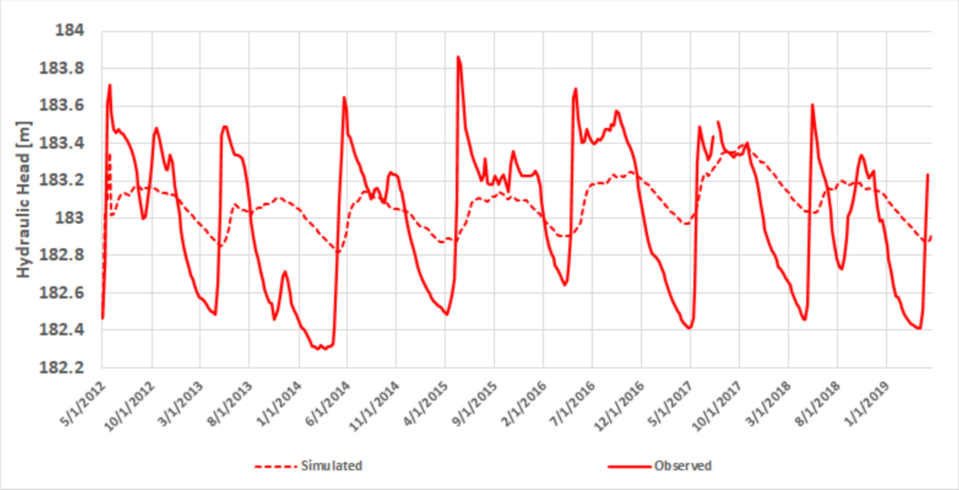

Figure 4: Simulated versus observed data for one of the groundwater monitoring wells from FEFLOW numerical modelling on the simplified assumption of homogeneity for a layered system

The other scenario, which involved a seamless integration of the CGM from Leapfrog Works into the numerical FEFLOW model, showed a good match between simulated and observed data after the model calibration (Figure 5). Although the authors agree that no model is perfect in terms of matching exactly real-world values, the integrated modelling approach provided better estimates of groundwater inflows than the case that incorporated modifications to geological features on the site.

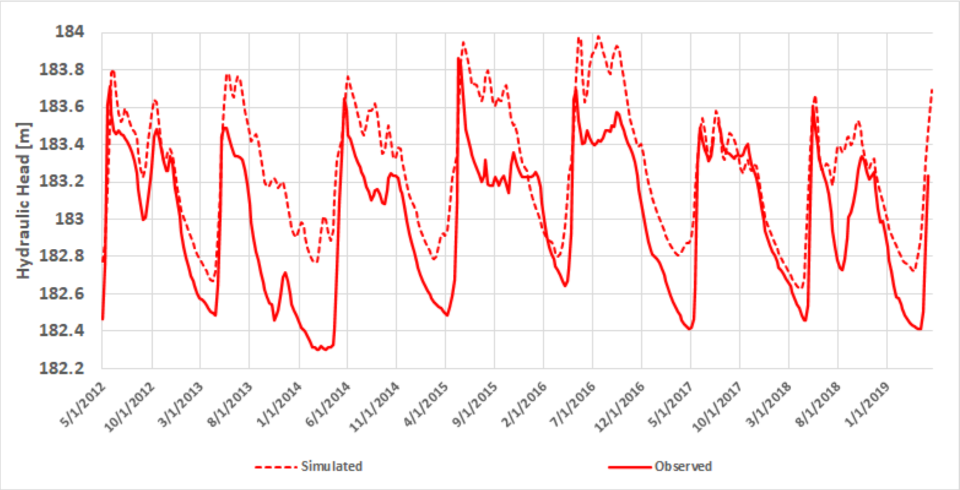

Figure 5: Simulated versus observed data for one of the groundwater monitoring wells from the numerical FEFLOW modelling after a seamless integration from the CGM

Conclusion

Developed numerical groundwater models often incorporate many modifications or simplifications of geological features that do not closely match their corresponding CGMs. This often results in simulated groundwater data not comparing well with observed real-world data. This study investigated a seamless integrated modelling approach from a Leapfrog Works CGM into a numerical FEFLOW groundwater model as a means of addressing the problem of oversimplification of geological features in groundwater models. Application of this approach to the development of a groundwater flow model for a mine site indicated that geological features in the CGM are not only retained in the numerical model, but also improve the groundwater modelling process by producing results which closely match observed data. This was confirmed by two FEFLOW groundwater modelling scenarios where the seamless integrated modelling approach produced better results than the case where geological modifications were incorporated in the modelled site.

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Investigating Ammonia Loading Mechanisms at an Underground Gold Mine

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Abstract

The use of ammonium nitrate based explosives is widespread in the hard rock mining industry. Nowadays, most mining operations rely on either ammonium nitrate based emulsion or ammonium nitrate fuel oil to fragment ore bodies. In both cases, it is commonly understood that a certain portion of the explosives brought to a blast zone will remain undetonated, and eventually be dissolved by mine water. Dissolution of ammonium nitrate leads to the presence of ammonia nitrogen in the water. Although several technologies are available to remove ammonia nitrogen from impacted water, reduction at the source is considered a best practice.

This paper documents the efforts aimed at reducing ammonia nitrogen loading at the Meliadine underground mine located in Nunavut, Canada. Loading mechanisms and resulting ammonia nitrogen concentrations in mine water are discussed and compared to other underground mine sites. The observed loading rates were found to be on the lower spectrum of available information found in the literature, averaging 7 g NH_3-N / kg of emulsion used in 2021. This study also revealed that tasks performed at the explosive storage facilities accounted for approximately 11% of all undetonated underground explosives, while development and production blasting operations contribute 43 and 46%, respectively.

Improvements in monitoring and interpretation of ammonia concentrations in mine water are also discussed, including the use of a key performance indicator to track monthly changes. Mitigation measures to reduce the ammonia loading rate are grouped in four categories: 1) data acquisition improvements, 2) behavioural changes, 3) engineered solutions and 4) governance. Preliminary results indicate a 19% reduction of the ammonia loading rate following the establishment of a training and awareness campaign. Upon completion of these mitigation measures, the mine is expecting a reduction of ammonia loading rate above 30%. Areas for further research, notably the quantity of undetonated explosives trucked to the surface alongside ore and waste material, are also discussed.

Introduction

Ammonium nitrate (AN) is commonly used in the hard rock mining industry as a base product for explosives. Nowadays, the most prevalent types of explosives found on mine sites are either emulsion (typically 70–80% AN, 10–20% water, 4% oil and 1–2% additives) or ammonium nitrate fuel oil (ANFO) (typically 94.5% AN and 4.5% oil) (Jermakka et al., 2015). It is commonly understood that a certain portion of the explosives brought to a blast zone will remain undetonated due to spillage or misfires. Even though emulsion is more water-resistant than ANFO, both products are eventually dissolved by mine water. Watson (1991) reported a nitrogen leaching rate of about 50% for ANFO after one minute of contact time, and 1.2% for emulsion, after 144 hours. For this reason, using a 100% emulsion approach is considered a best practice by many mining companies.

Once dissolved in water, AN dissociates into nitrate (NO_3^-), ammonium (NH_4^+) and ammonia (NH_3). The resulting proportion of NH_4^+ and NH_3 is a function of the pH and the temperature of the solution; in this paper, both species will be referred to as ammonia nitrogen (NH_3-N).

Although several technologies are available to remove ammonia nitrogen from impacted water, reduction at the source is also considered best practice.

Studied site overview

The Meliadine gold mine, operated by Agnico Eagle Mines, is located approximately 25 km north of Rankin Inlet and 80 km southwest of Chesterfield Inlet in the Kivalliq Region of Nunavut. The mine site is located on the peninsula between the East, South, and West basins of Meliadine Lake (63°01'23.8"N, 92°13'6.42"W). The area is accessible from the all-weather gravel road linking the Meliadine mine site with Rankin Inlet.

The current mine plan of Meliadine includes six gold deposits, and relies on both open pit and underground mining practices. This paper discusses activities at the underground mine targeting the Tiriganiaq zone (referred to as the Meliadine underground mine in this paper), which hosts the largest deposit to date and has a strike length of approximately 3 km and a known depth of 800 m. This mine is hosted in a magnetite-rich oxide iron formation, accessed by ramps, and relies on long-hole mining methods. At the time of writing this paper, the mine reaches a depth of 525 m.

Following best practices, the Meliadine underground mine uses bulk emulsion for both long-hole blasting operations (hereinafter referred to as production blasting), as well as blasting operations, to access the mineral deposit (development blasting). The Meliadine underground mine also relies on a combination of cemented pastefill, cemented rockfill (CRF) and dry rockfill to backfill its stopes. The pastefill is produced using filtered tailings from the Meliadine mill.

The mine is in an area of continuous permafrost, with an estimated base depth between 285 m and 430 m. Despite the presence of permafrost, underground excavations act as a sink for groundwater via the shallow flow regime located in the active layer (seasonally thawed), and most of all, the deep flow regime beneath the base of the permafrost. This deep flow regime is characterized by high levels of total dissolved solids (TDS). Groundwater samples collected beneath the permafrost since 2018 show TDS values between 40,500 and 71,000 mg/L, with an average of 55,900 mg/L.

To allow for recirculation of mine water, a water treatment system is present underground for total suspended solids (TSS) treatment. Apart from CRF operations, all underground tasks typically rely on recirculated water. A simplified diagram of the underground water balance of the mine site is presented in Figure 1. Inputs and outputs that are not captured in this figure are considered negligible. Any surplus of water pumped to the surface is stored in dedicated saline storage ponds. A water treatment plant is also present at the surface to treat this saline water for TSS and NH_3-N prior to being discharged to sea. All water discharged from Meliadine site must meet the water quality requirements set by Environment Canada and Climate Change within the Metal and Diamond Mine Effluent Regulations (MDMER). TSS treatment is performed using a high rate clarifier, while NH_3-N treatment relies on the breakpoint chlorination technology.

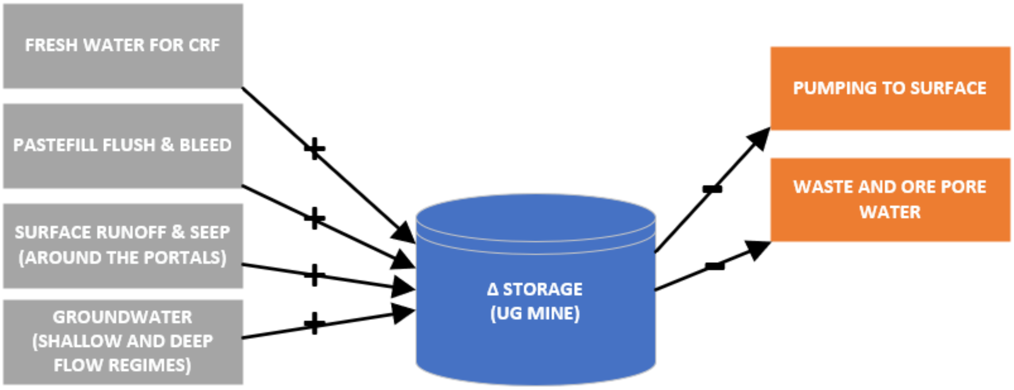

Figure 1: Simplified diagram of the underground water balance

Ammonia loading rate

The use of AN based explosives inevitably leads to leaching of NH_3-N in the water of the Meliadine underground mine. For this reason, NH_3-N is considered a key compound of interest, and is monitored for operational and compliance purposes. Part of this monitoring includes the concentration assessment of NH_3-N in the water pumped to surface, as presented in Figure 2.

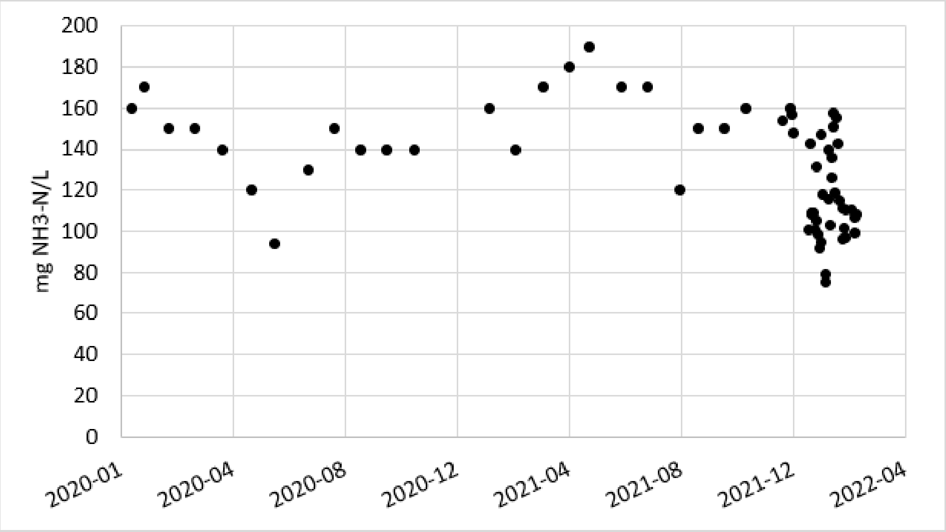

Figure 2: Ammonia concentration over time in the water pumped to surface

As shown in Figure 2, NH_3-N concentrations at this control point were measured monthly until November 2021, then more frequently afterward. Figure 2 also shows that NH_3-N concentrations range from 75 to 190 mg N/L, while most of the readings fall within the low to mid 100s. These values have, however, limited meaning by themselves. Factors such as water inflow entering the mine and the extent of blasting operation strongly influence NH_3-N concentrations in mine water. As an example, lower ammonia concentrations were reported in May 2020, which coincided with a period during which underground operations were scaled back due to the COVID-19 pandemic. A more meaningful value, referred as the ammonia loading rate in this paper, was calculated using the following formula:

$$Ammonia\ loading\ rate\ = \frac{Q_{inflow}\ x\ C_{NH3}}{M_{explosives}} \tag{1}$$

Where:

Q_{inflow} represents the calculated inflows (m^3/year).

$M_{explosives}$ represents the mass of explosives used (in kg/year).

C_{NH3} represents the ammonia concentration of the water pumped to surface (yearly average, in mg NH_3-N/L) of the following month.

This value then allows for comparison with other mine sites, as shown in Table 1.

Table 1: Comparison of measured ammonia loading rate with other underground mine sites

Mine sites	Location	Emulsion to ANFO ratio	Inflow rate (m^3/day)	Average explosive use (kg/day)	Average NH_3-N (mg/L)	g NH_3-N/ kg explosive
Meliadine underground mine (average 2020)	NU, CA	100:0	292	5200	155	8.6
Meliadine underground mine (average 2021)	NU, CA	100:0	259	5830	160	7.0
Lapa underground mine (average 2016 to Q1 2018)	QC, CA	78:22	949	706	10.7	14.4
Lapa underground mine (Q2 2018)	QC, CA	100:0	806	300	2.2	5.9
Undisclosed (Sidenko, 2018)	MB, CA	82:18	N/A	N/A	N/A	6 to 43[1]
Multiple mines (Morin and Hutt, 2009)	BC, CA	Mostly ANFO	N/A	N/A	N/A	20 to 47[1]
Multiple mines (Jermakka et al., 2015)	Finland	N/A	N/A	N/A	N/A	Up to 33[1]

[1] Assuming 70% AN in emulsion, and 94.5% AN in ANFO.

The Lapa underground mine (Quebec, Canada), which was in commercial operation between 2009 and 2018, is another Agnico Eagle property. This mine was of particular interest due to similarities with the Meliadine underground mine, such as limited supply of fresh water and recirculation of most of the process water directly underground. This mine site also gathered a high-quality dataset including NH_3-N concentrations, water inflows, and explosive consumption over the course of its operation. Notably, a transition from a mix of emulsion and ANFO to 100% emulsion can be observed in this dataset.

Averaging 8.6 and 7.0 g NH_3-N/kg explosive for 2020 and 2021 respectively, the ammonia loading rate of the Meliadine underground mine is similar to the Lapa underground mine when using 100% emulsion. This loading rate also appears to be on the lower spectrum of what is found in references such as Sidenko (2018), Morin and Hutt (2009) and Jermakka et al. (2015). However, all mine sites studied by these references relied on at least some ANFO explosives. Discrepancies with reported values in the literature could also be partially explained by underlying assumptions behind the ammonia loading rate calculation presented in this section. For one, this method fails to account for the undetonated explosives trucked outside of the mine alongside the ore and waste material.

Sources discrimination

A series of workshops and audits were performed to determine the main sources of NH_3-N in the Meliadine underground mine water. In addition to undetonated explosives, two other sources were identified:

- Natural occurrence in groundwater. Water samples collected from unimpacted groundwater since 2018 show an average of 5.3 mg NH_3-N/L.
- Nitrogen-based contaminants in pastefill bleed. The pastefill is produced using filtered tailings from the Meliadine mill. It is assumed that some of the moisture contained in the tailings becomes pastefill bleed and mixes with mine water. With an average concentration of 100 mg NH_3-N/L in the tailings water, there is little doubt that this source contributes to the ammonia loading underground. Also, cyanate (CNO-) present in the tailing water (average 290 mg-N/L) likely undergoes partial or complete hydrolysis to form NH_3-N once released underground.

Assuming complete CNO^- hydrolysis and using available information on the groundwater and pastefill bleed flowrates, the contribution of these three sources of NH_3-N in the Meliadine underground mine water was calculated, and is presented in Figure 3.

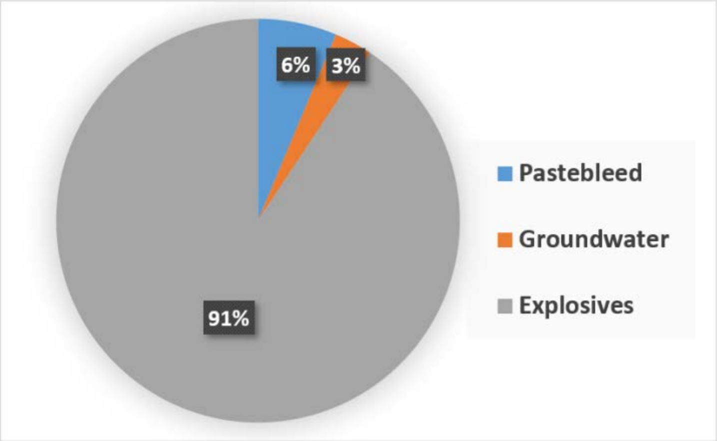

Figure 3: Suspected contributors of ammonia nitrogen in the underground mine water

Once it was determined that undetonated explosives were the main contributor to the ammonia loading rate observed at the Meliadine underground mine, further studies were performed to determine which tasks led to the most undetonated explosives.

Workshops and interviews were conducted with experienced blasters, drill and blast technicians, as well as third-party blasting experts. Following this exercise, the mining operations were subdivided into three categories: explosive storage facilities tasks, development blasting, and production blasting. For each category, the most likely events resulting in the release of undetonated explosives were identified. Assumptions were developed on the frequency of such events, as well as the likelihood and size of release. The results of this exercise are presented in Figure 4.

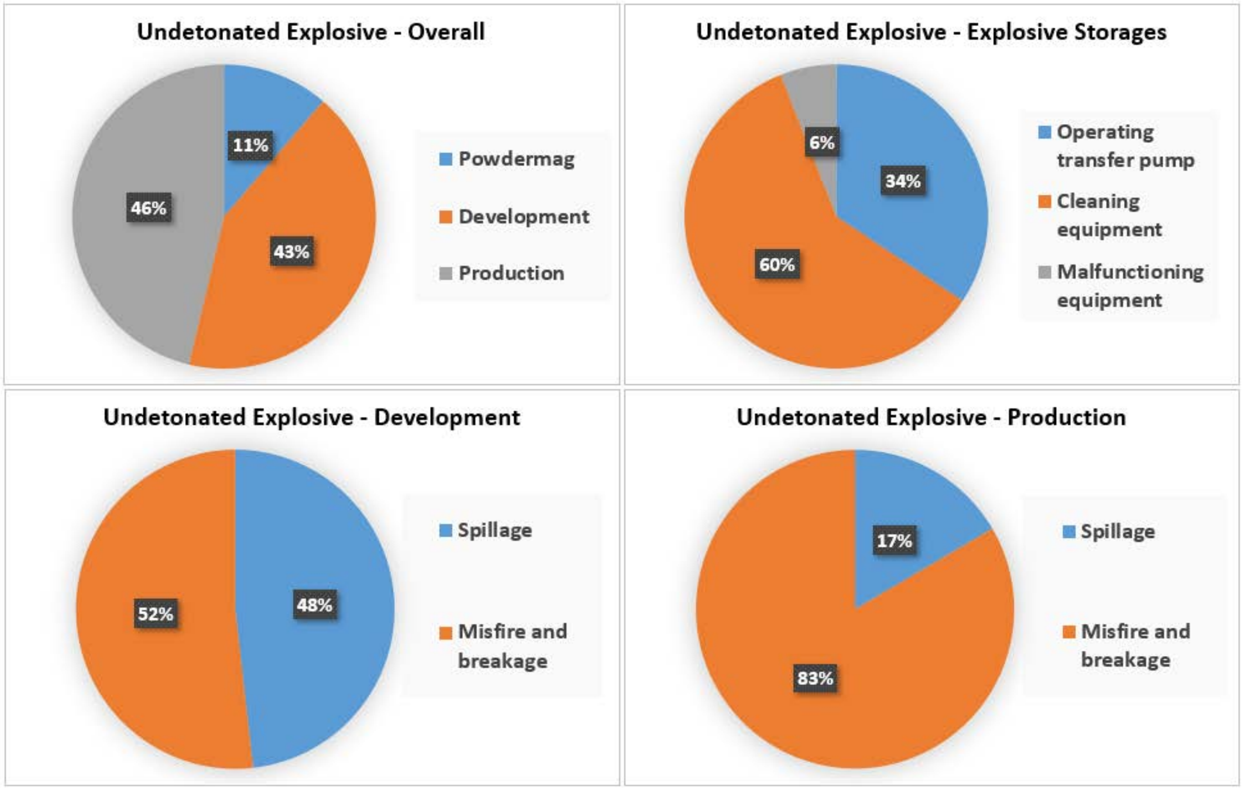

Figure 4: Breakdown of the various sources of undetonated explosives

Although a multitude of professionals were consulted while developing Figure 4, a high level of imprecision is to be expected of numerous assumptions supporting these graphs. Nevertheless, the degree of detail was deemed sufficient to guide future mitigation actions.

Figure 4 shows that tasks performed at the explosive storage facilities are suspected to generate approximately 11% of the overall release of undetonated explosives, whereas development rounds and production rounds equally share the remaining responsibility. This indicates that none of these areas should be considered insignificant. Undetonated explosives releases at the explosive storage facilities are mostly due to routine tasks, and could likely be mitigated by engineered solutions, establishment of Standard Operating Procedures (SOP), and training. About half of the suspected release from development rounds occur during routine tasks involving the handling of the emulsion hoses (i.e., spillage). Awareness campaigns, training, and SOP are the likely solutions to reduce these occurrences as well. The remaining half of the suspected release on development rounds appears to be due to breakage and misfires. Such events are suspected to represent over 80% of the overall release from production rounds. In both cases, improvement to the blasting patterns could reduce this source. These solutions are further discussed in the following sections.

Key Performance Indicator

To quantify the impact of mitigation measures on ammonia loading rates, the data presented in Table 1 were reported on a monthly basis and are used as a Key Performance Indicator (KPI) for emulsion handling underground (see Figure 5). To reach a wider audience, the units of this KPI were converted to percentage of undetonated explosive. This was done using a conversion factor of 0.81, while assuming 70% AN in the emulsion.

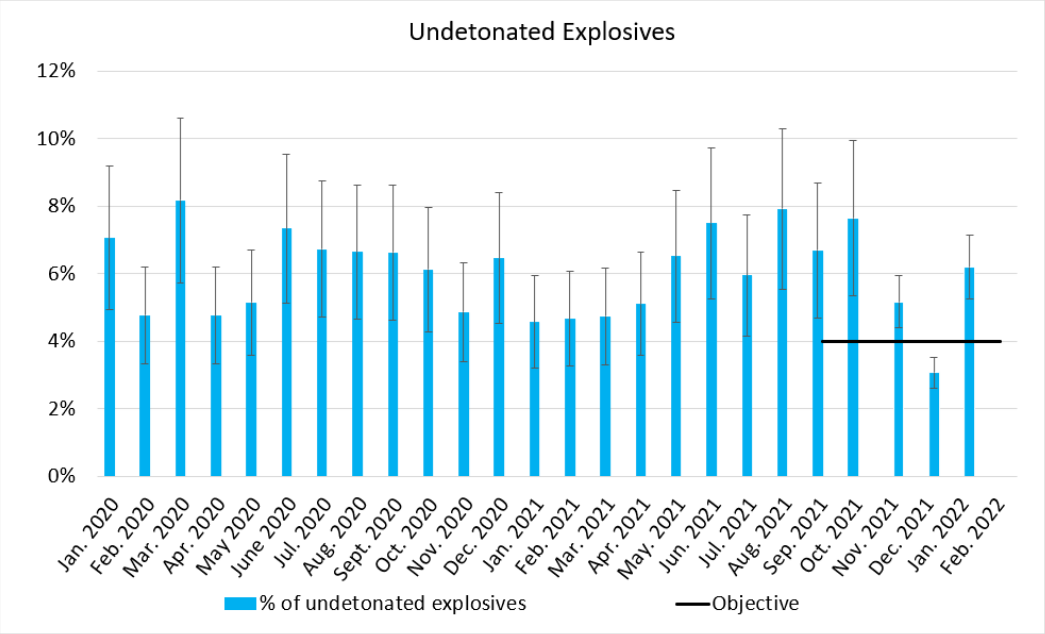

Figure 5: Key Performance Indicator to track handling of explosives underground

From January 2020 to November 2021, an accuracy of ±30% is assumed on this undetonated explosives KPI. Establishing an accuracy range was deemed important, since some of the values used to calculate this KPI have known uncertainties. For example, in February 2021, a sampling campaign performed over the course of 12 hours revealed large variations in the ammonia concentrations of the water pumped to surface. The data collected during this exercise suggests that relying on a single monthly analysis of NH_3-N to calculate the undetonated explosives introduces an inaccuracy of ±15% by itself. To mitigate this inaccuracy, the frequency of NH_3-N analysis was increased in December 2021. The remaining ±15% can be attributed to known uncertainties on the calculated inflows. The error margin on the mass of emulsion used per month is assumed to be inconsequential, based on discussions with the mining engineers responsible for reporting these values.

In September 2021, an internal objective of 4% undetonated explosives was set as an upper bound. Justified by the documented reduction of the ammonia loading rate following similar initiatives (Forsyth et al., 1995; Matts et al., 2007; Jermakka et al., 2015), this objective represents a 30% decrease compared to the 2021 average.

Mitigation measures considered

Mitigation measures to reduce NH_3-N loading are already documented by numerous authors in conference papers (Forsyth et al., 1995; Revey, 1996; Cameron et al., 2007), reports (Matts et al., 2007) and management plans (DBC, 2013; ERM, 2017; AKHM, 2019).

Based on the available information in the literature, the information presented in Figure 4, as well as the information collected during numerous workshops with experienced blasters and mining engineers, a list of mitigation measures was developed to reduce ammonia loading at the Meliadine underground mine. These mitigation measures include:

- Data acquisition improvements: refining the KPI assumptions, developing a spill tracking system, and improving ammonia monitoring underground.
- Behavioural changes: providing specific training on ammonia considerations to all employees handling explosives, as well as the engineering team.
- Engineered solutions: improving explosive storage facilities layout and lighting, reviewing designs of emulsion containers and transfer pumps, and substituting explosive material for perimeter holes on development rounds.
- Governance: reviewing SOPs for each task involving emulsion handling, updating the site's ammonia management plan, and establishing an auditing system to track best practice compliance.

To date, most of these mitigation measures are in progress. Since raising awareness and providing training were identified as low effort/high reward tasks, this mitigation measure is already well underway.

Interpretation of specific trends in the monthly KPI (Figure 5) prior to October 2021 would be hazardous due to the high level of imprecision on these values. On the other hand, this KPI is averaging 4.8% since November 2021. This represents a loading rate of 5.9 g NH_3-N/kg explosive, or about 19% below the 2021 average presented in Table 1. These preliminary results are deemed encouraging and seem to confirm the attainability of the company objective to reduce ammonia loading by more than 30%.

Conclusions and future considerations

Ammonia nitrogen is a common contaminant found in hard rock mining applications, and reduction of the contamination at the source is considered best practice. In this paper, ongoing efforts to understand and reduce ammonia loading rates at the Meliadine underground mine were documented. The main findings from these efforts are:

- With an average loading rate of 7.0 g NH3-N/ kg of emulsion used in 2021, the loading rate observed at the Meliadine underground mine is similar to what was previously observed at the Lapa underground mine. This loading rate also appears to be on the lower spectrum of what is reported in the literature, but limited information is available on mines using 100% emulsion.
- Spillage at the explosive storage facilities accounts for approximately 11% of the released undetonated explosives, whereas development rounds and production rounds accounted for 43% and 46% respectively.
- Release from breakage and misfires appears to represent 50% of all undetonated explosives linked to development rounds, and over 80% of the undetonated explosives linked to production rounds.
- Preliminary results indicate a 19% reduction of the ammonia loading rate following the establishment of a training and awareness campaign.

On a final note, the KPI discussed above does not capture how much explosive is used per ton of rock fractured, otherwise referred as the powder factor. There is little doubt that using fewer explosives to break the same amount of rock would reduce the mass of NH_3-N dissolved in the mine water. Furthermore, the findings and calculation methods presented in this paper do not account for the undetonated emulsion trucked outside of the mine alongside the ore and waste material. Considering the leaching rate reported by Watson (1991) for emulsion explosives (1.2% after 144 hours), large quantities of this explosive are likely to remain at the surface of such ore and waste material. According to Jermakka et al. (2015), this sink could account for as much as 50% of the total quantity of undetonated explosives. Recognizing this as a major factor influencing the concentration of ammonia in its mine water, the Meliadine underground mine will continue to study this occurrence.

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The Model is Wrong, Get Over It – Uncomfortable Truths and Decision Making with Mathematical Models

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Abstract

In engineering, mathematical modelling is ubiquitous and often an inter-disciplinary activity for many design processes. In the mining sector, it is frequently the case that the mathematical modelling output from one discipline becomes the input to another. This is particularly true with designs that are affected by surface water and groundwater systems, where water can be viewed simultaneously as a valuable resource, a nuisance, a hazard, and a critical component of our environment that must be protected. With this in mind, it is commonly thought that the purpose of a mathematical model is to help understand how a system works. While this perspective on mathematical modelling is largely true, for an engineer who is responsible for a design, the model's utility must be taken one step further by using the model results to make a decision. This additional step creates a significant challenge for the decision maker because a mathematical model is not a complete description of the system; in fact, it would be more accurate to describe a model as a reflection of what we know and don't know about the system. This inherent limitation to mathematical modelling is much more pronounced in surface and groundwater studies since unlike most engineering disciplines, modelling of natural water systems is exceptionally challenging due to extreme aleatory and epistemic uncertainties. Nonetheless, design decisions must still be made for a project to progress.

While science and engineering literature provides some useful guidance on creating and testing mathematical models, guidance on how to use a model to make a decision is difficult to find. This paper discusses the application of a decision framework for use with mathematical models of surface and groundwater systems through an iterative approach, as opposed to the more traditional linear planning process. Following this framework can dramatically improve the transparency and clarity of any mathematical model with a specific focus on the more challenging applications, such as in surface water and groundwater systems. Applying the framework will help determine the reliability of a model, highlight

what is known from what is not (of great importance for climate resilience), assist in preparing to procure modelling services and, importantly, facilitate communication of the decision-making process to all stakeholders.

Introduction

In engineering, mathematical modelling is ubiquitous and often an inter-disciplinary activity for many design processes. In the mining sector, it is frequently the case that the mathematical modelling output from one discipline becomes the input to another. This is particularly true with designs that are affected by surface water and groundwater systems, where water can be viewed simultaneously as a valuable resource, a nuisance, a hazard, and a critical component of our environment that must be protected. It is commonly thought that the purpose of a mathematical model is to help understand how a system works. While this perspective is largely true, for an engineer who is responsible for a design, the model's utility must be taken one step further by using the model results to make a decision. However, it is typically the case that the decision maker for a project is not the same person who produced the model. This creates a communication gap where the modeller's interpretation of the real-world system is usually perceived as a "black box" by the decision maker. This communication gap exists because there is a depth and nuance to mathematical modelling not conveyed in the conventional framework widely used in mathematical modelling. In this paper we review the Conventional Framework for modelling and provide additional steps intended to better bridge the communication gap between the modeller and the decision maker. We refer to this enhanced modelling framework as the Decision Framework.

The Conventional Framework

Figure 1 depicts the Conventional Framework for mathematical modelling promoted in literature. This framework has been widely adopted and discussed in surface and groundwater literature (which we will collectively referred to as "hydrology" in this paper). Although it is worth noting that in hydrology this Conventional Framework is often subdivided into additional steps which can be broadly listed as:

1. define the purpose,
2. create the conceptual model,
3. design the mathematical model,
4. calibrate the model,
5. conduct a sensitivity analysis,
6. verify the model,

7. create a prediction model, and
8. present results.

Note that there is no consensus on the number of sub-steps in hydrology literature, but they all follow the same general pattern (e.g., Anderson and Woessner, 2002; Kresic, 1997; Spitz and Moreno, 1996). It is interesting to note that in hydrology texts this framework is usually presented as part of the numerical modelling discussion, whereas in mathematical texts this framework is presented as a fundamental to all mathematical models and so is not linked to complexity (Meyer, 2004). We would suggest that this is because while many relatively simple models are regularly used in hydrology (e.g., Theis equation) they are usually not subject to calibration, so the Conventional Framework is perhaps being applied unconsciously in simple cases.

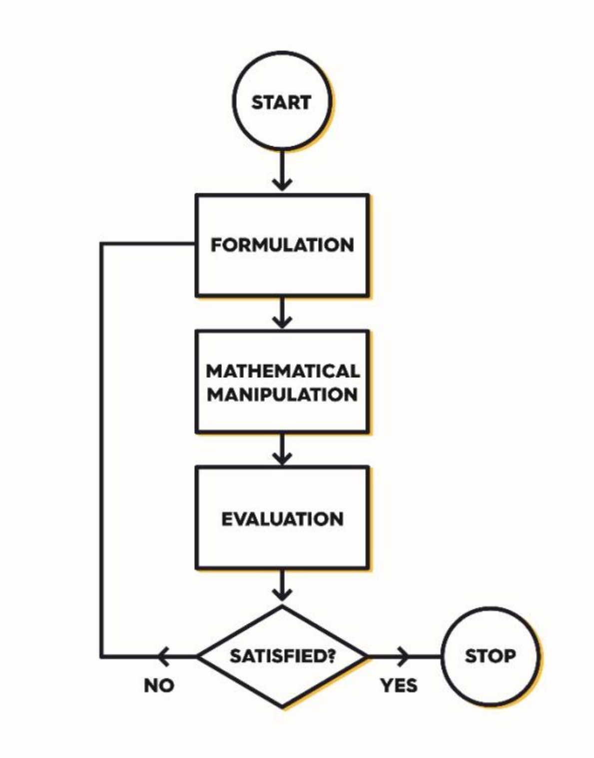

Figure 1: The Conventional Framework for modelling (after Meyer, 2004)

Although the Conventional Framework is widely published and accepted, it is not clear where it came from, and there is no clear rationale provided as to why we should use it. Dym (2004) offers a brief and plain explanation in that mathematical modelling is a principled activity and that the Conventional Framework allows one to simply determine the "intentions and purpose" of the mathematical model. While Meyer (2004) suggests that mathematical modelling cannot be done mechanically, so having some guidelines on how to proceed is merely helpful. From an application point of view, we could say that the

Conventional Framework provides steps to modelling that are listed in the order that are normally undertaken because they simply make sense. Suffice to say that this Conventional Framework has proven useful as it has been adopted by practicing engineers and hydrologists all around the world. However, given that the Conventional Framework is based on common sense rather than a rigorous algorithm, it would be amenable to reasonable changes.

Perhaps the most useful change to the Conventional Framework would be an improvement to the overall communication of the model. Note from Figure 1 that there is an iterative loop in the framework until a "satisfactory" model has been achieved. There are two communication issues here: 1) qualifying a model as satisfactory is subjective to the modeller, and 2) the results of the model are normally reported only after it is deemed satisfactory. In effect, the Conventional Framework promotes a "best explanation" approach to a mathematical model in a linear fashion from the data, through the model, to a result. It is important to note that in this context, the best explanation does not necessarily mean the best possible explanation, since it is impossible to prove that any single model is "correct". Rather the best explanation model is the one selected by the modeller because it seems to be the best-fit to the available observations. This approach may be considered adequate when the modeller is also the decision maker, as they would have the benefit of the insight developed through trial and error of the iterative loop. However, when the modeller needs to communicate the findings of the model to another person, the linear nature of the best explanation approach tends not to be very convincing.

The best explanation approach of the Conventional Framework is usually not very convincing because it is prediction focused, and from outside of the process, appears as a "black box" shielding the model from inspection. Engineers and scientists generally understand that a mathematical model is not a complete description of the system, but rather as a reflection of what we know and do not know about the system, and that models, mathematical or otherwise, usually provide only one possible explanation for the real-world observations. This nuance and depth of a model cannot be communicated through a single prediction. In fact, it is widely recognized that most of the insight and confidence in a model is not found in the numerical prediction, but rather developed as part of the modelling process (Kay and King, 2020; Tetlock and Gardner, 2015; Barbour and Krahn, 2004; Dym, 2004; Watson and Burnett, 1995). In fact, Pilkey and Pilkey-Jarvis (2007) document several real-life applications of mathematical models that fail as numerical predictions but were still qualitatively useful through the insights developed in the modelling process. In this way, the modelling process, or in our metaphor, the "stuff" hidden in the black box, is more important than the prediction because in the words of psychologist and economist Daniel Kahneman, "No one ever made a decision because of a number. They need a story."

This evolves into a communication dilemma for the modeller who follows the Conventional Framework, and it is a dilemma which compounds as the number of people who need to understand the model increases. In the mining sector, it is frequently the case that the mathematical modelling output from one discipline becomes the input to another, and consequently there are often many decision makers involved. Additionally, mining projects need to address outside stakeholders, which usually include regulators and the public. Therefore, mining companies have a clear need for better communication than can be offered through the Conventional Framework.

The Decision Framework

The Decision Framework modifies the Conventional Framework by assuming that the modeller and the decision maker are not the same person. The Decision Framework also contends that, for decision making, the qualitative sense of the model is more insightful than the numerical output. Therefore, the Decision Framework seeks to provide a more complete picture of the model by describing the process taken to reach the numerical output. Following this Decision Framework can dramatically improve the transparency and clarity of any mathematical model, as well as help determine the reliability of a model, highlight what is known from what is not, and facilitate communication of the decision-making process to all stakeholders. In effect, the Decision Framework seeks to make the modelling process transparent and interactive, which is beneficial to decision making because in the words of Bender (2000), "When any of us approaches a problem, we do so in a limited, biased fashion. The more open-minded, communicative, and creative we can be, the better our model is likely to be". Figure 2 depicts the Decision Framework which comprises a loop with six stages. The rationale for the loop and a description of the stages are provided in the following paragraphs.

The looping nature of the Decision Framework indicates that modelling is truly an ongoing process. This looping nature of the framework speaks to the timeless advice that we need to update our understanding of the system as we learn more about it (Kay and King, 2020; Tetlock and Gardner, 2015; Meyer, 2004; Bear, 1979; and Peck, 1969). This is increasingly important when we are modelling under conditions of extreme aleatory and epistemic uncertainty such as in hydrology, and particularly when we need to reuse the model continuously over very long periods (e.g., decades) such as mining projects. The loop can be applied in two general ways: 1) chronologically as new data becomes available through time, and 2) by evaluating the results of an initial model by running an alternative data set through the process. It should be obvious from the looping nature of the Decision Framework that as modellers we need to consider the decision maker's longer-term need for revisiting and updating the models. This means that we need to think about how to put more control over the legacy of our mathematical models into the hands of the decision makers, such that they own and can pass historical modelling efforts into the future.

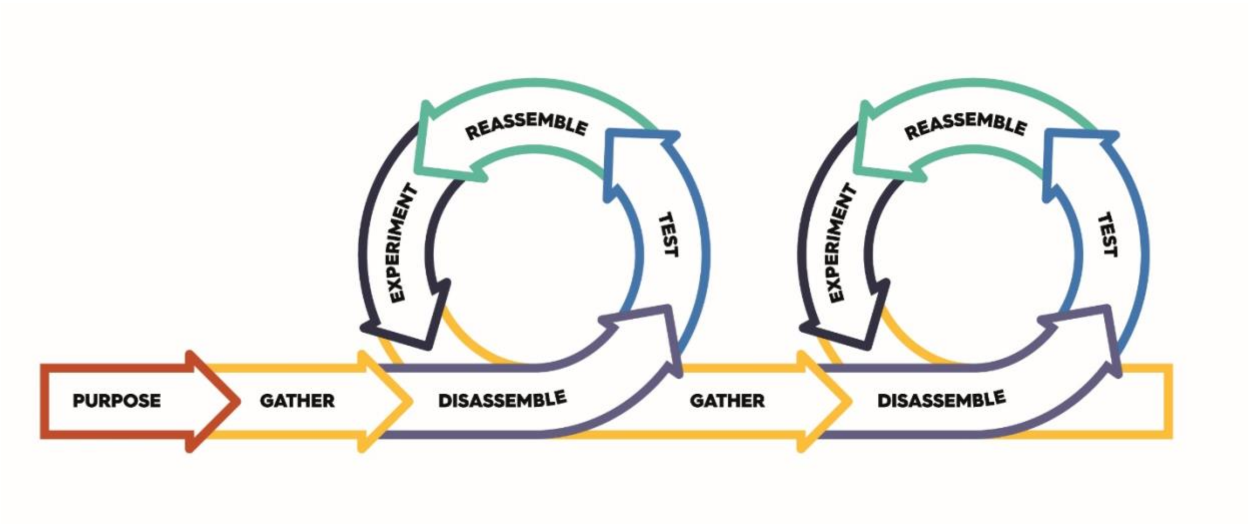

Figure 2: The Decision Framework for modelling

Purpose

The first stage is defining the purpose for the mathematical model. This stage is common to all mathematical models and as such it is also the first step in the Conventional Framework. Simply put, at this stage we must clearly and concisely identify what it is that we want to know. Having a clear purpose allows the modeller to design the appropriate model. It is interesting to note that uncertainty can and often does enter the process at this stage. This uncertainty is created by starting with a vague purpose, which can lead to modelling the wrong process.

Gather

During the gather stage we collate all the available information and make it spatially visible. However, at this stage it is equally important to highlight any critical data that is missing (e.g., precipitation data from the site). The gather stage allows us to critique the starting quality of the data, helps us to clearly articulate the current limits of our knowledge, and helps to inform the decision maker on which data should be targeted for future collection. Note that under the Conventional Framework it is typically assumed that the available data is of sufficient quality and quantity. However, communicating the gather stage as a distinct step in the process allows the decision maker to develop an initial qualitative sense of the model's reliability. It is also noted that the gather stage initiates subsequent loops in the Decision Framework.

Disassemble

The objective of this stage is to clearly identify and communicate what is objectively true from what needs to be assumed in the mathematical model. This stage comprises 1) data inspection, 2) identification of the important features and dynamics of the system, and 3) establishing a conceptual model of the problem. This stage has much in common with the conceptual model creation step in the Conventional Framework; however, this stage puts more emphasis on highlighting the clear distinction between objective truths and assumptions necessary to create the model. We believe this distinction to be important as it forms an important part of the discussion around aleatory and epistemic uncertainty. For example, in hydrology modelling, the quality and quantity of stream flow data (including missing data) are very important to the assumptions made, which can have a strong effect on the model results. If the objective truths and necessary assumptions are mixed, then the decision maker does not receive a fully transparent model.

Test

The objective of the test stage is to break the large system model, which is often intractable, into smaller and more tractable components. In the application of mathematical models breaking an intractable model into many tractable ones is considered best practice (Kay and King, 2020; Dym, 2004; Meyer, 2004; and Bender, 2000). In effect the test stage aims to demonstrate how the metaphorical black box of the mathematical model works by breaking it into smaller and more comprehensible components. This stage comprises: 1) a first principles deconstruction of the system, 2) application of simple models and hand calculations, and 3) benchmarking against similar problems.

This stage allows the modeller to provide the decision maker with multiple perspectives on the problem, and allows both a deeper exploration of aleatory and epistemic uncertainties and some ability to quantify the effects of these uncertainties. Under the Conventional Framework this step is not formally undertaken. This is regrettable because in our experience this testing stage provides the most convincing lines of evidence that reinforce the choices made by the decision maker, and it is relatively easy to do.

Reassemble

The reassemble stage of the Decision Framework comprises building a mathematical model that represents the whole system. Essentially, the reassemble stage is the Conventional Framework for modelling, and it is assumed that the reader is familiar with this general process. Within the Decision Framework the benefit of completing the previous four stages is that the decision maker is given the opportunity to see how the model was created. This transparency in the model development is not typically provided in the Conventional Framework, and it is this lack of transparency that understandably makes the decision maker skeptical about the model results. During this stage multiple models should be created to reflect alternative possible scenarios, and each model should include parameter uncertainty analysis.

Under the Conventional Framework there is no universally accepted means of creating a hydrology model; however, the common default is to create a very complex model to simulate the system. This can be problematic and unnecessary. It is problematic because increasing model complexity results in more time to create the model, increasing simulation runtimes, and it becomes more difficult to understand how the model parameters are interrelated. This in turn typically means that fewer models can be created to test alternative concepts of the hydrological system. It is unnecessary because increasing the complexity of the model does not ensure greater accuracy or a better predictive output. This is particularly true when the available data is sparse, which is usually the case in hydrology. In general, and regardless of the framework being used, the simplest model that captures the important features of the system is usually the best choice.

Experiment

With the acceptable mathematical model of the entire system completed during the reassemble stage, the experiment stage allows the model to become a useful proxy of the real-world system through an interactive sequence of "what-if" analysis. This "what-if" analysis is arguably the most useful aspect of mathematical models when used for engineering design. Under the Conventional Framework there is no specification for "what-if" type analysis; however, in hydrology "what-if" questions can be posed at the outset of a well-planned modelling project. Unfortunately, even a well-planned modelling project will result in additional "what-if" questions being asked at the end of the project. However, in hydrology, most conventional models are too complex to run quickly enough for near real-time "what-if" analysis, and they are typically too rigid to allow significant changes to the model domain. This limits the utility of many conventional hydrology models. One possible workaround to this complexity and rigidity problem is to complete "what-if" analysis during the Test Stage, where rapid, simple models can be easily developed for this purpose. Another option is to choose a modelling method during the reassemble stage that is both quick enough and flexible to allow for rapid "what-if" analysis. We recommend the latter approach.

Summary

Hydrological systems can have a profound effect on human endeavours, including mining. As such there is an ongoing need to understand how the hydrological system might impact the man-made system and vice versa. However, hydrological systems are complex and difficult to model. Yet modelling is still our best available tool to understand such systems and out interaction with them. Unfortunately, models are merely approximations, both in terms of how we think a system works and how we construct mathematical formulae to represent it. Therefore, our ability to accurately simulate hydrological systems is severely limited. Nonetheless, design decisions must still be made for a project to progress.

With respect to decision making, what mathematical models lack in predictive accuracy they make up through qualitative insights derived through the modelling process. However, this presents a challenge when the modeller and decision maker are not the same person. This paper discussed the application of a

Decision Framework for use with mathematical models of hydrology. This Decision Framework assumes that the modeller must communicate all the insights derived through the modelling process to the decision maker. Following this framework can dramatically improve the transparency and clarity of any mathematical model and facilitate communication of the decision-making process to all stakeholders. It is our hope that by following the Decision Framework the need to put more control over the legacy of our mathematical models into the hands of the decision maker will become a serious consideration. Doing so in the mining sector will allow the modeller and decision maker to effectively pass historical modelling efforts and the insights gained to their successors.

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Mineral Reaction and Solute Loading Rates from Field ARD Test Pads at the Bagdad Mine in Arizona

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Abstract

Standard laboratory tests are critical tools to predict the acid rock drainage (ARD) and metal leaching (ML) potential, and hence the long-term seepage water quality, from mine stockpiles. Due to differences in laboratory testing and actual field conditions, field testing is likely to represent more closely the internal conditions within a rock pile as well as the various mechanisms controlling ARD/ML generation. The objective of the field test pad study at the Bagdad mine in Arizona is to improve the prediction of ARD/ML potential and long-term seepage water quality from development rock and previously acid-leached ore materials under field conditions. To supplement the natural precipitation received at the relatively semi-arid site, water is applied via a network of driplines installed on the top surface and upper side slopes of the test pads.

For the development rock test pads, seepage pH and EC values have remained relatively constant throughout the study thus far at ~7.5–8.5 and ~2000–4000 µS/cm, respectively. Sulfate loading rates in the seepage have been used to estimate the reaction rates of the two acid-generating minerals present in the test pad materials – pyrite and chalcopyrite. Calcium and magnesium loading rates in the seepage have been used to estimate the reaction rates of the acid-neutralizing minerals calcite and biotite, respectively. Calculations using the mineral contents and average reaction rates predict that the acid-neutralizing minerals, especially calcite, are likely to remain available after the acid-generating minerals are consumed. Findings from this study indicate that seepage from the development rock materials is not likely to develop acidic pH levels in the future, due to excess alkalinity provided by calcite and the reactive silicate minerals.

Introduction

Acid rock drainage (ARD) is a natural phenomenon that is primarily caused by the oxidation of sulfide minerals. It is characterized by acidic waters and is typically, but not always, associated with metalliferous and sulfate-rich waters. Standard laboratory tests are critical tools to predict the ARD and metal leaching (ML) potential. However, there are wide differences in parameters that control ARD/ML generation, including particle size distribution, temperature, microbial activity, air-flow, and water movement within the materials in the laboratory versus in the field (Kempton 2012; Pearce et al., 2015). Lab tests also have the limitation of testing small amounts of materials that may have appreciable variability in mineralogy and ARD/ML potential. Hence, laboratory tests may provide a limited representation of future seepage water quality from these materials. A multi-pronged approach which includes field-testing of larger amounts of materials using constructed test pads is likely to provide a more representative demonstration of ARD and ML generation from mine stockpiles under normal field conditions.

A field test pad study is underway at the Bagdad mine in Arizona to evaluate ARD/ML potential and long-term seepage water quality from future development rock and leached ore stockpiles under field conditions. The Bagdad mine is an open-pit copper and by-product molybdenum mine operated by Freeport-McMoRan Bagdad Inc., a subsidiary of Freeport-McMoRan Inc. (FCX) located in Yavapai County approximately 210 km northeast of Phoenix, Arizona, USA. Average annual precipitation rate at the site is approximately 380 mm/year (WRRC, 2016). Average summer high temperature approaches 36 degrees Celsius (°C) in July, and the average winter low is just above 0°C in January. The results obtained from the study will be utilized in support of the on-going mine planning and permitting processes, and to provide guidance for developing any necessary measures to control and/or mitigate ARD and ML from future stockpiles. The objectives of this paper are to:

1. estimate reaction rates for sulfide mineral oxidation and dissolution of neutralizing minerals;
2. estimate the acid generation-neutralization balance based on solute loading rates; and
3. understand the long-term ARD potential from future stockpiles constructed with the development rock materials.

Test pad construction, operation and sampling

Error! Reference source not found. shows an aerial drone image of the six test pads (five development rock and one previously leached material) constructed as part of the Bagdad ARD test pad study. These rock types represented significant tonnage in the projected mine plan and were typically classified as having an uncertain ARD potential based on static testing, namely: Porphyry Quartz Monzonite (PQM), Quartz Monzonite (QM), and Precambrian Undifferentiated (pCundiff). Results from the leached ore test pad (TP8) will not be discussed here, as the focus for this test pad is to evaluate drain-down of previously leached material and is different from that of the five development rock test pads (TP3 to TP7). The final test pad shape resulted in the following configuration (plan view dimension): 9 m × 9 m top, 21 m × 21 m bottom, 5 m height from center of the stockpile, and side slopes of 1.5H:1V.

Eight 210-litre (L) barrels of material from each test pad were collected prior to pad construction and processed (composited/split) for geochemical and mineralogical analyses. Post-construction operation, monitoring and maintenance (OM&M) activities, including seepage sampling and analysis, began in 2019 and will conclude in 2022. Due to the relatively semi-arid conditions at the site, drip-line systems supplying water on the top surface and upper slopes of the test pads were installed to augment water received via natural precipitation. Supplemental water application is expected to accelerate the natural ARD/ML development, ensure sufficient toe seepage for water quality analyses, and facilitate a future water quality evaluation within the relatively short study duration of three years. A target application rate of ~3,800 L per week per test pad has been used. This is approximately three times the annual precipitation volume. Seepage from each test pad reports to a seepage collection system at the toe of the pad via a seepage collection pipe buried underneath the pad and collected into a 19-L sampling container. Test pad seepage has been collected and analyzed for field parameters and selected water quality constituents on a monthly/bimonthly basis. Detailed descriptions of test pad construction, material characterization, and OM&M activities are provided in Raghav et al. (2021).

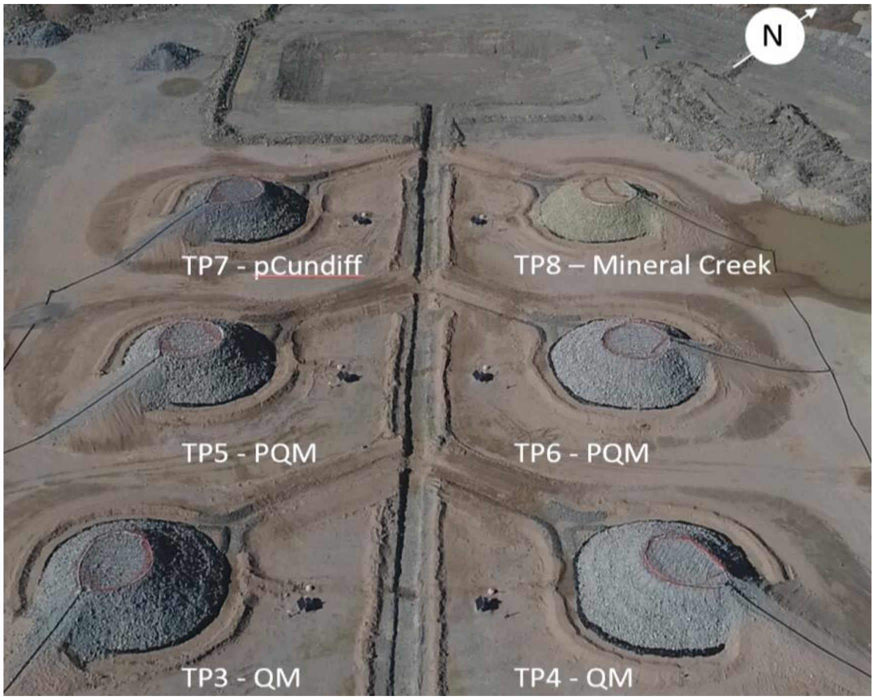

Figure 1: Aerial drone images of the test pads constructed as part of the Bagdad ARD test pad study. Note: QM – Quartz Monzonite; PQM – Porphyry Quartz Monzonite; pCundiff – Precambrain Undifferentiated; Mineral Creek – material from Mineral Creek leach stockpile

Results

Test pad seepage chemistry

Test pad seepage pH and electrical conductivity (EC) values have remained relatively constant throughout the study at 7.5–8.5 and 2,000–4,000 respectively. Fluctuations outside this pH range were observed from April through August 2021 (Figure 2). These have been attributed to unreliable readings due to normal wear-and-tear of the probe. Measurements obtained using a new pH probe since September 2021 have remained more stable. A sharp but short-lived decrease in pH has also been observed on selected occasions when pH measurements were obtained during or immediately following high-intensity precipitation events (e.g., late January 2021 and early December 2021). Higher water content in the test pads can result in higher internal carbon dioxide levels and decrease in pore water pH. However, the test pad seepage pH increased to the typical range within a week after draindown and increased carbon dioxide degassing to the atmosphere as has been observed in other studies (Peterson, 2014).

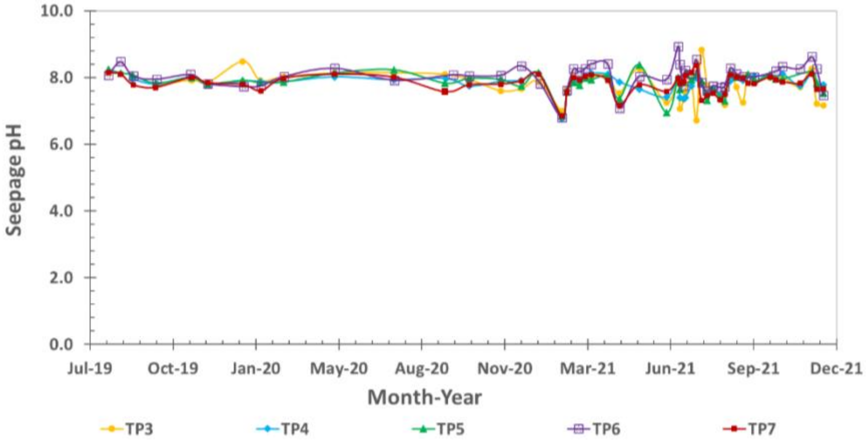

Figure 2: Test pad seepage pH

The degree of water saturation and flushing frequency can influence sulfide oxidation rates and solute loading in seepage (Herasymuik et al., 2006; Hollings et al., 2001). Water application was paused during periods of high-intensity precipitation to prevent constant flooding of pore spaces, which could slow down sulfide oxidation by limiting oxygen supply. Conditions within the pads are not oxygen limited based on consistently positive oxidation-reduction potential (ORP) data and moderate-high dissolved oxygen (DO) measurements (typical DO percent saturation of 50–80%). In addition, seepage sulfate concentrations have typically remained in the 1,000–2,000 mg/L range. Hence, the volume and frequency of water application are generally appropriate to promote sulfide oxidation by flushing out built-up oxidation products and exposing fresh mineral surfaces for further oxidation.

Test pad mineralogy

Based on X-ray diffraction (XRD) test results, chalcopyrite and pyrite are the two most likely sulfide minerals that upon oxidation can release acidity, sulfate, and metals into the seepage (Table 1). For TP5 and TP6, pyrite was not reported, but the total S data are consistent with pyrite being present below the XRD detection limit (0.3%). Hence, a pyrite concentration of 0.29% is assumed for these materials. No sulfate minerals were detected in any of the development rock types. However, based on total S data, it is possible that sulfate minerals may be present below the XRD detection limits in some or all the test pads. For the purposes of this evaluation, all sulfate loading in the seepage is assumed to be a result of sulfide mineral oxidation. No sulfate minerals are considered to be dissolving or precipitating.

Calcite, biotite, and chlorite are the minerals present in all test pads that are most likely to provide neutralization potential in the short to medium term (Table 1). Calcite is a “fast dissolving” carbonate that is most likely involved in the neutralization of the acidity generated from sulfide mineral oxidation. Biotite is a silicate mineral known to weather faster than other silicate minerals such as feldspars, plagioclase, etc. (Karlsson et al., 2018). Chlorite is another silicate mineral with intermediate weathering rate that may provide neutralization capacity, but has not been considered because the indicator solute in seepage (magnesium) is the same as for biotite. For this evaluation, all the magnesium in the test pad seepage is assumed to result from biotite dissolution.

Table 1: Pre-test rock characterization – XRD mineral content (weight %)

Description	TP3	TP4	TP5	TP6	TP7	Detection limit
Quartz	28.2	31.3	23.3	23.5	30.1	0.1
Plagioclase	21.0	19.0	24.4	28.3	16.7	0.5
K-Feldspar	27.3	25.8	34.5	29.1	22.0	0.5
Muscovite	6.2	6.8	5.5	6.0	9.9	0.5
Biotite	2.6	1.7	2.4	2.2	2.8	0.5
Chlorite	2.7	3.0	0.8	2.1	4.1	0.5
Kaolinite	2.4	3.6	2.4	1.6	2.6	0.5
CEC SC	6.2	5.2	4.6	5.1	6.6	0.01
Calcite	2.2	2.0	1.2	1.5	3.5	0.5
Pyrite	0.46	0.70	0.00	0.00	0.94	0.3
Chalcopyrite	0.68	0.74	0.87	0.75	0.80	0.3
Molybdenite	0.0	0.0	0.0	0.0	0.1	0.01
Gypsum	0.0	0.0	0.0	0.0	0.0	0.5
Jarosite	0.0	0.0	0.0	0.0	0.0	0.7
Sum	100	100	100	100	100	

Note: Minerals listed but reported as 0.0 did not have peaks above background levels (or above peak overlaps) and may be present below XRD detection limits. CEC SC refers to “Cation Exchange Capacity from Swelling Clays”.

Estimation of solute loading

Test pad seepage flow measurements typically included peak and low flow periods during the weekly water application cycles and hence, provide a reasonable estimation of seepage volumes. To estimate monthly seepage volume, an average of all the seepage flow rate measurements in the corresponding month was used. Solute concentrations in seepage have been measured on a monthly basis from August 2019 to March 2020 and every other month thereafter. Hence, solute loading rates, mineral reactions rates, and acid generation-neutralization balance are estimated on a monthly basis. The monthly solute loadings (moles) in seepage are calculated for sulfate, calcium, and magnesium using molar mass (g/mol), monthly seepage concentrations ($C_{Seepage}$, mg/L) and monthly test pad seepage volumes (L). In order to use sulfate loading in the seepage to estimate sulfide oxidation rates, the sulfate contribution from "water applied" on the test pads is subtracted. Similarly, the calcium and magnesium contribution from "water applied" on the test pads is subtracted when estimating calcite and biotite dissolution rates, respectively. This is important because a significant fraction of the "water applied" is stored within the test pads and not reported as seepage. To account for this, the fraction of "water applied" to the total water received is calculated $\left(f_{Water\ Applied} = \frac{Water\ Applied}{Water\ Applied + Precipitation}\right)$. For the purposes of this evaluation, the same fraction is assumed to apply to the seepage volume. In other words, the monthly seepage volume is multiplied by this fraction to estimate the volume of "water applied" that will contribute to the seepage. This adjusted volume is multiplied by solute concentrations in the "water applied" ($C_{Water\ Applied}$) to estimate the contribution of "water applied" to solute loading in the seepage.

$$\begin{aligned} &Adjusted\ solute\ loading\ in\ seepage\ (moles) \\ &\quad = Seepage\ Volume\ (L) \times \left[C_{Seepage}\left(\frac{moles}{L}\right) - C_{Water\ Applied}\left(\frac{moles}{L}\right) \times f_{Water\ Applied} \right] \end{aligned}$$

Figure 3 shows the adjusted loading of sulfate, calcium, and magnesium in seepage from TP3. Other development rock test pads show similar trends for adjusted loading of these solutes in seepage.

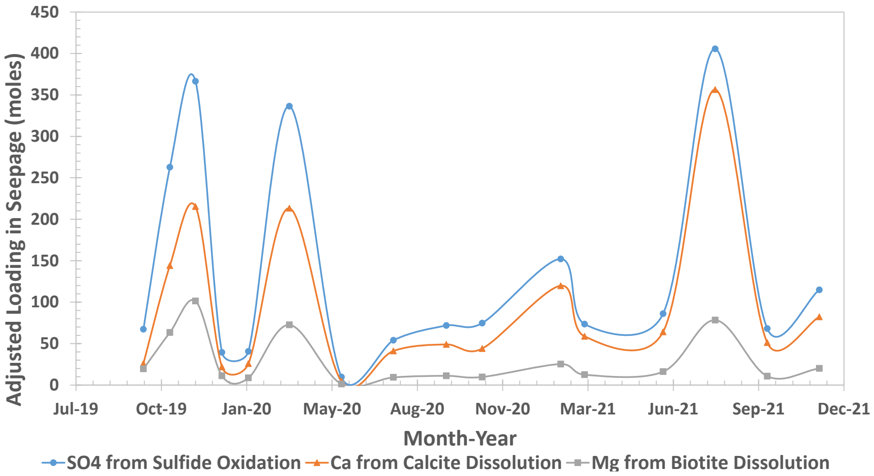

Figure 3: Adjusted solute loading in test pad seepage

Estimation of acid generation-neutralization balance

Based on the pyrite and chalcopyrite oxidation reactions below, two moles of sulfate are released per mole of pyrite or chalcopyrite oxidized. Two moles of H^+ are released per mole of sulfate released from pyrite oxidation, as opposed to one mole of H^+ released per mole of sulfate released from chalcopyrite oxidation. Based on test pad seepage chemistry observed, only abiotic sulfide mineral oxidation by oxygen is considered in this evaluation. Biotic sulfide oxidation by ferric iron is dominant only at low pH conditions (pH <4.5) due to the dependence of ferric iron solubility on pH.

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_3 + \boldsymbol{2SO_4^{2-}} + \boldsymbol{4H^+}$$

$$CuFeS_2 + \frac{17}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + Cu^{2+} + \boldsymbol{2SO_4^{2-}} + \boldsymbol{2H^+}$$

$$\boldsymbol{Total\ H^+\ released = (H^+\ moles\ released)_{Pyrite}} + \boldsymbol{(H^+\ moles\ released)_{Chalcopyrite}}$$

Two moles of H^+ neutralization is available for every mole of calcium released from calcite dissolution.

$$CaCO_3 + \boldsymbol{2H^+} \rightarrow H_2CO_3 + \boldsymbol{Ca^{2+}}$$

Based on the oxidative weathering reaction of biotite, one mole of magnesium is released per mole of biotite dissolved. Three moles of H^+ neutralization are available for every mole of magnesium released from biotite dissolution.

$$K(MgFe_2^{2+})(AlSi_3O_{10})(OH)_2 + \frac{1}{2}O_2 + 8H_2O + \boldsymbol{3H^+}$$
$$\rightarrow Al(OH)_3 + 2Fe(OH)_3 + K^+ + \boldsymbol{Mg^{2+}} + 3Si(OH)_4$$

$$\boldsymbol{Total\ H^+\ neutralization\ available}$$
$$= \boldsymbol{(H^+\ neutralization\ available)_{Calcite}} + \boldsymbol{(H^+\ neutralization\ available)_{Biotite}}$$

Alkalinity in the "water applied" is also a likely contribution to H^+ neutralization. However, alkalinity is reported based on laboratory titrations to a standard pH endpoint of 4.2. The (H^+ neutralization available)$_{\text{Water Applied}}$ cannot be accurately estimated using the laboratory reported alkalinity in the "water applied". Assuming two moles of H^+ neutralized for every mole of alkalinity, results in the contribution of "water applied" to "total H^+ neutralized" to be minimal. Figure 4 for TP3 shows that the "net H^+ neutralization available" in seepage is predominantly positive (excess neutralization available) when considering only calcite and biotite dissolution. Findings from other test pads are similar and consistent with the near-neutral pH and moderate alkalinity values (~60 mg/L as $CaCO_3$) of the seepage.

$$\boldsymbol{Net\ H^+\ neutralization\ available = Total\ H^+\ neutralization\ available - Total\ H^+\ released}$$

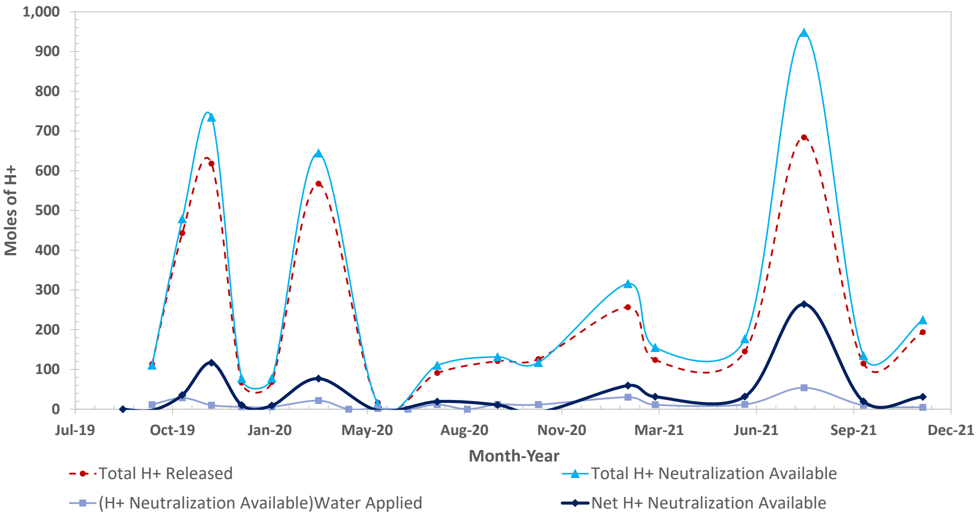

Figure 4: Estimated acid generation-neutralization balance

Estimation of mineral reaction rates

Adjusted sulfate loading is used to estimate pyrite and chalcopyrite oxidation rates in the test pads. In order to estimate the appropriate fraction of sulfate contributed by each mineral, a relationship between pyrite and chalcopyrite weathering is required. Sulfide mineral oxidation reactions are surface controlled kinetic reactions; hence, accessibility to the mineral surface strongly controls reaction rates. Steger and Desjardins (1978) showed with weathering experiments that the relative reactivity of pyrite is approximately two times that of chalcopyrite. Stromberg et al. (1994) proposed a linear dependence between mineral reaction rates for pyrite (R_{Py}) and chalcopyrite (R_{Cpy}), mineral abundance (mole/m^3) for pyrite (V_{Py}) and chalcopyrite (V_{Cpy}), and relative reactivity.

$$\frac{R_{Py}}{R_{Cpy}} = \left(\frac{V_{Py}}{V_{Cpy}}\right) \times 2$$

$$Mineral\ abundance, V\ (mole/m^3) = Pre - test\ mineral\ content\ \left({}^{mole}/_{kg}\right) \times Rock\ density\ \left({}^{kg}/_{m^3}\right)$$

The underlying assumption is that for both pyrite and chalcopyrite, the accessible surface areas for reaction are available in proportion to their relative mineral abundance in the corresponding test pad. This approach has been used in the literature to account for accessible surface areas of the sulfide minerals (Eriksson and Destouni, 1997). XRD mineral content (Table 1) and mineral molar mass are used to calculate the pre-test mineral content of pyrite and chalcopyrite in mole/kg. Assuming the test pads as truncated square pyramids, the volume of each test pad is estimated as 1,185 m^3. Assuming a rock density of 2,600 kg/m^3 and porosity of 30%, the bulk density is estimated as 1,800 kg/m^3 and mass of rock in each test pad as 2,100 metric tons. Adjusted sulfate loading from pyrite is used to calculate pyrite oxidation rate as shown below. Chalcopyrite oxidation rate is calculated similarly.

$$Sulfate_{Pyrite}\left(\frac{moles}{month}\right) = \left(\frac{\left(\frac{R_{Py}}{R_{Cpy}}\right)}{1+\left(\frac{R_{Py}}{R_{Cpy}}\right)}\right) \times Adjusted\ sulfate\ loading\ \left(\frac{moles}{month}\right)$$

$$Sulfate_{Chalcopyrite}\left(\frac{moles}{month}\right) = \left(\frac{1}{1+\left(\frac{R_{Py}}{R_{Cpy}}\right)}\right) \times Adjusted\ sulfate\ loading\ \left(\frac{moles}{month}\right)$$

$$R_{Py}\ \left(\frac{mole}{kg.s}\right) = \frac{Sulfate_{Pyrite}(moles/month)}{\left(\frac{2\ moles\ of\ sulfate}{mole\ of\ pyrite}\right) \times (kg\ of\ rock\ in\ test\ pad) \times \frac{days}{month} \times \frac{86400\ s}{day}}$$

Adjusted calcium loading and the stoichiometric relationship discussed earlier (1 mole of calcium per mole of calcite) are used to estimate the calcite dissolution rate. Biotite dissolution rate is calculated via a similar approach.

$$Calcite\ dissolution\ rate\ \left(\frac{mole}{kg.s}\right) = \frac{Adjusted\ Calcium\ Loading\ (mole/month)}{\left(\frac{1\ mole\ of\ calcium}{mole\ of\ calcite}\right) \times ((kg\ of\ rock\ in\ test\ pad) \times \frac{days}{month} \times \frac{86400\ s}{day}}$$

Figures 5 and 6 show sulfide oxidation and neutralizing mineral dissolution rates, respectively. Fluctuations observed in the rates are most likely due to variability in the monthly total water received. Peaks in reaction rates correspond to periods of high-intensity precipitation or unplanned increase in water application due to major leaks (e.g., TP3 in August 2021), which promote flushing of stored oxidation/weathering by-products. No long-term increasing or decreasing trends are observed in the reaction rates.

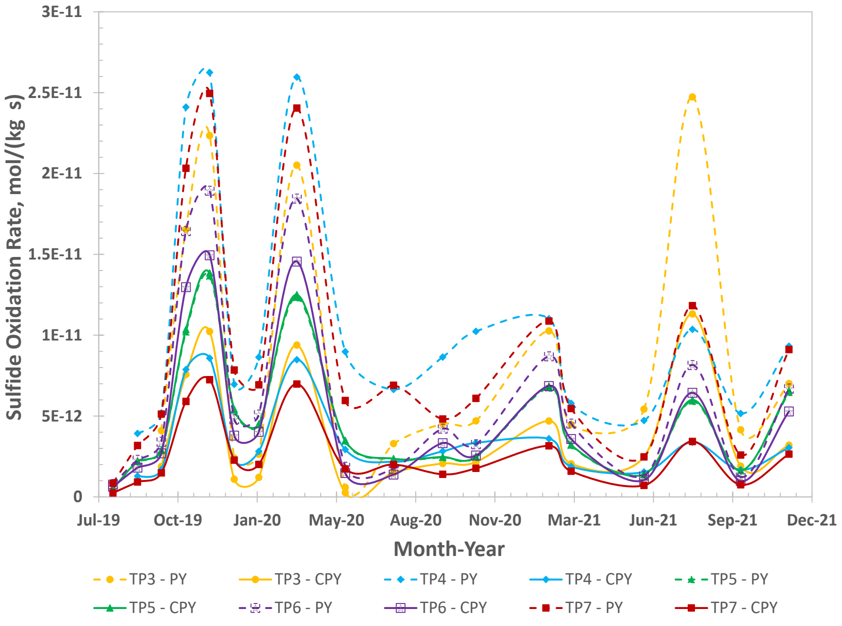

Figure 5: Estimated pyrite and chalcopyrite oxidation rates

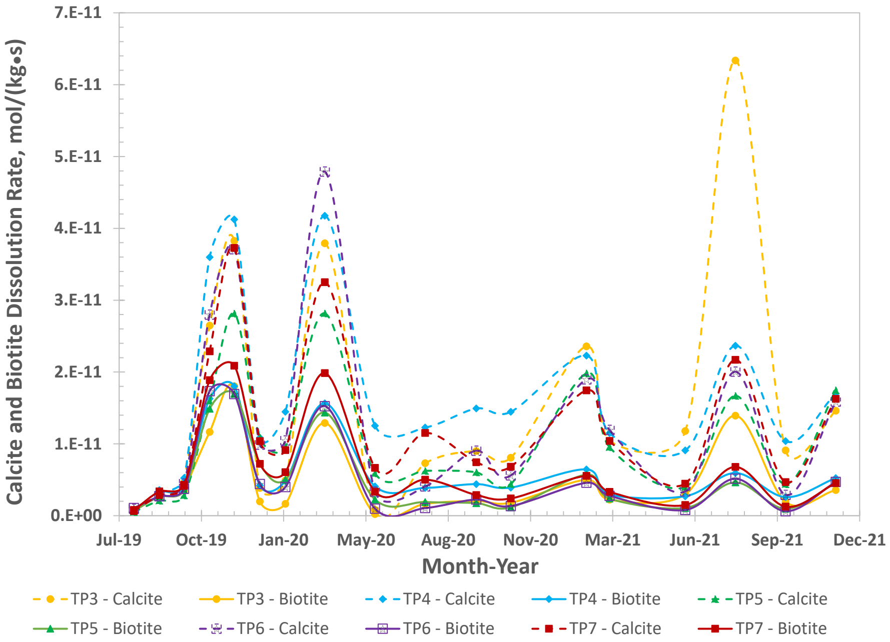

Figure 6: Estimated calcite and biotite dissolution rates

The estimated mineral reaction rates are within typical ranges reported in the literature from other laboratory and field studies (Stromberg et al., 1994; Peterson, 2014).

Estimation of time to consume minerals

The number of years to consume the primary acid-generating minerals (pyrite and chalcopyrite) and acid-neutralizing minerals (calcite and biotite) are estimated to understand if the test pad materials will eventually become acid generating. The current solute loading rates are assumed to be representative of the long-term minerals reaction rates.

$$Time\ to\ consume\ mineral\ (years) = \frac{Pre - test\ mineral\ content\ (mole/kg)}{Average\ mineral\ reaction\ rate\ \left(\frac{mole}{kg.s}\right)\left(\frac{365\ days}{year}\right)\left(\frac{86{,}400\ s}{1\ day}\right)}$$

This calculation assumes that all the pre-test mineral content is available for reaction, not just the fraction exposed on the surface. In addition, it does not consider that only a fraction of the rock surfaces are contacted by water and are available for active mineral-water interactions. Hence, the results from this calculation do not represent the actual time to consume the minerals. No data were collected regarding “water to rock” contact ratios and surface exposure, i.e., percentage of mineral exposed on the surface and available for reaction. However, assuming that all the minerals discussed have similar surface exposure, these estimates reasonably represent the relative time to consume the minerals. Figure 7 shows that for all the development rock test pads, the acid-neutralizing minerals, especially calcite, are likely to remain available after the acid-generating minerals are consumed. Hence, the development rock materials are not predicted to become acid generating in the future.

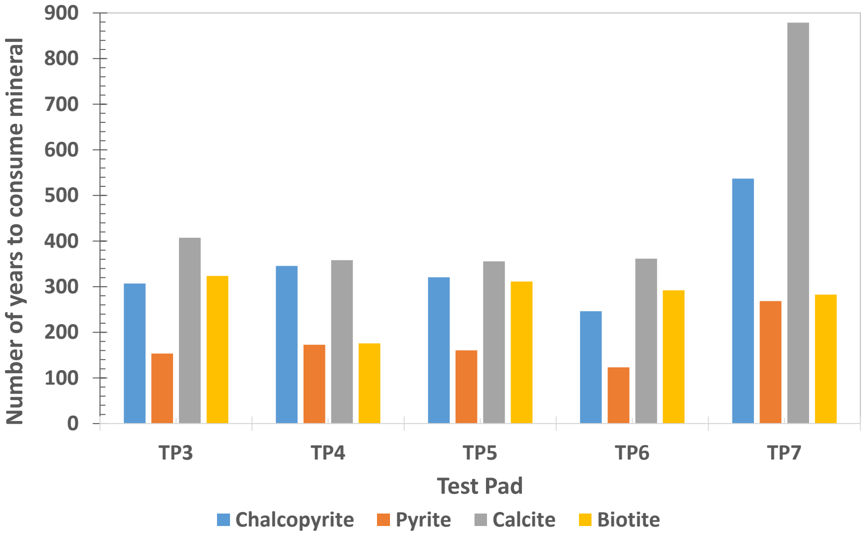

Figure 7: Estimated number of years to consume mineral

Conclusions

Field studies provide a more representative estimation of ARD potential of materials as compared to laboratory tests. This is especially true for mine sites in arid/semi-arid climates such as the Bagdad mine in Arizona. After approximately 2.5 years of weekly water application and natural precipitation, seepage pH from all development rock test pads have remained near-neutral (7.5-8.5) with moderate alkalinity (~60 mg/L as $CaCO_3$). These observations are consistent with the estimated acid generation-neutralization balance based on seepage solute loading rates and stochiometric solute-mineral relationships. Weekly water application employed in the study is expected to have accelerated the mineral oxidation and weathering reactions. Nevertheless, the mineral reaction rates estimated here provide a reasonable understanding of the long-term ARD potential. Future stockpiles constructed with the development rock materials included in this study are not likely to become acid generating based on the mineral contents and estimated reaction rates for pyrite, chalcopyrite, calcite, and biotite.

Acknowledgements

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Watershed Recovery in the Elliot Lake Area 20 Years Post Closure – Monitoring Program Design and Lessons Learned

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Abstract

Rio Algom Limited (RAL) owns, manages, and maintains nine uranium tailings management properties in the vicinity of Elliot Lake, located in northeastern Ontario (Appendix Figure A.1).[1] Uranium was mined in the Elliot Lake area of north-eastern Ontario for approximately forty years. The former Elliot Lake mines are generally located within the Serpent River Watershed (SRW), which is located between Sudbury and Sault Ste. Marie, Ontario. The watershed drains a land area of 1,376 km^2 and flows southward into Serpent Harbour at the North Channel of Lake Huron. The SRW is a chain-lake system containing more than 70 lakes.

The Elliot Lake mines generally operated from the late 1950s to the mid 1960s, and again from the early 1970s until the early 1990s, when most of the mines ceased operations (Table 1). In total, there are eleven decommissioned mining operations located in the SRW (Quirke [Quirke I and Quirke II], Panel, Denison, Spanish-American, Can-met, Stanrock, Stanleigh, Milliken, Lacnor, Nordic, and Buckles) and one other (Pronto) is located near the north shore of Lake Huron (Appendix Figure A.1). Associated with the mine sites are eleven decommissioned tailings management areas (TMAs), of which seven are flooded (Denison TMA 1, Denison TMA 2, Panel, Quirke, Spanish-American, Milliken, and Stanleigh) and four are vegetated (Lacnor, Nordic, Pronto, and Stanrock). Tailings were also historically deposited in Buckles Creek (adjacent to the Nordic TMA) and in Sheriff Creek (adjacent to the Milliken mine); these sites are included within the areas licensed by the Canadian Nuclear Safety Commission (CNSC). The main parameters of concern derived from the pyritic uranium ore tailings are acid, iron, and radium-226.

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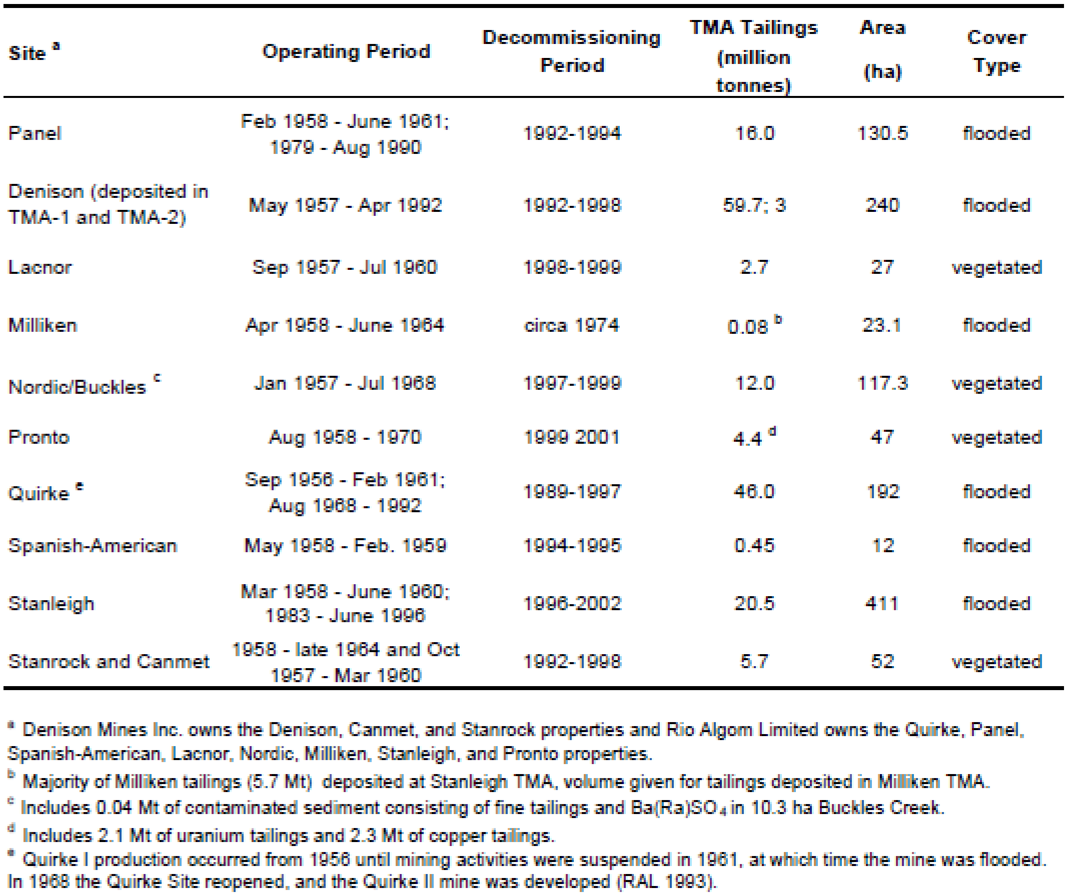
[1] There are three additional sites in the Elliot Lake area, owned, managed, and maintained by Denison Mines Inc. (DMI).

Final decommissioning and closure of the Quirke, Panel, Denison, Stanrock, and Spanish American properties was undertaken between 1992 and 1996. The Stanleigh, Lacnor, Nordic, and Pronto sites were decommissioned from 1997 to roughly 2000 and, in the case of Stanleigh, was not final until 2002 (i.e., when TMA flooding was completed). The TMAs are currently in long-term care and maintenance following closure that includes water collection, water management, effluent treatment (lime for pH adjustment and metals removal and barium chloride, or barite for radium-226 removal), source monitoring, watershed monitoring, and TMA management. All TMAs discharge to the SRW, except Pronto, which discharges to the north shore of Lake Huron.

Table 1: Elliot Lake mines – operating history, size, and cover type



Site [a]	Operating Period	Decommissioning Period	TMA Tailings (million tonnes)	Area (ha)	Cover Type
Panel	Feb 1958 - June 1961; 1979 - Aug 1990	1992-1994	16.0	130.5	flooded
Denison (deposited in TMA-1 and TMA-2)	May 1957 - Apr 1992	1992-1998	59.7; 3	240	flooded
Lacnor	Sep 1957 - Jul 1960	1998-1999	2.7	27	vegetated
Milliken	Apr 1958 - June 1964	circa 1974	0.08 [b]	23.1	flooded
Nordic/Buckles [c]	Jan 1957 - Jul 1968	1997-1999	12.0	117.3	vegetated
Pronto	Aug 1958 - 1970	1999 2001	4.4 [d]	47	vegetated
Quirke [e]	Sep 1956 - Feb 1961; Aug 1968 - 1992	1989-1997	46.0	192	flooded
Spanish-American	May 1958 - Feb. 1959	1994-1995	0.45	12	flooded
Stanleigh	Mar 1958 - June 1960; 1983 - June 1996	1996-2002	20.5	411	flooded
Stanrock and Canmet	1958 - late 1964 and Oct 1957 - Mar 1960	1992-1998	5.7	52	vegetated

[a] Denison Mines Inc. owns the Denison, Canmet, and Stanrock properties and Rio Algom Limited owns the Quirke, Panel, Spanish-American, Lacnor, Nordic, Milliken, Stanleigh, and Pronto properties.

[b] Majority of Milliken tailings (5.7 Mt) deposited at Stanleigh TMA, volume given for tailings deposited in Milliken TMA.

[c] Includes 0.04 Mt of contaminated sediment consisting of fine tailings and $Ba(Ra)SO_4$ in 10.3 ha Buckles Creek.

[d] Includes 2.1 Mt of uranium tailings and 2.3 Mt of copper tailings.

[e] Quirke I production occurred from 1956 until mining activities were suspended in 1961, at which time the mine was flooded. In 1968 the Quirke Site reopened, and the Quirke II mine was developed (RAL 1993).

As part of the closure and decommissioning process, RAL and DMI developed the Serpent River Watershed Monitoring Program (SRWMP). A central tenet of the monitoring framework for this program was that it should evolve in response to the observed changes in watershed conditions. Since decommissioning, conditions within the TMA basins have generally improved. TMA water quality is generally at or near Environment Impact Statement (EIS) predicted levels, with decreasing concentrations of radium-226, sulphate and uranium, as well as increasing pH levels. The improvements within the TMAs and at the TMA discharges have been reflected with improvements in the downstream receiving environment. As such, the SRWMP has evolved to reflect these changes. This presentation will focus on the SRWMP monitoring program design evolution of acceptability criteria and benchmarks, monitoring locations, monitoring parameters and monitoring frequency as the watershed has recovered, as well as lessons learned from the last twenty years.

SRWMP purpose and design basis

The SRWMP is an ecosystem-based aquatic monitoring program designed to evaluate cumulative effects of mine discharges on the SRW in relation to conditions predicted in EIS documents; and assess long-term trends in watershed quality. The program was designed with the following concepts/goals:

- assess mine-related impacts (i.e., mine indicator parameters);
- avoid redundancies between monitoring locations;
- monitor at a frequency equal to the ability to demonstrate change; and
- establish acceptability criteria to enable program modifications in response to measured conditions.

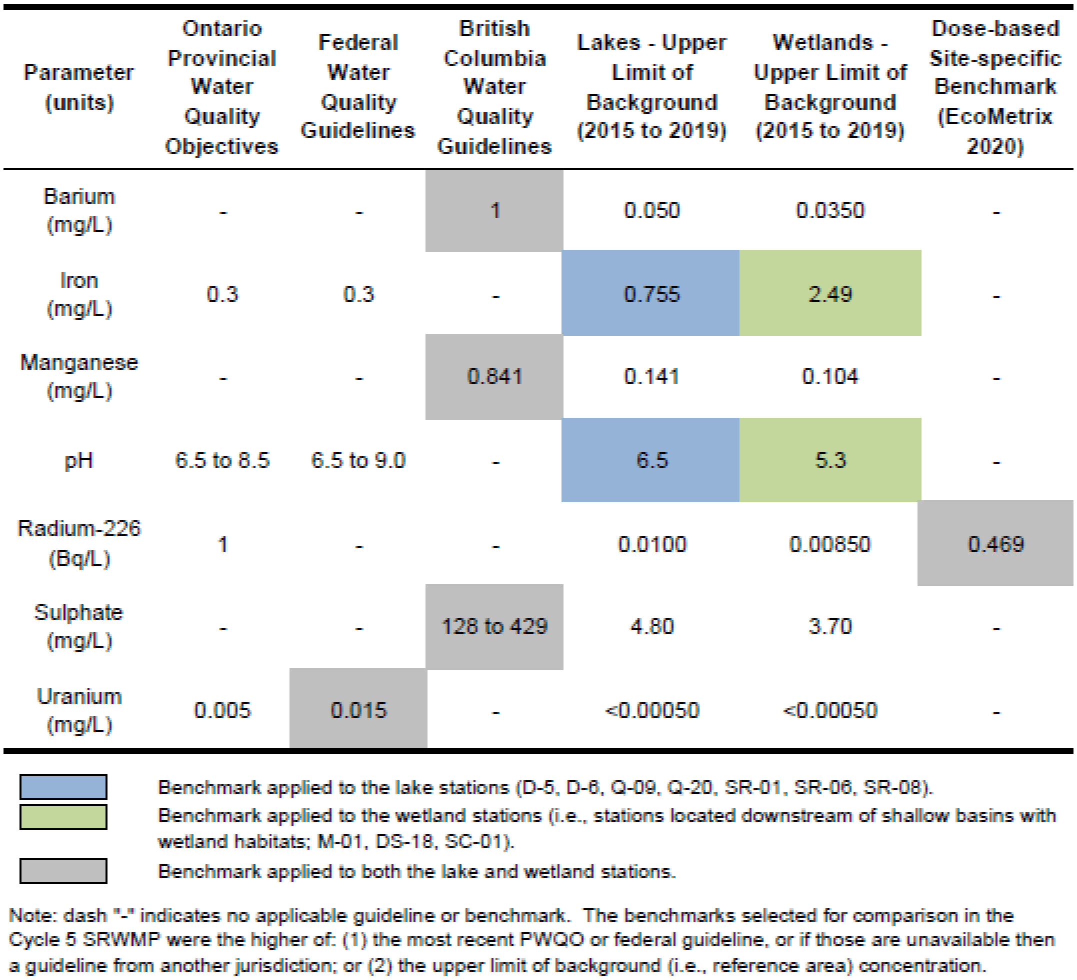
Every five years a study design is prepared that considers monitoring data results as well as the findings of any special investigations conducted to inform the program. As part of each study design, the methods, assessment benchmarks, monitoring locations, parameters, and the frequency of monitoring are reviewed and updated.

Acceptability criteria and benchmarks

Acceptability criteria were established that set the conditions for reducing or adding to the SRWMP scope. These criteria were based on achieving standards (which were termed benchmarks) as well as assessment of trend analyses. Achievement of the benchmark combined with improving trends would result in locations and parameters being eliminated from the study design or, alternatively, additional monitoring could be added in response to decreasing environmental quality. The foundation of the acceptability criteria was the establishment of benchmarks for water, sediment, and benthic invertebrate community monitoring, which were reviewed and updated with each progressive cycle of the SRWMP (every five years).

For water and sediment parameters, benchmarks were selected as the applicable water/sediment quality guideline, or the upper limit of background concentrations (reference stations), whichever was higher. By using the upper limit of background, data could be screened against local conditions. Through review of the benchmarks in relation to reference conditions, it became clear that mine-exposed stations require comparison to reference stations of similar habitat characteristics. Therefore, benchmark criteria were established for lake stations and wetland stations as these habitat types typically had differing water quality, particularly for parameters that can be influenced by dissolved oxygen or the organic content in water (e.g., iron and manganese). The benchmark criteria for barium, iron, manganese, pH, radium-226, sulphate and uranium were used in the most recent study design (Table 2).

Table 2: Water quality benchmarks of the cycle 5 SRWMP (Minnow, 2021)



Parameter (units)	Ontario Provincial Water Quality Objectives	Federal Water Quality Guidelines	British Columbia Water Quality Guidelines	Lakes - Upper Limit of Background (2015 to 2019)	Wetlands - Upper Limit of Background (2015 to 2019)	Dose-based Site-specific Benchmark (EcoMetrix 2020)
Barium (mg/L)	-	-	1	0.050	0.0350	-
Iron (mg/L)	0.3	0.3	-	0.755	2.49	-
Manganese (mg/L)	-	-	0.841	0.141	0.104	-
pH	6.5 to 8.5	6.5 to 9.0	-	6.5	5.3	-
Radium-226 (Bq/L)	1	-	-	0.0100	0.00850	0.469
Sulphate (mg/L)	-	-	128 to 429	4.80	3.70	-
Uranium (mg/L)	0.005	0.015	-	<0.00050	<0.00050	-

🟦	Benchmark applied to the lake stations (D-5, D-6, Q-09, Q-20, SR-01, SR-06, SR-08).
🟩	Benchmark applied to the wetland stations (i.e., stations located downstream of shallow basins with wetland habitats; M-01, DS-18, SC-01).
▨	Benchmark applied to both the lake and wetland stations.

Note: dash "-" indicates no applicable guideline or benchmark. The benchmarks selected for comparison in the Cycle 5 SRWMP were the higher of: (1) the most recent PWQO or federal guideline, or if those are unavailable then a guideline from another jurisdiction; or (2) the upper limit of background (i.e., reference area) concentration.

In addition, it is recognized that guidelines may evolve based on current research, and that generic guidelines may not be applicable in all scenarios. For example, multiple guidelines for radium-226 exist; however, they are derived based on the technical feasibility of water treatment methodology, or the assumption of dose to the specified receiver. In this instance, to provide a more conservative benchmark, site-specific water and sediment quality objectives were derived using site-specific doses calculated from measured radionuclide concentrations, as well as the current dose benchmarks (Ecometrix, 2019).

Acceptability criteria for benthic invertebrate community conditions were defined as no significant effects on downstream benthic communities relative to background (Beak, 1999a). Numerous endpoints were originally assessed and statistically compared as a part of the Cycle 1 and Cycle 2 benthic community assessments. To reduce redundancy and ensure unique and quantifiable measurements, Cycle 3 proposed five primary metrics: diversity, density, and correspondence analysis (CA) Axes 1, 2, and 3. To account for natural variation, ecologically meaningful was defined as differences greater than two standard deviations when comparing primary metrics from mine-impacted areas to reference conditions (Minnow, 2009).

Locations

When the program was initiated (in 1999), there was limited information on the geographical extent of effects associated with the history of mining on the downstream watershed (Beak, 1999a). To address this uncertainty, monitoring of water quality, sediment quality, benthic invertebrate communities and fish population health was conducted in lakes and streams spanning the watershed. Over time, these programs scaled back in response to data collected and changing conditions (Minnow, 2021).

Originally, samples for water quality analysis were collected at a total of 35 stations (Beak, 1999a; Appendix of this paper, Figure A.2). Over time, this was reduced to 16 stations by the most recent study design (Minnow, 2021; Appendix Figure A.3), which included the removal of mine-exposed stations based on performance (i.e., stable or decreasing trends of mine-related parameters), as well as the removal of reference stations due to redundancy and to maintain like-habitat with existing mine-exposed stations. In one instance, a previously removed station was re-added in response to changing TMA conditions.

In 1999, surficial sediment quality was monitored at 20 lakes in the Serpent River watershed to monitor the most recently deposited sediment (Appendix Figure A.4). This sediment quality scope has since been reduced based on performance to four near-field mine-exposed lakes and four reference lakes (Appendix Figure A.5).

The SRWMP initially included benthic invertebrate community monitoring at 20 lakes (lotic habitat) and 28 streams/rivers (erosional habitat) within the watershed (Appendix Figure A.4). Over time, the erosional locations (i.e., streams and rivers) and less depositional lakes (i.e., shallow lakes) were removed from the program, because the lakes downstream of mine discharges represented the primary depositional habitat for mine-related substances and had the most potential for mine-related impact on the benthic invertebrate communities. The reference lakes included in the program were also rationalized to match like-habitat of the mine-exposed lakes. Other lakes were removed from the program based on performance or redundancy. In the most recent study design, benthic invertebrate community monitoring was conducted in four near-field mine-exposed lakes and four reference lakes (Appendix Figure A.5).

In 1999, fish population health was assessed at three near-field lakes, two far-field lakes, and two reference lakes. Fish health was eliminated after two cycles, as there were no mine-related differences between mine-exposed lakes and reference lakes.

During the first three cycles of the SRWMP, fish tissue sampling was conducted across 20 lakes to support a human health risk assessment and a food chain dose assessment. This sampling was suspended after the third cycle as it was determined sufficient data were available to understand location dose and risk. Additional fish tissue data has been and will be collected periodically from only near-field lakes to update these assumptions.

Overall, the monitoring design was rationalized to focus on the near-field locations where changes in mine impact were the most relevant and most detectable.

Parameters

During operations the list of water quality parameters monitored had expanded (70 parameters) to address various operational effects questions, but had never been rationalized. The Cycle 1 SRWMP identified six parameters that were clearly elevated in downstream areas of the watershed and mine related, defined as "mine indicator parameters" (inclusive of uranium, radium-226, sulphate, iron, total dissolved solids [TDS] and pH). Potential mine indicators were also determined as changes in analytic methods, or method detection made it difficult to determine whether elevations in certain parameters were mine-related or were ecologically meaningful (aluminum, arsenic, cadmium, cobalt, copper, lead, manganese, nickel, selenium, and silver). Ancillary parameters were determined that would assist in data interpretation (hardness, dissolved organic carbon [DOC], alkalinity and total suspended solids [TSS]). Field measurements were also included to assist with data interpretation (pH, conductivity, dissolved oxygen, temperature, and flow).

During the Cycle 2 design, water quality data collected from Cycle 1 for source area and receiving environments were screened against water quality benchmarks to identify mine indicator parameters. The list of water quality parameters was then reduced to eleven mine-indicators (barium, cobalt, DOC, iron, manganese, radium-226, pH, selenium, silver, sulphate, and uranium) or influence parameters (conductivity and temperature; Table 3; Minnow, 2002). Based on performance, this has been further reduced to seven parameters in the current design (barium, pH, radium-226, sulphate, uranium, iron and manganese; Minnow, 2021).

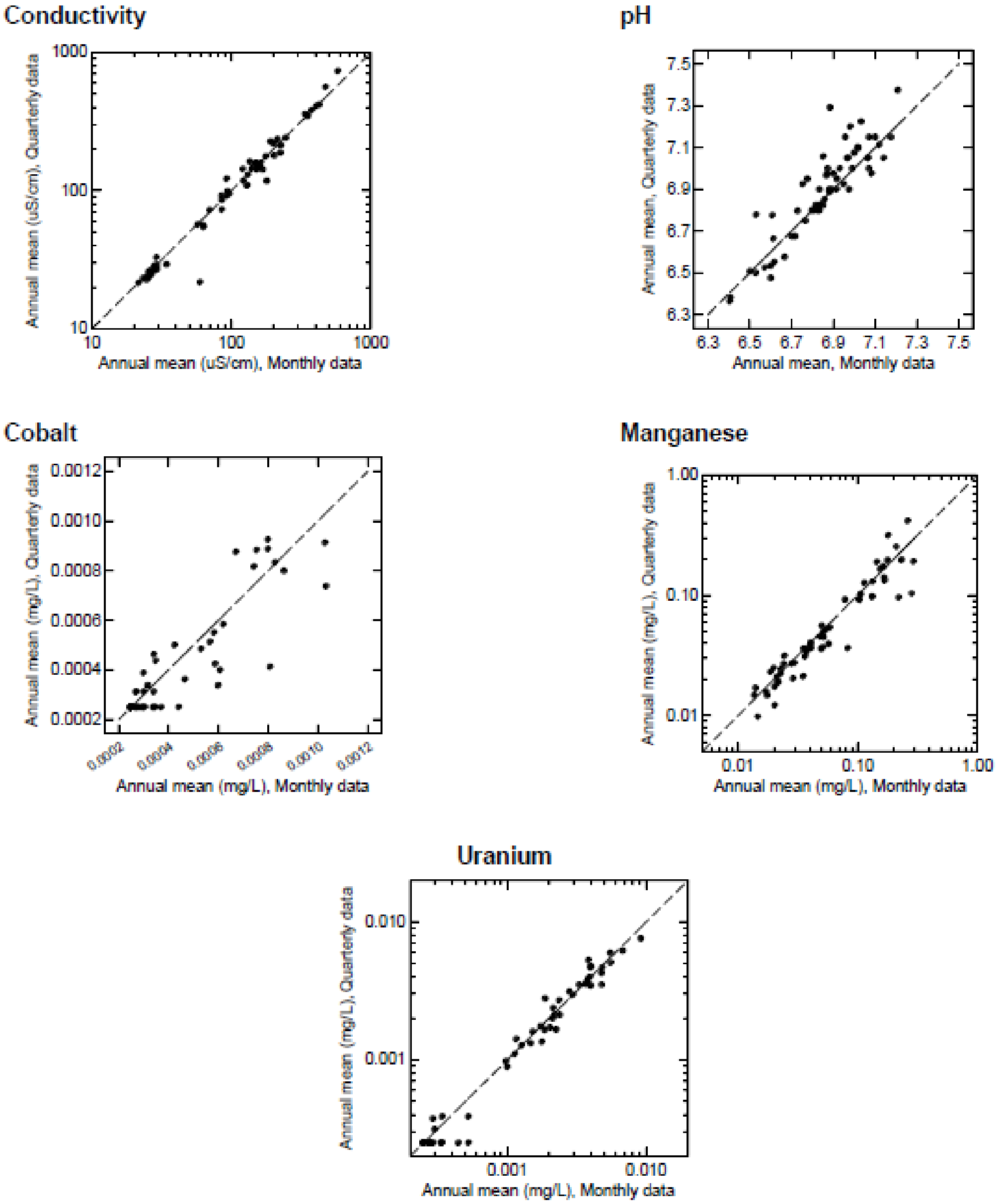
Sediment monitoring parameters followed a similar approach, whereby a comprehensive list of 15 parameters were measured during Cycle 1 and 2 (as sediment sampling was conducted once every 5 years originally). In Cycle 3, based on the statistical assessment of data relative to acceptability criteria, sediment parameters were reduced to seven mine-indicator parameters (barium, cobalt, iron, manganese, nickel, radium-226 and uranium; Minnow, 2009), which have remained consistent in the current study design (Minnow, 2021).

Table 3: Summary of water quality relative to evaluation criteria for SRWMP, SAMP and IBMP, SRWMP Cycle 2 study design (Minnow, 2002)

Parameter	Screening Benchmark	SRWMP		Source Area Monitoring Program (SAMP)		In Basin Monitoirng Program (IBMP)	
		Number of Samples	Samples Exceeding Benchmark (%)	Number of Samples	Samples Exceeding Benchmark (%)	Number of Samples	Samples Exceeding Benchmark (%)
Chloride	background	33	91%	8	100%	8	88%
Sulphate	background	257	86%	145	96%	125	99%
Strontium	background	204	76%	53	83%	52	100%
Hardness	background	200	76%	56	80%	38	100%
Magnesium	background	206	74%	93	89%	59	95%
TDS	background	261	73%	231	92%	138	99%
Sodium	background	20	70%	62	92%	20	90%
Manganese	background	208	63%	88	86%	77	78%
Potassium	background	28	61%	20	85%	13	100%
Barium	background	207	53%	64	70%	53	70%
Silicon	background	20	50%	18	67%	11	64%
Selenium	background	206	44%	50	50%	51	43%
Silver	background	203	41%	52	40%	52	56%
Uranium	PWQO	235	22%	155	59%	105	70%
Iron	PWQO	251	22%	124	56%	177	59%
Arsenic	PWQO	209	17%	65	26%	59	41%
Cadmium	background	169	17%	63	16%	52	6%
Cobalt	PWQO	205	16%	87	62%	74	57%
DOC	background	197	15%	49	39%	38	8%
Copper	background	221	13%	92	34%	82	39%
Aluminum	PWQO	209	11%	63	35%	52	19%
Alkalinity	background/PWQO	258	10%	219	6%	247	4%
Lead	background	221	9%	84	4%	75	8%
Thallium	background	170	8%	53	32%	52	38%
Titanium	background	203	8%	50	6%	51	8%
pH	PWQO	258	6%	835	6%	780	5%
Phosphorus	PWQO	168	1%	53	2%	56	4%
TSS	CWQG	210	1%	451	0%	202	0%
Zinc	PWQO	220	0%	103	18%	84	15%
Ammonia	PWQO	183	0%	90	17%	87	11%
Nickel	PWQO	222	0%	102	5%	84	2%
Boron	PWQO	20	0%	19	5%	12	0%
Chromium	PWQO	205	0%	50	2%	51	2%
Radium-226	PWQO	263	0%	224	0%	205	6%
Beryllium	PWQO	203	0%	55	0%	52	0%
Molybdenum	PWQO	205	0%	50	0%	51	0%
Vanadium	PWQO	205	0%	52	0%	53	0%
Zirconium	PWQO	20	0%	18	0%	12	0%
Nitrate	background	-	-	130	42%	63	35%
210Polonium	background	-	-	24	17%	33	30%
Total Thorium	background	-	-	27	15%	38	21%
210Lead	background	-	-	24	8%	32	22%
Nitrite	CWQG	-	-	10	0%	15	0%

"-" indicates that parameter was not measured as part of the SRWMP.

▨ Shade indicates parameter was recommended for on-going water quality monitoring program.


Conductivity

pH

Cobalt

Manganese

Uranium

Figure 1: Annual station means for conductivity, pH, and selected metals for quarterly versus monthly samples; receiving environment stations. The dashed line indicates a 1:1 relationship (quarterly = monthly; Minnow, 2009)

Frequency

While locations and parameters of the SRWMP have been reviewed relative to acceptability criteria and benchmarks, changes to monitoring frequency have been considered relative to the ability of the system to demonstrate change. As part of the original SRWMP design, water sampling frequency at the outlet of lakes was established based on the hydraulic retention time of the lake (Beak, 1999b). Generally, upstream source areas were sampled monthly, and downstream areas were sampled either once or twice per year. As part of the Cycle 3 study design, the sampling frequency at many of the monthly monitoring stations was reduced to quarterly based on statistical assessment of approximately 10 years of monitoring data, which indicated there would be no difference in the ability to detect mine-related changes, concentrations above benchmarks, or temporal trends (Minnow, 2009). Annual means calculated with monthly versus quarterly datasets showed excellent agreement (Figure 1), as did trends identified through Spearman rank correlations between annual means and year for quarterly versus monthly datasets (Figure 2; Minnow, 2009).

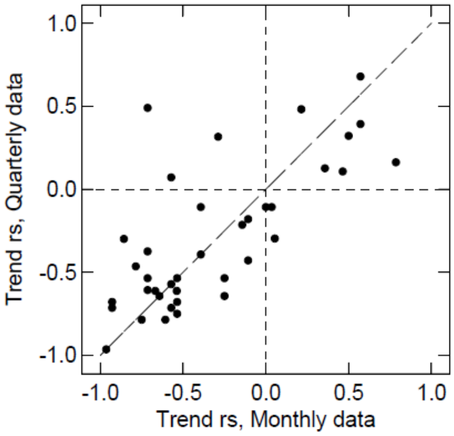


Figure 2: Trends (Spearman rank correlations [rs] between annual station means and year) for quarterly versus monthly samples; receiving environment stations. The dashed line indicates a 1:1 relationship (quarterly = monthly). Based on trends for conductivity, pH, cobalt, manganese, and uranium (Minnow, 2009)

In the initial SRWMP design, the sediment and benthic invertebrate community sampling monitoring frequency was once every five years, based on a depositional rate determined in a sediment depositional study conducted during operations (McKee et al., 1987; Beak, 1999b). After 15 years of monitoring, water quality had dramatically improved, but a commensurate improvement in sediment was not observed (Minnow, 2011). To investigate this discrepancy, a second deposition rate study was conducted to determine if sediment deposition rates were lower post-closure compared to during operational periods, using sediment traps and core profiling (Minnow, 2013). Sediment dry weight and bulk density data obtained from sediment traps were used to calculate sediment deposition rates rate (Minnow, 2013). For sediment core sections, sediment deposition rates were estimated based on time markers and were determined using caesium-137 peaks[2], radium-226 and sulphur concentrations in the context of changes in mining practices over time, as well as titanium concentrations that helped to differentiate natural variation in inorganic

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[2] This is a widely used technique based on atmospheric nuclear testing that resulted in caesium-137 peaks in 1963 and 1958 (Klaminder et al., 2012).

deposition from inorganic deposition associated with mining activity (Minnow, 2013). Deposition rates estimated using sediment traps and core profiling generally agreed (Minnow, 2013). It was determined that even at the most rapidly depositing lake it would take over ten years to accumulate 1 cm of sediment. To reflect this slower rate of change, the frequency of sediment and corresponding benthic invertebrate community sampling was reduced to once every 10 years (Minnow, 2016).

Conclusion

The SRWMP successfully evolved in response to the observed changes in watershed conditions to maintain a relevant and risk-based monitoring program, including design updates to acceptability criteria and benchmarks, monitoring locations, monitoring parameters, and monitoring frequency. The SRWMP has shown that the SRW has responded to improvements in the TMAs over the past twenty years, as demonstrated by surface water quality consistently achieving the SRWMP benchmarks and acceptability criteria, with few exceptions. In addition, the SRWMP has indicated that SRW water quality has improved more rapidly than sediment and benthic invertebrates. The SRWMP design evolved as these improvements were demonstrated. By designing a program that incorporates adaptive management with well-defined criteria for the basis of change, monitoring programs can achieve efficiency as well as provide adequate focus on potential areas of risk or concern. As the monitoring program is able to evolve in response to changing conditions in the watershed, it allows for the realization and application of lessons learned through a consistent approach, ensuring the efficient use of resources as well as decreasing unnecessary worker exposure risks (such as working on water) for the collection of unnecessary samples.

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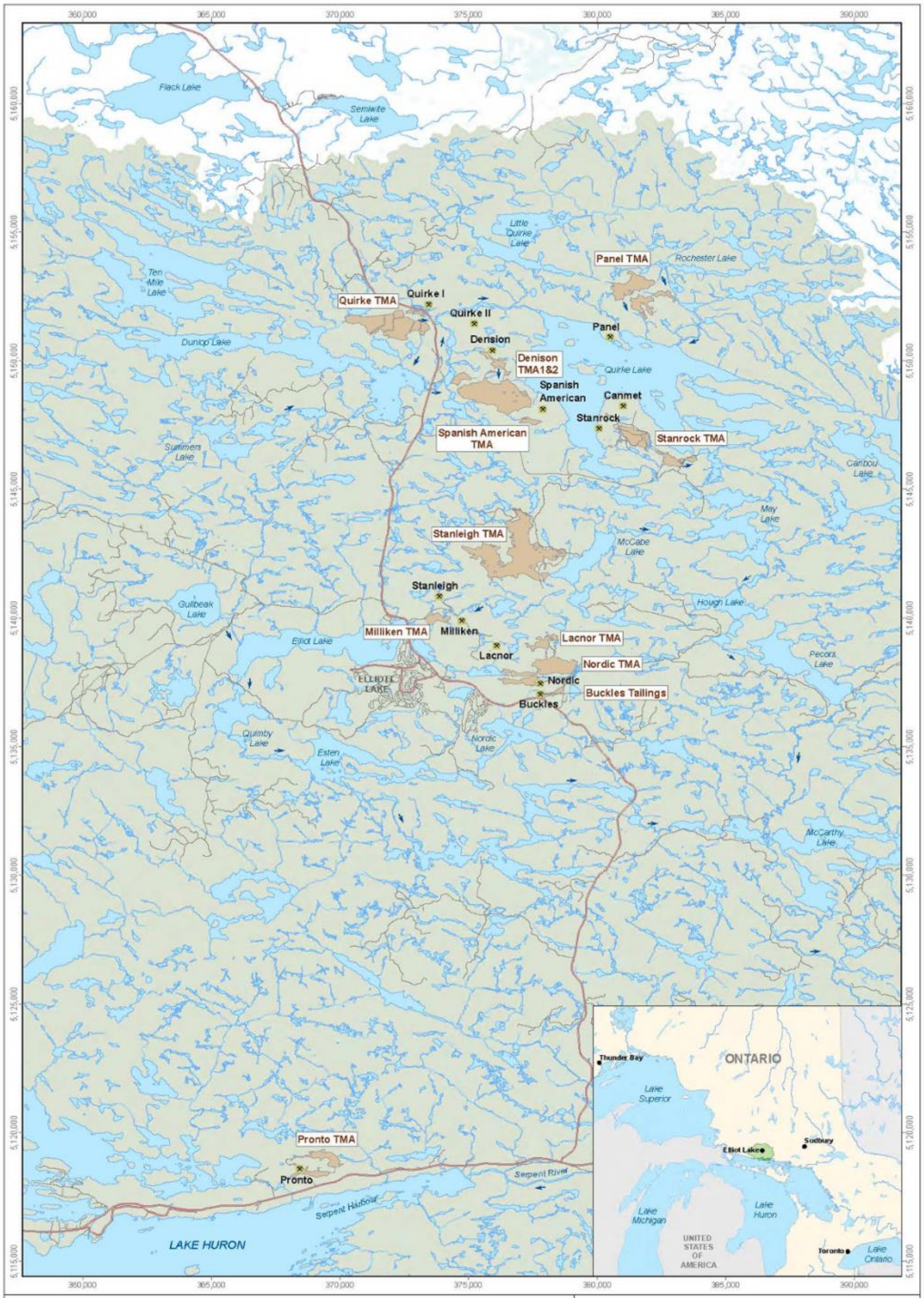
Appendix: Supporting maps



LEGEND

- ● Mine Site
- 🟫 Tailings Management Area (TMA)
- 🟩 Serpent River Watershed

Serpent River Watershed and Location of Former Mines and Tailings Management Areas

Map Projection: UTM Zone 17 NAD 1983
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Date: March 2021
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Figure A.1

Document Path: C:\Users\MLaPalme\Trinity Consultants, Inc\BHP - 197202.0041 - Cycle 5 SOEM - GIS\Cycle 5 Report\19-41 Figure 1.1 Serpent River Watershed and Location of Former Mines.mxd

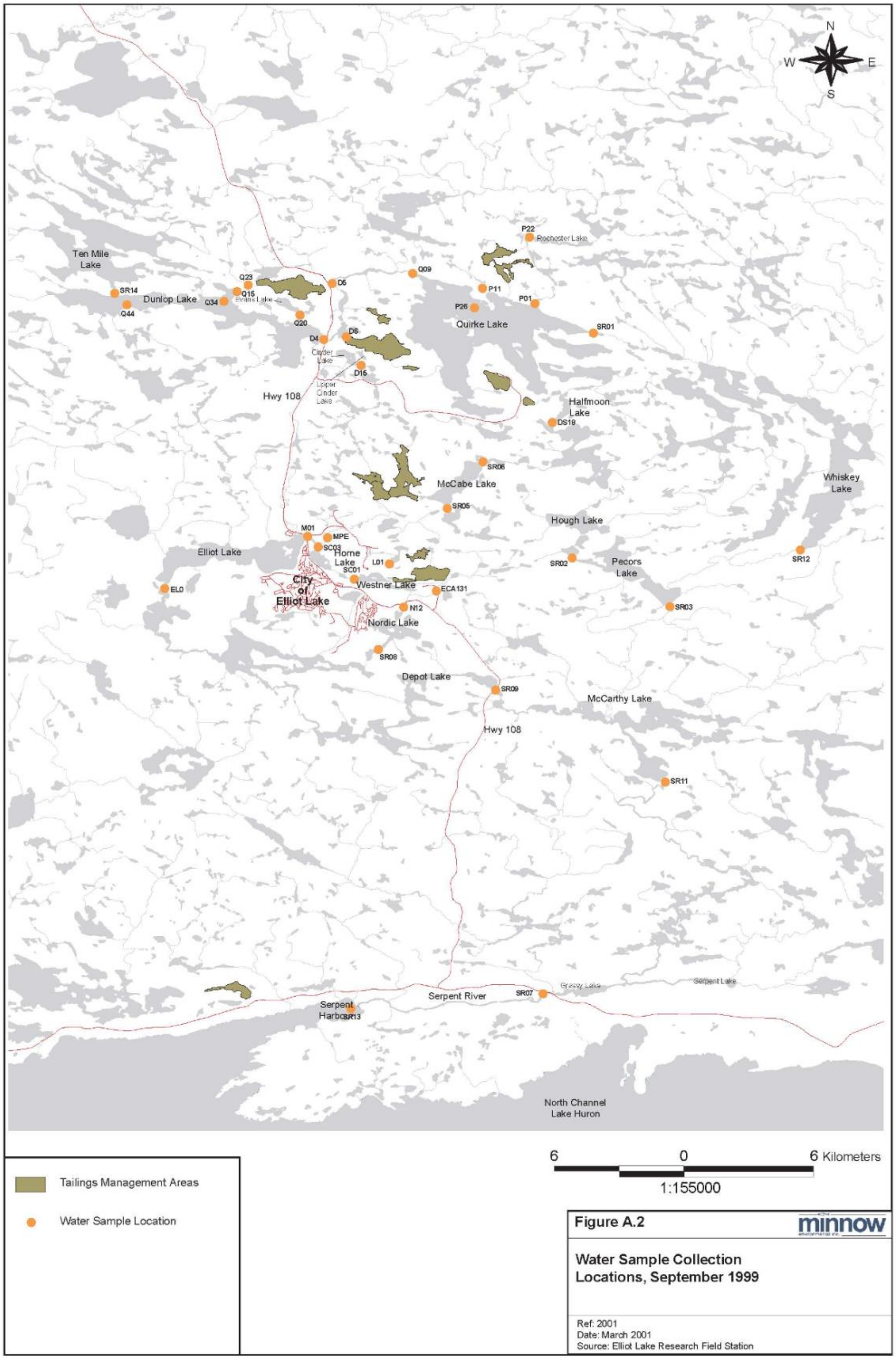
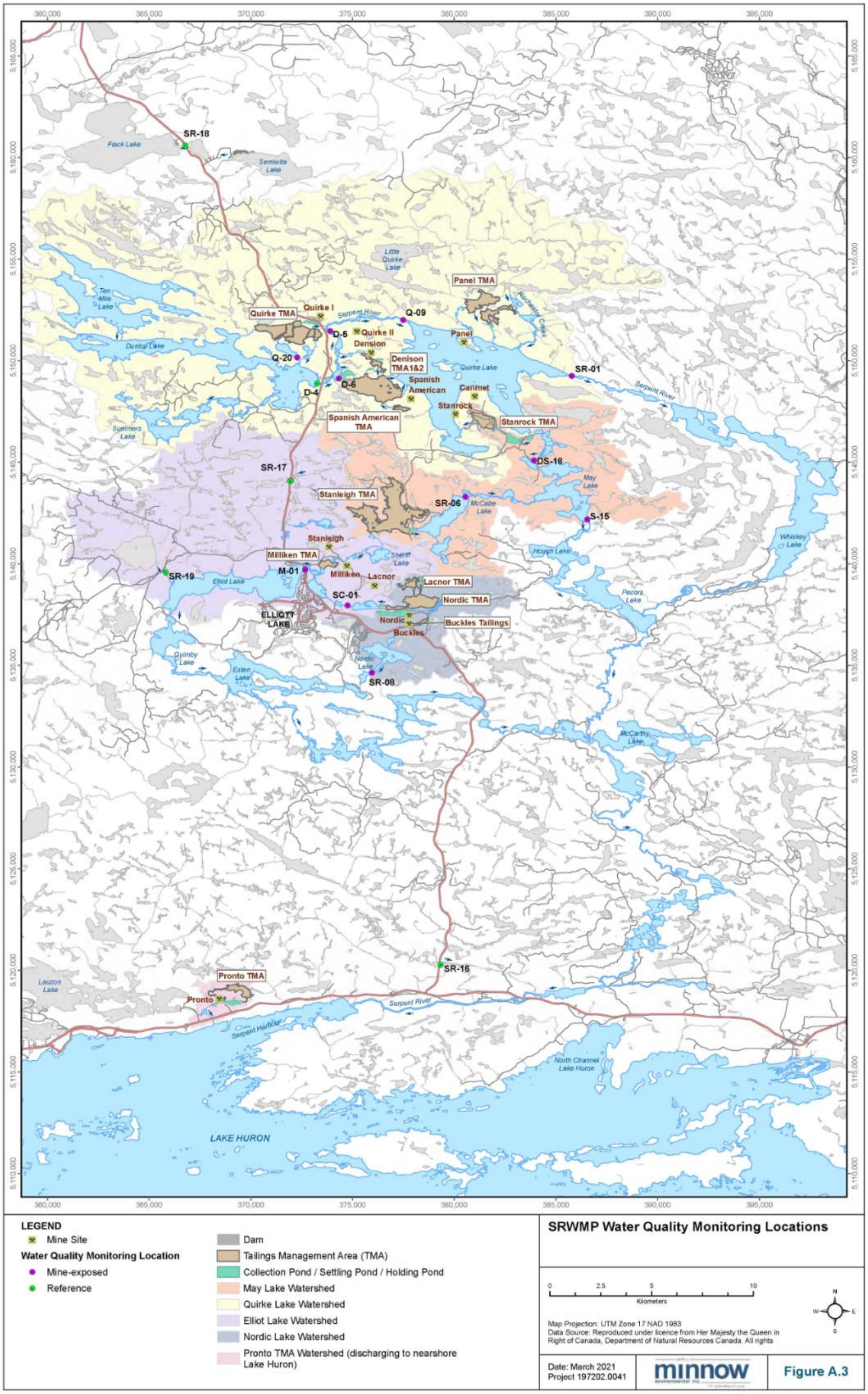


Figure A.2

Water Sample Collection Locations, September 1999

Ref: 2001
Date: March 2001
Source: Elliot Lake Research Field Station



SRWMP Water Quality Monitoring Locations

Figure A.3

Document Path: C:\Users\MLaPalme\Trinity Consultants, Inc\BHP - 197202.0041 - Cycle 5 SOE\4 - GIS\Cycle 5 Report\19-41 Figure 2.1 SRWMP Water Quality Monitoring Locations.mxd

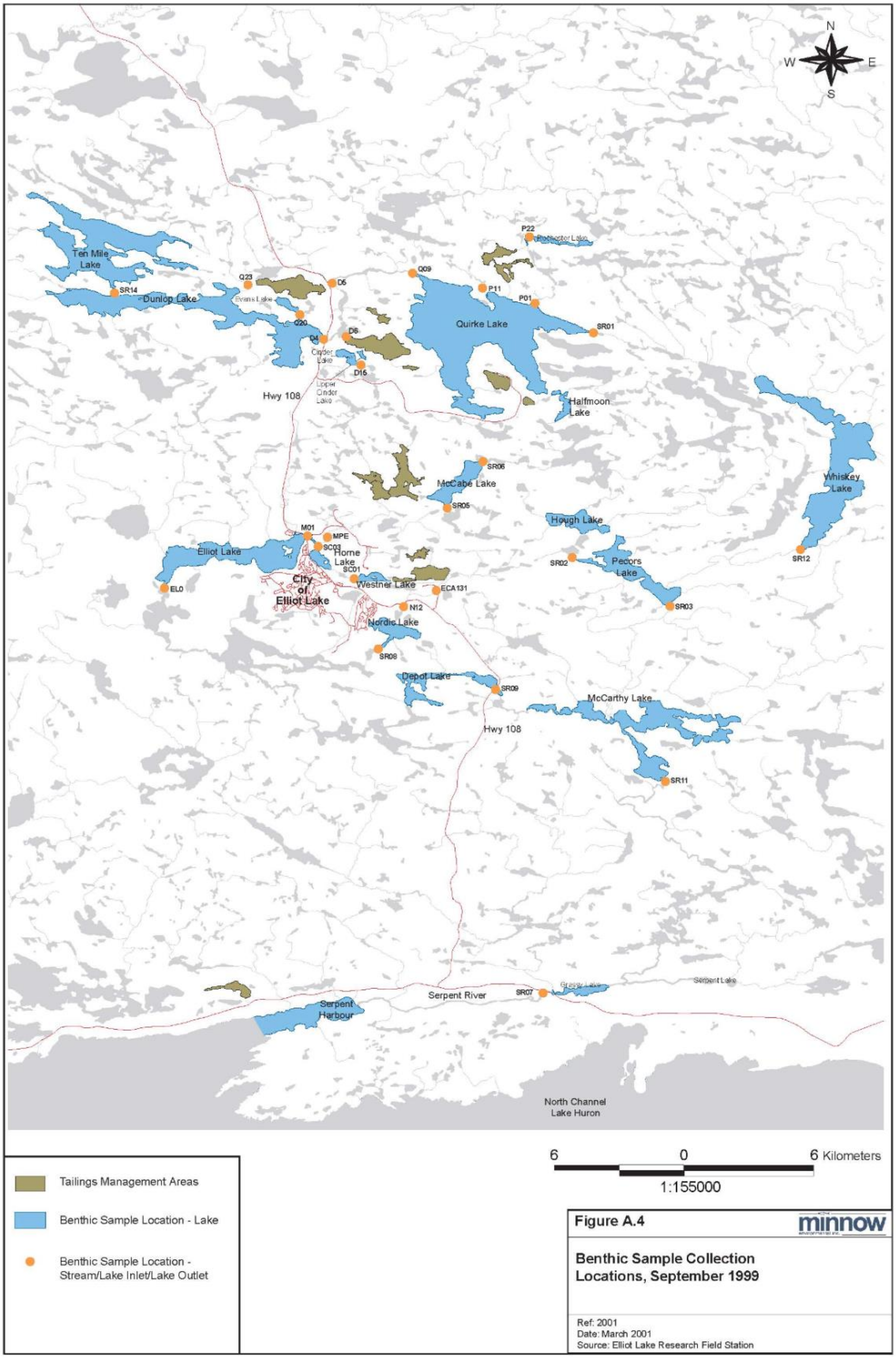


Figure A.4

Benthic Sample Collection Locations, September 1999

Ref: 2001
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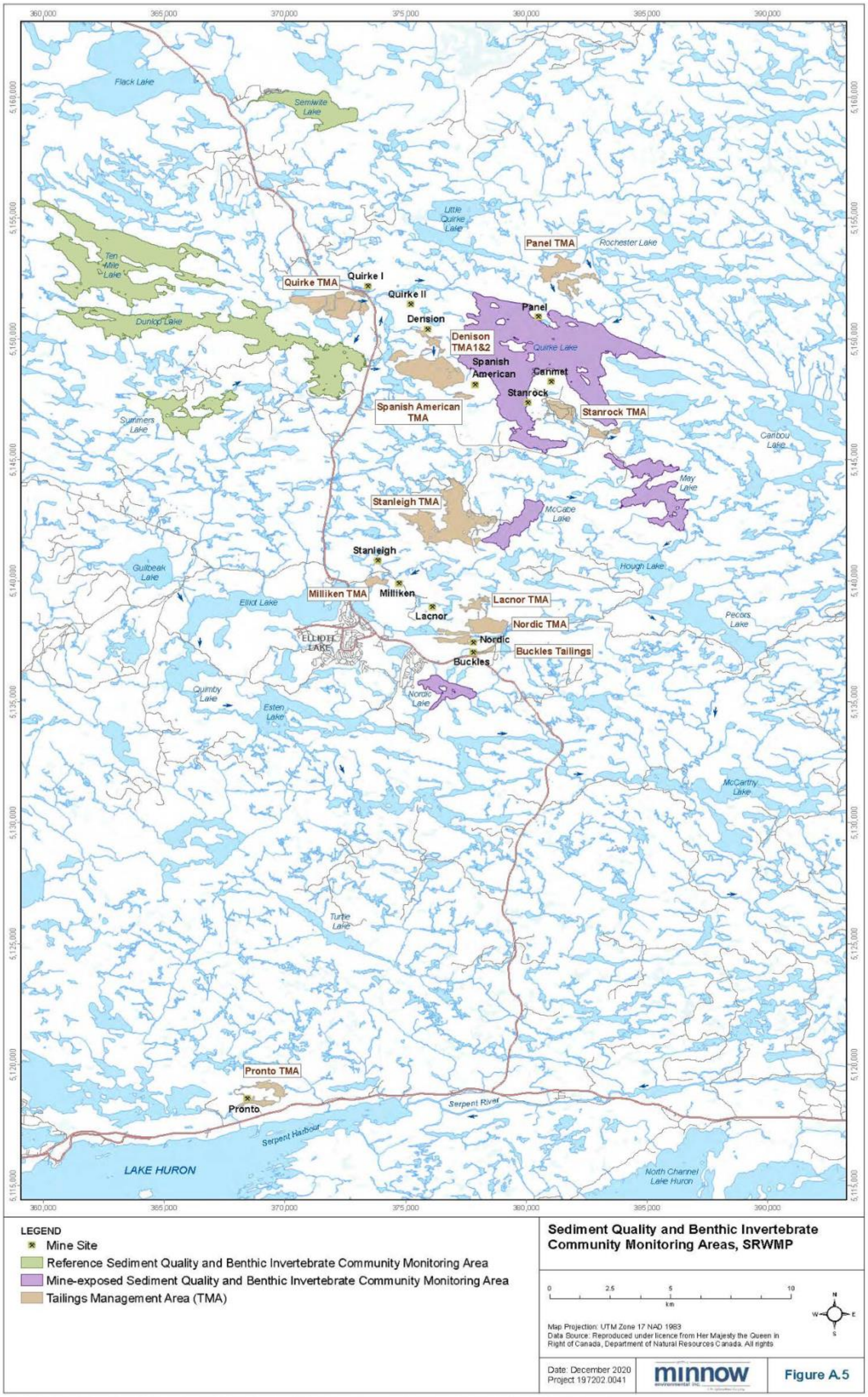
Source: Elliot Lake Research Field Station



Sediment Quality and Benthic Invertebrate Community Monitoring Areas, SRWMP

Figure A.5

Document Path: C:\Users\MLaPalme\Trinity Consultants, Inc\BHP - 197202.0041 - Cycle 6 SOEM - GIS\Cycle 6 Report\19-41 Figure 2.3 Sediment Quality and Benthic Invertebrate Community Monitoring Areas, SRWMP.mxd

Chapter 3:
Water Treatment

Thermally Activated Minerals and Waste for Mine Water Treatment

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Abstract

Mine drainage results from the interaction between the run-off and the bedrock, mine waste, or tailings. Its passive treatment is a challenge due to the variable charge in metals, metalloids, sulfate, and also variable concentrations range and season impacted flow. Moreover, environmental impacts of mine drainage may persist hundreds to thousands of years after mine closure. Accordingly, mine drainage treatment is mandatory, in order to limit the discharge of contaminants into the environment. Mining companies are continuously searching for treatment technologies to reduce their environmental footprint and the cost of water treatment. Therefore, the utilization of waste materials in water remediation is attracting more attention. Moreover, physicochemical and mineralogical modification of waste materials prior to their use enhance their metal removal capacity and their mechanical and chemical stability. Consequently, modified waste becomes an interesting option for both active and passive treatment of the mine drainage.

Several underutilized natural, or various waste materials resulting from diverse human activities, can be modified for water treatment through simple procedures. These include: chemical activation with oxidants, acids, or bases; coating; grafting of metal or organic functional groups; and thermal activation (calcination, pyrolysis, alkaline fusion, hydrothermal treatment). Among these, thermal activation by calcination can greatly improve the water treatment performance of materials by means of a relatively low cost, simple procedure. Calcination modifies chemical composition and mineralogy, as well as surface charge and oxidation-reduction potential; enhances neutralizing capacity and alkalinity generation, as well as specific surface and porosity; and reduces grainsize. In our studies, dolomite [$CaMg(CO_3)_2$] was partially decomposed in calcite ($CaCO_3$) and periclase (MgO) by calcination for one hour at 750°C. The new material showed improved efficiency for Mn treatment, which was reduced from 0.65 to 0.05 mg/L in a contaminated neutral mine drainage (CND), and also for As treatment, reduced from 196 to 2 μg/L in CND. Moreover, eggshells calcined for one hour at 900°C and employed in a 0.3% solid: liquid ratio increased the pH of acid mine drainage (AMD) from 2.5 to 6.9 at 20°C, and to 9.2 at 4°C, respectively. Various contaminants concentrations were reduced as follows: As <0.0005 mg/L, Cd 0.00022 and 0.00009 mg/L, Cu 0.0061 and 0.0091 mg/L, Co 0.0338 and 0.0016 mg/L, Cr 0.0015 and 0.0022 mg/L, Fe <0.01 mg/L, Ni 0.0291 and 0.0024 mg/L, Se 0.0033 and 0.0044 mg/L, Zn 0.007 and 0.022 mg/L, at 20°C and 4°C respectively. Eggshells mineralogy changed from 99.43% calcite ($CaCO_3$) before calcination, to 51.4% calcite ($CaCO_3$) and 48.6% portlandite [$Ca(OH)_2$] after calcination. Finally, paper sludge was employed to treat Zn from a CND (pH 7.72). While the raw material reduced Zn from 9.72 mg/L to 1.99 mg/L, calcined material (6h at 700°C) reduced Zn below 0.01 mg/L. To conclude, thermal activation by calcination for different underutilized materials or waste locally available (to reduce transport costs) can be considered and optimized for mine drainage treatment.

Introduction

Mine drainage is unique among contaminated waters, given its mechanism of generation, charge and flow, and environmental impacts, which may persist hundreds to thousands of years after mine closure (Sapsford, 2013; Kučerová et al., 2014; Frau et al., 2015). Mine drainage can be acidic (acid mine drainage [AMD]; pH<6), circumneutral (contaminated neutral drainage; CND; 6<pH<9), basic (pH>9), diluted, mineralized, or saline (Nordstrom et al., 2015). The AMD is characterized by the presence of elevated concentrations of various inorganic contaminants such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), nickel (Ni), mercury (Hg), manganese (Mn), iron (Fe), selenium (Se), copper (Cu), vanadium (V), and zinc (Zn) (Nordstrom et al., 2015). The CND contains significant concentrations of metals and metalloids that are soluble at near-neutral pH (As, Sb, Se, Ni, Zn, Mn), and which are increasingly being recognized as an environmental concern (Stantec, 2004; Bright and Sandys, 2015). The above contaminants are harmful to humans and environment, rendering their treatment mandatory (Etteieb et al., 2021).

Mine water treatment methods include the following processes: chemical precipitation, coagulation-flocculation, flotation, filtration, solvent extraction, electrochemical treatment, ion exchange, complexation, evaporation, distillation, crystallization, oxidation, reduction, phytoremediation, and adsorption (O'Connell et al., 2008; Sandy and DiSante, 2010). However, treatment is challenging as mine waters contain mixes of contaminants, while optimal treatment conditions can be contaminant-specific (Calugaru et al., 2018). Water pH and Eh (redox potential) are important parameters as they influence elemental speciation and solubility, and thus treatment options (Calugaru et al., 2021b). Other significant issues are the potential for metals recovery (Rakotonimaro et al., 2017) and water recovery and reuse (as water is a limited but reusable resource). Finally, site-specific, regulatory, economic, environmental, and social factors represent additional constraints for the selection of a remediation system. As the global commitment to sustainable development and sustainable remediation have increased, the mining industry has been searching for treatment technologies that reduce the environmental footprint of water treatment, considering, among other factors, the utilization of waste and underused materials in water remediation (Favara and Gamlin, 2017; Hengen et al., 2014). Moreover, modification of readily available materials enables the reutilization and stabilization of residues (Vadapalli et al., 2010), decreases manufacturing and transportation costs (Hengen et al., 2014), offers flexibility in terms of treated pollutants (and to flow and charge variations), and allows metal recovery and sorbent regeneration (O'Connell et al., 2008).

Several mineral and organic materials can be easily modified for application in wastewater treatment. Chemical and mineralogical modification can be performed: by calcination of seashells, eggshells, dolomite, sewage sludge, paper sludge; by alkaline fusion and hydrothermal treatment of coal, bagasse, and waste incineration fly ashes, for zeolite fabrication; and by pyrolysis of various organic waste for biochar production (Calugaru et al., 2018). Chemical activation can be performed by: oxidation (e.g. of peanut hull biochar and cellulose); alkali activation (e.g. of switchgrass biochar and wood residues); Fe (III) impregnation (e.g. of activated carbon, biochar, peat, agricultural residues, sand, cellulose, zeolite); acid hydrolysis (e.g. of wood residues, chitin, seashells); and grafting of metal-binding functions (e.g. on cellulose, wood residue, chitosan, bacterial and fungal biomass) (Calugaru et al., 2018).

The aim of this paper is to present the improved performance by calcination with three largely and readily available materials: dolomite, eggshells and paper sludge, for mine drainage treatment.

Methodology

The dolomite was supplied at Temiska Silice (Saint-Bruno-de-Guigues, Quebec). Its thermal activation (half-calcination) was carried out in a furnace (Thermolyne Furnace type 30400, Barnstead International), at 750°C, for one hour (Calugaru et al., 2016).

The eggshells were recovered from a local cafeteria, washed with deionized water, and dried at 100°C in an oven (Heratherm, Thermo Scientific). Then, they were crushed for 30 seconds in a ring grinder (SRM type, model C+RC, Rocklabs). Afterwards, eggshell powder was calcined in the oven (Thermolyne Furnace type 30400, Barnstead International), for one hour, at 800°C, 850°C, and 900°C (Calugaru et al., 2022).

The paper sludge was sampled at the pulp mill Nordic Kraft (Lebel-sur-Quevillon, Québec). Its calcination was carried out in an oven (Lindberg Blue M), for six hours, at 500, 600, 700, 800, and 900°C.

Characterization of solids was performed by X-ray diffraction (XRD) using a Bruker AXS D8 advance X-ray diffractometer. The DiffracPlus EVA software was used to identify mineral species, and the TOPAS software implementing Rietveld refinement was used to quantify the abundance of all identified mineral species (Calugaru et al., 2016; Calugaru et al., 2022). The loss of ignition was evaluated by 16 hour calcination at 375˚C in a Thermolyne Furnace (type 30400 from Barnstead International), according to standard Method MA. 1010-PAF 1.0. The organic matter was evaluated by charring at 550˚C in an oven

(Thermolyne Furnace type 30400, Barnstead International). Thermogravimetry analysis (TGA/DSC, model STA449FS, Netzsch) was performed to evaluate the thermal decomposition. Granulometry was evaluated (Microtrac) and the specific surface was measured (model vacprep061, Micro metrics) as the particle size is supposed to decrease and the specific surface is supposed to increase after calcination. Paste pH was measured (Hach HQ30d Flexi multimeter) after one hour of contact in ratio solid: liquid (deionized water) of 1: 10 (Method D 4972-95a, 1995, ASTM). Then, PZC pH (the pH for the material which has a zero electrical surface charge) was determined by the salt (solid) addition method (Bakatula et al., 2018). Acid digestion followed by elemental qualitative and quantitative analysis was performed using microwave plasma atomic emission spectrometer (Agilent Technologies Spectrometer 4200 Series, Santa Clara, CA, USA) (Calugaru et al., 2016; Calugaru et al., 2022).

Mine effluents were sampled on sites of gold and zinc active mines in the Abitibi-Temiscamingue region of Quebec, Canada. The effluents were preserved at 4°C prior to analysis and testing. Qualitative and quantitative elemental analysis of the mine effluents before and after treatment was performed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800). The Eh and pH were measured with a Hach HQ30d Flexi multi-meter.

Results and discussion

Half-calcination at 750°C, for one hour, of dolomite ($CaCO_3 \cdot MgCO_3$), lead to its decomposition in a mixture of calcite ($CaCO_3$) and periclase (MgO) (Calugaru et al., 2016).

Half-calcined dolomite was found effective for the treatment of Mn in a gold mine CND (pH 4.8÷8.1) during six months of column testing, for six hours of hydraulic residence time (HRT). Previously, the efficiency of raw dolomite vs. half-calcined dolomite was evaluated in batch testing with synthetic DNC and Mn removal by raw dolomite and was found to be very poor: 11,9% Mn removal (Table 1, Calugaru et al., 2021a).

Half-calcined dolomite was also found effective for the treatment of As (V) (Table 1, Braghiroli et al., 2020). Synthetic CND of pH 7 containing 850 mg As (V) / L was put into contact with half-calcined dolomite in a solid: liquid ratio of 1% in batch testing. After eight hours, the As concentration was below the detection limit (BLD), whereas the maximum As removal of half-calcined dolomite was found to be 820 µg As/g. For column testing, a gold mine CND (pH≈7) was employed. For an HRT of two hours, the As concentration was decreased from 196 µg/L to 0.5÷1.9 µg/L. When the test was ended (after 112 days), the half-calcined dolomite was still efficient.

Calcination of eggshells ($CaCO_3$), at 800°C, 850°C, and 900°C, for one hour, leads to mixtures of calcite ($CaCO_3$) and portlandite [$Ca(OH)_2$] in the ratios : 80% calcite to 20% portlandite; 66% calcite to 34% portlandite; and 50% calcite to 50% portlandite, respectively (Calugaru et al., 2022).

Table 1: Performance of raw and calcined materials for mine effluent's treatment

Material	Effluent characteristics	Treatment conditions	Results
Raw dolomite $CaCO_3 \cdot MgCO_3$	Synthetic CND, pH 7.2 49.6 mg Mn/L	Batch testing, 48 h Solid: liquid ratio 0.75% 25°C, 300 rpm	11,9% Mn removal pH 7.0
Half-calcined dolomite $CaCO_3 \cdot MgO$	Synthetic CND, pH 6.1÷7.2 49.6 ÷ 892 mg Mn/L		≥ 97.2% Mn removal pH 9.7÷10.6
Half-calcined dolomite $CaCO_3 \cdot MgO$	Real CND, pH 4.8÷8.1 Mn ≈ 0.645 mg/L	Column testing, 6 months 203g material 20°C, 18mL/h, HRT=6h	≥ 90% Mn removal pH 6.7÷9.82 Mn ≈ 0.052 mg/L
Half-calcined dolomite $CaCO_3 \cdot MgO$	Synthetic CND, pH 7 850 µg As (V)/L	Batch testing, 48h Solid: liquid ratio 1% 20°C, 500 rpm	[As] BDL after 8h Q_{max} = 820 µg As/g
Half-calcined dolomite $CaCO_3 \cdot MgO$	Real CND, pH 6.5÷7.8 196 µg As/L	Column testing, 112 days 120g material 20°C, 0.5 mL/min, HRT=2 h	0.5÷1.9 µg As/L
Raw eggshells $CaCO_3$	Real AMD, pH 2.25÷2.62 Fe 219 mg/L Zn 1.61 mg/L Cu 0.7141 mg/L	Batch testing, 2 h Solid: liquid ratio 1% 20°C, 300 rpm	pH 5.92 Fe 85.6 mg/L Cu 0.108 mg/L Zn 3.18 mg/L
Calcined eggshells, 800°C 80% $CaCO_3$, 20% $Ca(OH)_2$		Batch testing, 2h Solid: liquid ratio 0.5% 4°C, 20°C, 300 rpm	pH 6.66÷6.84 Fe ≤0.12 mg/L Zn ≤0.367 mg/L Cu 0.0109 mg/L
Calcined eggshells, 900°C 50% $CaCO_3$, 50% $Ca(OH)_2$		Batch testing, 2 h Solid: liquid ratio 0.3% 4°C, 20°C, 300 rpm	pH 6.89÷9.22 Fe <0.01 Zn ≤0.022 mg/L Cu ≤0.0091 mg/L
Raw paper sludge	Real CND, pH 7.3÷7.7 Zn 9.72÷13.42 mg/L	Batch testing, 24 h Solid: liquid ratio 1%, 20°C, 300 rpm	pH 7.4 Pb 0.0924 mg/L Zn 1.99 mg/L
Calcined paper sludge		Pilot testing 18 L, 0.5 h Solid: liquid ratio 0.05%, 20°C	pH 8.8 Pb <0.01 mg/L Zn <0.01 mg/L

To comparatively evaluate the efficiency of raw vs. calcined eggshells, a gold mine AMD (pH 2.25÷2.62) was employed. The AMD contained significant concentrations of Fe (219 mg/L), Zn (1.61 mg/L) and Cu (0.7141 mg/L). The raw eggshells raised the pH of the effluent, and significantly (60%) reduced the concentration of Fe. However, the treated effluent did not conform with Québec and Canadian regulations. In contrast, calcined eggshells succeeded in producing an effluent that did conform with Québec and Canadian regulations, after two hours of contact time, at 4°C and 20°C (Table 1). Moreover, calcined eggshells were characterized by XRD after the treatment of the AMD, and gypsum was identified and quantified in a significant amount (Table 2). Therefore, sulfate (SO_4^{2-}) was also treated.

Table 2: Post characterization XRD analysis of eggshells effective for AMD treatment

	Crystalline phase, %			Amorphous phase, %
	Total	$CaCO_3$, %	$CaSO_4 \cdot H_2O$, %	
Calcined eggshells, 800°C, 0.5%	71.1	40.4	59.6	28.9
Calcined eggshells, 900°C, 0.3%	69.7	45.2	54.8	30.3

Paper sludge was calcined at 500°C, 600°C, 700°C, 800°C and 900°C, for six hours (Jha et al., 2006). Thereafter, to comparatively evaluate the efficiency of raw vs. calcined paper sludge, a Zinc mine CND (pH 7.3÷7.7) was employed. It was noticed that although the raw paper sludge significantly (80%) reduced the concentration of Zn, the final effluent did not conform with Québec and Canadian regulations. Moreover, for the solid: liquid ratio of 1%, a non-negligible concentration of Pb was measured in the final effluent (0.0924 mg/L). Consequently, increasing the solid: liquid ratio was not considered for enhancing Zn removal (to achieve the effluent conformity). In contrast, paper sludge calcined for six hours at 700°C produced an effluent that did conform with Québec and Canadian regulations, after 30 minutes of contact time, in pilot testing (18 L), for a solid: liquid ratio of 0.05% (Table 1).

It can be observed that all materials presented in this paper show significant improvement of their efficiency for mine drainage treatment, by calcination, compared to raw materials.

For the case of dolomite, conversion of $MgCO_3$ into MgO enhances its neutralizing capacity and increases the effluent's pH, which is an important parameter for Mn removal (Calugaru et al., 2021a). Moreover, CO_2 elimination enhance porosity and specific surface (Calugaru et al., 2016), calcite availability, and therefore As removal (Salameh et al., 2015; Braghiroli et al., 2020). It is also notable that for dynamic (column) testing, dolomite rocks (diameter 0.5 cm) were employed, which is interesting for a passive treatment, whereas for batch testing, dolomite was used as fine powder.

In the case of eggshells, one hour of calcination at 800°C led to the decomposition of 20% of the calcite ($CaCO_3$). Therefore 20% of CO_2 was liberated into the atmosphere, which is inferior when compared to the CO_2 liberated in the complete decomposition of the calcite. The resulting material was able to treat the AMD in both cold and mild temperature conditions. Moreover, a waste was used. Also, for use in a dynamic regime, the crushing of eggshells is not necessary as it can reduce hydraulic conductivity.

Paper sludge underwent the most important mass loss by calcination, among the materials evaluated in this study. Its calcination at 700°C produced only 1.78% ash, because paper sludge had 70% humidity and contained 86% organic matter. Therefore, ≈ 7% ash could be obtained, if two weeks of air drying are allowed before calcination of the paper sludge. The ash produced showed a good adsorption for Zn, while the solid: liquid ratio employed (0.05%) led to a very low amount of treatment sludge, which settled fast. Moreover, a waste generated in high amounts and having few opportunities for recovery was used.

Conclusion

Calcination can greatly improve the efficiency of different waste and underused materials for mine drainage treatment. However, field scale testing as well as technical-economic analysis still have to be done, considering transport cost, calcination cost, mine water treatment cost, and sludge management. The global ecological footprint of employing calcined waste for mine water treatment should be compared with that of engineered materials. Moreover, calcination enhances the mechanical and chemical stability of waste, while products are safe to handle. Employing readily available waste also reduces exploitation of natural resources. Therefore, calcined waste and underused materials could be considered as green alternatives for mine water treatment in batch or in dynamic regime, for active or passive treatment, post-closure and restoration, in multistep treatment, or included in a multicomponent/multistep treatment system such as biofilter, barrier, drain, et cetera.

Currently, a project is ongoing at CTRI. Passive treatment solutions including thermally activated minerals and waste are being evaluated for the treatment of an exfiltration AMD issued from the passive treatment system already in place. Filters and sulfate-reducing passive biofilters composed of various materials at various proportions are being evaluated at laboratory scale (batch and column testing), to determine their hydraulic residence time and life time. Technical-economic analysis will be performed, and then the best option will be applied at field scale.

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Complete Nitrate Removal Using a Novel Ion Exchange and Encapsulated Bacteria System

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Abstract

Nitrate pollution is a serious problem across industries, and the severe ecological damage that can occur when discharging to sensitive waterways has led to many regions of the world mandating strict nitrate discharge limits of 1 mg/L. Traditional water treatment methods can struggle to meet these low levels, with membrane solutions such as reverse osmosis reaching the level, but creating a difficult to manage concentrated nitrate brine, and other methods such as wetlands requiring large footprints. This paper introduces Clean TeQ Water's BIONEX™ technology, which is specifically designed to selectively remove nitrate from water to achieve very low concentrations, with a small footprint and minimum waste production.

BIONEX™ is a combination of our Continuous Ion Filtration (CIF®) technology to concentrate nitrate into a brine stream, which is treated by our proprietary lens encapsulated bacteria, BIOCLENS®. The CIF® stage removes inorganic nitrates to <1 ppm consistently, and the movement of resin ensures there are minimal effects of fouling, which is a limiting factor for using batch ion exchange systems. This is particularly the case for waste waters, where bacteria and sludge can infiltrate systems. BIOCLENS® treated brine is then filtered and returned for regeneration. A small waste flow is typically purged from the brine loop, usually less than 1% of the feed flow, and in most cases can be returned upstream to the front of the wastewater treatment plant, or blended with the product where possible, to enable a zero liquid discharge approach to be achieved.

In recent piloting of BIONEX™ in China, NOx-N in the feed was consistently reduced from 20 mg N/L to <1 mg N/L, and the NOx-N in the brine was reduced from 200 mg N/L to <20 mg N/L, a level suitable to reuse the brine to regenerate the ion exchange resin. These results form the basis for large-scale water treatment plants that can polish nitrate to very low levels, such as the 12 MLD plant that Clean TeQ Water is currently installing in China.

Introduction

Effects of nitrate

Nitrate is often present in waters associated with mining as a result of blasting activities using ammonium nitrate. It can also be present in groundwater and surface water in agricultural areas from fertilizer use, and is often present in municipal and industrial waste streams following the aerobic degradation of ammonia. Even moderate nitrate concentrations can lead to eutrophication of natural water bodies, causing algal blooms that severely harm the aquatic environment. In 2020 alone, the Harmful Algae Event Database (HAEDAT) reported almost 600 harmful algal bloom events globally (UNESCO, 2021). Moreover, the USA's Environmental Protection Agency's 2013–2014 National Rivers and Streams Assessment rated 43% of rivers and streams as having poor quality in regard to their nitrogen content (EPA, 2020).

Infant methemoglobinemia (blue baby syndrome) has well-established links to high nitrate levels and is one of the main reasons for nitrate concentration limits being set for drinking water around the world (Shuval and Gruener, 2013). Recent literature reviews of over 30 global epidemiologic studies have found increasing links to various forms of cancer, even when concentrations are below the current drinking water limits (Ward et al., 2018). For these reasons, governments and water authorities around the world are placing increasingly strict regulations on nitrate concentrations in waters for discharge to the environment, and for drinking. These stricter limits are appearing at the same time as nitrate levels in water-stressed areas are increasing, leading to a need to urgently upgrade water treatment infrastructure (Abasscal et al., 2022). For too long, nitrogen issues have been growing unnoticed, and governments and authorities are now acting to avoid long-term knock-on effects to their critical and ever-declining clean water resources.

Conventional nitrate removal methods

Conventional bacteria treatment methods such as CAS (conventional activated sludge), BNR (biological nutrient removal), MBBR (moving bed bio-reactor), and MBR (membrane bio-reactor) can struggle to reduce effluent nitrate concentrations below 1 mg/L, especially in cold climates (Magdum and Kalyanaraman, 2017). While reverse osmosis and ion exchange can treat these concentrations, they produce large volumes of waste that can be difficult to manage. Wetlands can be effective for nutrient reduction, but have extremely large footprints and can struggle to meet the nitrate limits at low temperatures.

Clean TeQ Water's BIONEX™ technology is specifically designed to deal with these nitrate issues in an environmentally friendly and cost-effective manner. By combining two of our innovative water treatment technologies, continuous ionic filtration (CIF®), and lens encapsulated bacteria (BIOCLENS®), the process electively removes nitrate/nitrite from water sources and converts it to harmless nitrogen gas.

Continuous ion exchange

Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange, while simultaneously performing physical filtration, tolerating suspended solids in the feed. The ion exchange resin is periodically moved around the system for reconditioning. Additional information about CIF® can be found in the Appendix of this paper.

Encapsulated bacteria

Clean TeQ Water's BIOCLENS® lenses contain living bacteria that are encapsulated in a stable, porous polymer gel matrix. As the lenses are stirred in a reactor, water and dissolved impurities diffuse through the lenses and encounter the bacteria, where targeted reactions occur. Specifically selected bacteria with high nitrification or denitrification activity are used in the lenses, resulting in high removal activity. The encapsulation protects bacteria in saline environments and from potentially toxic compounds in the feed.

The compact and regulated conditions of the bioreactor also promote complete reactions, which means potentially lower nitrous oxide emissions. A diagram of a BIOCLENS® lens is shown in Figure 1.

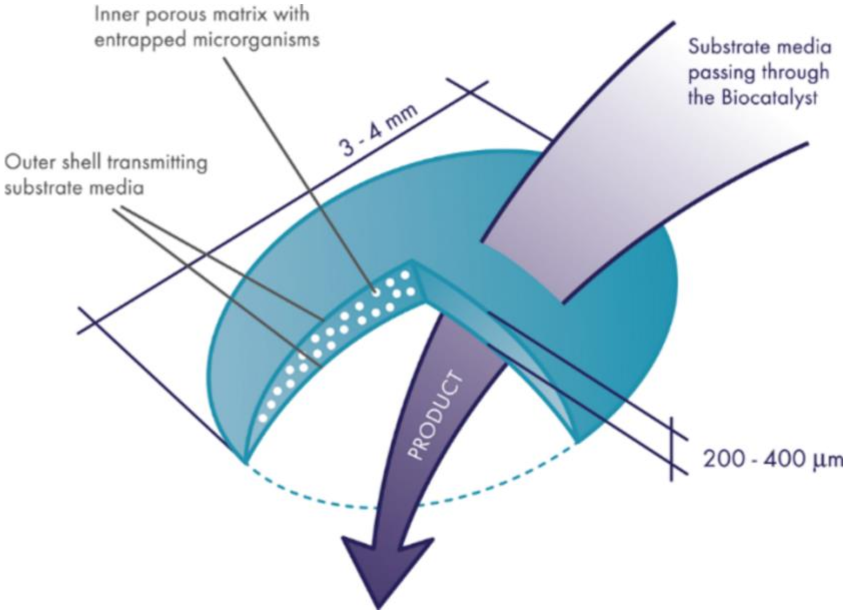

Figure 1: Diagram of a BIOCLENS® lens

Since the bacteria are encapsulated, as opposed to being free cells as in traditional treatment technologies, they remain protected in harsh environments and can cope with the high ammonia and nitrate concentrations and osmotic pressures that are seen in salt-laden brines. Testing has shown that extremely high activity rates are still observed in the presence of high salt concentrations of 50,000 mg/L.

BIONEX™ technology

BIONEX™ combines CIF® and BIOCLENS® in a complementary fashion to remove nitrate and convert it to nitrogen gas. The process diagram of a BIONEX™ system can be seen in Figure 2. The concentrated nitrate brine stream from ion exchange resin desorption is treated by lens encapsulated bacteria, typically removing nitrate to under 10 mg/L. The brine is then filtered, and returned to the desorption column, where it is reused for resin regeneration.

Less than 1% of the feed flow is purged from the brine loop in order to prevent build-up of contaminants. The waste stream typically has a TDS of 10,000 mg/L with 10 mg/L nitrate. In most cases, the small waste stream can either be returned upstream to the front of the wastewater treatment plant and/or can be blended with the product as a zero liquid discharge (ZLD) solution.

Salt usage is minimized since most of the brine is reused and not discharged. This is often a downfall of batch ion exchange processes, where high volumes of nitrate-bearing brines are discharged from the system and need to be managed. The recycling of the brine reduces the operating expenditure of the process with typical treatment costs of US$0.10–0.15/$m^3$ water treated, compared to typically US$0.15–0.20/$m^3$ for conventional ion exchange and reverse osmosis, and US$0.40/$m^3$ for biology.

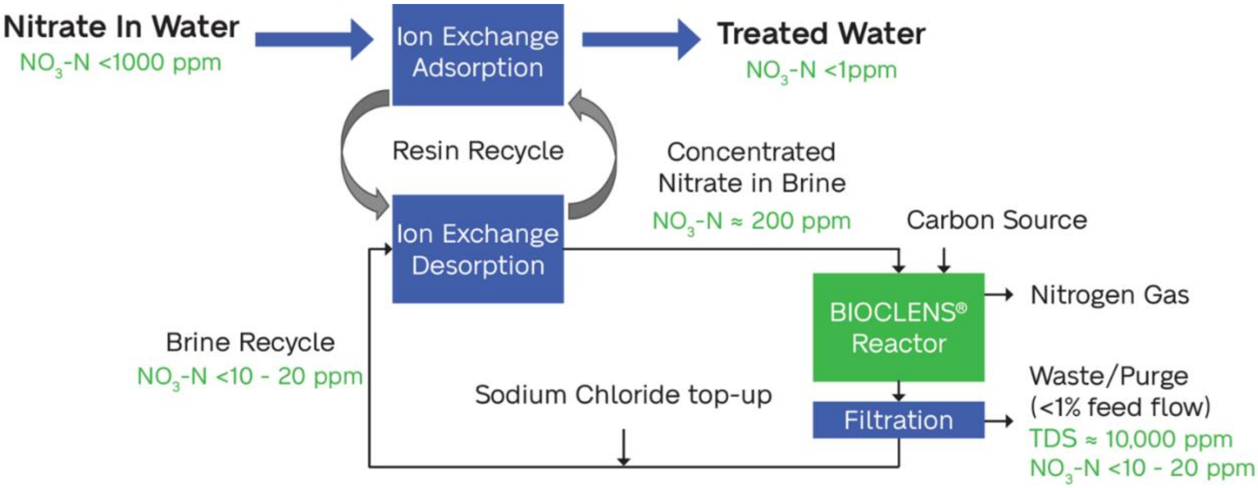

Figure 2: BIONEX™ flowsheet

Piloting methodology

Initial laboratory testing

A range of laboratory-scale experiments were initially undertaken to assess the performance of BIOCLENS® in relation to a range of operating conditions such as temperature, hydraulic residence time, salinity, pH, dissolved oxygen, mass-to-volume ratio of catalyst, carbon source type, and carbon-to-nitrogen dosing ratio. Results have shown that activity rates of the biocatalyst are consistently high, depending on influent nitrogen levels, and at low levels of catalyst loading can yield even higher activity rates of greater than 5,000 mg NOx/kgh, which is otherwise unheard of in conventional technologies.

Further process development and testing that we carried out has resulted in the ability of BIONEX™ to be tuned to provide a unique sulfate desorption step to ensure low nitrate levels can be maintained consistently when sulfate-to-nitrate ratios in the feed are high, enabling a high degree of nitrate polishing to be sustained during long-term operation, without producing any additional waste.

Pilot plants

A pilot-scale project was carried out in Taiping, China, treating up to 100 kL/d of industrial wastewater containing 15 ppm NO3-N and reducing it to less than 1.5 ppm. For this plant a fixed-bed ion exchange system was used, and the waste brine was treated with lens encapsulated bacteria. It was found that the fixed bed resin quickly suffered from extensive fouling and the flow was severely restricted.

A second pilot plant has been operating in Tianjin, China from early 2021 to provide proof of concept to the client whose current wetland treatment plant was unable to achieve <3 ppm nitrate concentrations. The pilot plant shown in Figure 3 currently treats up to 100 m^3/d and consists of a CIF® plant, and two stages of BIOCLENS® reactors. A proprietary self-cleaning screen keeps the lenses within the reactor, while allowing treated water to pass through (right of Figure 3). The bioreactors have a two-hour residence time at 25°C. Carbon dosing is controlled to optimize the activity of the lens encapsulated bacteria reactors. The pH and temperature of the system was controlled automatically during operation.

Figure 3: Photograph of the pilot plant equipment, CIF® (left), BIOCLENS® reactors (middle), self-cleaning screen (right)

Results and discussion

The results in Figure 4 show the nitrate is consistently removed to less than 1 ppm (undetectable levels), apart from three instances during periods of maintenance/shutdown. This resulted in a brine containing 200 ppm nitrate being fed to the lens encapsulated bacteria reactors.

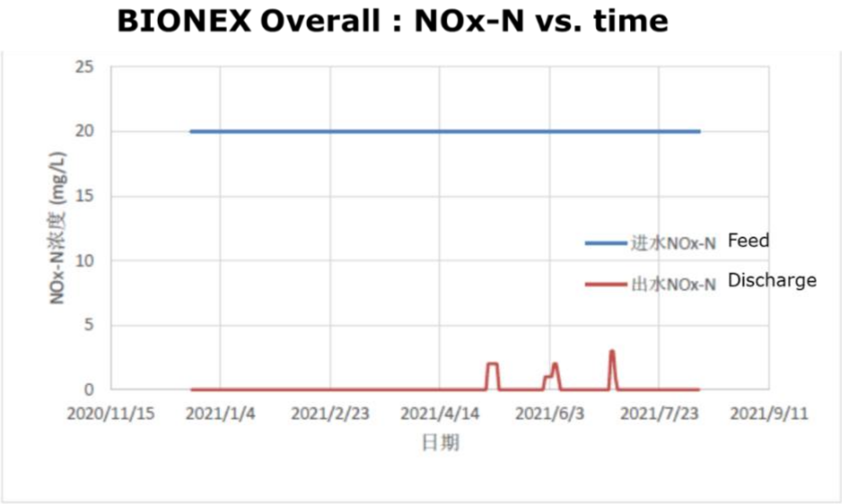

Figure 4: Feed and effluent nitrate concentrations of the pilot plant

Figure 5 shows the activity of the lens encapsulated bacteria reactors over time. After a few days for bacteria to acclimatize from cold storage, the two-staged reactor system consistently removed nitrate in the desorption brine to <10 ppm, which allows for efficient regeneration of the loaded resin in the continuous ion exchange system. The two-stage system was optimized by reducing the carbon-to-nitrogen ratio, with the activity rates seen across both reactors peaking at around 1,000 mg NOx-N/kgh at higher carbon levels.

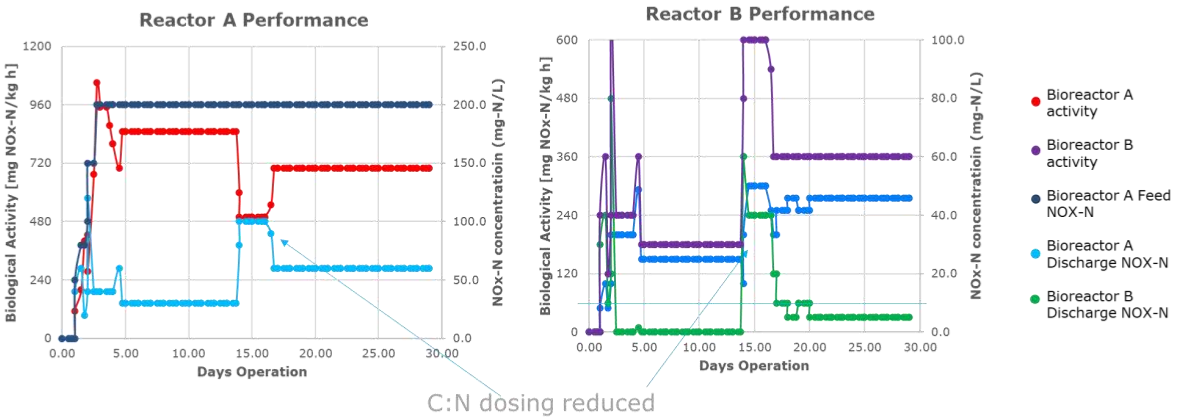

Figure 5: Biological activity of BIOCLENS® reactors during piloting

Piloting confirmed that the BIONEX™ system was able to consistently achieve <1 ppm nitrate in the effluent, and that lens encapsulated bacteria removes sufficient nitrate from the brine for it to be reused with minimal salt top-up required. These results form the basis for large-scale water treatment plants that can polish nitrate to very low levels with low chemical consumption, low waste production, and small footprints.

Current applications

Clean TeQ Water is currently delivering a flagship first-of-its kind 12 MLD BIONEX™ plant in Ordos, Inner Mongolia, China, which will reduce the total nitrogen from the wastewater treatment plant effluent from a coal mine from 5 ppm to less than 1 ppm. As of the first of March 2022, the plant is in the hot commissioning phase. A photo of the plant can be seen in Figure 6.

Figure 6: Photo of the BIONEX™ nitrate removal plant in Ordos, China

BIONEX™ has the potential to be the missing piece for existing water treatment plants looking to intensify their nitrate removal capacity. Meanwhile, Clean TeQ Water's BIOCLENS® technology also offers the ability to retrofit existing treatment systems, or to be used on its own to treat concentrated nitrogen-polluted feed waters. It can be enclosed within existing activated sludge reactors to enhance ammonia or nitrate removal.

Conclusions

Novel technologies such as BIONEX™ can offer superior treatment to achieve stricter regulatory requirements (<1 ppm TN) for discharge to the ocean and surface water, with biological treatment able to manage highly saline brines with minimal resource consumption and waste production. BIONEX™ plants typically operate with >99% recovery, with significantly lower waste and operating costs than batch ion exchange or reverse osmosis plants, meaning brine evaporation ponds and liquid waste handling can be eliminated when a zero liquid discharge approach is possible.

The results of piloting have major implications for mine water treatment, with BIONEX™ providing cost-effective nitrate removal with a small footprint. The technology allows users to meet ultra-low nitrate concentrations that are often mandated by regulating bodies with minimal resource consumption and waste production. In addition, it is a key enabler for reuse of wastewater for irrigation, industrial, mining, agriculture, and aquaculture purposes, reducing demands on clean drinking water, while reducing harmful algal blooms and eutrophication of sensitive water bodies.

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Appendix

Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange, while simultaneously performing physical filtration, tolerating suspended solids in the feed, and allowing for cheaper reagents such as sulfuric acid and lime to be used. These usually cannot be used in conventional batch ion exchange systems since the precipitates that form cause the system to block up during desorption. CIF® is also more resistant to resin bed fouling compared to conventional ion exchange approaches since the ion exchange resin in periodically moved around the system. Higher removal efficiencies are also achieved in CIF® due to the counter-current movement between the feed solution and ion exchange resin. The system can also tolerate up to 150 mg/L of suspended solids in the feed, and perform physical filtration if required.

In CIF®, ion exchange resin is continuously moved around the system for regeneration. Water treatment occurs in the adsorption column, which uses a moving packed bed of ion exchange resin. It can be likened to the continuous sand filtration process; however, the ion exchange resin continuously removes dissolved ions through ion exchange while simultaneously filtering solids if required. CIF® consists of a series of vertical columns, as seen in Figure 8, with one column treating the water, and the rest used to recondition the ion exchange resin as part of a continuous process.

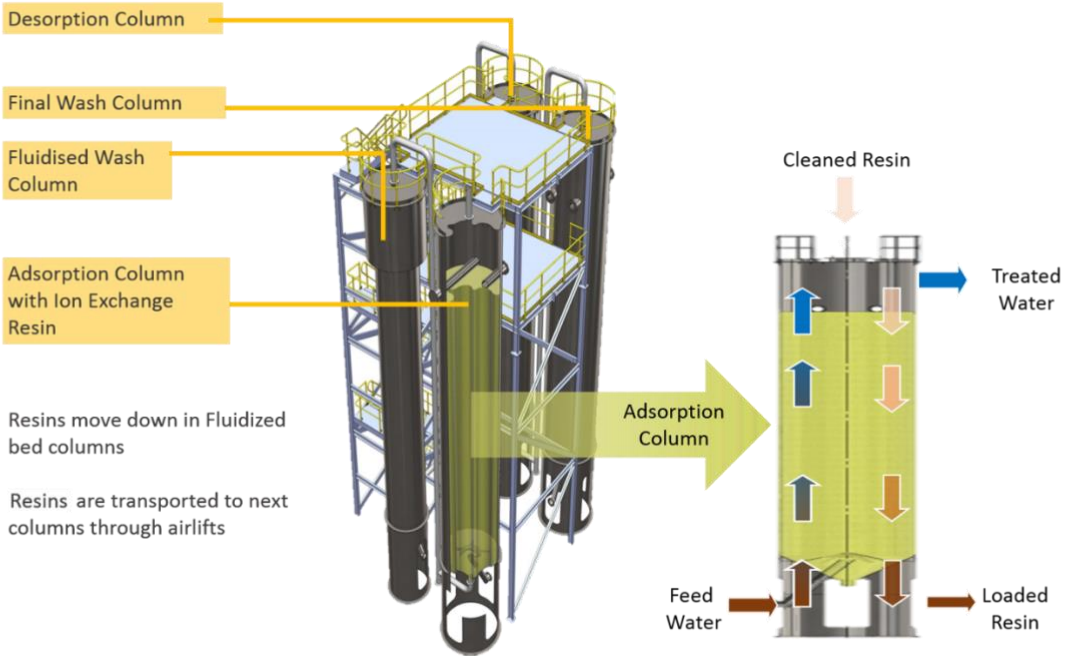

Figure 7: Diagram of a typical CIF® system

A Novel Photocatalytic Approach to Passive Mine Water Treatment

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Introduction

Vast amounts of mining process-affected water are produced during mine operations and closure, which may have an impact on the local environment, community health, and overall sustainability due to contaminants, odours, and fugitive emissions. Typically, active mine effluent and tailings treatments require chemical additives or separation technologies that are capital and energy intensive. These methods are often operationally complex and require a high degree of maintenance oversight to operate successfully. Alternative passive-treatment technologies, such as wetlands, offer solutions but are not well integrated with existing active treatment methods and are unable to provide the high-strength chemical oxidation required to effectively treat contaminants and emissions of concern.

To this end, H2nanO Inc. has developed SolarPass, a novel buoyant photocatalytic treatment system for passive advanced oxidation of dissolved contaminants. This treatment system naturally forms a floating reactive barrier that also intercepts and treats volatile emissions. The SolarPass system can be deployed and recovered in-situ for off-grid, high-strength oxidative treatment of recalcitrant mining contaminants without the need for chemical or electrical inputs. Further, SolarPass can be continuously operated without gas handling, operator intervention, or adsorbent regeneration/disposal.

Previous bench-scale research has validated this floating solar-photocatalytic process for recalcitrant naphthenic acids treatment in mining process-affected water (Leshuk et al., 2018). In addition, photocatalysis has been successfully demonstrated for the treatment of mining wastewater and tailings applications targeting ammonia (Altomare et al., 2012), cyanide (Chiang et al., 2003), and selenium (Holmes et al., 2022). Building upon previous work, H2nanO further validated the efficacy of the SolarPass system for two in-situ mine treatment applications: the bench-scale (1 L) treatment of organoselenium and the pilot-scale (500 L) treatment and mitigation of reduced sulfur emissions from a mining tailings pond containing anaerobic sludge.

Methodology

The preliminary evaluation of SolarPass for the oxidative treatment of selenomethionine as a representative organoselenium compound was performed at the laboratory scale (1 L) under artificial UV light, using solutions of 25 mg/L and 25 µg/L seleno-L-methionine in deionized water to accurately quantify the reaction products. Treatment experiments were also performed using a simulated mine-water matrix (Holmes et al., 2022). The organic fraction of selenomethionine was quantified using low-range chemical oxygen demand (COD) measurements, while the selenium species were quantified using ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS) by Brooks Applied Labs.

In addition, SolarPass was validated for the treatment and containment of volatile reduced sulfur emissions using an outdoor pilot-scale system (500 L) for water containing biogenic H_2S from a tailings pond containing anaerobic sludge. Sulfurous compounds were tracked and quantified using in-field online measurements (electrochemical handheld sensors) and high-resolution laboratory analysis (colourimetric assays and inductively coupled plasma optical emission spectroscopy [ICP-OES]) to establish the effective conversion of volatile sulfurous compounds to sulfate.

Results and discussion

Organoselenium photocatalytic treatment results

The objectives of these experiments were to demonstrate an initial proof of concept for the photocatalytic treatment of selenomethionine at an elevated concentration, while confirming the selenium mass balance. Organoselenium compounds are significantly more toxic and bioaccumulative than Se(VI) for various aquatic biota (Lemly et al., 1993) and therefore, oxidative conversion of organoselenium to Se(VI) can significantly reduce the toxicity of selenium-containing effluents. Figure 1 presents the selenium speciation results during photocatalytic treatment and a control (UV exposure, no catalyst). The total selenium present (average of 9,828 ± 134.5 µg/L) matched the theoretical selenium added with the selenomethionine stock solution (10,000 µg/L Se) and remained constant during the experiment duration. Through photocatalysis, selenomethionine was treated from an initial concentration of 9,140 µg/L to 2.19 µg/L, demonstrating a >99.97% reduction in the initial selenomethionine concentration with conversion to 98.1% selenate. Compared to the photocatalytic experiment, the UV control (no catalyst) showed only a 9.4% decrease in the initial selenomethionine concentration, while receiving a similar UV dose. In addition, the selenate concentration in the UV control only increased by 63.7 µg/L compared to 9460 µg/L using SolarPass, validating that UV exposure is insufficient on its own to effectively treat selenomethionine.

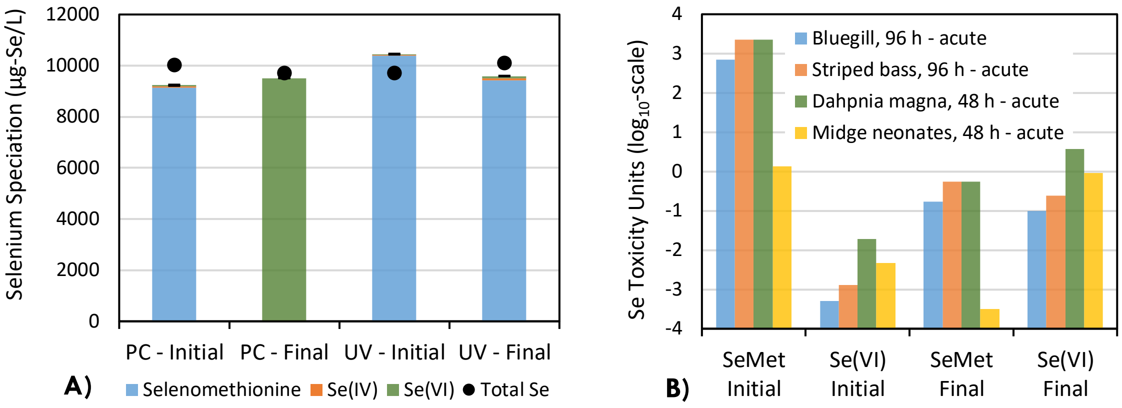

Figure 1: A) Selenomethionine photocatalytic (PC) treatment results compared to a UV control. B) Selenium species toxicity reduction results (toxicity units derived by normalizing Se concentration by LC50 values obtained from Lemly et al., 1993)

Based on reported selenomethionine toxicity (Lemly et al., 1993), the initial solution in this study exceeds the LC50 concentration for bluegill juveniles (96 h acute), striped bass fingerlings (96 h acute), *Daphnia magna* (48 h acute), and midge neonates (48 h acute). Except for *Daphnia magna*, the selenomethionine levels were converted to non-toxic levels of Se(VI) via photocatalysis. These results demonstrate that photocatalysis is an effective method for the elimination of selenomethionine by converting it to selenate and significantly reducing the bioavailability and toxicity of selenium-contaminated effluent.

Reduced sulfide treatment results from biogenic sources

At the pilot scale (500 L), the diurnal H_2S emissions were compared between two closed-cell reactors, one with the floating reactive barrier (FRB) and a bare control. To better elucidate the emissions blocking performance of the FRB at a larger scale, the initial aqueous sulfide concentration for both reactors was increased to 76 – 115 mg/L S^{2-}, approximately 4.5 times greater than the expected concentration in the mine tailings water. During this experiment there was a notable diurnal effect on the temperature profile and the H_2S emissions (Figure 2). Compared to the bare control, the FRB reduced H_2S emissions by >94% over the duration of the study, with negligible diurnal effects on the emission reduction. This proves that even during periods of low UV exposure the FRB is still an effective barrier for volatile sulfurous emissions. During this period, there was significant treatment of aqueous sulfide by either air oxidation in the control (55% decrease) or photocatalytic activity in the FRB reactor (71% decrease). Notably, while the FRB reactor reduced H_2S emissions by >95%, the decrease in the aqueous sulfide concentration proceeded at a rate 1.5 times faster than the air oxidation rate in the control.

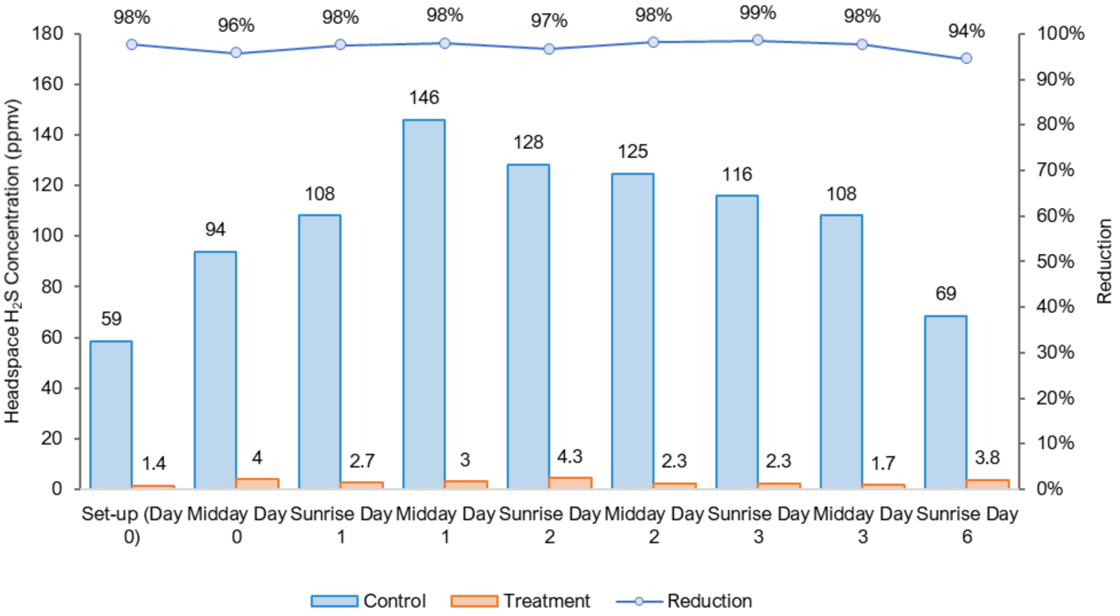

Figure 2: Field-scale headspace H_2S reduction results (control vs. treatment – day/night)

Conclusion

As a standalone process or as part of a larger treatment system, SolarPass is a promising low-cost platform for the photocatalytic treatment of mine water contaminants, including persistent organics, organoselenium, and sulfur compounds. Under laboratory-scale simulated solar conditions, SolarPass effectively eliminated selenomethionine via photocatalysis by converting the organoselenium into the less toxic and bioavailable selenate. Further, when demonstrated at pilot-scale, SolarPass effectively mitigated volatile sulfur emissions while providing simultaneous passive aqueous treatment. These results demonstrate that SolarPass provides an effective solution for passive tailings management and can address diverse challenges in mining-impacted waters.

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Biogeochemical Attenuation of Selenium and Nitrate in Mine Contact Waters

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Abstract

Conuma Resources Ltd. (Conuma) operates three mines that produce steelmaking coal. These mines are in northeast British Columbia, Canada, in Treaty 8 Territory. The main parameters of potential concern (POPC identified in the mine contact water that require treatment include selenium (Se) and nitrate ($N0_3$-). Selenium originates primarily from weathering of exposed mine waste materials (i.e., waste rock), while nitrate is released via leaching of blasting residues associated with ammonium nitrate-based explosives. Elevated concentrations of these POPCs, particularly selenium, have the potential to impact the health of the aquatic ecosystem. To treat and reduce concentrations of Se and $N0_3$- in the mine contact waters, in-situ anaerobic semi-passive biological treatment systems, commonly referred to as biochemical reactors, (BCRs) were constructed. Design and operational controls that were incorporated in the mitigation measures included lateral water flow within the in-situ anaerobic bioreactors to allow for attenuation of Se and $N0_3$-. The results show evidence of effective denitrification (up to 100 %) with concentrations of $N0_3$- decreasing from 49 mg/L to <10 µg/L in the outflow of the anaerobic bioreactors. Selenium shows pronounced removal (up to 94%) with concentrations decreasing from ~200 µg/L to 20 µg/L. The reduction in Se concentration was accompanied by a shift in Se speciation from dominantly selenate (SeVI) to selenite (SeIV) and/or to elemental selenium via dissimilatory microbial reduction under anaerobic conditions. The data also suggest that Se remobilization via direct oxidation pathways may be occurring after the treated water has gone through the aeration process; however, the rate is too insignificant to be of concern. Collectively, the water chemistry results indicate that the biochemical reactors are an effective technology for the bioremediation of Se and $N0_3$- in coal mine affected waters under suboxic conditions. Optimization of the operational design of the biochemical reactors currently underway is expected to improve Se and $N0_3$- removal performance and achieve better outcomes of water treatment.

The engagement and involvement of First Nations in the design, implementation, and operation of water management systems, as well as environmental monitoring, is ongoing. Information gathered will be

shared in a coordinated manner through multiple forums, including the environmental monitoring compliance committee (EMCC).

Introduction

Discharges from coal mines into receiving waters downstream of mine sites are required to meet applicable ambient water quality guidelines for constituents of potential environmental concern (i.e., national, [CCME], federal [ECCC], and provincial). In British Columbia (BC), guidelines can be modified on site-specific bases into "in-stream" water quality objectives to address specific receiving water issues (e.g., high background). Science-based environmental benchmarks (SBEBs) are developed into Site Performance Objectives (SPOs) that are specified in environmental management permits and are established with associated monitoring frequency and reporting requirements (BCMOE, 2016).

Selenium (Se) and nitrate (NO_3) are parameters of potential concern (POPC) at coal mine operations throughout the world. Selenium is a naturally occurring substance and an essential element required for the health of humans, animals, and some plants. Selenium is released to the environment via weathering of exposed surfaces of mine waste materials (e.g., waste rock, pit walls, coarse rejects, and tailings). Nitrate is released primarily via dissolution of blasting residues associated with ammonium nitrate-based explosives (Mahmood et al., 2014).

In the environment, Se is present in five oxidation states including Se(IV), Se(VI), Se(0), Se(-1) and Se(-II). Among these species, the reduced forms of selenium (i.e., Se(0), and Se(-II)) are insoluble in water and less bioavailable, while selenate (SeO_4^{2-}) and selenite (SeO_3^{2-},) are highly soluble oxyanions and are predominant in most industrial wastewaters and mine contact waters. Both selenate and selenite are bioavailable and have the potential to bioaccumulate.

Several technologies, including physical, chemical, and biological, are available for selenium and nitrate treatment. Selenate removal has been reported to be typically not feasible using conventional physical/chemical technologies. Removal of selenite can occur using iron co-precipitation, a conventional physical/chemical technology. However, meeting stringent regulatory discharge limits (in µg/L) may not be possible (NAMC-SWG, 2020). Over the past two decades, technology development for selenate removal has progressed and biological treatment has emerged as the most promising method (Golder Associates, 2020). Microbial reduction of Se oxyanions to insoluble elemental selenium has been applied successfully for removal of selenium from wastewater or process water using diverse types of bioreactors (Rittmann, 2006; van Hullebusch et al., 2003).

This paper presents data derived from using anaerobic biochemical reactors (BCRs) for the in-situ treatment of selenium and nitrate in contact water from the Brule Mine. BCRs are a proven and effective biological technology that are used as an alternative to active mechanized physical/chemical treatment and engineered water treatment plants to meet SPOs. In addition to their effectiveness in removing selenate, the in-situ BCRs are cost effective.

Methods

Site description and BCR technology

Consistent with other proponents within the mining industry, Conuma has implemented BCRs as the treatment systems of choice to treat and remove nitrates and selenium from mine contact water before discharge into the environment. In the more than five years of its operation of the Brule mine, Conuma has continued to develop and implement progressive generations of BCRs with the help of industry experts and third-party qualified professionals who have worked successfully with BCRs in North American mining applications. The progression of BCR treatment technology at Brule is consistent with other mining operations in North America, as best practices are adapted to the conditions in Northeast British Columbia.

BCRs utilize organic substrate to create an environment where microbes consume and scavenge oxygen beginning with free oxygen, then nitrates, and then reduce selenate to selenite and eventually to elemental selenium. BCRs are generally operated as a gravity downflow system, although upflow configurations are also possible with hydraulic retention time being a key design parameter. BCRs generally have lower capital and operational costs, although they require daily interaction and adjustment of the systems. With proper design, BCRs can operate with minimal energy or chemical inputs, and can operate reliably in cold climates without external heat inputs. Conuma currently operates two BCRs at Brule mine (BCR1 and BCR2). For the purposes of this paper, only BCR1 is discussed.

The BCR1 treatment system at Brule mine was initially designed and constructed in 2015. In 2017, BCR1 was optimized by improving composition and layering of the treatment media. The reactor cell media installed in 2017 for BCR1 consisted of three distinct layers of limestone, sawdust and wood chips, and hay. These two previous BCR1 designs utilized the "horizontal flow" system, where water entered BCR1 through an influent manifold pipe situated in the upper interval of the BCR and nested in mixed media. Water then flowed horizontally through a treatment media layer across the reactor, then downward into an underlying limestone drain layer, and discharged through a manifold situated within the limestone layer. Water levels within BCR1 were controlled by stop logs located within the Agridrain. From the Agridrain, the effluent flowed into an aeration pond. Although this system was progressively more functional, uniformity of influent flow (and thus effectiveness of treatment) posed operational challenges and there was increased evidence of water forming preferred flow paths, and thus not receiving full treatment.

As a result, BCR1 was optimized for the second time by installing a bottom-up vertical flow system that addressed the flaw observed in the horizontal flow system. Conuma retained Navigator Environmental & Technical Services to optimize BCR1 and incorporate design improvements recommended by third-party independent reviewers who completed an evaluation of BCR Technology and its application to cold climates.

In October 2021, BCR1 was drained. This is an anticipated and planned maintenance function for all BCR and indeed most active treatment systems. The spent media was removed and ultimately replaced. The following design improvements were implemented:

- the gravel bed on the bottom of the BCR was extended the full length of the BCR;
- an extensive underdrain system was installed in the gravel bed;
- a system of standpipes was installed to introduce water into the BCR at the top of the treatment media in order to conserve heat and provide uniform flow across the BCR;
- the underdrains were plumbed into manholes to collect treated water;
- new treatment media with substantially more wood fibre was carefully prepared and installed;
- new insulating hay was installed on top of the treatment media; and
- pumps were installed in the manholes to remove treated water from the system.

These changes converted BCR1 from a horizontal flow BCR to a vertical downflow BCR. This new configuration promotes more uniform flow and uniform treatment, limiting channelling of contact water and promoting uniform residence time. The changes were completed in mid-November 2021 and the first samples from the optimized BCR1 were collected on November 22, 2021.

In the optimized BCR1, water enters the BCR through an influent manifold pipe situated in the upper interval of the BCR and nested in mixed media (BCR1-IN). Water then flows vertically through a mixed-treatment media layer across the reactor and then downward into the underlying limestone drain layer. Treated water (i.e., effluent) discharges from BCR1 through Agridrain1 or is pumped from the manholes into an aeration pond. There the anaerobic effluent is aerated prior to discharge into the main sediment pond via an open channel into the southwestern corner (MSP-IN1). There it flows towards the discharge end of MSP (MSP-D) and then to the downstream receiving environment (Blind Creek), before reaching the Compliance point BC-01a.

Figure 1 shows the location of the BCRs, and Figure 2 presents the water management through the BCR and surrounding infrastructures. The breakdown of the organic media over time provides electron donors to support the development of reducing conditions required for the reduction of nitrate to nitrogen gas and selenium to SeO_4^{2-} and SeO_3^{2} and then to Se(0), which is precipitated within the BCR through microbially-mediated processes.

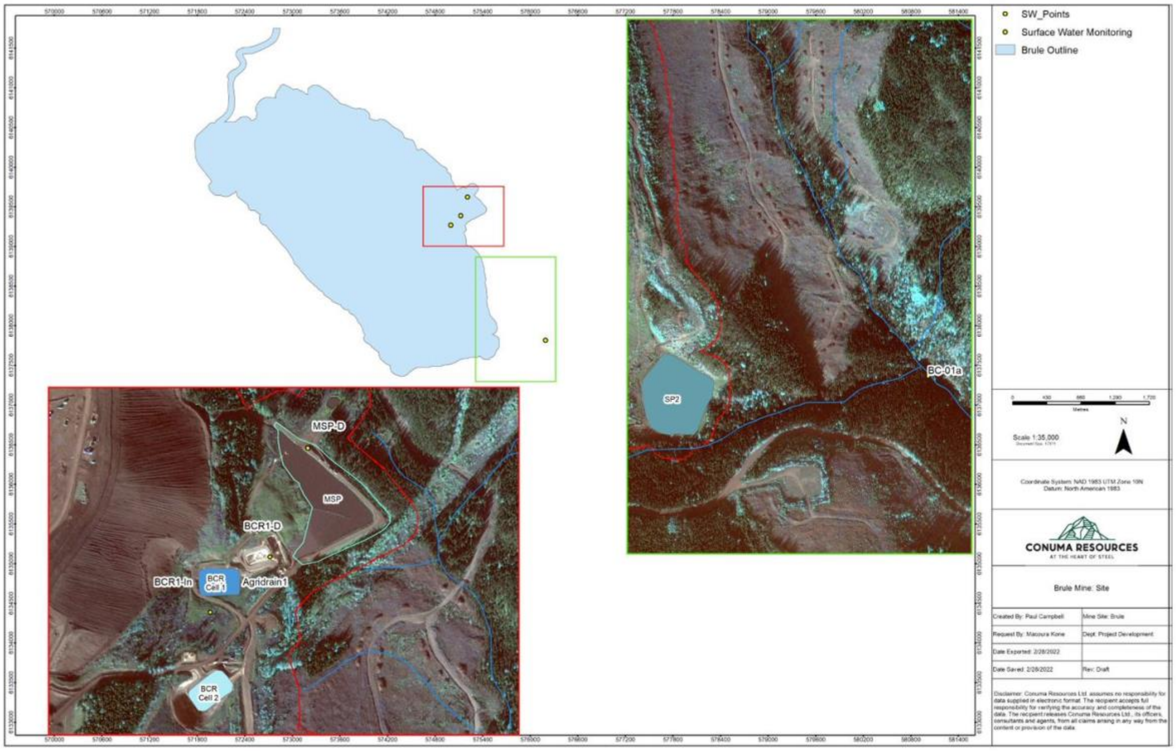

Figure 1: Location of the BCRs

Figure 2: Water management through the BCRs

Monitoring

Water samples were collected from the monitoring sites shown in Figure 2 and sent to an accredited laboratory for comprehensive analysis of geochemical parameters including physical parameters, nutrients, sulfide, anions, total/dissolved trace elements metals, and selenium species. Trace element concentrations were determined via inductively coupled plasma mass spectrometry (ICP-MS), while anions were analyzed via ion chromatography. Solid and water samples were analyzed for microbial community by DNA sequencing and quantification of specific bacteria by qPCR tests.

Results

The results are presented in the following sections.

Table 1: Hydrochemistry of influent, effluent and receiving waters

	DO (mg/L)	ORP (mg/L)	pH	Se (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Ammonia (mg/L)
BCR1-In	0 –15	0 – 176	6 – 8	0.009 - 0.199	0.013 – 49.2	317 - 712	246 – 605
Agridrain	<0 – 5	-482 – 39	6 – 8	0.002 – 0.1	0.001 – 28	306 - 721	288 – 732
BCR1-D	<0 – 18	-187 – 169	7 – 9	0.006 - 0.089	0.001 – 28.7	322 - 728	294 – 802
BC-01a	0 –124	0 -169	8 -9	0.001 – 0.061	1.01 – 47.9	41 – 618	116 – 530

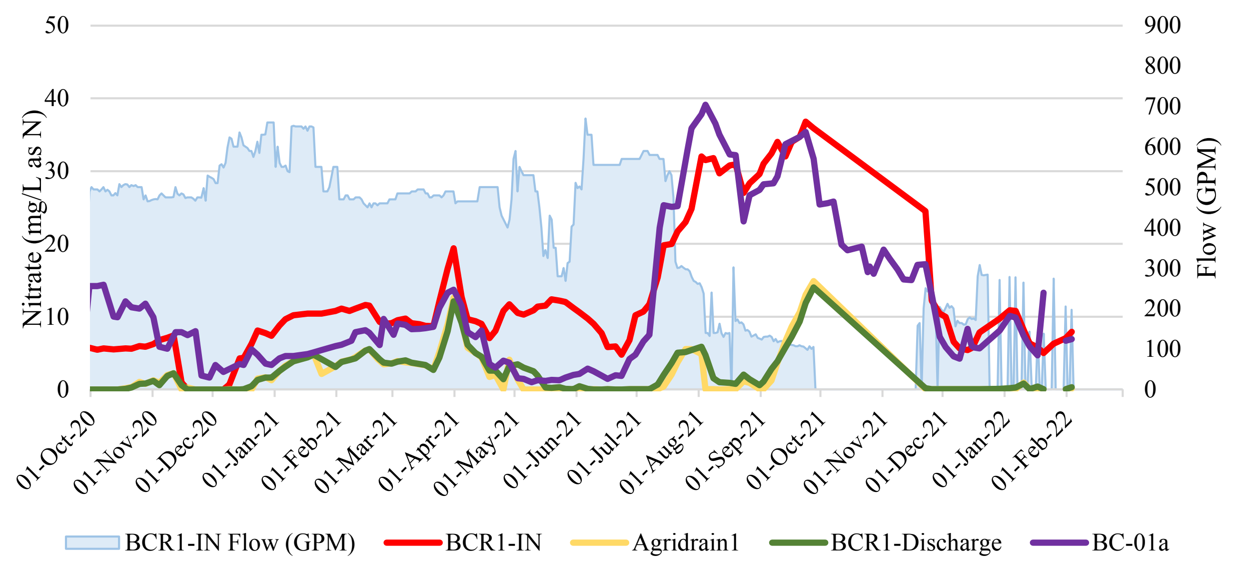

Figure 3: Time series of nitrate in influent, effluent and receiving environment

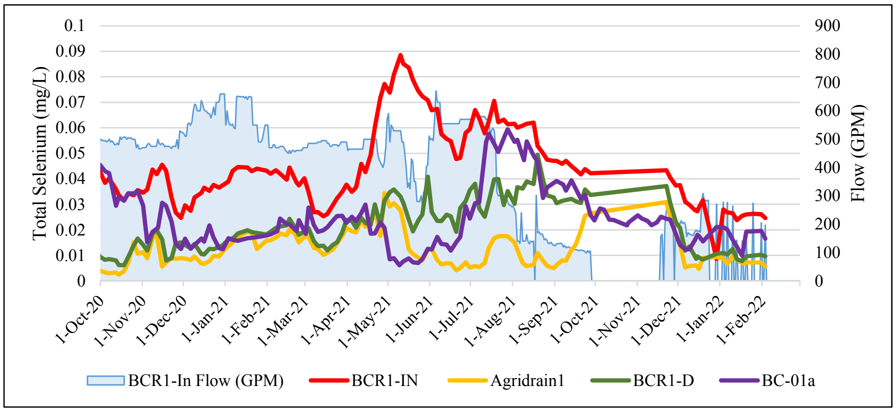

Figure 4: Time series of total selenium in influent, effluent, and receiving environment

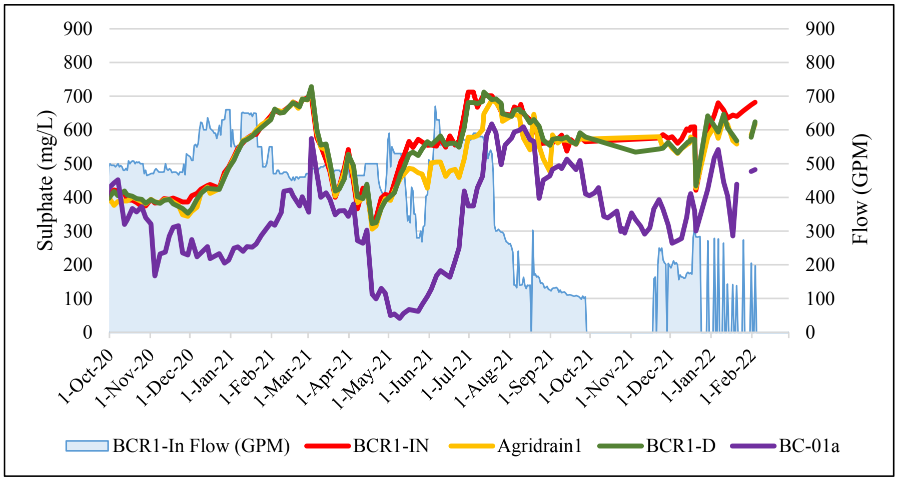

Figure 5: Time series of sulfate in influent, effluent, and receiving environment

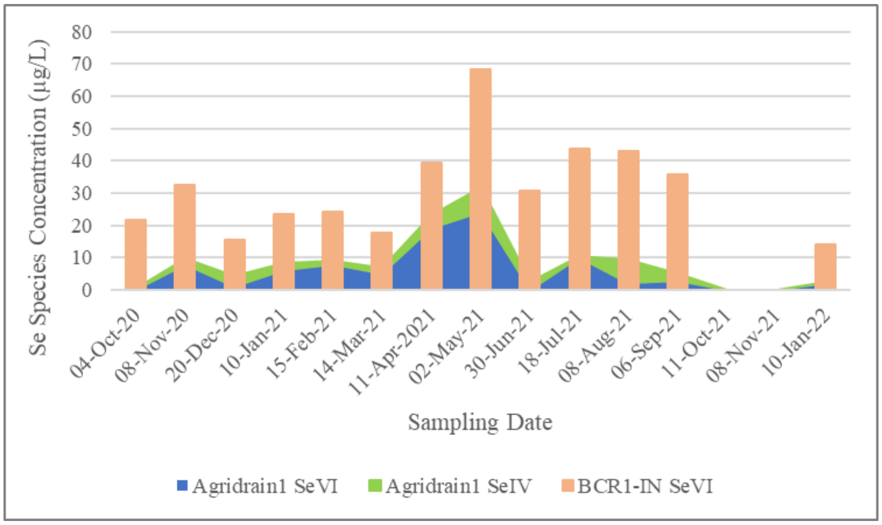

Figure 6: Selenium speciation species in influent and Agridrain effluent

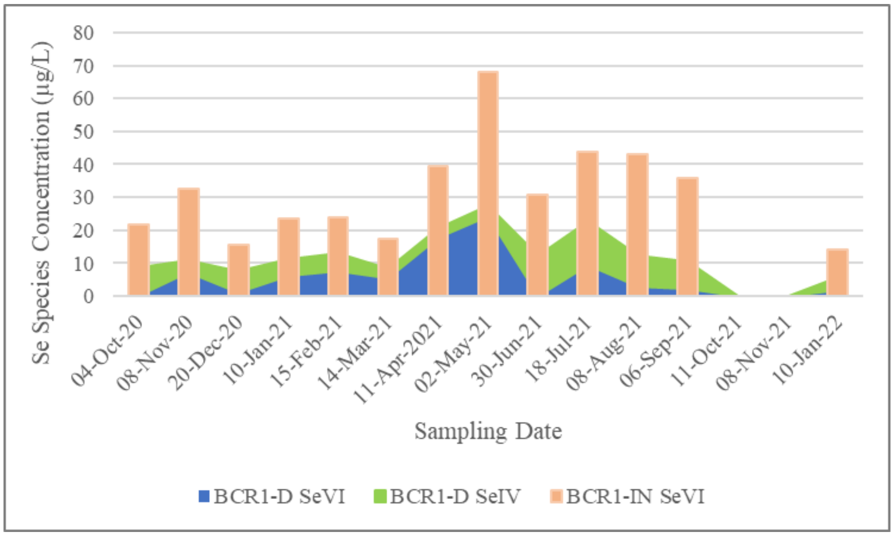

Figure 7: Selenium speciation species in influent and BCR1-D effluent

Discussion

The data for redox proxies in the Agridrain are indicative of mildly suboxic conditions, as inferred by the absence of DO, the values of oxidation-reduction potential (ORP), and the presence of ammonia (Table 1). Indicators of more strongly reducing conditions, as would be revealed by sulfate reduction and/or reductive dissolution of Fe oxide, were not observed. Concentrations of Fe were below the detection limits, and no decreases were observed for sulfate (Figure 5).

Nitrate concentrations in the untreated influent water (BCR1-IN) show mine-related signature, attributed to residual ammonia-nitrogen-based blasting residues. Concentrations ranged from <1 to 49 mg/L. After treatment in the bioreactor, concentrations of nitrate in the outflow of the bioreactors (Agridrain) decreased to less than 1 mg/L, with pH ranging from 6 to 8 (Table 1). These results show evidence of effective denitrification (i.e., microbially-mediated nitrate reduction) up to 100 % by nitrate-reducing bacteria (NRB) such as *Thiobacillus, Acinetobacter, Pseudomonas, Sulfuricumonas* identified in the bioreactor and the Agridrain. These results support earlier findings that demonstrated the use of these bacteria for the reduction of nitrate (Lortie et al., 1992; Torrento et al., 2010). Similarly, concentrations in the discharge effluent water (BCR1-D) were below the regulatory limit of 10 mg/L (Figure 3).

Selenium shows removal rate of up to 94% with concentrations decreasing from ~200 µg/L to less than 20 µg/L at pH 7-9 (Table 1), attributed to selenium reducing bacteria (SeRB) such as *Pseudomonas, Bacillus,* identified in the bioreactor and the Agridrain. These results are consistent with earlier findings that demonstrated the use of these bacteria for the reduction of selenium oxyanion, selenate (SeVI) and selenite (SeIV) (Lortie et al., 1992) and production of insoluble elemental selenium (Stolz et al., 2006; Lenz and Lens, 2009) (Figure 4). The reduction in Se concentration was accompanied by a shift in Se speciation from dominantly selenate (SeVI) to selenite (SeIV) and/or to insoluble elemental selenium (Figures 6 and

7) via dissimilatory microbial reduction under suboxic to anaerobic conditions. The influent is characterized by selenate (SeVI), while selenite (SeIV) is predominant in BCR-treated waters. Both selenate and selenite yielded lower concentrations in BCR effluents (Agridrain and BCR1-D) than influent (BCR1-IN), indicating that the BCRs can reduce selenate to selenite and then to insoluble elemental selenium believed to be adsorbed into mixed media in the BCRs. Other forms of Se evaluated, include organic Se compounds and selenocyanate, which were at trace levels (i.e., selenocyanate, dimethylselenide, methylselenic acid, and unknown selenium compounds) or with concentrations less than analytical detection limits (i.e., selenomethionine and dimethyl diselenide).

The results presented here show simultaneous and significant selenate and nitrate reduction within the bioreactors under suboxic to anoxic conditions, consistent with findings reported earlier by Oremland et al. (1999) and Bianchin et al. (2013). Nitrate in the treated effluent (Agridrain) were near complete consumption and below the regulatory limits, while selenium concentrations, though below the regulatory limits, in most instances do not perform as well as nitrate. These results also support findings by Zhao et al. (2014), who demonstrated that near complete removal of nitrate may be required for significant selenate reduction to occur. Concentrations of nitrate have mostly been below the SPO limit at the compliance site (BC-01a) for the last three months. However, selenium in the receiving environment (BC-01a) remains above the SPO limit. Recent optimization of BCR1 and the proposed construction of additional water management structures are expected to improve contact water management, influent, and downstream receiving water quality.

Conclusion

The use of biochemical reactors for the attenuation of selenium and nitrate are integrated in the Brule Mine design and water management plans. The results presented in this paper demonstrate that BCRs can be used as in-situ bioremediation technology for effective reduction of Se and NO_3 in mine contact waters so as to meet regulatory limits.

There is an opportunity to enhance Se removal and rapidly meet regulatory limits via the addition of organic substrates (i.e., molasses) or defined organic amendments (i.e., acetate and lactase) to the bioreactors as carbon source and electron donors to facilitate growth and reduction of Se oxyanions to elemental selenium (USEPA, 2001, Park et al., 2006).

Certainly, improvement of water management structures for the interception and collection of contact water for treatment and source control measures will limit the release of constituents of concern into the environment.

The engagement and involvement of First Nations in the design, implementation, and operations of water management systems, as well as environmental monitoring, is ongoing, and information gathered is shared in a coordinated manner through multiple forums, including the environmental monitoring compliance committee (EMCC).

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Asset-Level Benchmarking of Water Use and Production Risk in the Mining Industry

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Abstract

There is a growing requirement for comparable transparent water use in the mining industry for its potential impact on production and cost at asset, company, and country level. In response, Skarn Associates have developed a novel methodology by normalizing key water indicators, while applying a mining analyst's approach: using technical, operational, and commercial data to contextualize water management at each site, with transparent benchmarking and estimating where necessary.

This bottom-up approach enables the review and evaluation of water management data at mine, corporate, and country level. This converts into a powerful tool to ascertain the complexity of the water management by a particular operation and serves as an indication of the level of resilience the operation has when facing a drought period. When overlaying climatic precipitation trends, it is even possible to estimate the volume of metal that is produced in regions that are facing a negative trend in annual rainfall.

While there are a multitude of environmental social governance (ESG) benchmarking tools on the marketplace, the Skarn Mine Water Benchmarking Tool is a mining-specific water bottom-up quantitative analysis tool, which combines disclosed water asset-level and external public data with contextual mine water management knowledge. This allows for a valid comparison of water impacts on ESG metrics, economical and risk quantification, at asset, company and regional level.

Introduction

Over the last decade, several organizations have intensified their warnings on water-related risks for the mining industry. In 2019 CDP, a non-profit group that runs a global disclosure system, reported exposure to water-related risks in the mining sector totalling US$24.9 billion, with just under half of the CDP respondents having already been impacted by water-related financial losses amounting to US$11.8 billion during the previous five years. These losses only relate to water as a revenue risk factor. To illustrate the importance of water availability in mining, BHP, one of the major diversified mining companies, indicates: "Without water, our business simply could not operate. And without water, the communities we operate in wouldn't survive".

Water is also a major reputational and transition risk factor, where significant investments are made to mitigate environmental issues through remediation systems, or through billion-dollar seawater desalination installations. Simultaneously, population growth and climate change conditions are applying even greater stresses on the mining industry, which is an important local competitor for available water. This has already resulted in numerous examples where legal and community conflicts have reduced or even completely cut off access to water for mining operations, resulting in disruptions to production and a direct loss of revenue and increased operational costs, and even leading to the stranding of valuable mineral deposits. As the international Climate Disclosure Standards Boards (CDSB) confirms: "Water is arguably the medium through which we feel the effects of climate change most". For many mining companies over the last few years, water has converted from an operational back-end "nuisance" that was managed at operational level (only-cost, no-benefit), to a front-end corporate strategic, operational, and transition risk factor.

The complex and localized nature of water and climate change, and the mix of qualitative and quantitative information available, makes it difficult for investors and other mining industry stakeholders to incorporate water risk data into their company analyses. Until now, little information or suitable methodologies have existed to help quantify operational water data into relevant information for corporate and external stakeholder decision-making.

In response to this growing requirement for simple, transparent, and comparable water use in the mining industry, Skarn Associates have developed a proprietary methodology, normalizing key water indicators, while applying a mining analyst's approach: using technical, operational, and commercial data to contextualize water management at each site and the resulting impact on production and costs at an asset level. Skarn utilizes a combination of actual reported data (where available) and benchmarking of water use parameters where necessary that allows for mining operations and/or companies to be compared on a like-for-like basis.

The challenge

As mentioned, water is a direct revenue risk factor for the mining industry. It is also a complex parameter to evaluate as it requires combining local climate context together with an understanding of the operation's water use and resilience to external water-related factors. Skarn has identified three main reasons why most of the currently available water-risk tools do not fully satisfy the requirement to identify water-related business risk for mining companies and their stakeholders.

First, there are several different types of reporting standards and guidelines, which makes it difficult for companies to report within a common framework. This can be seen in the following figure, which represents a selection of mining related reporting standards and guidelines on water, environment, sustainability, climate change, accounting, etc., that contain definitions on water parameters.

Figure 1: Mining related reporting standards, guidelines and organizations

The complexity around these different standards is that they are not all aligned when it comes to parameter definitions, resulting in indicators that can be interpreted differently depending on the standard that is used. This is especially complex for companies that are committed to report following multiple guidelines, resulting in inconsistent or conflicting reported data. Furthermore, qualitative reporting standards provide little use for quantitative and benchmarking analysis.

A second issue, as noted in several publications, is that one of the main complications for water-risk analysis in the mining industry is the lack of consistency in water data reporting by mining companies. Not all companies disclose their full asset level water performance data in a consistent way, year-on-year, using the guideline definitions as claimed. Examples include: mining companies reporting water data only at corporate aggregated level, limited parameters, or even reporting negative water consumptions. The last-mentioned example typically results from under-reporting water withdrawals, due in part to not accurately recording all captured rainwater, run-off, or dewatering volumes.

However, one of the most crucial problems is the complexity of contextualization and the translation of available water use data into useful financial risk quantification. This requires asset-level evaluation and cannot be executed through top-down analysis. Water risk impact is not uniform throughout the mining industry globally, or within a company portfolio. Negative effects related to drought or flooding depend on a combination of external, local, and site-level operational conditions and factors. These external and internal parameters are often very localized and as such have direct impact on water management for each mine. This limits the validity of a top-down analysis approach in evaluating water impact for the mining industry, as it does not allow for differentiation at mine or even company level.

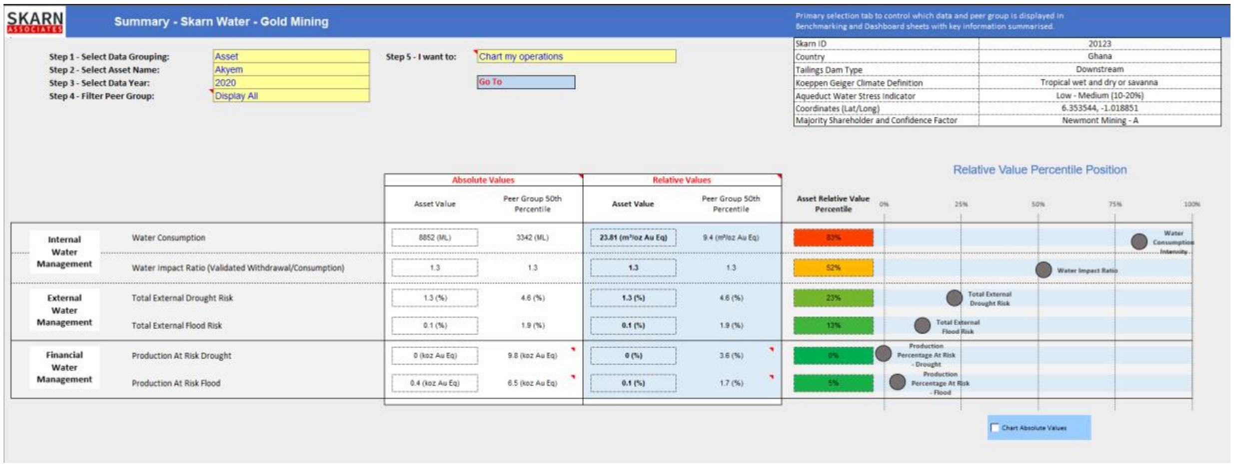
Several of the existing water reporting guidelines used by the mining industry, such as GRI and ICMM, recognize the importance of the external climate context and recommend the use of tools such as

WRI Aqueduct or WWF Water Risk Filter to identify a mine's baseline water stress level as a trigger for more detailed water disclosure requirements. Unfortunately, these water stress indicators tell only part of the story, as they do not evaluate water use or operational resilience to water variability factors, nor do they flag the direct external water exposure of a mine. Furthermore, the major use of these tools relates only to potential drought conditions, and does not provide information relating to production risk from excess water, such as flooding events.

As a result, Skarn Associates has developed a simple tool that enables external stakeholders to evaluate and compare relevant water-related information and impacts at both a mine and company level; taking into consideration the lack of reporting consistency, variety of standards in use, incomplete or erroneous asset level reporting, and the lack of contextual impact evaluation and comparison.

The solution

In response to the above, Skarn recently launched two separate tools: Skarn Water – Gold and Copper, which provide a detailed bottom-up evaluation of water management at a mine, company, and country level for the gold mining industry. The tools help to simplify the complexity of water management at a particular mine and highlight the resilience an operation has to potential drought conditions. By combining climatic precipitation trends and drought data, the tools allow the estimation of the metal production at risk and the overall financial impact to a mine or company.



Primary selection tab to control which data and peer group is displayed in Benchmarking and Dashboard sheets with key information summarised.

Step 1 - Select Data Grouping: Asset
Step 2 - Select Asset Name: Akyem
Step 3 - Select Data Year: 2020
Step 4 - Filter Peer Group: Display All
Step 5 - I want to: Chart my operations

Skarn ID	20123
Country	Ghana
Tailings Dam Type	Downstream
Koeppen Geiger Climate Definition	Tropical wet and dry or savanna
Aqueduct Water Stress Indicator	Low - Medium (10-20%)
Coordinates (Lat/Long)	6.353544, -1.018851
Majority Shareholder and Confidence Factor	Newmont Mining - A

		Absolute Values		Relative Values		
		Asset Value	Peer Group 50th Percentile	Asset Value	Peer Group 50th Percentile	Asset Relative Value Percentile
Internal Water Management	Water Consumption	8852 (ML)	3342 (ML)	23.81 (m³/oz Au Eq)	9.4 (m³/oz Au Eq)	83%
	Water Impact Ratio (Validated Withdrawal/Consumption)	1.3	1.3	1.3	1.3	52%
External Water Management	Total External Drought Risk	1.3 (%)	4.6 (%)	1.3 (%)	4.6 (%)	23%
	Total External Flood Risk	0.1 (%)	1.9 (%)	0.1 (%)	1.9 (%)	13%
Financial Water Management	Production At Risk Drought	0 (koz Au Eq)	9.8 (koz Au Eq)	0 (%)	3.6 (%)	0%
	Production At Risk Flood	0.4 (koz Au Eq)	6.5 (koz Au Eq)	0.1 (%)	1.7 (%)	5%

Figure 2: Skarn Water Gold Mining – main menu

The Skarn Water tool main menu screen allows users to group data by asset, company, or country for a selected year and view a summary of six key indicators. Users can also select a comparison peer group such as mine, process, tailings dam, or climate zone type, or default to a global comparison.

The summary view shows the three key indicator classes:

- **Internal water management**: The physical water context of the mining operation, represented by its water consumption (total and intensity), and Water Impact Ratio (a Skarn defined indicator, representing both water efficiency and environmental impact).
- **External water management**: Flood and Drought Risks based exclusively on external climatic parameters and historic climate data.
- **Financial water management**: Production at risk due to flood and drought factors, evaluating current water use on site to determine resilience and operational exposure.

Global coverage

Skarn currently covers detailed water use for the majority of listed gold mining companies globally, representing around 50 million ounces of gold production. The forthcoming Skarn Water Copper Mining tool will cover over 18 million tonnes of global copper production, equivalent to over 85% of mine supply.

Results

Gold mining is a water intensive industry: in 2020 over 2 billion cubic meters of water were withdrawn from the environment to produce 50 million ounces of gold. However, only half of that volume was consumed (following GRI and ICMM definitions) with the remainder discharged to the environment as (treated) effluent.

Skarn estimates that in 2020 the copper mining industry withdrew greater volumes of water than gold at around 3.6 billion cubic metres. The higher volume largely reflects larger scale operations in copper mining; however, surprisingly, the industry discharges a similar volume of water back to the environment as gold, or around 28% of the water withdrawn.

Several general conclusions can be drawn from this. First, and this can be verified at an individual mine operation level, copper mines operate in drier climate locations than gold mines, forcing them to be more water efficient. The direct implication is that copper mining, in general, is more exposed to drought risk, whereas gold mines are more likely to be impacted by flood risk events.

Skarn has identified that well over 4% of annual gold production is at risk due to flood or drought related events, associated to trends in recent climatic precipitation – taking into account asset-level exposure and resilience of mining operations to external climatic factors. Although 4% might sound manageable, it does represent over US$ 3 billion of annual revenue losses based on current gold prices. However, the main issue is that this risk is not evenly spread among the mining companies: 80% of the total water-related production revenue risk is represented by just 51 mining operations.

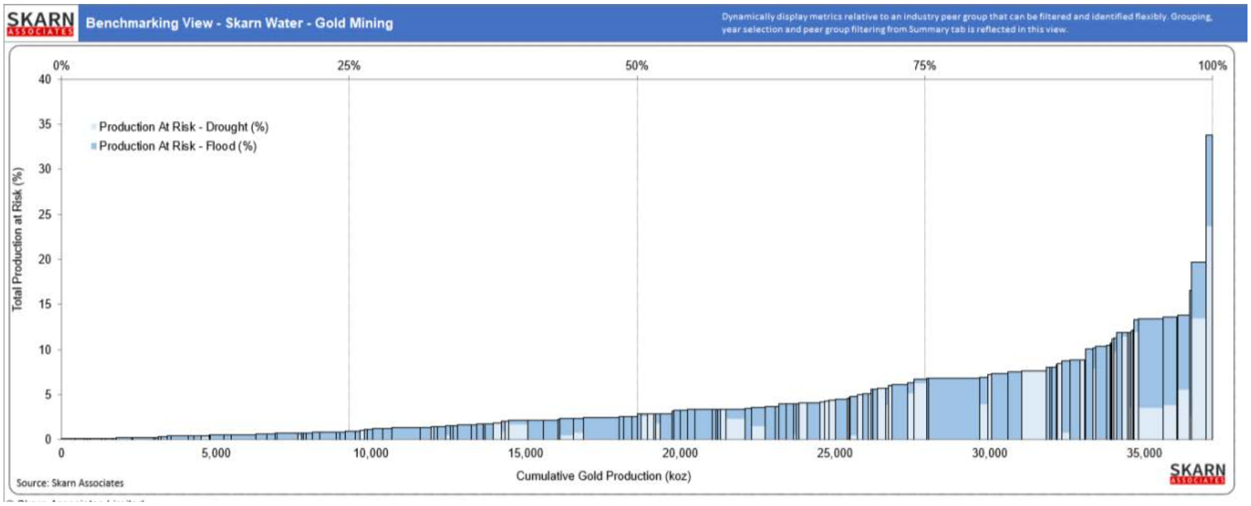


Figure 3: Skarn Water Gold Mining – % gold production at risk – asset level

Figure 3 shows asset level production at risk, based on 2020 production data that is overlain with contextual information on internal water management, resilience, and exposure to water availability based on the matrix of water sources used at the mine site, and external climatic data.

In the case of copper mining, total production at risk due to flood and drought conditions, based on reported data and current production conditions, exceeds US$ 5 billion, with only 25 operations accounting for well over 70% of that risk.

From an investor's perspective, water risk analysis and differentiation at the asset level not only drives environmental and sustainability aspects, it also influences economic value and returns evaluation.

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Innovative Approach to Active and Passive Water Treatment for Complex Water Quality Applications: The Removal and Recovery of Transition, Post-transition, Lanthanide, and Actinide Metals

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Extended Abstract

The rare earth elements (REEs) or rare earth metals consist of seventeen chemical elements, the fifteen lanthanides, scandium, and yttrium (Connelly et al., 2005). Scandium and yttrium are considered rare earth metals since they exhibit similar chemical properties to the lanthanides and are found in the same ore deposits as the lanthanides. REEs are typically categorized into two sub-groups, the cerium sub-group of "Light" rare earth elements (LREE), which includes lanthanum to europium, and the "Heavy" rare earth element (HREE) subgroup, which includes gadolinium to lutetium in addition to yttrium (Gupta and Krishnamurthy, 1992). Except for radioactive promethium, REEs are moderately abundant in the Earth's crust, with some REEs more abundant than copper, lead, and gold. Despite this relative abundance, most REEs are not found in concentrations great enough to make them economically exploitable (USGS, 2007). The REEs are never found as pure metals but rather exist in a variety of minerals including silicates, oxides, carbonates, phosphates, and halides (Vijayan et al., 1989). The USA, once able to domestically produce sufficient REEs, has for more than 20 years become almost totally reliant on imports, primarily from China, because of the low cost of operations (USGS, 2002).

Most REEs are found in deposits of the minerals bastnaesite, monazite, and xenotime (Reisman et al., 2013). Over 90% of the world's economically recoverable REEs are found in primary mineral deposits, with bastnaesite deposits in the USA and China accounting for the largest concentration of REEs (Jackson and Christiansen, 1993). Ideally, bastnaesite, a low-thorium mineral, is preferred over thorium-containing monazites, because of concerns over the radioactive hazards associated with the element thorium. However, monazites generally contain more of the high-value heavy REEs. Bastnaesite and monazite account for approximately 95% of the current sources for the LREEs, while xenotime is the primary mineral source for the HREEs and yttrium (Zhang, 2014).

To meet growing global demand, alternative sources for REEs are currently being explored. These include phosphate mining waste products, coal combustion residues (CCRs or coal ash), bauxite residue (red mud), and shale drill cuttings. It is estimated that 100,000 tons of REEs are co-mined with 170 million tons of phosphate rock annually (Zhang, 2014).

While numerous procedures to extract and recover REEs from these alternative sources have been reported, none have yet seen widespread commercial acceptance due to various limitations, such as high cost, low efficiency, lack of specificity, impact on primary product purity and yield, temperature sensitivity, environmental impact, and the inability to economically extend the technologies to large-scale operations. Clearly, there is a need to improve the extraction and recovery technology of REEs and other valuable metals.

One way to achieve a commercially viable separation scheme is to employ a polymer compound that will selectively bind to and remove various REEs and other valuable metals in the presence of potential interfering ions, such as calcium, magnesium, and iron. Furthermore, this process should be economically viable, efficient, scalable, applicable to environments with high total dissolved solid (TDS) concentrations, relatively insensitive to ambient temperature, and have minimal environmental impact. Periodic Products has previously (Laurino, 2008) reported on a series of novel, non-toxic, water-insoluble polymer compounds that rapidly and efficiently remove several metal ions, including both light and heavy REEs, from aqueous media. This report summarizes the performance characteristics of these polymer compounds in several REE and related mining applications.

In laboratory studies, these polymers exhibit the specific, selective, and fast complexation of transition, post-transition, and lanthanide metal ions, in addition to demonstrating the reusability of the chelating polymeric ligands. The adsorption capacity of these polymers for the transition, post-transition, lanthanide, and actinide metals is substantially higher than other heterogeneous adsorbents and is equivalent to those obtained with homogeneous sorbents. In addition, the ease of separation of polymer from aqueous media via gravity filtration avoids the use of high-pressure ultrafiltration associated with the separation of aqueous ion solutions and homogeneous sorbents. Lastly, the polymers exhibit second-order adsorption kinetics over a pH range from 1.5 to 14 and are not affected by high concentrations of Group I or Group II metals, such as sodium, calcium, and magnesium.

The impact of temperature and TDS concentration on this technology was investigated in two separate studies. In a year-long field study in West Virginia conducted under temperatures ranging from 10ºF to 95ºF, polymer-filled geotextiles passively removed selenium and manganese from a coal mine tailing pond to discharge-compliant levels. In a second study, the polymers selectively removed transition metals and lanthanides from undiluted copper mine pit water with a TDS greater than 100,000 milligrams per liter (mg/L). This pit water contained a mixture of 18 transition and lanthanide metals with a total concentration of 13,000 mg/L. Polymer treatment reduced the total concentration of these 18 metals to less than 4 mg/L. In addition, due to the presence of coordinate-covalent bonding in these polymer species, metals existing primarily in their anionic form were also removed. Arsenic concentrations were reduced from 0.589 mg/L to <0.10 mg/L and chromium concentrations were reduced from 1.384 mg/L to <0.10 mg/L. Lastly, the mixture of metals was quantitatively removed from the polymer and recovered. Thus, the performance of the polymer technology was not affected by ambient temperatures of 10ºF to 95ºF or TDS concentrations of at least 100,000 mg/L.

The use of the polymer compounds in the extraction and recovery of REEs from phosphate rock and three phosphate fertilizer waste by-products, phosphogypsum, amine tailings, and waste clay, was investigated. As the study was narrowly focused to examine the suitability of the polymers to bind metals in crude waste extracts, extraction procedures were not optimized. Overall extraction and recovery yields were between 80% for gadolinium and 8% for praseodymium from amine tailings, between 70% for terbium and 7% for praseodymium from phosphogypsum, between 56% for scandium and 15% for praseodymium from phosphate rock, and between 77% for samarium and 31% for praseodymium from waste clay. The polymers effectively bound 100% of the REEs extracted from the solids. Interestingly, the polymers also bound 100% of the uranium in the amine tailing and waste clay extracts, and 82% and 83% of the uranium in the phosphogypsum and phosphate rock extracts, respectively. In addition, the polymer bound 100% of the thorium extracted from the amine tailings, phosphogypsum, and waste clay. Thorium was not extracted from the phosphate rock under the conditions investigated.

In a series of other investigations, these polymer compounds have also been shown to bind 98% to 100% of the REEs extracted from Marcellus Shale cuttings, bauxite residues, and coal ash residues.

The results of these studies suggest that this polymer technology represents a highly efficient and cost-effective method for the removal and recovery of REEs and other metals from several mining waste streams. The rapid kinetics, metal selectivity, and pH stability, along with the ability to reuse the adsorption polymers, increases the economic viability of this process for transition, post-transition, lanthanide and actinide metal extraction and recovery from previously unrealized sources. As a result, this polymer technology represents an opportunity for the production of REEs as well as water treatment applications.

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Removal of Selenium by Reduction to Selenite and Surface Complexation

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Abstract

Selenium is now a well-known pollutant, present in various coal and hard-rock mines and some thermal power plant effluents throughout the world. Veolia Water Technologies Canada has developed the Tracer^{TM} Se process (patent pending), which is a new method for selenium removal based on biological reduction of selenium to selenite, its subsequent removal from water using surface complexation on ferric oxyhydroxide, and further biological oxidation of the treated water. The mechanisms by which selenium is understood to create toxicity in the environment will be reviewed, as well as some of the leading existing technologies for removing selenium. The Tracer Se process will then be described, and test results presented.

Introduction

Selenium, like sulfur, is widely present in the environment, albeit at usually low concentration. Like sulfur it is mostly present in the environment at higher oxidation states, i.e., as selenites and selenates (+4 and +6 oxidation states respectively); rarely as selenides (–2 oxidation state). It is almost never found as the element (0 oxidation state), but it is often produced in that state in biological treatment processes.

Selenites and selenates are generally soluble in water, more so than sulfites and sulfates. As such they cannot easily be removed from water by precipitation. Selenites can form insoluble surface complexes with metal oxides such as ferric hydrous oxide and manganese hydroxide, and can therefore be removed that way. Elemental selenium can also be produced from selenites or selenates by using a reduction process, biological or otherwise. It is a solid, and it is possible to remove it from water in that form. Because of their acute toxicity, selenides need to be handled with care, and if present can also form insoluble metal salts or, at low pH, be emitted as H_2Se, a noxious and highly toxic gas.

Organo-selenium species are important in understanding selenium toxicity. There are a great number of these species. Basically, any organic species that contains sulfur has an equivalent that contains selenium. As an example, the substitution of oxygen by sulfur in the cyanate ion gives thiocyanate, and the substitution of sulfur by selenium gives selenocyanate (OCN^-, SCN^- and $SeCN^-$ respectively).

Of particular interest is the substitution of sulfur by selenium in the two sulfur-bearing amino acids, cysteine and methionine, giving selenocysteine and selenomethionine. Methylseleninic acid (CH_3SeO_2H) is another organo-selenium species which has been detected in water treated by biological processes and which is biologically active.

Selenium toxicity – an overview

The issue of selenium toxicity is complex, but reducing toxicity is the main objective behind the development and commercialization of the Tracer Se process.

In recent years a number of large-scale bird mortality incidents have been associated with selenium. Examples include birds feeding and nesting at the Kesterson Reservoir in the San Joaquin Valley, California, between 1983 and 1985; eared grebes at the Salton Sea, California, in 1992; and, again, eared grebes at the Great Salt Lake, Utah, in 2011. While selenium has been associated with the die-offs, the mechanism involved is not well understood.

Acute toxicity

Table 1: Acute toxicity of some selenium species

Species	Toxicological endpoint	Selenium form	Result in mg/L	Toxicity category	Reference
Cerodaphnia dubia	LC50 24 hours	Selenite	0.44	Highly toxic	Beatty & Russo, 2014
Cerodaphnia dubia	LC50 48 hours	Selenate	1 to 9.3	Moderately toxic	Brix et al., 2001
Daphnia magna	LC_{50} 48 hours	Selenious acid (selenite)	0.43	Highly toxic	Beatty & Russo, 2014
Daphnia magna	LC_{50} 48 hours	Selenite	0.55	Highly toxic	Maier et al., 1993
Daphnia magna	LC_{50} 48 hours	Selenate	2.84	Moderately toxic	Maier et al., 1993
Hyallela azteca	LC_{50} 96 hours	Selenite	0.34	Highly toxic	Beatty & Russo, 2014
Hyallela azteca	LC_{50} 96 hours	Selenate	6 to 32	Slightly to moderately toxic	Brix et al., 2001
Oncorhynchus mykiss	LC_{50} 96 hours	Selenate	4.5 to 9	Moderately toxic	Beatty & Russo, 2014
Oncorhynchus tshawytscha	LC_{50} 96 hours	Selenite	3.5 to 13.6	Slightly to moderately toxic	Beatty & Russo, 2014
Oncorhynchus kisutch	LC_{50} 96 hours	Selenite	8.1 to 23.4	Slightly to moderately toxic	Beatty & Russo, 2014

To help understand toxicity data such as LC_{50} (the concentration at which 50% of the test organism will die after a stated time), the US EPA (2021) uses five toxicity categories. We can use this system to characterize the acute toxicity of selenium for a few aquatic organisms, as shown in Table 1.

As can be seen in Table 1, selenium is more acutely toxic for species lower in the food chain such as *C. dubia*, *D. magna,* and *H. azteca* than for salmonids such as *O. mykiss*, *O. tshawytscha*, and *O. kisutch*. In cases where acute toxicity data is available for both selenites and selenates, selenites are generally more toxic than selenates. Given that selenates are the dominant form of selenium in the aerobic aquatic environment, one could conclude that selenium is only slightly to moderately acutely toxic for most fish species, but can be highly toxic for small crustaceans such as *D. magna* and *C. dubia*.

Chronic toxicity

Chronic toxicity is a different issue. Quoting Beatty and Russo (2014): “since ambient Se concentrations rarely reach levels that result in acute effects, the more common situation resulting in Se toxicity occurs at much lower chronic exposures.” The literature on selenium chronic toxicity is vast and confusing. Here are some key points from the Beatty paper:

> “Bacteria, fungi, algae, and invertebrates are fairly tolerant to elevated Se concentrations, and the more important role these organisms play is in the rapid transformation and transfer of Se into the aquatic food web. However … there is a high degree of variability in the toxic effects on algae and invertebrate taxa based on water Se concentrations, suggesting that Se uptake is very different among species at a given water concentration. …
>
> “Fish and bird species have the highest sensitivities to both Se-related embryo mortality and developmental deformity, although amphibians and reptiles may also be sensitive to Se. … Reproductive and non-reproductive toxic effects may be seen in fish from chronic Se exposure. Reproductive effects are those originating from the maternal transfer of Se, while non-reproductive effects refer to the direct toxic impacts Se may have on juveniles and adults. Both reproductive and non-reproductive effects result primarily from the dietary intake of Se. There is also evidence that waterborne Se can elicit non-reproductive effects albeit at higher aqueous concentrations. …
>
> “Many of the sublethal effects of Se in fish are similar to those found in birds… The more sensitive chronic effects in birds are related to reproductive impairment.”

One of the difficulties in assessing the chronic toxicity of selenium is that its uptake by living organisms depends on its speciation. Most laboratory studies have been done using selenites or selenates, as these chemicals can easily be purchased and dosed at controlled concentration in the water. The issue is that the concentration of selenium in the tissues of living organisms does not depend on the total concentration of selenium in the water, but rather on the concentration of the various selenium species.

Besser et al. (1993) calculated the bioconcentration factor[1] of selenium for three organisms depending on the selenium speciation. All experiments used a total concentration of 10 µg Se/L in the water, but the selenium speciation varied.

Table 2: Bioconcentration factors

Organism	Exposure	Selenium speciation	Bioconcentration factor
Chlamydomonas reinhardtii (a green algae)	24 hours	Selenate	428
		Selenite	1,440
		Selenomethionine	5,320
Daphnia magna (a crustacean)	96 hours	Selenate	293
		Selenite	570
		Selenomethionine	30,300
Lepomis macrochirus (a fish)	30 days	Selenate	20
		Selenite	20
		Selenomethionine	5,000

In the same paper, Besser et al. also reported that the speed of selenium uptake by the organisms studied also varies with the selenium speciation, with selenomethionine uptake being much faster than selenite, and selenite uptake being faster than selenate.

A decade later, Amweg et al. (2003) did another study that looked at the potential for bioaccumulation of various selenium species. In this case Amweg et al. were looking at a process named algal-bacterial selenium reduction (ABSR), in which inorganic selenium is converted to elemental selenium by a combination of algae and bacteria, and then is removed from the water. This process is not widely used nowadays, but was considered for a time for treating agricultural waste water containing large concentrations of selenium. Amweg et al.'s study "was intended to monitor Se concentrations in invertebrates found in the ABSR system and assess the effect of ABSR treatment on Se bioavailability."

Amweg et al. (2003) found that while the treatment managed to reduce the total selenium in the water by 60%, the bioconcentration factor for two algae species was actually increased by an order of magnitude after treatment. Overall, "[r]esults indicate that Se within and discharged from the ABSR was more bioavailable than that in the untreated drain water, and that except in the algal bioaccumulation test, organisms accumulated more Se exposed to ABSR-treated water than if exposed to untreated water." Amweg et al.'s conclusions are damning for the ABSR process:

> "We believe that production of organo-Se by microbial activity… and reduction of selenate to selenite which is then accumulated by algae … and incorporated into algal selenoproteins, caused the increased Se bioavailability seen after ABSR treatment. Higher organisms generally accumulate Se

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[1] The bioconcentration factor, or BCF, is the ratio of an element in the tissue to the concentration of the same element in water.

> through their diet … and this Se-rich algal biomass presumably served as a Se source for the other invertebrates of the ponds. … Increased Se bioavailability is inherent in the system design due to its dependence on microbial Se reduction. … [G]iven that organic Se forms are approximately 1000 more bioavailable than selenate … the system would have to be extraordinarily effective to achieve less bioaccumulation from the effluent than from the influent. Hypothetically, if the influent contained entirely selenate and the effluent contained entirely organic Se, the system would have to achieve greater than a 99.9% reduction in total Se concentration in order to be judged a success by the criterion of less bioaccumulation from the effluent."

An adage of modern toxicology is that "solely the dose determines that a thing is not a poison"[2]: there is a relationship between the concentration of a substance and its effect. What is important, however, is not the concentration in the environment, but the concentration in the tissues.

Selenium is only moderately acutely toxic in water, especially when present as selenate. Because of the widely different values for the bioconcentration factor of the various selenium species and the lack of information on the selenium speciation in most papers looking at chronic toxicity, its chronic toxicity is difficult to assess. For biological treatment at least, the question of bioavailability of the selenium in the treated water is highly relevant in assessing the performance of the treatment system.

Even neglecting the effect of selenium on the reproduction success, the well-publicized die-off events mentioned above are a good example of selenium toxicity. It is however likely that these die-offs are complex events caused by bioaccumulation of selenium through the food chain up to a point where the selenium concentration became high enough that it caused acute toxicity in the predators. It is also likely that many species have issues with reproduction success because of a similar chain of events, even if the selenium concentration in the tissues is not sufficient to cause acute toxicity.

Current approaches for selenium removal in water

Given the toxicity of selenium and the difficulty of removing it, it is not surprising that many competing technologies have been developed to try to remove it from waste water. We will try to broadly describe the main approaches that are currently in use, but the interested reader can refer to the excellent review by Golder (2020) titled *State-of-Knowledge on Selenium Treatment Technologies*, which itself refers to numerous papers on the subject.

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[2] Paraphrased from Paracelsus' "Alle Dinge sind Gift, und nichts ist ohne Gift, allein die Dosis macht dass ein Ding kein Gift ist", which can also be translated to "All things are poison, and nothing is without poison, the dosage alone makes it so a thing is not a poison."

Physico-chemical treatment options

Physico-chemical treatment options include reverse osmosis, ion exchange, and chemical reduction. Because they are not biological, they produce very little or no organo-selenium species, thereby reducing potential toxicity issues.

Reverse osmosis separates molecules based on their size. As selenites and selenates are relatively large molecules, it is quite easy to separate them. However, in mine effluents there are many large molecules. In the presence of scaling molecules such as silica and gypsum, it becomes difficult to achieve a high recovery, that is to have a large fraction of the water produced as clean water (permeate). The other issue with reverse osmosis is that it only moves selenium to a more concentrated stream. Given that in typical mine water the concentrated stream is 30% of the feed flow, one ends up with 70% of the feed being clean water ready for discharge and 30% of the flow having three times the selenium concentration that needs to be disposed of.

Ion exchange is similar to reverse osmosis, except that separation is based on the charge of the molecules rather than their size. Ion exchange resins have been developed that can bind selenites and selenates quite effectively, but they are subject to competition from other molecules, notably nitrates and sulfates. This increases the requirements for column regeneration, increasing the volume of waste to reject. In water with low nitrates and sulfates this volume can however be managed. Electro-reduction has been used with some success for this situation, but other techniques could also be used. In water with high nitrate or sulfate, the volume of waste water produced rapidly becomes unmanageable.

Chemical reduction with zero-valent iron (ZVI) was studied extensively for a time and has been installed at some sites. With this approach selenates are reduced to selenites, producing ferrous iron, and are then co-precipitated on iron hydroxide flocs. There are a number of variations on this process, including the use of sulfur-modified iron. While the process works, there are a number of practical considerations that make it quite complex. First, ZVI iron will also reduce nitrates to nitrites. This both consumes part of the ZVI and produces nitrites, a by-product toxic to many fish species. Secondly, ZVI effluent contains a lot of soluble iron, mainly ferrous iron, another toxic element which must be removed before discharge. Finally, ZVI media has had a tendency to plug, reducing the flow in the reactor to a point where the media need to be replaced entirely. Newer media formulations are said to be less affected by this issue.

Biological treatment options

Biological treatment systems are based on the fact that bacteria and archaea can, in the right conditions, reduce selenites and selenates to elemental selenium, which is essentially insoluble in water. Elemental selenium can then be removed to produce selenium-free water.

All biological treatment options share some characteristics:

- Nitrates compete with selenites and selenates, and when present in high enough concentration must be removed from the water before selenium reduction can occur effectively.
- Elemental selenium particles are both very small and not electrically charged, which makes their removal from water challenging.
- Elemental selenium particles are easily oxidizable, and care must be taken through the process to prevent this from occurring.
- Reaction kinetics are slow, which translates into large reactors and hence high costs.
- By their nature all these processes will convert a fraction of the selenium to organo-selenium, with the potential toxicity issues that this may cause.
- Biological treatment systems have difficulty *consistently* achieving the 10 µg/L of total selenium that will possibly become the new selenium criteria for Canadian coal mines (ECC Canada, 2022; Golder, 2020).

There are many biological reduction processes available, and biological reduction is by far the most common selenium treatment process. The reader is referred to Golder (2020) for a more detailed introduction to these processes and some case studies.

Veolia's Tracer Se process

In this section, Veolia's Tracer Se process will be presented. We will then present preliminary results and some advantages of this process.

The process

Veolia's Tracer Se process combines biological reduction of selenates to selenites, removal of selenites and biomass under reducing conditions, and reoxygenation of the selenium-free water. See process schematic:

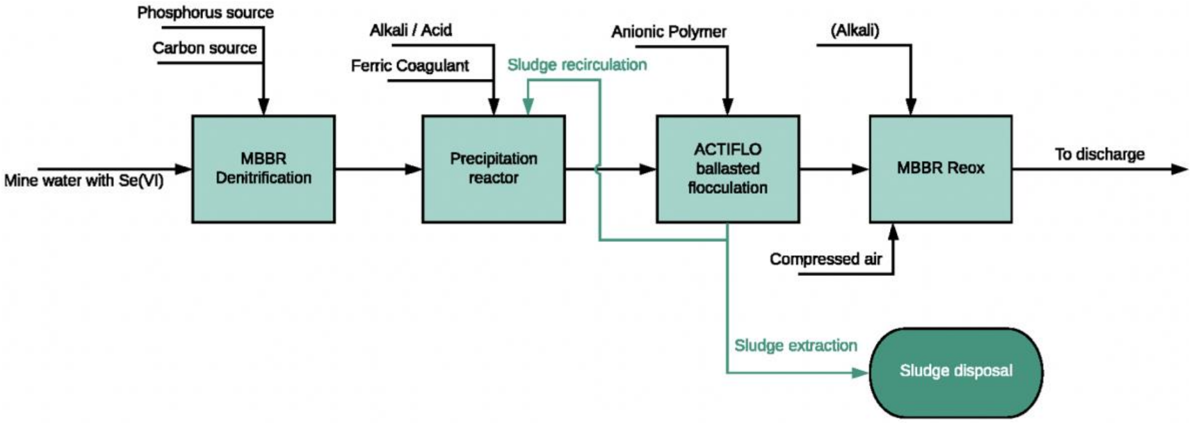

Figure 1: Tracer Se schematic diagram

First, water is directed to a biological reduction reactor containing biomass and operated under anaerobic or anoxic conditions. A moving bed biofilm reactor (MBBR) can be used for this purpose. In this reactor, selenates are biologically reduced by the biomass to selenites, or absorbed on the biomass. At the same time nitrites and nitrates, if present, are being reduced to nitrogen gas. The conditions in this reactor are controlled to minimize further reduction of selenites.

The water containing the selenites and any sloughed biomass is then directed to a precipitation reactor. While maintaining reducing conditions, a coagulant such as a ferric or aluminum salt is mixed with the water. By controlling the pH and using sludge recirculation to age the sludge, solids having adsorption sites are formed. Selenites are adsorbed onto these sites. Thereafter, the solids with adsorbed selenites, in addition to the sloughed biomass containing adsorbed selenium, are separated from the water. A ballasted flocculation settler such as Veolia's Actiflo is well suited for this application.

The water is further treated in a second biological reactor under aerobic conditions where the water is subjected to reoxygenation. In the process, reduced selenium species present in the water are oxidized to selenate, thus reducing the final toxicity of the final effluent.

Preliminary results

Two laboratory studies have been completed so far. The first study, a proof-of-concept test, was conducted on a coal mine effluent. No detailed speciation was conducted and the test was stopped once removal of selenium was confirmed. Note that in this test the sequence was Reduction > Reox > Selenium removal.

Table 3: Proof-of-concept test results

Parameters	Units	Raw water	After treatment
Se total	µg Se/L	344	38.4
Se dissolved	µg Se/L	311	–
Selenites	µg Se/L	< 1	8.1
Selenates	µg Se/L	308	< 1

These results were encouraging; hence, a second test was started. In this trial water from a hard-rock mine was used. The second test was longer in duration and detailed analyses were conducted to try to understand the mechanisms involved in each reactor. The reactor sequence was also changed to reduction > solid removal > reox, in the hope that this would improve selenium removal and decrease the concentration of selenites in the treated water.

For total recoverable and dissolved Se, each sample was digested in a closed vessel (bomb) with nitric and hydrochloric acids. The resulting digests were analyzed for Se content via inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS). Particulate selenium was calculated by difference.

The sample analyzed for dissolved selenium was filtered on a 0.45 µm filter. It should be noted that a significant fraction of any elemental selenium present in the water will pass through such a filter.

For the selenium speciation, each aqueous sample was analyzed using ion chromatography inductively coupled plasma collision reaction cell mass spectrometry (IC-ICP-CRC-MS). In this process, selenium species are chromatographically separated on an ion exchange column and then quantified using inductively coupled plasma collision reaction cell mass spectrometry (ICP-CRC-MS).

Two detailed speciation campaigns were undertaken. The first campaign was initiated three months after the start of the test and focused on the reduction and solid removal steps. No sampling of the Reox reactor was done in this campaign.

The main observations from this first speciation (shown in Table 4) are the following:

- The measured dissolved selenium concentrations are close to the calculated total of the speciation species detected in the sample for all samples. This would be indicative of a low concentration of elemental selenium[3].
- Selenium "disappears" in the reduction stage. This suggests that the system was not yet stabilized and that there was significant absorption of selenium on the biomass.

Table 4: First speciation campaign's results

Parameters	Units	Raw water	Reduction	After solid removal
Macro parameters				
Total recoverable selenium	µg Se/L	47.1	6.13	3.36
Particulate selenium (calculated)	µg Se/L	3.5	4.21	0.78
Dissolved selenium	µg Se/L	43.6	1.92	2.58
Speciation				
Sum of dissolved selenium species (calculated)	µg Se/L	45.32	1.126	2.762
Dimethylselenoxide	µg Se/L	< 0.01	0.024	< 0.01
Methylseleninic acid	µg Se/L	0.046	< 0.01	< 0.01
Selenites	µg Se/L	0.219	0.377	0.186
Selenates	µg Se/L	45	0.17	2.27
Selenocyanate	µg Se/L	< 0.01	< 0.01	< 0.01

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[3] Because of the small size of elemental selenium particles, the measured "dissolved" selenium will include a large fraction of any elemental selenium present. However, elemental selenium being electrically neutral, it is not measured in the speciation analysis.

Parameters	Units	Raw water	Reduction	After solid removal
Selenomethionine	µg Se/L	< 0.01	< 0.01	< 0.01
Selenosulfate	µg Se/L	< 0.01	< 0.01	< 0.01
Unknown Se speciation	µg Se/L	< 0.01	0.515	0.256

- Most of the total selenium remaining in the reduction stage is in particulate form.
- Selenium speciation in the reduction stage shows a high concentration of unknown selenium species. The organoselenium concentrations are low.
- Most of the selenium remaining after solid removal is in dissolved form, and mostly as selenate.
- After selenium removal, organoselenium concentrations are below detection limits. Some unknown selenium species are still present in the clarified water.

The second campaign was conducted a month later, four months after the test was started. For this test, the reox was operated for a week with water from the selenium removal. Prior to this the reox was fed directly from the reduction step. This time the selenium mass balance was much better.

The main observations from this second speciation are the following (see Table 5):

- The measured dissolved selenium concentrations are close to the sum of the dissolved species detected in the sample for the raw water and in the reduction step, which is indicative of a low concentration of elemental selenium.
- The total selenium concentration in the reduction step is the same as in the raw water. The reduction reactor now seems at equilibrium, at least for selenium.
- Most of the total selenium in the reduction step is in particulate form and is likely associated with sloughed biomass.
- Selenites are the main dissolved selenium species in the reduction step.
- After selenium removal most of the selenium remaining is in dissolved form. Selenocyanates and selenites are the most common species identified.
- The total selenium concentration in the reox reactor is higher than in the water after selenium removal. This is likely due to the reox not being at equilibrium.
- Most of the selenium remaining in the reox is in dissolved form, and mostly as selenite and selenate. Organoselenium species concentrations in the reox step are lower than after selenium removal, suggesting at least a partial oxidation of these species in the reox.

Table 5: Second speciation campaign's results

Parameters	Units	Raw water	Reduction	After selenium removal	Reox
Macro parameters					
Total recoverable selenium	µg Se/L	47.9	47.8	3.55	6
Particulate selenium (calculated)	µg Se/L	1.2	43.71	0.97	0
Dissolved selenium	µg Se/L	46.7	4.09	2.58	6.03
Speciation					
Sum of dissolved selenium species (calculated)	µg Se/L	45.015	3.709	1.145	2.908
Dimethylselenoxide	µg Se/L	< 0.01	0.067	0.045	0.026
Methylseleninic acid	µg Se/L	0.136	0.014	0.031	0.03
Selenites	µg Se/L	0.529	1.49	0.324	1.71
Selenates	µg Se/L	44.3	0.039	0.01	0.926
Selenocyanate	µg Se/L	< 0.01	0.767	0.501	0.141
Selenomethionine	µg Se/L	< 0.01	0.168	< 0.01	< 0.01
Selenosulfate	µg Se/L	< 0.01	0.202	0.034	0.041
Unknown Se speciation	µg Se/L	< 0.01	0.962	0.19	0.024

Advantages

Compared to existing treatment processes the Tracer Se has the following advantages:

- Nitrites and nitrates are not detrimental to the process, and might in fact be required.
- Kinetics are much faster than with a process where there is biological reduction to elemental selenium. This should translate into smaller size and lower costs.
- The process minimizes the production of the more toxic forms of selenium.
- Preliminary results indicate that the process will be able to meet the proposed Canadian Coal Mine Effluent Regulation of 10 µg/L. Pilot tests will be required to confirm the process performance.

Future work

At this point we believe that the Tracer Se process shows a lot of potential, but further work is required before it can be commercialized.

A third laboratory trial is being planned. In this trial, the reox reactor will be fed on a continuous basis with water after solid removal, which should solve the equilibrium issues experienced in the preceding trial. This will allow a better understanding of the change in selenium speciation in the reox reactor.

Laboratory trials are useful, but at some point, pilot tests will have to be undertaken. A few sites have shown an interest, but setting up these tests is a long process, and it is likely that these tests will not start until fall of 2022, or perhaps spring of 2023.

An important aspect of the pilot tests will be to monitor the long-term system performance when the raw water characteristics change, such as changes in concentration or temperature.

Like most treatment processes, the sludge produced in the Tracer Se process is susceptible to oxidation. It is not really possible to characterize the sludge at laboratory scale; a pilot is required to produce enough sludge to allow testing. Once the sludge is available, various options for safe long-term sludge storage can be studied.

Conclusion

Selenium in wastewater effluent can be a major issue due to the complexity of its removal as well as the possibility to result in a more toxic effluent after treatment, due to the modification of the bioavailability of the selenium through different processes. A new treatment process for removal of selenium, the Tracer Se process, which combines biological and physico-chemical processes, is being developed by Veolia. While the development is still in the early phases, preliminary results have shown that there is potential for excellent performance, both in terms of total selenium and low concentration of known bioavailable, hence toxic, organo-selenium forms in the treated water. Tests are ongoing and we will publish new results as they become available.

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Laboratory-Scale Bioremediation Treatability Studies for Legacy Mines and Lessons Learned

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Abstract

This paper presents results and lessons learned from laboratory-scale treatability studies evaluating passive bioremediation as a potential treatment strategy for mining-influenced water (MIW) emerging from two legacy mines in Montana, USA. MIW influent from both mine sites was acidic with a mean pH of 2.46 and 4.01, had low to moderate total dissolved solids, and contained constituents of concern (CoCs) such as Al, As, Be, Cd, Cu, Fe, Pb, Tl, and Zn that exceeded potentially applicable water quality benchmarks. Passive, biologically-based water treatment can be a cost-effective technology for treating MIW, particularly at legacy mine sites. The primary goal of these studies was to assess the effectiveness of sulfate-reducing biochemical reactors (SRBRs) and treatment wetlands for improving the quality of MIW discharges from two historical mines. SRBRs can increase pH and alkalinity of MIW while producing sulfide, which, in turn, removes aqueous metal ions through precipitation as metal sulfides. Constructed treatment wetlands can be designed to promote oxic and aerobic conditions, thereby improving the quality of SRBR-treated water. Laboratory-scale SRBRs and wetlands were evaluated for their ability to improve the quality of MIW collected from both mines. The studies were conducted with oversight by the U.S. Environmental Protection Agency and the Montana Department of Environmental Quality.

Each stage of the treatment systems effectively removed potential CoCs for MIW from each mine site by promoting the necessary geochemical and biological processes. The conditions necessary for biological sulfate reduction and metal sulfide precipitation were maintained in the SRBRs operated at design flow rates, while the conditions necessary for the oxidation of biochemical oxygen demand and manganese, and removal of residual CoCs, were maintained in the treatment wetlands. Treatment systems operating at design flow rates provided ample sulfate reduction, sulfide generation, metal sulfide precipitation, and alkalinity to significantly improve MIW quality. Despite a change in performance associated with increasing flow rates in some SRBRs, the treatment wetlands were able to continue removing residual CoCs from SRBR effluents.

Introduction

Passive, biologically-based water treatment can be a cost-effective and low-maintenance technology for treating MIW, particularly for remotely located legacy mine sites. This paper describes two laboratory-scale treatability studies developed with oversight by the U.S. Environmental Protection Agency and the Montana Department of Environmental Quality, with the goal of assessing passive bioremediation as a potential treatment option for MIW emerging from two historical mine sites. The Danny T mine adit (referred to as the Danny T mine), is located within the Barker Hughesville Mining District (BHMD) Superfund Site in Cascade and Judith Basin Counties, Montana. The Haystack Creek mine (referred to as the Haystack Creek adit), is located within the Carpenter Snow Creek Mining District (CSCMD) Superfund Site in Cascade County, Montana. Mining activities in the region occurred from the later part of the 19th and early 20th centuries until the mid-20th century after silver, lead, and zinc deposits were discovered in the districts.

The focal technologies considered were biologically-based and included sulfate-reducing biochemical reactors and constructed treatment wetlands. Biological sulfate reduction accomplished by sulfate-reducing bacteria increases alkalinity and pH of MIW while producing sulfide anions, which, in turn, remove aqueous metal ions through precipitation as metal sulfides (see Sheoran et al., 2010, for a review). Treatment wetlands can be designed to target removal of other metals not removed by SRBRs, such as manganese (Hedin and Nairn, 1993; Kadlec and Wallace, 2009). Bioremediation technologies, such as the two evaluated here, can potentially reduce operation, maintenance, and monitoring costs compared to active MIW treatment strategies, while potentially achieving water quality objectives. Ultimately, these evaluations provide critical information for determining whether passive bioremediation treatment strategies are feasible for implementation, as well as providing insight into potential design of full-scale systems.

Methods

MIW was collected from the two mines during the summer of 2017 in 55-gallon barrels, which were then sealed and transported to a testing laboratory in Tucson, Arizona. The MIW was held in climate-controlled storage until ready for use in the laboratory-scale study.

The aluminum and ferric iron typically found in MIWs may lead to clogging within SRBRs due to precipitation of aluminum and iron hydroxide and oxide minerals. This fouling may render the SRBR less effective, require increased levels of maintenance, and shorten the longevity of the treatment system. Therefore, we evaluated the need for, and effectiveness of, limestone pre-treatment by operating a subset of SRBRs with and without pre-treatment. The pre-treatment stage was designed to increase pH above 4.5 s.u. to promote the precipitation and removal of Al and Fe (oxy)hydroxides. Reactors were filled with 1 to

1.5-inch diameter limestone. Half of the Danny T SRBRs were provided with limestone pre-treated water and the other half of the SRBRs were provided raw MIW. The SRBRs receiving raw MIW were larger to accommodate a higher acidity and metal loading; thus, they were constructed from 8-inch diameter PVC pipe fashioned into 46-inch tall columns (Figure 1). The bottom 4 inches of the column was filled with pea gravel (for increased hydraulic conductivity at the effluent port), followed by 36 inches of substrate mixture. Finally, at least 2 inches of MIW at the top (inflow side of the column) will be maintained during operations. The four SRBRs receiving pre-treated water, as well as the Haystack Creek SRBRs, were smaller due to the reduced acidity and metal load and were constructed from 4-inch diameter PVC pipe fashioned into 46-inch tall columns. The bottom 4 inches of the column was similarly filled with pea gravel (for increased hydraulic conductivity at the effluent port), followed by 36 inches of substrate mixture, and finally at least 2 inches of MIW at the top. All SRBRs contained a mixture of labile and recalcitrant carbon sources, which serve as electron donors for the sulfate-reducing bacteria, as well as limestone as an alkalinity source.

In addition, a small amount of manure was added to the reactor as an inoculant to stimulate biological colony growth. Two SRBR organic substrate mixtures were evaluated, differing only in the amounts of woodchips and walnut shells. The mixtures consisted of alfalfa hay (10% wt.), woodchips and sawdust (10 or 30% wt.), walnut shells (30 or 50% wt.), and limestone (30% wt.).

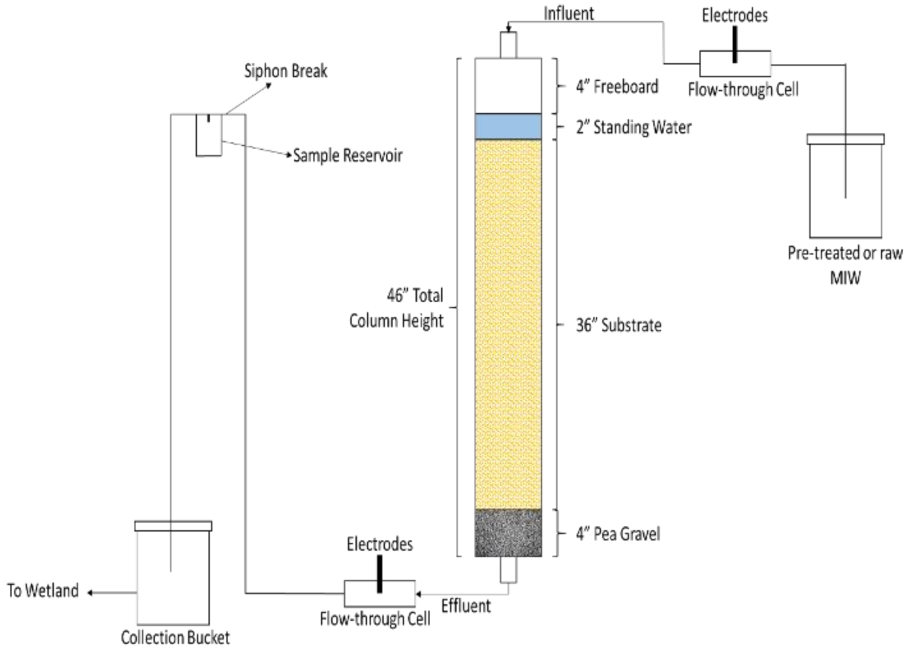

Figure 1: Schematic of the 4-inch and 8-inch diameter SRBR columns used in the treatability studies. Depicted here is a Danny T SRBR, as indicated by the SRBR-treated water being directed to a VFW

For the Danny T MIW, a third treatment stage was evaluated; vertical flow wetlands (VFWs) for removing BOD and Mn were added after the SRBRs (Figure 2). VFWs were constructed using 45-gallon polyethylene tanks (24 in. × 24 in. × 18 in.) containing 16 inches of media consisting of 8 inches of washed coarse sand placed on top of 8 inches of round, washed gravel (0.2 to 0.5 inches diameter). Influent water was distributed across the surface of the sand and gravel bed planted with wetland vegetation. Wetland plants promote an environment conducive to microbes that passively treat water, and root systems help maintain hydraulic conductivity of the media. This type of wetland has the added advantage of maintaining activity during the winter because water is distributed below the surface of the topmost media, thereby helping to maintain temperatures above freezing (Kadlec and Wallace, 2009), which would be important for any full-scale system to be considered for the site.

Figure 2: Laboratory-scale treatability study setup.
***Left*: Sample reservoirs, multi-meters, and flow-through cells on the back side of the rack.**
***Right:* Columns are on the front side of the rack and treatment wetlands on the right**

Treatability of the adit discharge was assessed by quantifying metal removal efficiency and changes in concentrations of the primary constituents of concern (CoCs) based on multiple aqueous chemical and physical parameters. Aqueous samples were routinely collected from the influent feed and from the effluent feeds of each treatment system stage and analyzed for pH, electrical conductance (EC), oxidation-reduction potential (ORP), dissolved oxygen (DO), and temperature. Samples were also analyzed for total and dissolved cations, anions, alkalinity, acidity, and biochemical oxygen demand (BOD). A set of probes were installed in a flow-through cell to record field chemistry parameters in real time, but later discontinued because of fouling issues. Routine sampling continued throughout the study. For the purposes of this paper, emphasis will be placed on results at end of pipe rather than individual treatment stages.

Results and discussion

Danny T mine MIW is acidic with a mean pH of 2.9, has moderate total dissolved solids, and contains concentrations of Al, As, Be, Cd, Cu, Fe, Pb, Tl, and Zn that exceed identified water quality benchmarks. The Haystack Creek MIW is milder, but still acidic with a mean pH of 4.0, has low total dissolved solids, and contains concentrations of Al, Be, Cd, Cu, Fe, Pb, and Zn. Results from historical periodic monitoring at both sites indicate seasonal variation in adit water quality, which is likely related to seasonal changes in flow rates associated with spring runoff.

The Danny T passive treatment system without pre-treatment markedly improved the quality of the MIW influent. Water quality indicator parameters (e.g., DO, ORP) indicate that anoxic and anaerobic conditions were maintained in all SRBRs, as required for sulfate reduction, and oxic and aerobic conditions were restored in the VFWs (Figure 3). Water treated by this two-stage system was circumneutral and net alkaline. Treated effluent was also characterized by metal concentrations at or below the identified potentially applicable benchmarks, with the exception of total arsenic, copper, and strontium. Concentrations for these metals did not decrease below the identified benchmark until the latter half of the study or they occasionally exceeded the identified benchmark. It is worth noting that strontium is not an identified CoC at the site; it was, however, leached from the substrates used in the study, highlighting the importance of characterizing potential substrates to better understand what might be added to treated water.

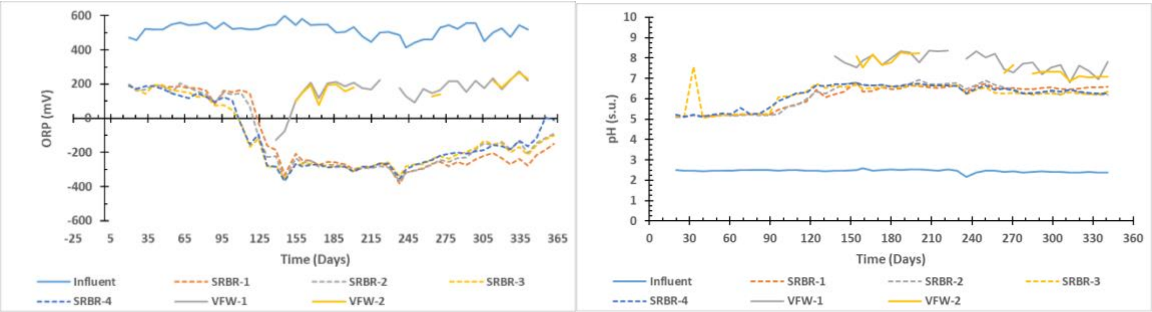

Figure 3: Oxidation-reduction potential (ORP; *left*) and pH (*right*) readings recorded during weekly sampling events in MIW influent (blue line), SRBRs (dashed), and VFWs (solid) from two-stage system (i.e., without pre-pretreatment)

The Danny T three-stage passive treatment system (with limestone pre-treatment) similarly improved the quality of the MIW influent with each stage of the three-stage system effectively removing potential CoCs as intended. Following pre-treatment, pH increased from a mean of 2.9 s.u. in the MIW to a mean of 6.6 s.u. due to alkalinity generated during the dissolution of limestone. Increased pH and reduced acidity following pre-treatment likely improved environmental conditions for sulfate-reducing bacteria, as well as other essential fermenters and methanogens within the SRBRs (Johnson and Hallberg, 2005; Sheoran et al., 2010). Pre-treatment of the MIW largely removed Al and Fe while also decreasing As, Be, Cu, and Pb concentrations. Potential CoCs relatively unaffected by the increased pH during pre-treatment were Ni, Se, Cd, Tl, Mn, and Zn. Water quality indicator parameters (e.g., DO, ORP) indicate that anoxic and anaerobic conditions were maintained in all SRBRs and oxic and aerobic conditions were restored in the VFWs throughout the study. The conditions necessary for biological sulfate reduction and metal sulfide precipitation were maintained in the SRBRs operated at design flow rates, while the conditions necessary for the oxidation of BOD and Mn, and removal of residual CoCs, were maintained in the VFWs. In fact, incorporating pre-treatment allowed the SRBRs to achieve operating conditions approximately 60 days earlier than the two-stage treatment system. Water treated by the three-stage system was circumneutral and net alkaline. Treated effluent was also characterized by metal concentrations below the identified benchmarks during the latter half of the study.

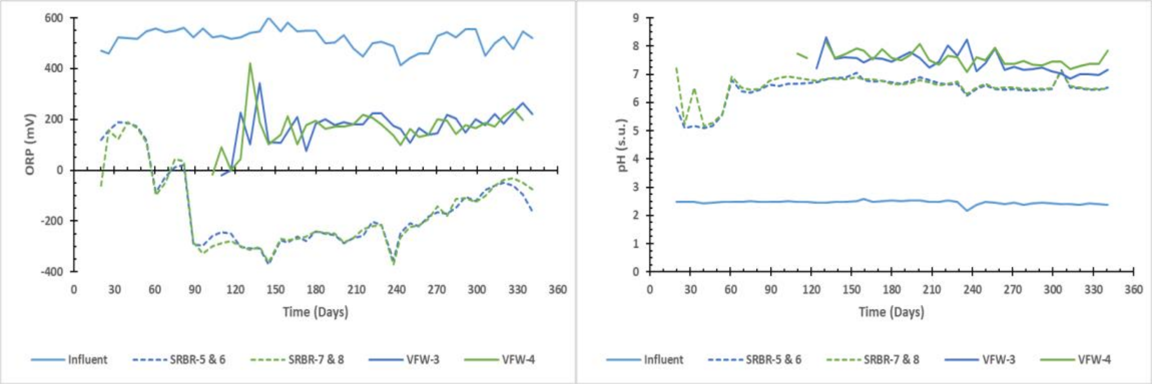

Figure 4: Oxidation-reduction potential (ORP; left) and pH (right) readings recorded during weekly sampling events in MIW influent (blue line), SRBRs (dashed), and VFWs (solid) from three-stage system (i.e., with pre-pretreatment)

The Haystack Creek SRBRs, which lacked pre-treatment and post-treatment wetlands, also successfully treated the relatively milder MIW, producing effluent that was net alkaline with a mean pH of 6.9 s.u. and

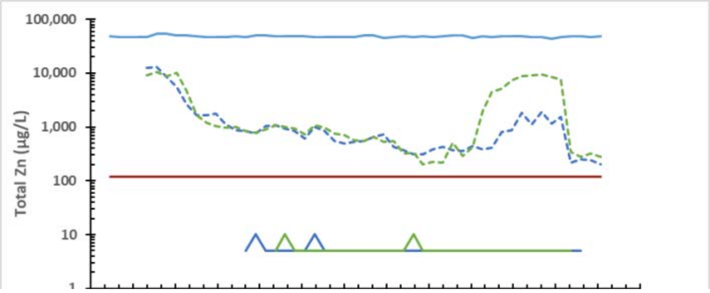

Figure 5: Total zinc concentrations (log scale) in MIW influent (blue line), SRBRs (dashed lines), and VFWs (solid lines) relative to the identified potential water quality benchmark (red lines). Zn was removed below detection levels by the VFWs

metal concentrations that were at or below the identified benchmarks, with the exception of total Zn. Zinc particulates are very small and likely were incompletely filtered out by the SRBRs. Results from the Danny T two- and three-stage systems, however, show that VFWs are an effective filtering mechanism for the total iron and zinc particulate material that was not effectively removed or retained by the SRBRs (see Figure 5 for an example). A subset of SRBRs used for both sites were periodically subjected to increased flow rates, while others were left as is. Metal removal rates increased with increasing flow rates, suggesting still greater capacity for metal removal. Yet the SRBRs operated at the (unchanged) design flow rate exhibited the most strongly anoxic and anaerobic conditions, while the SRBRs operated at higher flow rates showed signs of weakening anoxic and anaerobic conditions. For example, Danny T SRBRs 2 and 4 in Figure 3 exhibit the highest ORP values during the final 40 days of the study when they were operated at a flow rate twice as high as the design flow rate. This observation suggests that the increased mass loading of oxygen inhibited sulfate reduction. Increased oxygen loading is the likely cause of the observed increase in DO and ORP and concomitant decrease in sulfate reduction rates (not shown). However, higher oxygen loading rates do not explain the similar, but less dramatic, increase in DO and ORP and decrease in sulfate reduction rates observed in SRBRs that remained at a constant flow rate (see SRBRs 1 and 3 in Figure 3 for an example). It is possible that these SRBRs shifted to a new pseudo steady-state condition as microbial communities matured or as the availability of critical nutrients shifted (Kleinmann et al., 2021).

Another objective of the study was to refine the mixture of organic and inorganic substrates used in each treatment system component. Proper characterization and selection of organic and inorganic substrates would mitigate the observed leaching of CoCs into the water being treated and would therefore increase the likelihood of meeting all treatment goals. Moreover, selecting the appropriate mix of organic substrates offers additional benefits to SRBR performance (Sheoran et al., 2010), as suggested by the improvement in SRBRs containing a higher percentage of wood chips and sawdust relative to walnut shells. The organic carbon associated with the woodchips and sawdust may have been more readily available to the microbial community to support sulfate reduction relative to what was available in walnut shells. It is possible that more substantial differences in substrate performance may have become evident later as the contribution of more recalcitrant organic matter sources becomes more important.

Conclusions

Overall, the passive treatment systems operating at design flow rates markedly improved the quality of MIW from both mines, producing effluent that was circumneutral and net alkaline. Incorporating pre-treatment allowed the SRBRs to achieve operating conditions approximately 60 days earlier than the two-stage treatment system. The three-stage system with pre-treatment also reduced CoCs below the identified benchmarks earlier in the study. Improvements in water chemistry following pre-treatment (increased pH and reduced acidity) likely improved environmental conditions for sulfate-reducing bacteria and therefore improved its performance.

The success of all treatment systems operated at the design flow rates suggests that the initial flow and mass loading calculations provided an appropriate starting point for design and operation. Results showing metal removal rates increasing in several SRBRs with increasing flow rates suggests still greater capacity for metal removal. However, the data also indicate that there are limits to metal removal. Differences in performance became evident as flow rates were increased to each treatment system. In the system without pre-treatment, anoxic and anaerobic conditions were maintained in all SRBRs throughout the study. In the system with pre-treatment, the SRBRs operated at the highest flow rate began exhibiting signs of failure, as indicated by a near complete, but potentially temporary, loss of anoxic conditions by the end of the study. Results suggest performance decreased in these high flow rate SRBRs due to excessive oxygen loading.

Overall, results from this study highlight the value in designing passive bioremediation systems with components that target different subsets of potential CoCs. In this study, the conditions necessary for biological sulfate reduction and metal sulfide precipitation were promoted in the SRBRs, while the conditions necessary for the oxidation of BOD and Mn, and removal of residual CoCs, were promoted in the VFWs. CoCs targeted for removal by the SRBRs, but which were not completely removed, were subsequently removed by the VFWs.

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Treatment of a Thickener Overflow in Metal Mining Using Membrane Separation Technologies

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Abstract

In this study, the feasibility of treating a thickener overflow stream from a North American copper and nickel concentrator using membrane separation technologies was evaluated. Performances of pressure driven technologies including a combined ceramic membrane microfiltration (MF) and reverse osmosis (RO), and an electrochemically driven technology, electrodialysis (ED), were compared.

The results show that both RO and ED technologies were effective at reducing the concentration of the major salts and contaminants in the thickener overflow (including calcium and magnesium) below the detection limit of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). This can result in a significant alleviation of the build-up of salts in the recycled water stream, and will reduce its negative impact on the effectiveness of the flotation process in the recovery of nickel and copper. During RO separation, the permeate flux decreased over time. This could be attributed to membrane fouling caused by a high concentration of calcium sulfate in the thickener overflow streams. This negative phenomenon could be minimized via electrodialysis reversal (EDR). The results of this study showed that both RO and ED are potential candidates for mine water treatment applications in milling operations. In addition, ED can be a promising alternative to RO, as ED requires less pre-treatment in applications for water streams with high scaling potentials.

Introduction

Milling processes including grinding, flotation, and thickening are the most water-intensive parts of the mining industry. The overflow stream from the thickening process is normally recycled and reused in grinding and flotation. This is done to minimize the demand for fresh water. The remainder of the water balance is made up of process water that comes from the tailings treatment process. The thickener tank overflow water has a much higher total dissolved solids (TDS) than that of the process water (Di Feo et al., 2020). While the recycling of this stream reduces the intake of fresh water, it also results in a build-up of salts and contaminants. This in turn leads to a decreased effectiveness of the flotation process. It has been shown in laboratory tests that the nickel + copper grade versus nickel recovery curve decreased when thickener overflow was used (Di Feo et al., 2021). More precisely, the nickel + copper grade of the primary rougher concentrates decreased relative to that obtained with process water (Di Feo et al., 2021).

The objective of this work was to evaluate the effectiveness of two membrane separation technologies including reverse osmosis (RO) and electrodialysis (ED) to treat the thickener overflow stream. Reducing the concentration of salts and contaminants in a thickener overflow stream can result in maintaining the grade of nickel + copper in the flotation process. Figure 1 presents the flowsheet diagram of a copper and nickel concentrator with the proposed membrane separation stage to treat the thickener overflow stream before being recycled and reused in grinding and flotation.

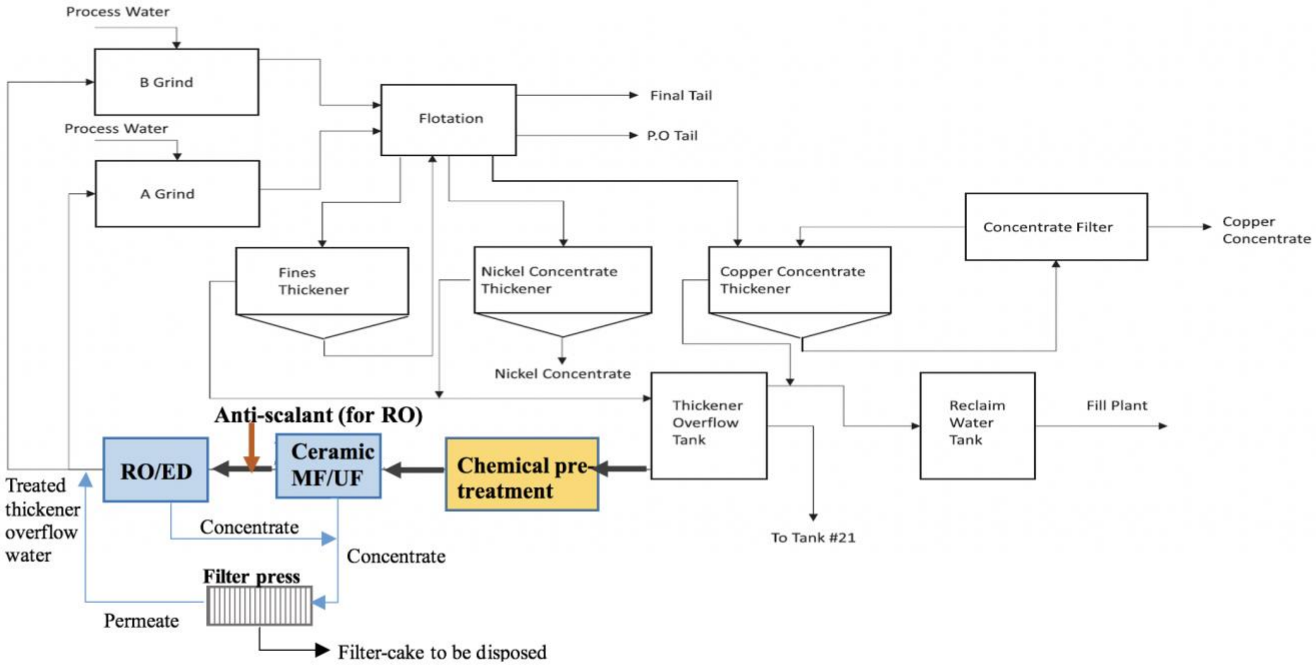

Figure 1: Flow diagram of a copper and nickel concentrator (modified from Di Feo et al., 2020)

Methodology

Two test systems were used in this study: a) a pilot-scale RO system, manufactured by BluMetric Environmental Inc., Canada, containing a standard GE-Osmonics RO membrane with a Molecular Weight Cut-off (MWCO) in the range of 200–250 Daltons and maximum operating pressure of 400 psi (Figure 2); and b) a pilot-scale ED system manufactured by Electrocell North America Inc., USA, with ten pairs of

Neosepta anion exchange (CEM) and cation exchange membranes (AEM), stacked in an alternating configuration (Figure 3). The systems were utilized to treat the thickener overflow samples from a North American copper and nickel concentrator. As a pre-treatment step, a single ZrO_2/Al_2O_3 ceramic microfiltration (MF) membrane with 19 channels and a pore size of 110 nm was employed to remove suspended solids (SS). Detailed descriptions of ED and RO operations were presented in previous publications (Di Feo et al., 2021; Mosadeghsedghi et al., 2020). During ED, operation polarity was switched to reversal mode at specific intervals for 15 seconds.

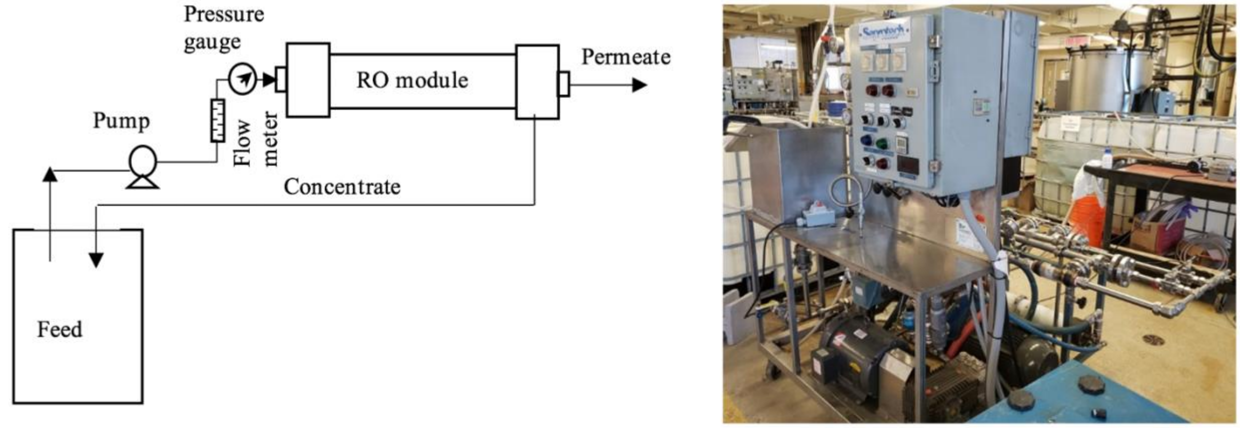

Figure 2: Schematic of the BluMetric Environmental RO system

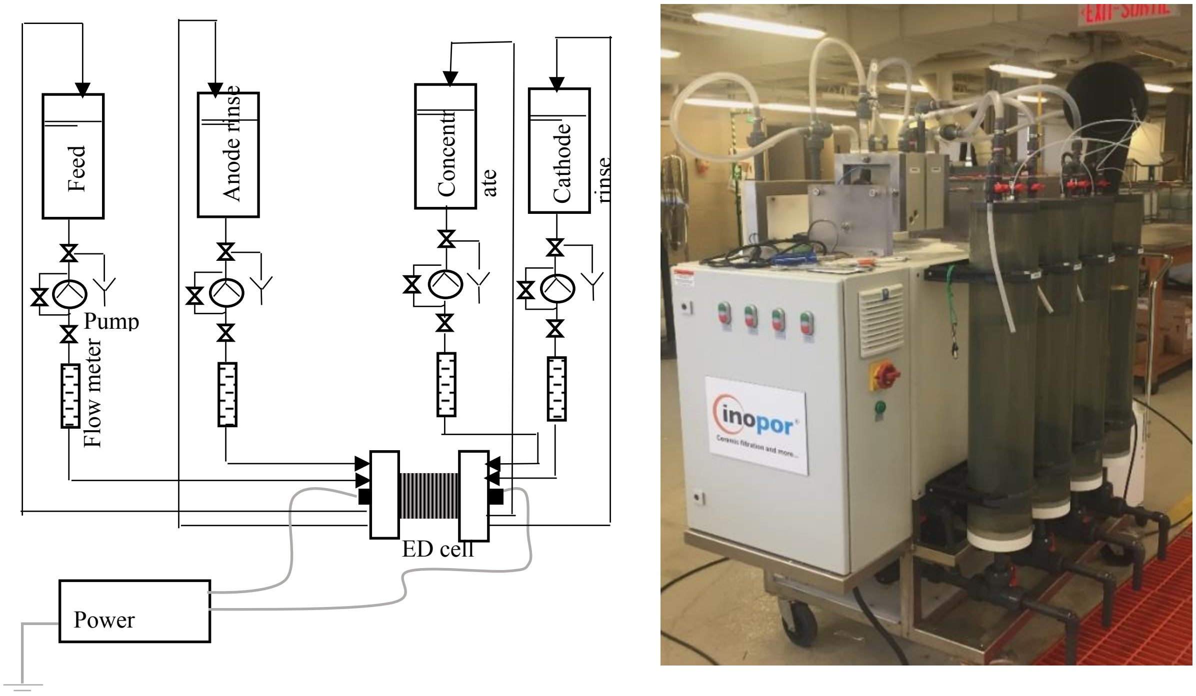

Figure 3: Schematic of the ElectroCell laboratory-scale ED system

In both operations, samples of 50 mL were taken in specific intervals for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis. The percentage of ion rejection (R) was calculated using the following equation:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \ \ (\%)$$

Where:

C_0 = the concentration of a specific element in the initial thickener overflow feed sample.

C_t = the concentration of a specific element at *t* minutes of operation, in the permeate and in the feed respectively for RO and ED operations.

To measure the permeate flow rate in RO operation, the time for collecting 500 mL of permeate is measured at specific intervals. Permeate flux describes the quantity of permeate produced during RO separation per unit of time and membrane area (Alonso et al., 2020). The permeate flux was calculated using the following equation:

$$P_v = \frac{F_P}{S}$$

Where:

P_v = the permeate flux.

F_p = the permeate flow rate

S = the area of the membrane, which was 7.9 m^2 for GE-Osmonics RO.

Results and discussion

The elemental composition of the raw thickener overflow, as well as the treated samples using RO and ED, are presented in Table 1.

Table 1: ICP-AES elemental composition data for the raw and treated thickener tank overflow

Element	Raw feed concentration (mg/L)	Concentration after RO (mg/L)	Concentration after ED (mg/L)
Al	0.295	<0.077	<0.077
B	<0.096	<0.096	<0.096
Ba	0.114	0.003	<0.003
Bi	<0.430	<0.430	<0.430
Ca	701.000	6.310	1.230
Cd	<0.023	<0.023	<0.023
Co	<0.120	<0.120	<0.120
Cr	<0.053	<0.053	<0.053
Cu	0.032	<0.008	<0.008
Fe	<0.026	<0.026	<0.026
K	48.660	21.130	<0.058
Li	<0.042	<0.042	<0.042
Mg	0.027	0.007	0.001
Mn	<0.004	<0.004	<0.004
Mo	<0.048	<0.048	<0.048
Na	112.000	32.230	0.560
Ni	<0.140	<0.140	<0.140
P	<1.530	<1.530	<1.530
Pb	<0.140	<0.140	<0.140
S (ICP)	792.000	<17.500	<0.730
Sb	<0.090	<0.090	<0.090
Se	<0.340	<0.340	<0.340
Si	0.931	<0.096	<0.096
Sr	1.650	0.0132	<0.010
Te	<0.170	<0.170	<0.170
Zn	<0.024	<0.024	<0.024
Zr	<0.014	<0.014	<0.014
TDS (mg/L)	2416.000	247.000	189.000

The ICP-AES results (Table 1) show that the raw thickener overflow (before membrane treatment) contained calcium and sulfur (in the form of sulfate salts) at concentrations of around 700 mg/L and 790 mg/L, respectively. Membrane scaling will occur during RO treatment at these concentrations, and will result in permeate flux decline over time (Ashfaq et al., 2020). This phenomenon was observed during treatment of the thickener overflow using RO (Figure 4).

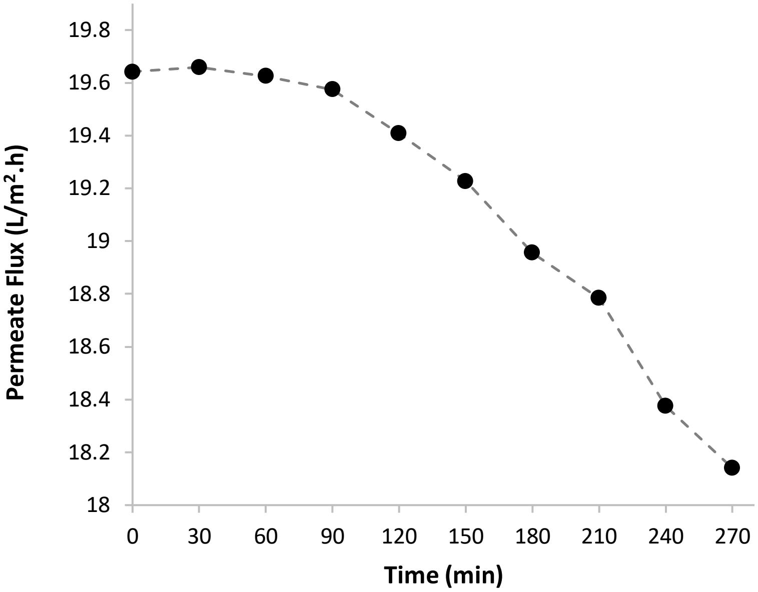

Figure 4: Permeate flux vs. time during RO separation

Scanning Electron Microscopy (SEM) images of a scaling layer on a RO membrane are shown in Figure 5. It was suggested that the addition of polyphosphates such as sodium hexamtaphosphate (SHMP) as anti-scalants can retard the precipitation of the scale-forming sulfate and carbonate salts. However, their use can cause the formation of phosphate scaling (Mortazavi et al., 2008).

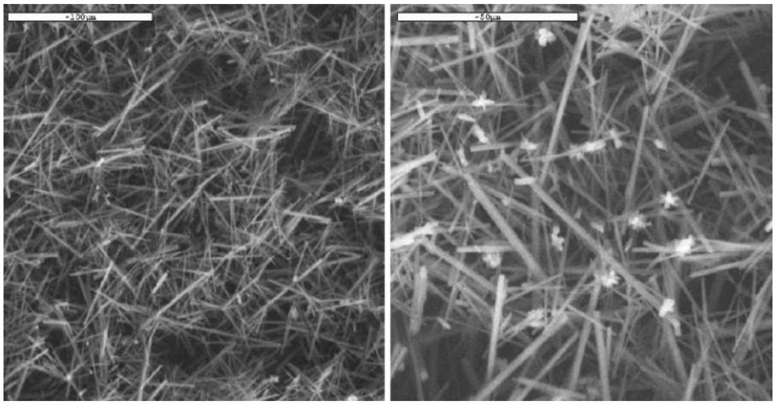

Figure 5: SEM of a scaling layer deposited on the surface of the RO membrane

This negative phenomenon was minimized via electrodialysis reversal (EDR) and the reversal polarity mode of ED operation. Due to its scaling-prevention feature, ED was suggested to be used before membrane separation technologies. This can significantly reduce the scaling and fouling issues during nanofiltration

(NF) and RO operations (Geluwe et al., 2011). Figure 6 shows that using both RO and ED, high removal rates were obtained for most dissolved components of the thickener overflow.

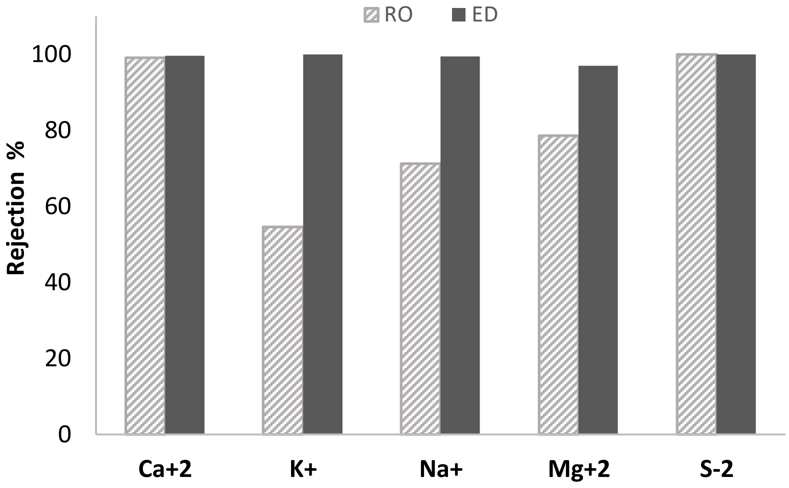

Figure 6: The percentage of ion rejection using RO and ED treatments

The quantities of calcium and sulfur, the two most concentrated constituents in the feed, removed using RO were 99% and 100%, respectively. In comparison, the quantities removed by ED were 99.6% and 100%, respectively. In addition to calcium and sulfur, potassium was present in feed water samples at considerable concentrations. The concentration of potassium in initial samples was approximately 49 mg/L, and a complete removal of 100% was achieved by ED, which was around 45 percentage points higher than that of 54.6% obtained by RO. Accordingly, the total dissolved solids concentration (TDS) of the thickener overflow stream was effectively reduced by more than 90% using either technology.

Conclusion

The thickener overflow stream of a North American copper and nickel concentrator was effectively treated using membrane separation technologies including RO and ED, before being recycled and reused in grinding and flotation. The TDS content of the thickener overflow was reduced by over 90% after being treated by either of the two discussed technologies. Membrane scaling occurred during RO operation due to high calcium sulfate concentrations in thickener overflow samples. This negative phenomenon could be prevented via ED due to its reverse polarity feature (EDR).

Conclusively, both RO and ED can be used to reduce the accumulation of contaminants in recycled streams in milling operations. ED seems to be more advantageous than RO as it is more resistant against scaling and organic fouling. ED is also advantageous from an operating cost point of view as it does not rely on pressure.

Recommendations for future work

The present study focuses on minimizing the constituents in the thickener overflow stream in order to alleviate their negative impact on the nickel + copper grade in the flotation process. However, there are still gaps in the understanding of how the chemistry of recycled water can influence the recoveries and grade of nickel + copper. A detailed study on the effect of constituents' concentrations of thickener overflow stream on flotation will be the subject of our future studies. The ultimate objective is not to fully treat the thickener overflow recycled stream, but to maintain certain concentrations of the constituents within the operating limits of the flotation process. In order to obtain the operating limits of flotation for the constituents' concentrations, the following approaches will be taken: a) partially treat the entire thickener overflow stream to different levels of constituents concentrations; and b) completely treat a split stream (20%-70%) of the thickener overflow stream and recombine the treated split with the untreated stream. Ultimately, the treated thickener overflow stream from the above-mentioned approaches will be combined with process water at different ratios (20%-50%) and will be recycled to the grinding and flotation circuit.

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A Selective Sulfate Removal Plant Using an Innovative Approach to Ion Exchange

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Abstract

This paper details a 2 MLD plant which selectively removes arsenic, antimony, iron, hardness, and sulfate from mining water; designed to meet environmental quality indicators. The client, Fosterville Gold Mine Pty Ltd, is owned by Kirkland Lake Gold and is one of the world's highest grade gold mines. The site is located near Melbourne, Australia and it had identified a risk of reduced mine water storage capacity due to surface run-off and increased dewatering of the underground mine at depth. Clean TeQ Water carried out the project management, process design, procurement, and commissioning for the plant, which was handed over in August 2020.

The plant uses Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology, which uses both ion exchange chemistry and filtration to remove pollutants from water. Unlike conventional ion exchange (IX) systems which use static beds, CIF® uses a moving packed bed of ion exchange resin that provides optimized chemistry and the ability to filter solids when needed. Two CIF® modules were placed in series for the plant to form a DESALX® system. The first module removes multivalent cations (such as calcium, magnesium, and metals such as manganese and iron), and the second module removes multivalent anions (such as sulfate). During the treatment process, monovalent ions such as sodium and chloride pass through, and a gypsum-based brine is created that can be sent to existing lime precipitation systems for a zero liquid discharge solution.

The water produced by the DESALX® plant meets the performance criteria for sulfate, iron, arsenic, and antimony, with chemical usage below the design criteria. It also meets the quality indicators required by the State Environment Protection Policy for Waters; thereby potentially allowing the mine site to consider other water management best practices, such as managed aquifer recharge (MAR).

Introduction

Mine water treatment

Mine water has some unique challenges, often being high in suspended solids, metals, high or low pH, and with varying water flowrates and qualities (Brown et al., 2002). One of the most difficult mine water challenges is dealing with the brine left over from physical separation processes, such as reverse osmosis (RO). RO has long been accepted as the technology of choice for mine water treatment. However, it is susceptible to scaling and fouling due to cations such as calcium, magnesium, strontium, barium, aluminium, iron, or manganese, reacting with anions such as sulfate, phosphate, carbonate, or silicate in the feed. Due to the presence of these species, water recovery is often limited to below 70% during treatment, producing a large volume of difficult-to-manage saline brine. The resultant brine ponds to manage this brine are often expensive to install, require large surface areas, can be unsightly, and are very expensive to decommission. In addition to low recovery, scaling and fouling results in low RO membrane life, increased costs due to membrane replacement, and additional downtime and chemical use due to CIP (clean-in-place).

Continuous ion exchange

Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange, while simultaneously performing physical filtration, tolerating suspended solids in the feed. The ion exchange resin is periodically moved around the system for reconditioning. Additional information about CIF® can be found in the Appendix.

DESALX® technology

DESALX® combines two CIF® units in series. The first removes the divalent cations such as calcium, magnesium, and other metals, before the second stage removes multivalent anions such as sulfate. In the first stage, the strong acid cation resin in hydrogen form is regenerated using sulfuric acid, and in the second stage the weak base anion resin in free base form is regenerated using lime.

When calcium sulfate (gypsum) precipitation is expected during desorption, an additional agitated desorption column is used in the process to prevent blocking up. This column uses either physical mixing or air agitation in a Pachuca column depending on the characteristics of the water. The gypsum formed is removed with the spent solution during the resin transfer step. This is a process that cannot be achieved with batch IX processes, as solids block the system.

DESALX® selectively removes the multivalent cation and anions, letting the majority of monovalent anions through. Using sulfuric acid and lime as reagents creates gypsum in both stages, allowing DESALX® brine to be dewatered or combined with high-density sludge (HDS) systems to achieve a zero liquid discharge outcome.

DESALX® can be used to treat a variety of mine water types, including acid mine drainage, pit water, surface runoff, tailings water, excess water from underground mines, and process water. Hardness, metals, and sulfate are commonly present in mining wastewater as a result of processing, acid mine drainage, or the use of sulfuric acid on site.

The water treatment plant for Fosterville gold mine

Fosterville gold mine

The Fosterville gold mine is located two hours north of Melbourne, Australia. It is the state's largest gold producer and one of the highest-grade gold mines in the world. The underground mine has been in operation since 2005.

When mining started in 2005 there was an excess water problem. The excess water was initially stored in some of the old open cut pits, and as these started to fill up, the thinking moved to reinjecting the water back into the aquifer. The technology that first came to mind to reach the required quality for managed aquifer reinjection (MAR) was ultrafiltration (UF) followed by RO, however this approach was expected to only achieve 50% water recovery. Initial modelling of the system showed DESALX® offered lower operating costs and higher water recovery, reducing the volume of brine that would need to be stored on site. The ability to send the softened water to a reverse osmosis plant for polishing was also identified, achieving higher RO recovery and reducing the potable water makeup required for the mine's processing circuits.

The management at Kirkland Lake Gold (now Agnico Eagle) saw the benefits that the DESALX® technology would bring and decided to proceed with the technology, making it the largest DESALX® installation to date. The contract was awarded in 2017 and design work and construction followed shortly after.

Design phase

The flowsheet for Clean TeQ Water's scope can be seen in Figure 1, and a labelled render of the plant layout can be seen in Figure 2. The plant includes a ferric chloride precipitation system to reduce the arsenic and antimony in the feed water. The treated water then moves to the first stage of DESALX®, where cations such as iron, calcium, and magnesium are removed. The sulfate is then removed from the water in the second stage. Two modules consisting of adsorption, desorption and wash columns operate in parallel to accommodate the 2 MLD flowrate.

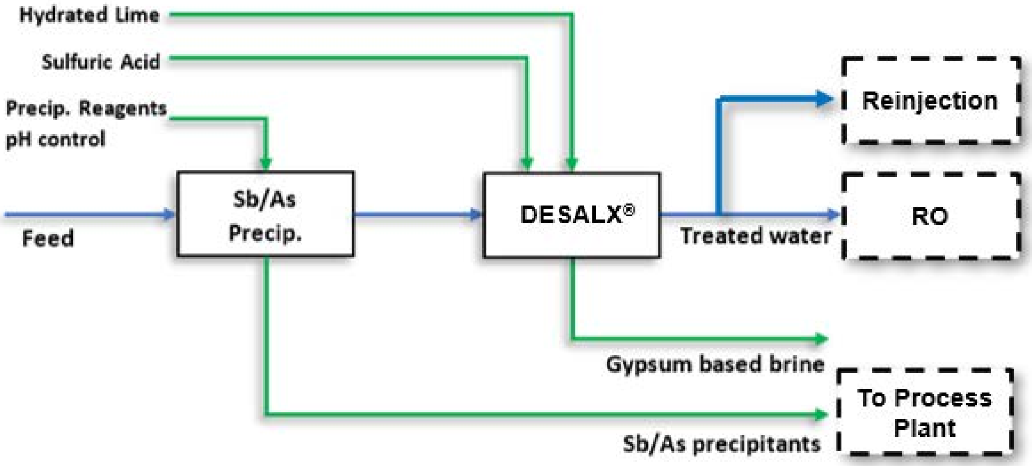

Figure 1: 2 MLD sulfate removal plant flowsheet

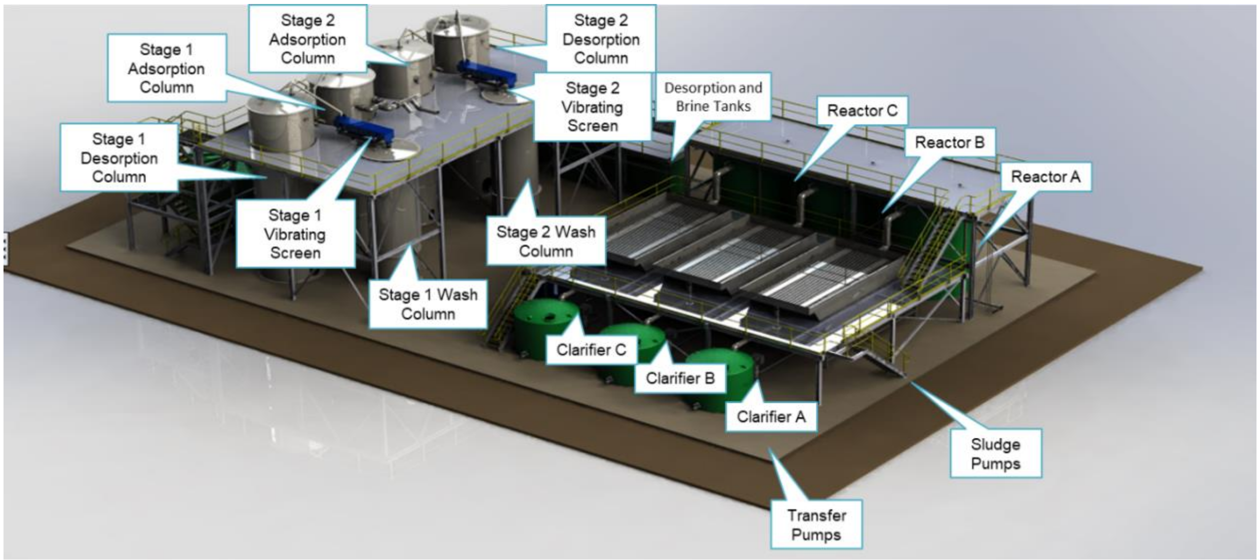

Figure 2: Layout of the plant

Project schedule

The project kicked off at the start of 2018 and included laboratory trials, a laboratory pilot, and a site pilot to optimize the design and verify the performance. Long lead items were ordered, and the fabrication of equipment continued in 2018. The final HAZOP/process review was completed, and construction finished in October of 2019. Commissioning was completed in December of 2019, with ongoing operations troubleshooting and support continuing, and the RO system being ramped up. Final handover of the plant occurred in August of 2020. A photograph of the completed plant can be seen in Figure 3.

Figure 3: Photograph of the completed plant

Performance

The design basis and performance of the plant is summarized in Table 1. The water produced by the DESALX® plant meets the performance criteria and the quality indicators required by the State Environment Protection Policy for Waters, making it of suitable quality that it can be reinjected into the aquifer. As of 15 April 2022 the mine is still a zero liquid discharge site, and water is sent to the downstream RO for process water reuse. The downstream RO is achieving a recovery of 85% given the reduced scaling risks and lower turbidity. The plant's resin flowrates can be adjusted if needed to increase and decrease the cation and anion removal extents.

Table 1: Design basis and plant performance (bolded species indicate performance criteria)

		Design basis			Plant performance
Species	**Unit**	**Before precipitation**	**Before DESALX®**	**After DESALX®**	**After DESALX®**
Total dissolved solids	ppm	7,400	7,400	5,848	5,410
Calcium	ppm	300	300	85	107
Magnesium	ppm	321	321	96	223
Sulfate	ppm	1,515	1,515	1,000	790
Iron (soluble)	ppm	1	5	0.1	0.05
Total arsenic (soluble)	ppm	0.5	0.03	0.03	0.001
Antimony (soluble)	ppm	13	0.05	0.05	0.025

Keys to successful project delivery

Several factors contributed to the successful delivery of the project, including these:

- Strong relationship formed between Clean TeQ Water and all parties involved.
- Openness to using new ion exchange technology for mine water treatment.
- Two rounds of piloting (one on site and one in the lab) for the smooth scale-up and optimization of design parameters.
- Collaborative engagement with the client and contractor to seamlessly integrate the plant with existing operations.
- On-the-job training of operators allowing smooth operation beyond commissioning.
- Remote access to the PLC allowing for quick assistance when required during the early days of the plant.

Lessons learned

Being the first large-scale installation of the technology for mine water treatment there were a number of lessons learned and improvements to the process:

- A better understanding of the hydraulics of moving large resin beds between columns was obtained, and of the forces that are exerted on various components, was obtained.
- The design of the resin screens was improved early in the project following deeper collaboration with suppliers.
- Improvements were made to arsenic and antimony sludge management using seeding and recycling to further reduce footprint and maintenance requirements.
- The size of buffer storage between DESALX® and RO was increased to ensure easy operation at higher capacities.

Looking ahead, Clean TeQ Water has already started:

- Further reducing acid consumption to near molar stoichiometric ratio.
- Improving the in-column aeration design to optimize the air usage when resin is transferred.
- Implementing high-velocity columns to allow for a more compact system.

Conclusions

The 2 MLD DESALX® plant at the Fosterville gold mine was successfully delivered to assist the client in managing their excess water. The water produced by the DESALX® plant meets the performance criteria for sulfate, iron, arsenic, and antimony, meeting the quality indicators required by the State Environment

Protection Policy for Waters and allowing the mine site to consider managed aquifer recharge. Conventional batch ion exchange systems have often struggled to find a place in mine water flowsheets, particularly when suspended solids and the risk of precipitation are present. This plant confirms Clean TeQ Water's moving bed technology as a viable and beneficial ion exchange based mine water treatment method.

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Appendix

Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange while simultaneously performing physical filtration, tolerating suspended solids in the feed, and allowing for cheaper reagents such as sulfuric acid and lime to be used. These usually cannot be used in conventional batch ion exchange systems since the precipitates that form cause the system to block up during desorption.

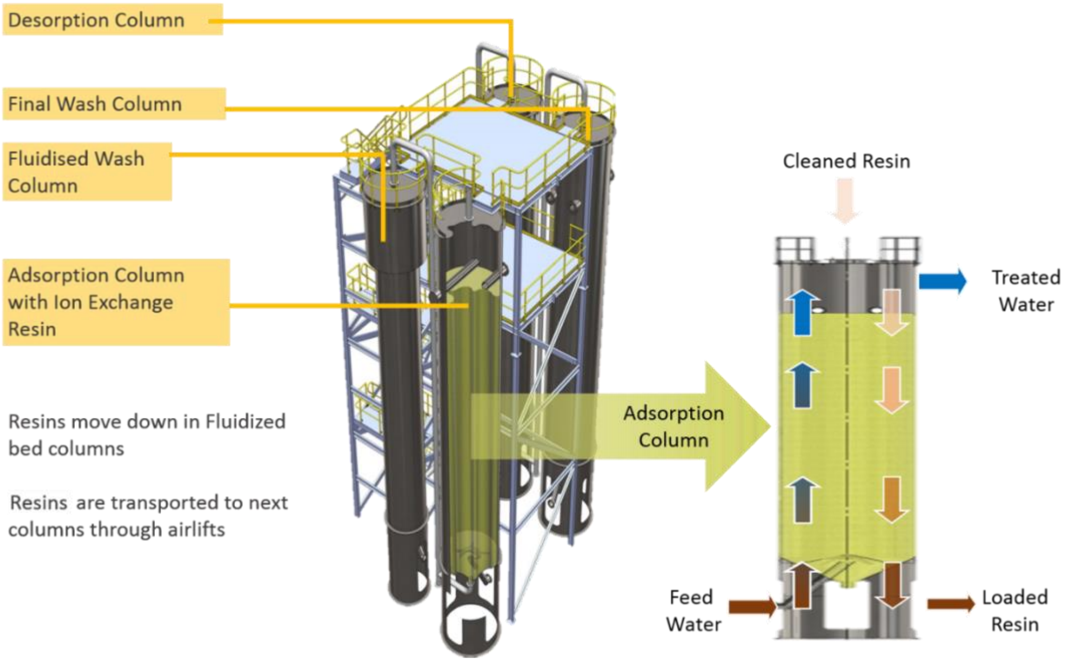

Figure 4: Diagram of a typical CIF® system

CIF® is also more resistant to resin bed fouling compared to conventional ion exchange approaches since the ion exchange resin in periodically moved around the system. Higher removal efficiencies are also achieved in CIF® due to the counter-current movement between the feed solution and ion exchange resin.

The system can also tolerate up to 150 mg/L of suspended solids in the feed and perform physical filtration if required.

In CIF®, ion exchange resin is continuously moved around the system for regeneration. Water treatment occurs in the adsorption column, which uses a moving packed bed of ion exchange resin. It can be likened to the continuous sand filtration process; however, the ion exchange resin continuously removes dissolved ions through ion exchange while simultaneously filtering solids if required. CIF® consists of a series of vertical columns, as seen in Figure 4, with one column treating the water, and the rest used to recondition the ion exchange resin as part of a continuous process.

Heavy Metal Removal from Polluted Waters Using *Schoenoplectus californicus* and *Phragmites australis*

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Abstract

Acid mine drainage (AMD) is one of the most significant environmental challenges facing the mining industry worldwide. Furthermore, in many countries, the relationship between the mining industry, land, water, and communities is very close. In Peru this relationship goes beyond economic factors. Often, the negative effects of AMD can reduce the quality of water resources and affect communities. For this reason, many methods have been developed for AMD treatment, with wetlands being a good option for heavy metal removal. In wetlands, the use of green plants and their associated microbiota seems to be a good technique to remove, contain, or render harmless environmental contaminants.

In this paper, we present the efficacy of *Schoenoplectus californicus* and *Phragmites australis* in a laboratory test for the removal of heavy metals from an aqueous solution. Both plants are Peruvian native Andean plants, and were tested using artificial solutions containing heavy metals such as copper, iron, lead, and zinc. From binary solutions of copper-iron, zinc-iron, and lead-iron, *Schoenoplectus californicus* removes 82%, 75%, and 88% of copper, zinc, and iron respectively; while the recovery of copper and lead in a quaternary solution of copper-zinc-lead-iron was 90 and 92% respectively. On the other hand, in the case of *Phragmites australis,* recoveries are slightly lower. From binary solutions the removal was 68% of copper, 53% of zinc, and 20% of lead; while the recovery in quaternary solutions was 97 and 95% for copper and zinc, respectively. Based on the results, it is concluded that *Schoenoplectus californicus* and *Phragmites australis* have a potential to be used in wetlands, especially in high Andean mining areas in Peru, to avoid possible contamination of natural water bodies in those areas.

Introduction

Acid mine drainage (AMD) and the possible contamination of nearby water sources and soils is one of the more serious environmental problems in the mining industry. For this reason, many remedial treatments for

AMD have been developed in recent years (Rodríguez-Galan et al., 2019). AMD remediation techniques can be classified as active and passive treatments, with active methods being the most widely used (Obreque-Contreras et al., 2015). Passive treatments, being relatively inexpensive and environmentally friendly, have recently become a viable implementation alternative. There are several types of passive treatment systems (Costello, 2003; Sheoran and Sheoran, 2006; Skousen et al., 2017; Ziemkiewicz et al., 2003). These systems are summarized in Table 1.

Table 1: Passive treatment systems

Passive treatment methods	
Aerobic wetlands (AeW)	Open limestone channels (OLC)
Anaerobic wetlands (AnW)	Permeable reactive barriers (PRB)
Anoxic limestone drains (ALD)	Pyrolusite® limestone beds
Reverse alkalinity producing systems (RAPS)	Slag leach beds (SLB)
Limestone diversion wells (LDW)	Successive alkalinity producing systems (SAPS)
Limestone leach beds (LSB)	Sulfate reducing bioreactors (SRB)
Microbial reactor systems (MRS)	Vertical flow wetlands (VFW)

In wetlands, the use of green plants and their associated microbiota seems to be a good technique to eliminate or reduce the concentration of environmental pollutants (Hallberg and Johnson, 2005; Klein et al., 2014; Mojiri et al., 2017). In addition, there are several factors that influence the effectiveness of plants. Ideal plants must be: hardy; able to tolerate low nutrient levels; resistant to weather shifts; and able to uptake more contaminants than normal plants. Various plants for heavy metals removal have been evaluated in pilot and constructed wetlands (Table 2).

Table 2: Plants used in passive treatment systems

Plant	Reference
Cyperus esculentus	Folsom and Lee, 1981
Eichhornia crassipes	Mishra, 2008
Phragmites australis	Bonanno and Giudice, 2010; Lee and Scholz, 2007; Southichak et al., 2006
Pista stratitoes	Miretzky et al., 2004
Schoenoplectus californicus	De Lange et al., 1998; Vymazal, 2013
Scirpus lacustris	Vymazal, 2011
Typha domingensis	Dunbabin and Bowmer, 1992; Vymazal, 2011
Vetiveria zizanioides	Borralho et al., 2020

Phragmites australis and *Schoenoplectus californicus* are the most used plants due to their wide tolerance to changes in pH (4–10), salinity (20–45 mg Cl/L), temperature (10–32ºC) (Neubauer et al., 2012; Reddy et al., 1990; Reddy and D'Angelo, 1997; Stein and Hook, 2005).

Schoenoplectus californicus grows in the coastal and riparian regions of southern North America (Mason, 1957) to Chile and Argentina (Wagner et al., 1990). This plant is also found in some Pacific islands such as the Cook Islands, Easter Island, New Zealand, and Hawaii (Hidalgo-Cordero and García-Navarro, 2017). It also frequently found in the high Andean areas of South America (Blanco, 2019). In fact, this plant is found at elevations from sea level to 3,800 m.a.s.l. Growing in extreme habitats, *Schoenoplectus californicus* has developed the ability to withstand fluctuations in temperature and volumes of water, high levels of ultraviolet-visible (UV-Vis) radiation, high salt content (areas near the beach), and potential polluting elements such as arsenic of natural origin (Montoya et al., 2009).

Schoenoplectus californicus is a perennial herbaceous plant. Its stem can measure between one and four meters, and occasionally reaches six meters, depending on the variety. The habitats of *Schoenoplectus californicus* are marshes, the banks of rivers and lakes, as well as areas prone to seasonal flooding. Its roots can extend to great depths of water varying from 2.5 to 3 m. However, this plant can grow and develop without problems in water depths of between 30 cm and 70 cm (Hidalgo-Cordero and García-Navarro, 2017; Neubauer et al., 2012).

It is believed that *Phragmites australis* was a plant native to Europe and the Canary Islands, and from there it was introduced to other parts of the world. It is currently one of the largest plants in the world. Specimens can be found from greater than 70°N to the equatorial regions and south to Tasmania (Australia) and the cone of South America (Weber, 2003). *Phragmites australis* is a plant with great adaptability to fresh water, brackish water (up to 10,000 ppm total dissolved salts) (Sainty and Jacobs, 1988), and alkaline wetlands in temperate zones world-wide (Roman, 1984). It also grows in natural and artificial wetlands, ditches, marshes, swamps, bogs, and prairie potholes as well as in artificial canal systems in agricultural areas (Roman et al., 1984). *Phragmites australis* has been reported in various climatic zones ranging from cold zones between 70°N and 43°S (Dahl, 1934; Haslam, 1972; Isacch et al., 2006; Packer et al., 2017) to tropical zones such as the Equator (Haslam, 1972) and arid zones such as Australia (Davies et al., 2010; Pfadenhauer and Klötzli, 2014).

Phragmites australis is a grass species that can grow up to four meters in height (Hanganu et al., 1999). It reaches high densities and forms monospecific stands (Hudon et al., 2005). The phragmite family have an estimated average lifespan of 4.5 years, but can live up to 6 years (Haslam, 1972). It has been shown that it is possible to adapt *Phragmites australis* to altitudes between 400 to 2,360 m.a.s.l. (Jiao et al., 2020; Klimeš et al., 1999; Klimeš, 2000).

Due to their great versatility and ability to adapt to different climates and temperatures, this study has used *Phragmites australis* and *Schoenoplectus californicus* for the design of wetlands. The aim of this research is focused on the evaluation of heavy metal removal by using *Phragmites australis* and *Schoenoplectus californicus* in laboratory wetlands under controlled conditions.

Materials and methods

Collection of plants

Phragmites australis and *Schoenoplectus californicus* were collected in the southern area of Lima, Peru. The collected plants were washed with tap water and deionized water, in order to remove dust.

Wetlands systems

Figure 1: Wetlands facility details

Polycarbonate cells with a width, height, and length ratio of 1:2:4 respectively were designed and constructed according to EPA recommendations (EPA, 2015). Four specimens of each plant were placed on each cell, with a distance of 20 cm between them. Then, 15 liters of an artificial effluent containing copper sulfate (0.063 mM), zinc sulfate (0.062 mM), iron sulfate (0.062 mM) and lead sulfate (0.033 mM) was added at a rate of 3 ml/min. This flow was simulated in order to generate an adaptation of the plants to the environment. The wetlands facility is presented in Figure 1.

The experiment was carried out at 16°C to 18°C, 450 m.a.s.l., with a humidity of approximately 65%. These conditions are similar to those of some mining operations that take place in Peru. In fact, mining in Peru takes place mainly in the high Andean zone (above 3,800 m.a.s.l.). However, some important operations are carried out on the coast with altitudes that range between 50 and 10,00 m.a.s.l. Among these we can mention: María Teresa (25 to 200 m.a.s.l.), Condestable (100 and 450 m.a.s.l.), Veta Dorada (115 m.a.s.l.), Los Incas (585 m.a.s.l.), San Juan (800 m.a.s.l.), Doble D (1,200 m.a.s.l.) and Cerro Lindo (1,820 m.a.s.l.). Likewise, San Vicente (1,400 to 2,000 m.a.s.l.) and Palmapeta (1,500 m.a.s.l.) are located on the edge of the jungle, where the humidity (90%) can be very similar to that of the city of Lima.

Water and plants sampling

Water samples from the eight constructed wetlands cells were collected in 100 ml plastic bottles over 7 days. 80 ml of each sample was filtered using 0.45 µm cellulose acetate filters (Sadler and Rynja, 1992). The other 20 ml was kept as an unfiltered sample and was used to measure turbidity. The concentrations of ammonia and nitrate were determined using the colorimetric method. The remaining concentrations of copper, zinc, and lead in the water were determined by flame atomic absorption spectroscopy (AAS) (O'Halloran et al., 1997).

The plants were carefully removed from the cells, rinsed with water, divided into aerial parts and roots, and placed in paper containers. Then they were taken to an oven to be dried at 60°C, to eliminate humidity. Later, the samples were pulverized with a grinder. Before determining the heavy metal concentration with AAS, a wet digestion process was performed. One gramme of dried sample was weighted into a porcelain crucible and then calcinated at 500°C for 12 hours in a muffle (Akinyele and Shokunbi, 2015; Hoening, 2005; Onianwa et al., 2001). In order to dissolve the organic material, the ash obtained was placed in a glass beaker with 15 ml of HNO_3 (1.0 M). The beaker was heated for 30 minutes in a hot plate, where the temperature increased to 100 °C. The residue was filtered into a 25 ml volumetric flask using a filter paper (Whatman, No. 42); the volume was completed with HNO_3 (1.0 M).

Metal removal

AAS was used to determine the concentration of heavy metal in water and in plants. To stablish the accuracy of the measurement of metal concentration with this method, blanks and standards were prepared based on the standard procedures (Ipeaiyeda and Ayoade, 2017; Padmavathiamma and Li, 2007; Radulescu et al., 2014; Soylak and Kizil, 2004).

During the analysis, a blank solution with 2 ml of 0.50% aqueous nitric acid (HNO_3) was prepared. Next, with the dilution of 1,000 ppm of the stock with 0.50% aqueous HNO_3, three standard solutions (100 mL) for each metal were prepared (see Table 3). The blank, standard (from lowest to highest concentration) and sample solutions were placed in that order on the autosampler. At the end, all absorbance results were registered.

Table 3: Instrumental conditions of the metal analysis by AAS

Parameters	Zn	Fe	Pb	Cu
Wavelength (nm)	213.9	248.3	283.3	324.8
Calibration range (mg/L)	0.2–1	1–5	2–10	1–5
Lamp current (mA)	9	15	10	8
Slit (nm)	1	0.2	1	0.5
Flame composition	air/acetylene			
Oxidant pressure (bar)	0.758			

Results and discussion

Metal removal

The variation of metal concentrations in the different samples was analyzed. The results obtained from the initial day and from the eighth day are summarized in Table 4 and Table 5 for *Phragmites australis* and *Schoenoplectus californicus* respectively. The efficiency of absorption of heavy metals by the plant is expressed by:

$$Efficiency = \left(\frac{C_f - C_0}{C_0}\right) x\ 100$$

Where, Cf and Co are the final and initial concentration of the metals in the solution.

The translocation factor (TF) is defined as the concentration of heavy metals in the shoot tissue divided by the concentration of heavy metals in the root tissue (Ipeaiyeda and Ayoade, 2017). Taking into account that if TF>1, the plant is a hyperaccumulator; if TF <1, it is a phytostabilizer.

Phragmites australis

The variations of the metal concentrations in binary and quaternary solutions are indicated in Figure 2 a. The removal of copper is greater in the quaternary solution than in the binary one. The same trend can be observed in zinc and lead.

However, the removals are minor in the case of lead. Only 4% of iron can be removed from the quaternary solution. It is observed that in binary solutions, iron interferes more in Pb removal than in Cu and Zn removal. An interference trend can be established in the following binary solutions, Pb-Fe > Zn-Fe

> Cu-Fe. In the quaternary solution a greater removal of zinc and copper is observed, and less lead removal is noticed. A removal trend can be established, Zn > Cu > Pb >> Fe.

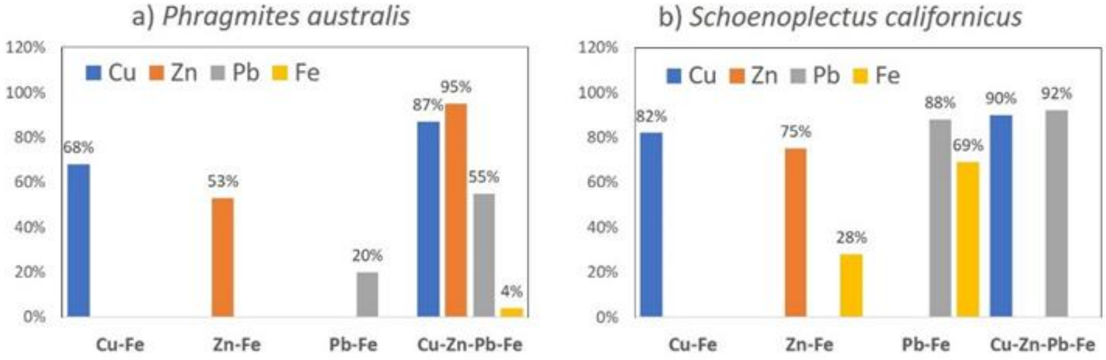

Figure 2: Metal removal percentages in each wetland

Table 4: Heavy metal concentrations (mg/L) in *Phragmites australis*, determined by AAS

		Solutions			
Metal	**Day**	**Cu-Fe**	**Zn-Fe**	**Pb-Fe**	**Cu-Zn-Pb-Fe**
Cu (mg/l)	Day (0)	0.50	---	---	0.97
	Day (9)	0.16	---	---	0.13
Zn (mg/l)	Day (0)	---	0.45	---	1.49
	Day (9)	---	0.21	---	0.08
Pb (mg/l)	Day (0)	---	---	0.46	0.31
	Day (9)	---	---	0.37	0.14
Fe (mg/l)	Day (0)	0.26	0.35	0.47	0.28
	Day (9)	0.64	1.33	0.54	0.27

Schoenoplectus californicus

The variations of the metal concentrations in binary and quaternary solutions are indicated in Figure 2 b. Iron can only be removed in the quaternary solution and in the leaded binary solution. The removal of copper is greater in the quaternary solution than in the binary one. The same trend can be observed in lead and iron. However, the removals are minor in the case of iron. It is observed that in binary solutions, iron interferes more in Zn removal than in Cu and Pb removal. An interference trend can be established in the following binary solutions, Zn-Fe > Cu-Fe > Pb-Fe. In the quaternary solution a greater removal of lead and copper is observed. In this case, a trend can be established and removal, Pb > Cu.

Table 5: Heavy metal concentrations (mg/L) in *Schoenoplectus californicus*, determined by AAS

		Solutions			
Metal	**Day**	**Cu-Fe**	**Zn-Fe**	**Pb-Fe**	**Cu-Zn-Pb-Fe**
Cu (mg/L)	Day (0)	0.50	---	---	0.71
	Day (9)	0.09	---	---	0.07
Zn (mg/L)	Day (0)	---	0.83	---	0.24
	Day (9)	---	0.21	---	0.64
Pb (mg/L)	Day (0)	---	---	0.33	0.66
	Day (9)	---	---	0.04	0.05
Fe (mg/L)	Day (0)	0.26	0.18	0.29	0.36
	Day (9)	0.55	0.13	0.09	0.71

Metal accumulation in plant species

The final concentration of heavy metal in each part of the plants were measured with the method described above. The results are summarized in Table 6 and Table 7. It is important to note that the Fe concentrations are the highest compared to the other heavy metals. Likewise, the Fe concentration in the roots of *Schoenoplectus californicus* is higher than in the roots of the *Phragmites australis*.

Phragmites australis

In this case, the metals are adsorbed on the roots, with the highest root/stem ratio for Fe in the binary solution (Cu-Fe and Zn-Fe) and Cu in quaternary solution. A greater fixation of iron in the roots is observed for all solutions, and is slightly greater for the binary solution of Zn-Fe.

In addition, it is observed that the *Phragmites australis* accumulates iron (95%) and copper (92%) in the root part in the binary (Cu-Fe) and quaternary solution respectively. Nearly 65% of Pb is accumulated in the roots in the binary (Pb-Fe) and quaternary solution. The translocation factor (TF) shows that the plant is a phytostabilizer.

Table 6: Final concentrations (ppm) of heavy metals in different parts of *Phragmites australis*

		Solutions			
Metal	**Part**	**Cu-Fe**	**Zn-Fe**	**Pb-Fe**	**Cu-Zn-Pb-Fe**
Cu (mg/l)	Roots	0.95	---	---	2.44
	Stems	0.55	---	---	0.22
	TF	0.58	---	---	0.09
Zn (mg/l)	Roots	---	1.47	---	2.36
	Stems	---	0.26	---	1.08
	TF	---	0.18	---	0.46
Pb (mg/l)	Roots	---	---	0.82	0.56
	Stems	---	---	0.47	0.29
	TF	---	---	0.57	0.51
Fe (mg/l)	Roots	27.35	36.30	22.25	28.10
	Stems	1.59	2.69	6.63	4.08
	TF	0.06	0.07	0.30	0.15

Table 7: Final concentrations (ppm) of heavy metals in different parts of Schoenoplectus californicus

		Solutions			
Metal	**Part**	**Cu-Fe**	**Zn-Fe**	**Pb-Fe**	**Cu-Zn-Pb-Fe**
Cu (mg/l)	Roots	7.36	---	---	5.14
	Stems	0.80	---	---	0.39
	TF	0.11	---	---	0.08
Zn (mg/l)	Roots	---	2.19	---	4.38
	Stems	---	0.87	---	1.38
	TF	---	0.40	---	0.31
Pb (mg/l)	Roots	---	---	2.07	1.42
	Stems	---	---	1.09	1.59
	TF	---	---	0.53	1.12
Fe (mg/l)	Roots	102.30	110.93	160.23	107.91
	Stems	10.29	19.68	6.30	13.51
	TF	0.10	0.18	0.04	0.13

Schoenoplectus californicus

In this case, the metals are adsorbed on the roots. With the exception of lead in the quaternary solution, where this metal is absorbed in the stem. The highest root/stem ratio is observed for Fe in the binary solution

(Pb-Fe) and Cu in the quaternary solution. Likewise, it is observed that the *Schoenoplectus californicus* mainly retains the ions in its roots, copper (93%), zinc (76%) and iron (96%). The lowest root metal content is observed for Pb in the quaternary solution. The translocation factor (TF) shows that the plant is a phytostabilizer.

Conclusion

Phragmites australis and *Schoenoplectus californicus* can successfully remove heavy metals such as Cu and Zn, and to a lesser extent Pb.

In wetlands with *Phragmites australis*, Fe appears to interfere with the removal of other metals when it is in a binary solution, with the greatest impact on lead removal (only 20%). However, in the presence of more metals, the interference of iron decreases considerably, allowing a good removal of Cu (87%) and Zn (95%), and greatly improving the removal of Pb (55%).

In wetlands with *Phragmites australis*, the interference of Fe seems to be lesser, especially in binary solutions, in which despite its presence, a good percentage of Cu (82%), Zn (75%) and Pb (88%) can still be removed. In the quaternary solution, a preferential recovery of Cu (90%) and Pb (92%) is observed, to the detriment of Zn and Fe.

In general, we can conclude that the studied plants have a potential to be used in wetlands. This provides scientific support for the replication of this process with these plants, either in the laboratory under different conditions, or on a larger scale. Nonetheless, the effect of the species in Fe concentration requires additional study, due to the reverse effect that has been observed.

Acknowledgements

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Metals Removal in a Two-Stage HDS Pilot Study on Concentrated Mine Water

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Abstract

The closure of inactive mine sites requires the management and disposal of water that has over time accumulated onsite. In the specific case that is the subject of this paper, a large volume of water had accumulated from mining operations. The water is characterized as being highly acidic, with a high sulfate and TDS concentration, and large concentrations of a variety of metals and metalloids. The volume of water is sufficiently large that treatment will take over a decade. A number of processes were evaluated for removal of the bulk of the wastewater constituents, including sulfate, fluoride, aluminum, copper, iron, and host of metals and metalloids at lower concentrations. As an initial evaluation, the high-density sludge (HDS) process was selected for a laboratory-scale pilot study. Lime was used as the neutralizing agent, due to cost considerations. Limestone was also evaluated. The study was conducted in HDR's process research laboratory in February and March of 2021. An additional run was conducted in May of 2021. The pilot system operated at a flowrate of nominally 100 ml/min, under a variety of operating conditions. The high strength of the wastewater and the resulting high solids formed in neutralization presented major challenges. This paper describes the wastewater characteristics, pilot system configuration, overall pilot system performance, and the degree of removal of some of the specific metals present.

Introduction

A mining company is in the process of closure of a non-operational copper mine site in the southwestern USA, which has accumulated a substantial volume of wastewater. This water is acidic and contains high concentrations of sulfate, copper, aluminum, and other metals. The accumulated water volume, along with the continuing inflow of groundwater and drainage, must be treated prior to discharge or reuse. There are many options for handling this wastewater, including resources recovery options (recovery of metals), traditional treatment and disposal options (like HDS), and evaporative solutions.

One approach under consideration is the high-density sludge (HDS) treatment. This process was initially developed by Bethlehem Steel in the 1960s to improve the treatment of acid mine drainage. HDS improves on simple hydroxide precipitation by modifying process conditions in such a way as to create a denser sludge and use chemicals most efficiently. This is critical because chemicals (lime) and sludge disposal are usually the two largest contributors to operating costs. These process conditions focus on driving the precipitation reaction for metal hydroxides and insoluble salts onto the surface of recycle solids, as opposed to occurring in solution. This results in the formation of larger particles, and if done properly, generates more uniform particle sizes that thicken and dewater more effectively. Typically, this process is used on streams in which the precipitated solids total in the hundreds to low thousands of parts per million (ppm). In this case, the concentration of precipitated solids is over 70,000 ppm.

Raw water characteristics

Four totes of water from the site were used as raw wastewater during the HDS testing described in this paper. These four totes were collected in a single sample event from the larger of the two pits at the site, as the water quality in the pits was similar. Runs #1 through #4 were performed using pit water from Tote #1. Mid-way through Run #4, the raw wastewater from Tote #2 was used. Run #7 was run on concentrated pit water from Tote #3. This tote was deliberately concentrated by blowing air through it to evaporate water. The concentration factor for this tote was approximately 15%.

It is suspected that a sampling anomaly resulted in Tote 2 having higher concentrations than other totes for most parameters. The sampling was done using an existing pumping system and piping, and it is possible some material in the line originated at another pit and was in the line at the start of sampling. The analytical data for each tote is detailed in Table 1 below. It was expected that the water quality in the pit was relatively homogenous based on past studies.

The characteristics of the water in the totes varied to a greater degree than expected. This is evident in the data presented. For example, for aluminium data where the concentrated tote (Tote 3) was concentrated over Tote 1, but Tote 2, which was not concentrated prior to use, was higher still in aluminum and most other parameters. Also, it should be noted that Tote 4 was much higher in several parameters, including sulfate, than the other totes.

The data in Table 1 reflects missing data for fluoride and sulfate in Totes 2 to 4. This results from analytical error on the part of the outside laboratory performing the analyses.

Table 1: Raw pit water from totes used during pilot

Analyte	Units	Tote 1	Tote 2	Tote 3	Tote 4
Aluminum	mg/L	6,400	7,800	7,200	11,000
Antimony	mg/L	0.0037	0.0042	ND	0.0046
Arsenic	mg/L	0.37	0.45	0.40	0.39
Beryllium	mg/L	2.1	2.3	2.2	2.5
Cadmium	mg/L	4.6	5.4	4.9	5.4
Calcium	mg/L	420	490	520	240
Chromium	mg/L	2.6	3.0	2.8	3.0
Cobalt	mg/L	10	12	11	12
Copper	mg/L	610	690	830	820
Fluoride	mg/L	840	–	–	–
Iron	mg/L	130	150	140	<0.39
Magnesium	mg/L	4,100	4,600	4,300	5,000
Manganese	mg/L	240	280	250	350
Mercury	ng/L	3.6	3.5	4.6	2.6
Molybdenum	mg/L	0.0042	0.0079	0.0099	0.0027
Nickel	mg/L	20	24	22	23
Potassium	mg/L	200	220	190	210
Selenium	mg/L	0.29	0.33	0.36	0.4
Silver	mg/L	<0.0041	<0.0082	<0.0082	<0.0041
Sodium	mg/L	300	310	310	320
Strontium	mg/L	3.5	4.0	3.8	3.2
Sulfate	mg/L	56,000	–	–	70,000
Thallium	mg/L	0.020	0.015	0.019	<0.010
Tin	mg/L	<0.042	<0.084	<0.084	<0.042
Total dissolved solids	mg/L	84,000	87,000	82,000	91,000
Total suspended solids	mg/L	170	210	96	26
Uranium	mg/L	2.8	2.3	3.0	2.6
Vanadium	mg/L	0.055	0.21	0.14	0.16
Zinc	mg/L	75	91	84	87

Discharge criteria

There are several options for discharge of the water after treatment and all have different discharge criteria. One attractive option is partial treatment and conveyance to an adjacent active mine site. Other options include discharge to groundwater, discharge to surface water, and use for livestock watering. Table 2 summarizes critical parameters of the potential discharge criteria versus the characteristics of the pit water.

Based on these data, the parameters of greatest concern include aluminum, arsenic, cadmium, chromium, copper, fluoride, iron, manganese, nickel, selenium, sulfate, total dissolved solids, total suspended solids, uranium, and zinc. The option of sending water to a neighbouring mine is attractive, as only pH and total suspended solids (TSS) requirements need to be met. However, most of the lime demand has to be satisfied to increase the pH to safely over 6, and to do this economically still requires treatment and solids/liquid separation. Of the other options, livestock watering is the most attractive set of criteria, but any of the discharge criteria may require polishing treatment beyond the HDS process.

Table 2: Potential effluent concentration requirements

Analyte	Units	Tote 1	Adjacent facility	Groundwater	Surface water	Livestock watering
pH	**Std units**	**2.0**	**>6**			
Aluminum	mg/L	6,400			0.243	
Arsenic	mg/L	0.37		0.01	0.15	0.2
Boron	mg/L	<0.025		0.6	187	
Cadmium	mg/L	4.6		0.005	0.00147	0.05
Chromium	mg/L	2.6		0.1	0.23	1
Cobalt	mg/L	10		0.875	0.042	
Copper	mg/L	610		1.3	0.0291	0.05
Fluoride	mg/L	840		4	140	
Iron	mg/L	110			1	
Manganese	mg/L	240		1.6	3.39	
Molybdenum	mg/L	0.0042		0.04		
Nickel	mg/L	20		0.1	0.168	
Selenium	mg/L	0.29		0.05	0.002	0.05
Sulfate	mg/L	56,000				
Total dissolved solids	mg/L	84,000				
Total suspended solids	mg/L	170	500			
Uranium	mg/L	2.8		0.02	2.8	
Zinc	mg/L	75		2	0.38	25

HDS system configuration

There were several concerns with the raw water characteristics that made the configuration of the pilot critical. These included:

1. The very high sulfate concentration >56 grams/litre (g/L). Given the pH below 3, a large amount of lime is required, and this potentially represented the production of as much as 76.5

g/L of calcium sulfate. The HDS process has some limitations in this area, and with the other precipitates present, the potential to reach 100 g/L solids formed exists, which is high for effective treatment. The limiting factor here is solids recycle, the homogeneity of the reaction tank contents, and the solids flux limitation on thickening. To counter this, effluent recycle was provided as well as solids recycle, so that the solids level was diluted.

2. Aluminum was the highest concentration metal present at over 6,400 mg/L. Precipitated as aluminum hydroxide, this would yield a solids-formed concentration of about 14.5 g/L TSS. Aluminum hydroxide is more difficult than other metals to form HDS solids. Improvement in solids characteristics is achievable, but the solids produced are smaller, and less dense than other metals. Aluminum hydroxide is amphoteric, starting to increase in solubility above pH 6.5. To remove the optimal amount of aluminum, solids liquid separation should occur near that pH.
3. A number of metalloids are effectively removed by coprecipitation at a pH below 7. These include arsenate, molybdenum, and selenite.
4. Magnesium is present at over 4,000 mg/L. The conventional wisdom is that magnesium hydroxide does not precipitate until a pH of over 10, and that is true when the concentration of magnesium is small. The solubility curve for magnesium hydroxide is steep, but at a pH of 9, a review of published solubility curves for magnesium hydroxide indicates a solubility as magnesium in the vicinity 3,400 mg/L at a pH of 9.4, and slightly over 4,000 mg/L at a pH of about 9. On a theoretical basis, some amount of magnesium hydroxide would precipitate in a second stage operated at about 9.
5. Most of the lime demand and most of the solids formed are generated at a pH below 6. This includes most of the calcium sulfate (from neutralization of the bulk of the free acidity plus that associated with aluminum, iron and copper sulfates). The metals precipitating at higher pH levels (zinc, nickel, cadmium) are low in concentration compared to aluminum, iron, and copper.

Observations from previous studies (single-stage HDS) indicated that a two-stage process was needed to effectively remove aluminum and other metals. The pilot HDS system was a two-stage system, consisting of reaction tanks and a clarifier operated at a pH of about 6, and reaction tanks and a clarifier operated at a pH of 9. The configuration of the pilot system is shown in Figure 1.

Recycle solids are initially mixed with lime slurry in an alkalization tank. The alkalization tank discharges to the neutralization tank, where it mixes with the influent water and recycle effluent for dilution. The neutralization tank overflows to an aging tank, which allows completion of calcium sulfate precipitation. The aging tank overflows to a vessel we have termed a sand trap. Our preference would have been a hydrocyclone, but the flows were too low. Heavier solids settle out in the sand trap and are pumped from the bottom. The intent is to remove some of the larger solids so that the recycle solids would be finer, and have more opportunity for growth. The sand trap overflows to a floc tank, and then on to the clarifier. The first stage normally operated at a pH of about 6. The clarifier effluent was then pumped to the second stage, which essentially duplicated the first stage without a sand trap.

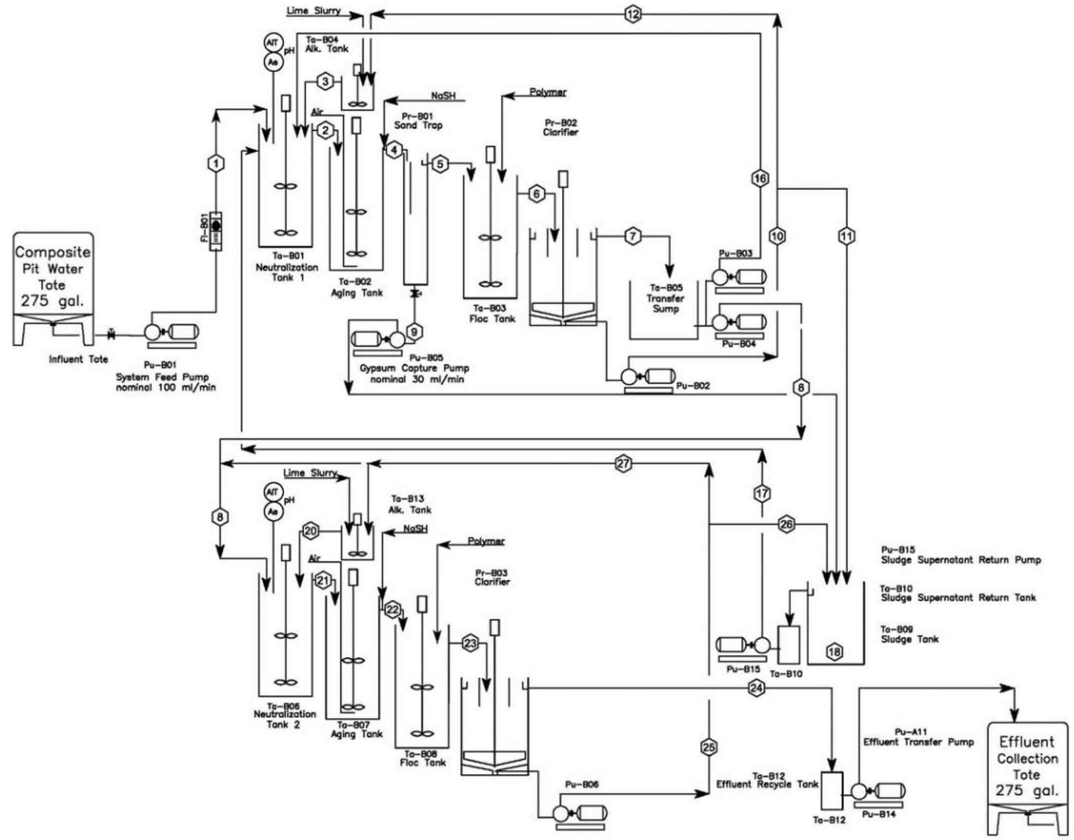

Figure 1: Flow diagram

Chronology

Rather than a detailed operating chronology, which would take more space than available in this paper, Table 3 shows the test runs that were conducted and their key parameters. Operationally, there were several issues that affected the outcome of the study. In no particular order, these were:

1. The solids-formed was measured on most runs, and was found to vary with minor modification of test conditions, including time between additions, mixing intensity and amount of reagent added at a time. The method was standardized using an intensely stirred 2-litre beaker with a reaction tank mixer to produce very aggressive mixing, and adding lime

in relatively small increments, typically allowing 5 minutes between additions. All solids formed values measured were higher than expected. It is possible that unreacted lime could have contributed to the solids formed measurement, but the mixing in the beaker was very aggressive.

Table 3: Study operating conditions

			Recycle ratio		Clarifier Effl pH				
Run	**Days**	**Configuration**	**#1**	**#2**	**#1**	**#2**	**Lime-stone**	**Aeration**	**NaSH**
1	6	Startup-maximize recycle	1.2	69	6.67	9.28	No	Both	No
2	5	Maximize recycle rate	5.75	91.3	6.85	9.33	No	Both	No
3	5	Limestone to first stage alkalization tank	3.98	215	6.59	9.46	Yes	Both	Stage 1
4	5	Impact of aeration	3.38	271	6.23	9.22	No	no	Stage 2
5	5	Maximize sludge from sand trap	4.05	298	6.65	9.14	No	Stage 2	Stage 2
6	5	Lower pH setpoint	4.39	208	6.0	8.63	No	Stage 2	Stage 2
7	5	Concentrated influent	4.75	175	6.35	8.91	No	Stage 2	Only last day
8	5	Single stage	2.7	XX	9.1	XX	No	Yes	No

2. Because of the higher than expected solids-formed, it was not possible to get the recycle ratio high enough in Stage 1 to produce very dense particles.
3. Sludge recycle and high suspended solids in the Stage 1 reaction tanks also presented problems related to plugging during start-up. Plugging dropped off with routine operation, which may reflect on the particle size distribution or operational adjustments.
4. Stage 2 exhibited much lower than expected lime demand, and much lower than expected solids formed. It was very rare to waste solids from this system. Lime demand in some runs was managed manually with a dropper, as pumping on a timer caused overshooting of the pH setpoint.

Summary of solids characteristics by runs

A total of 8 runs were conducted, each with over 40 hours of operating time. As would be expected, the first run exhibited continually improving Stage 1 and Stage 2 clarifier underflow (CU) concentrations. A critical parameter in this study is that of Ultimate Density (UD). The UD test is done by gravity settling a sample of sludge for a period of 24 hours, and determination of the solids concentration of the thickened sludge.

Stage 1 exhibited continued improvement in UD and CU in Run 2, but saw a decrease in both parameters in Run 3, in which limestone was added to the influent. As a point of comparison, UD at the end of Run 2 was about 220 g/L, but dropped to under 150 g/L at the end of Run 3. CU at the end of Run 2 was 150 g/L, and also dropped in Run 3 to a final value of about 75 g/L. CU and UD improved in Run 4, with the UD once again reaching 200 g/L. CU and UD continued to improve in Run 5, with a peak UD of 250 g/L at the end of Run 5. Note that in Run 5, all sludge was wasted from the sand trap, whereas in other runs the sand trap flow was set and excess solids were also wasted intermittently from the clarifier underflow.

Run 6 involved reducing the pH setpoints for both stages. The impact on Stage 1 was a rapid decrease in both CU and UD, with some improvement during the week. At the end of Run 6, CU improved to 100 g/L, well below the 175 g/L value at the end of Run 5. UD at the end of Run 6 was 180 g/L. Run 7 reflected improvement to near Run 5 levels for both CU and UD. Run 8 was the single-stage run. At the higher pH in the initial stage, there was greater lime demand and higher solids formed. As a result the recycle rate was lower, which may account for the lower CU (about 130 g/L at the end of the run) and UD (about 160 g/L). As shown in Table 3, recycle ratios were between 3/1 and 6/1. This range is not ideal, but the limitation on maintaining a reasonable solids concentration in the reaction tanks, while trying to achieve a recycle ratio of 15/1 or 20/1, would have resulted in a huge upsizing of treatment equipment due to the need for substantial effluent recycle, and performance at this level was thought to be adequate in terms of indicating reagent utilization efficiency and overall removal of the various components.

The second stage of the process, which increased the pH from 6 to 9, experienced a lower-than-expected solids production. Lime demand was so low that even using a timer to control lime addition for a few seconds every few minutes could not provide a consistent pH level in the reaction tanks. At times, lime slurry was manually added using a dropper. The solids-formed level was much lower than expected in Stage 2. In terms of clarifier underflow and ultimate density, there was a consistent upward trend from start-up through the end of Run 5, which peaked at about 200 g/L CU and 380 g/L UD. Run 6 (lower pH setpoints) exhibited a drop in CU to about 100 g/L, with an associated UD of under 200 g/L. These parameters trended up in Run 7, but due to the low solids formed, the rate of change was limited. There was no second stage in Run 8. Because of the lower-than-expected solids formed, and the need to maintain velocity in sludge tubing, the recycle ratio in Stage 2 was consistently above 100/1.

Removal of major contaminants

Aluminum, sulfate, and magnesium were the three parameters with the greatest concentrations in the influent wastewater.

Aluminum

Aluminum removal was typically to under 2 mg/L as dissolved aluminum in the effluent from Stage 1, and slightly better in Stage 2. Given the initial concentration of over 6,400 mg/L this represents greater than 99.97% removal. Although the theoretical solubility of aluminum in Stage 1 is lower than this, given the matrix of soluble components, this still represents a high level of removal. The single-stage effluent in Run 8 was an order of magnitude higher at an average of 16 mg/L for days 4 and 5 of the run. This is in agreement with past studies using a single-stage HDS pilot, which saw effluent concentrations of 10.6 mg/L aluminum at pH 9.0 and 15.0 mg/L at pH 9.6, both with an influent concentration of under 5,000 mg/L aluminum.

Sulfate

Effluent sulfate concentrations in the Stage 2 effluent were ranged between 12,000 and 14,000 mg/L for the two-stage process. The run using a single-stage configuration showed an effluent sulfate concentration of about 2,500 mg/L. This run also exhibited a higher lime demand, and the reduced sulfate concentration likely results from the additional calcium added.

Magnesium

Magnesium removal, expected to be negligible, was observed to drop from an influent of over 4,000 mg/L to a Stage 1 effluent ranging from 2,700 to 3,600 mg/L. A slight decrease was observed across Stage 2.

Removal mechanisms for trace contaminants

When discussing individual components of the wastewater, several factors must be kept in mind:

1. The amount of calcium sulfate formed is massive. The solids formed measurements indicated a solids production rate of 80 to 100 g/L. The aluminum hydroxide contribution to this total was typically about 14.5 g/L, which is the only other major component of the solids besides calcium sulfate. The shear mass of precipitation occurring would be expected to trap some of the metals present in the precipitation solids matrix.
2. Coprecipitation with iron and aluminum is commonly seen to remove small amounts of other metals that would not be expected to precipitate at the pH levels used here.
3. The weak adsorption of alkali on the surface of recycle particles, which is the core mechanism for development of dense solids in HDS, causes precipitation of metal oxides and hydroxides at the surface of the particle instead of in solution. At the particle surface the pH close to the particle is thus higher than the pH in the bulk solution. Typically, metal precipitation in a well-designed HDS process exhibits removal characteristic of a higher pH than indicated by pH measurement.

This study did not make an attempt to investigate which of the aforementioned mechanisms was responsible for removal of a specific wastewater component. It is expected that the net effect of all three results in the observed removals as identified below. It should also be noted that the effluent from the Stage 1 clarifier normally had a relatively high TSS, over 50 mg/L. While total and soluble concentrations were measured for the various parameters listed below, the use of soluble concentrations is more useful in evaluating performance, as the carryover solids would be expected to have trace contaminants present that contribute to the total but not soluble values.

Removal of trace contaminants

Antimony

Influent values were all near 0.004 mg/L. Effluent values from Stage 1 all were near or below detection limit (nominally 0.000043 or 0.000086 mg/L).

Arsenic

Shown below in Table 4 is the data summary for arsenic for the various runs.

Table 4: Arsenic removal

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	Run	Day	TJ Pit	Total	Dissolved	Total	Dissolved	Units
2/22/2021	1	6	0.37	0.0072	0.009	0.0083	0.0076	mg/L
3/1/2021	2	5		0.008	0.006	0.009	0.0079	mg/L
3/8/2021	3	5		0.0063	0.0073	0.0064	0.0052	mg/L
3/15/2021	4	5	0.45	<0.0049	<0.0025	<0.0025	0.0052	mg/L
3/22/2021	5	5		0.0048	0.0046	0.0049	0.0049	mg/L
3/26/2021	6	4		0.0041	0.0028	0.0035	0.003	mg/L
3/27/2021	6	5		<0.0049	<0.0049	<0.0049	<0.0049	mg/L
4/1/2021	7	4	0.4	<0.0049	<0.0049	<0.0049	<0.0049	mg/L
4/2/2021	7	5		<0.0049	<0.0049	<0.0049	<0.0049	mg/L
5/26/2021	8	3	0.39	NA	NA	0.07	0.0073	mg/L
5/27/2021	8	4		NA	NA	0.093	0.0079	mg/L
5/28/2021	8	5		NA	NA	0.0084	0.008	mg/L

Table 4 indicates influent arsenic concentrations were in the range of 0.37 to 0.45 mg/L. Arsenic in the arsenate form can be co-precipitated with iron below pH 7. The best removals observed in Stage 1 were in runs 4, 6, and 7. None of these runs had aeration in Stage 1, but the only aeration in Stage 1 was in Run 3. These three runs achieved the lowest Stage 1 pH, as they operated between pH 6.0 and 6.35. The other runs all operated between pH 6.5 and 7.0. This would fit with iron (or possibly aluminum) hydroxide coprecipitation. The worst performance was observed in the single-stage run (Run 8). The soluble arsenic in Run 8 was about 0.008 mg/L, which is not that far from the best performance of <0.0025 mg/L soluble arsenic in Run 4. The difference in performance is likely not significant.

Beryllium

Shown in Table 5 are the data for beryllium in the study. As shown, the influent beryllium ranged between 2.1 and 2.5 mg/L. Effluent dissolved concentrations were below detection limits for both stages in all runs. Total beryllium was measurable in the first stage effluent as part of the solids carried over from the clarifier.

Table 5: Beryllium removal

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	**Run**	**Day**	**TJ Pit**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Units**
2/22/2021	1	6	2.1000	0.0029	<0.000067	<0.000067	<0.000067	mg/L
3/1/2021	2	5		0.0027	<0.000067	<0.000067	<0.000067	mg/L
3/8/2021	3	5		0.0031	<0.000067	<0.000067	<0.000067	mg/L
3/15/2021	4	5	2.3000	0.000067	<0.000067	<0.000067	<0.000067	mg/L
3/22/2021	5	5		0.0011	<0.000067	<0.000067	<0.000067	mg/L
3/26/2021	6	4		0.0077	<0.000067	<0.000067	<0.000067	mg/L
3/27/2021	6	5		0.0036	<0.000067	<0.000067	<0.000067	mg/L
4/1/2021	7	4	2.2	0.0033	<0.000067	<0.000067	<0.000067	mg/L
4/2/2021	7	5		0.0041	<0.000067	<0.000067	<0.000067	mg/L
5/26/2021	8	3	2.50000	NA	NA	<0.000067	<0.000067	mg/L
5/27/2021	8	4		NA	NA	<0.000067	<0.000067	mg/L
5/28/2021	8	5		NA	NA	0.0016	<0.000067	mg/L

Beryllium is commonly precipitated at pH 6.5 as an hydroxide, but like aluminum the solubility increases with increasing pH above that point.

Cadmium

Shown in Table 6 are the analytical results for cadmium. Cadmium is present in this water in concentrations of 4.6 to 5.4 mg/L. Cadmium is theoretically soluble at neutral pH levels to about 8 mg/L as an hydroxide, and as cadmium sulfide is soluble to less than 0.0001 mg/L. For Stage 1 removals, the best performance was found in Run 7, with a soluble cadmium of 0.05 mg/L. Runs 1, 2, 4, and 5 had Stage 1 soluble effluent concentrations of 0.14 to 0.20. Runs 3, 6, and 7 had higher effluent cadmium values. Sulfide was added to the first stage in Run 3 only, and cadmium removal was not exceptional. No other variables were identified linking either the low values or high values related to first-stage performance.

On the other hand, Stage 2 provides more insight. Note that in Run 7, there are values shown for day 4 and day 5. Days 1 through 4 of Run 7 had no sulfide addition to the second stage. Day 5 did have sulfide addition to the second stage. As shown, the cadmium concentration decreased by an order of magnitude due to sulfide addition as the only variable change. Other comparably low values were seen in Runs 4, 5, 6, and 8. Runs 4, 5 and 6 all included sulfide addition to Stage 2. Runs 1, 2, most of 7, and Run 8 had no sulfide addition. Sulfide precipitation of cadmium would be viewed as less than optimal compared to lab data, and likely indicates the sulfide dosage was low. The worst Stage 1 removal was about 90%, and the worst Stage 2 effluent provided 98% removal. However, the lowest values produced were from the final run, single-stage operation, with no sulfide addition. The only possible explanation is that the additional solids formed helped remove cadmium.

Table 6: Cadmium removal

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	**Run**	**Day**	**TJ Pit**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Units**
2/22/2021	1	6	4.6	0.2	0.2	0.026	0.025	mg/L
3/1/2021	2	5		0.2	0.2	0.021	0.02	mg/L
3/8/2021	3	5		0.46	0.46	0.023	0.024	mg/L
3/15/2021	4	5	5.4	0.14	0.14	0.0068	0.0057	mg/L
3/22/2021	5	5		0.27	0.2	0.032	0.0058	mg/L
3/26/2021	6	4		1.2	1.3	0.039	0.0076	mg/L
3/27/2021	6	5		1.1	1.0	0.026	0.0057	mg/L
4/1/2021	7	4	4.9	0.52	0.54	0.094	0.08	mg/L
4/2/2021	7	5		0.5	0.5	0.025	0.0083	mg/L
5/26/2021	8	3	5.4	NA	NA	0.01	0.0099	mg/L
5/27/2021	8	4		NA	NA	0.0026	0.00066	mg/L
5/28/2021	8	5		NA	NA	0.0038	0.00066	mg/L

Chromium

Chromium in the influent varied between 2.8 and 3.0 mg/L. Based on hydroxide precipitation curves, chromium should not precipitate in the first stage, but in all runs the Stage 1 effluent was below 0.1 mg/L. This must be from coprecipitation. Chromium was observed to be near or below the analytical laboratory reported detection limit (typically 0.00085 mg/L, lower for Run 8) for all runs except Run 8 (single-stage operation).

Cobalt

Influent Cobalt varied between 10 and 12 mg/L. Stage 1 effluent Cobalt was lowest in Runs 1, 2, and 4, and highest in Runs 3 and 6. All values from the second stage were less than <0.00066 mg/L, except Runs 6 and 7. Run 6 was the run at lower pH setpoints. In run 7, day 4, without sulfide addition, was less than detectable, but day 5, with sulfide addition, had a soluble cobalt concentration of 0.013. All values from single-stage operation were <0.00066 mg/L. Runs 1, 2, part of 7, and 8 had no sulfide addition to the second stage. Runs 3 and 6 both had sulfide addition.

Manganese

The influent manganese concentration ranged between 240 and 280 mg/L, except for the feed to Run 8, which was 350 mg/L. Manganese is typically removed either by precipitation as an hydroxide at pH 10+, or by reaction with an oxidant at pH 8. Most of the manganese is removed in Stage 1, with an average soluble manganese in the Stage 1 effluent of 42 mg/L. In Stage 2, the average across all runs was 16.6 mg/L soluble manganese. There were 5 values for dissolved manganese that were above 10 mg/L, and 10 that were single digits. The best Stage 2 performance came from Run 8, where the final two days effluent soluble manganese were 0.053 and 0.026 mg/L. The worst performance was in Run 6 (lower pH setpoints) where the average effluent was 46 mg/L. It should be noted that aeration in Stage 1 was provided in Run 3 only, which did not offset the impact of limestone addition and the resulting loss in solids density and recycle ratio. Run 4 had no aeration in Stage 2, and the effluent manganese concentration was not appreciably higher. This indicates that removal via coprecipitation may have been more significant that oxidation and precipitation mechanisms.

Table 7: Manganese data

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	**Run**	**Day**	**Total**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Units**
2/19/2021	1	5	240		0.58		31	mg/L
2/22/2021	1	6		37	38	7.7	7.8	mg/L
2/26/2021	2	4			21		5.5	mg/L
3/1/2021	2	5		36	36	1.9	1.7	mg/L
3/4/2021	3	3			66		0.28	mg/L
3/5/2021	3	4			72		2.4	mg/L
3/8/2021	3	5		73	74	4.7	4.5	mg/L
3/12/2021	4	4			3.3		50	mg/L
3/15/2021	4	5	280	33	34	6.8	6.8	mg/L
3/19/2021	5	4			47		1.2	mg/L
3/22/2021	5	5		32	33	9.5	6.4	mg/L
3/26/2021	6	4		68	72	38	36	mg/L
3/27/2021	6	5		59	57	43	61	mg/L
4/1/2021	7	4	250	50	49	9.9	9.1	mg/L
4/2/2021	7	5		49	49	20	18	mg/L
5/26/2021	8	3	350	NA	NA	2.6	1.9	mg/L
5/27/2021	8	4		NA	NA	0.099	0.053	mg/L
5/28/2021	8	5		NA	NA	0.17	0.026	mg/L

Nickel

Shown in Table 8 is the accumulated data for nickel. Influent nickel concentrations ranged between 20 and 24 mg/L. Effluent dissolved nickel concentrations for Stage 1 were lowest in Runs 4 and 5 (0.23 and 0.33 mg/L respectively) and highest in Runs 3 and 6 (1.6 and 1.9/1.3 mg/L respectively). Effluent soluble nickel from Stage 2 was lowest in Runs 2, 4, 5, and 8. Runs 2, 4, 5, and 8 had Stage 2 pH levels greater than 9.1, whereas Run 6 Stage 2 pH was 8.63, and Run 3 was the run using limestone. The results seem to indicate that sulfide had some benefit, as it was used in Stage 2 on Runs 4, 5, and 6. Note that Run 6 had the lower pH setpoints. Run 8 also produced very low Stage 2 effluent soluble nickel concentrations. The theoretical solubility of nickel sulfide at pH 9 is less than 0.0001 mg/L. As before, this seems to indicate that the sulfide added was either not used efficiently, or insufficient in dosage, for the metals that can be precipitated as sulfides.

Table 8: Nickel data

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	Run	Day	TJ Pit	Total	Dissolved	Total	Dissolved	Units
2/22/2021	1	6	20	0.46	0.46	0.0052	0.011	mg/L
3/1/2021	2	5		0.56	0.54	0.01	0.0052	mg/L
3/8/2021	3	5		1.5	1.6	0.01	0.015	mg/L
3/15/2021	4	5	24	0.24	0.23	0.0052	0.0052	mg/L
3/22/2021	5	5		0.48	0.33	0.07	0.0052	mg/L
3/26/2021	6	4		1.9	1.9	0.074	0.037	mg/L
3/27/2021	6	5		1.4	1.3	0.056	0.032	mg/L
4/1/2021	7	4	22	0.71	0.71	0.022	0.011	mg/L
4/2/2021	7	5		0.62	0.62	0.053	0.02	mg/L
5/26/2021	8	3	23	NA	NA	0.0052	0.015	mg/L
5/27/2021	8	4		NA	NA	0.0052	0.0052	mg/L
5/28/2021	8	5		NA	NA	0.012	0.0052	mg/L

Selenium

Selenium in the influent ranged between 0.29 and 0.4 mg/L. First-stage removal typically achieved soluble and total selenium concentrations in the range of 0.13 to 0.11 mg/L. Run 7 was the outlier, with a final day dissolved selenium concentration of 0.061 mg/L. Run 8 averaged 0.042 mg/L over the last two days. In Run 7 there was not a substantial difference between the days without sulfide addition and the single day there was sulfide addition. Run 7 did benefit from a higher recycle ratio than any of the two-stage runs except Run 2. There is an indication from the literature that a small amount of selenium can be removed in the precipitation of calcium sulfate.

Uranium

The uranium concentration in the influent ranged between 2.3 and 3 mg/L, as shown in Table 9. Most removal occurred in the first stage, with the dissolved uranium concentration ranging between 0.015 and 0.037 mg/L. Greatest removal in Stage 1 occurred in Runs 6 and 7, which averaged under 0.016 mg/L. Poorest removal occurred in Runs 4 and 5. Runs 6 and 7 had slightly lower pH levels and slightly higher recycle ratios. Uranium, like aluminum, has a low solubility as an hydroxide at pH 5.5 to 6, and as pH increases from that point, solubility does as well. It should be noted that uranium behaves consistently from a chemical standpoint regardless of which isotope it is. The data reflects limited removal in the second stage, as one would expect. The single-stage system (Run 8) achieved the lowest uranium concentration, with the final two days of Run 8 averaging 0.0025 mg/L. This is unusual, given that the solubility of uranium hydroxide at pH 9 is much greater than at pH 6. This likely results from the additional solids produced in the single-stage process, and the greater impact of adsorption/coprecipitation on uranium removal.

Table 9: Uranium data

			Raw	Stage 1 effluent		Stage 2 effluent		
Date	**Run**	**Day**	**TJ Pit**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Units**
2/22/2021	1	6	2.800	0.028	0.024	0.012	0.012	mg/L
3/1/2021	2	5		0.04	0.037	0.015	0.016	mg/L
3/8/2021	3	5		0.028	0.026	0.02	0.018	mg/L
3/15/2021	4	5	2.300	0.038	0.0350	0.023	0.024	mg/L
3/22/2021	5	5		0.029	0.029	0.025	0.02	mg/L
3/26/2021	6	4		0.026	0.017	0.022	0.021	mg/L
3/27/2021	6	5		0.020	0.0150	0.021	0.02	mg/L
4/1/2021	7	4	3.000	0.024	0.015	0.019	0.018	mg/L
4/2/2021	7	5		0.02	0.016	0.019	0.018	mg/L
5/26/2021	8	3	2.600	NA	NA	0.0099	0.0096	mg/L
5/27/2021	8	4		NA	NA	0.0041	0.0036	mg/L
5/28/2021	8	5		NA	NA	0.0035	0.0014	mg/L

Zinc

The influent zinc concentration during the study were between 75 and 91 mg/L. The theoretical solubility of zinc hydroxide at pH 7.5 is over 100 mg/L. And yet, in the first stage of the two-stage process, the zinc is almost completely removed. Nearly all effluent zinc values were less than or equal to 0.0019 mg/L, including Run 8. Similar results were seen for nickel and cadmium. The sizing of the lime feed for the second-stage reaction was based on a lime demand for these metals. It is apparent that they were coprecipitated to a great extent in the first stage, which limited the solids formed and lime demand in the second stage.

Observations and conclusions

Based on the previous descriptions and data, the following conclusions are drawn:

1. The removal of aluminum in stage 1 was less than hoped for, but still greater than 99.95% for two-stage operation. The clarifier effluent from the first stage was cloudy, and solids carryover resulted in higher aluminum concentrations entering Stage 2, which would then be solubilized at the higher pH levels and exit the second-stage clarifier. Effluent aluminum concentrations were an order of magnitude higher in the single-stage process.
2. Lime demand and solids production was much higher in the single-stage process, but some metals concentrations were lower. The reduction in lime consumption is significant, and an important economic driver for the increased cost of a two-stage HDS process.
3. Magnesium removal was greater than expected in the first stage of the two-stage process and negligible in the second stage.
4. Metals that precipitate at high pH tend to coprecipitate in the first stage to a greater extent than anticipated. It might be desirable to operate the pH of the first stage lower or the second stage slightly higher to force more lime demand in the second stage.
5. Of the metals and metalloids evaluated, cadmium, manganese, selenium, and uranium were more effectively removed in a single-stage HDS process, whereas arsenic and chromium were more effectively removed in the two-stage process. There was no appreciable difference between one-stage and two-stage processes for antimony, beryllium, nickel, and zinc. Aluminum was more effectively removed in the two-stage process, whereas magnesium achieved much lower effluent concentrations in the single-stage process.

Overall, the benefits of the two-stage HDS process in this instance involve savings in lime consumption over conventional neutralization approaches, and greater removal of some metals.

Evaluating Novel Organic Substrates for Sulfate-Reducing Biochemical Reactors Treating Mine Water

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Abstract

Sulfate-reducing biochemical reactors (SRBRs) have been used for decades to passively treat mining-influenced water. SRBRs rely on microbially-mediated processes such as fermentation and sulfate-reduction to remove metals and sulfate from water and increase pH. Passive SRBRs typically consist of a biodegradable organic medium through which mine water passes. The complex community of microbes formed in SRBRs includes cellulolytic bacteria responsible for initial breakdown of lignocellulose that provides more readily bioavailable carbon to fermenters and sulfate-reducing bacteria. A wide range of organic media have been evaluated in the literature for effectiveness in SRBRs, and identification of effective lignocellulosic media is critical for short- and long-term SRBR performance.

In this study, we conducted screenings of SRBR media, as well as collaborated with universities in the USA and Indonesia. Media evaluated included coconut trees and coconut shells, rice husk, cassava, sugarcane bagasse, and spent brewer's grains. Using laboratory-scale SRBRs and synthetic mine water, media were screened for their ability to support sulfate-reduction via monitoring of the oxidation-reduction potential, dissolved O_2 concentration, and pH, and metal removal and sulfate-reduction rates. A subset of media was evaluated for treatment performance, lignocellulosic composition (cellulose, hemicellulose, and lignin before and after operation), available carbon sources, and microbial community composition. As expected, results varied among organic materials evaluated. A small number of substrates evaluated (coconut husk, coconut palm wood, and merbau) failed to achieve the conditions necessary to support sulfate reduction. The remaining substrates (*Phragmites*, corn stalk, date palm, coconut husk, sweet potato, vegetable waste, king grass, spent brewing grains, and sugarcane bagasse) successfully supported the conditions necessary for sulfate reduction. Metal removal rates for these substrates ranged from 37–98%. Results stemming from these screenings can provide insights into the type of lignocellulosic media with potential for sustaining essential SRBR microbial processes in short- or long-term operation. Variation in microbial communities among SRBRs was attributed to organic composition, with sulfate reduction proportional to the amount of readily available carbon (e.g., cellulose, hemicellulose).

Introduction

A multitude of historical mine sites exist throughout the western United States, with a portion of these releasing mining-influenced water (MIW) into the environment. Passive, biologically-based water treatment strategies can be a cost-effective and low-maintenance technology for treating MIW, particularly for remotely located legacy mine sites. One such technology is sulfate-reducing biochemical reactors (SRBRs), which have been used for decades to treat MIW (see Kleinmann et al., 2021 for a historical perspective). SRBRs rely on microbially-mediated processes such as fermentation and sulfate reduction to improve water quality by increasing pH and removing metals and sulfate from water (see review by Sheoran et al., 2010). Under anoxic conditions, sulfate-reducing bacteria (SRB) utilize a carbon source to complete dissimilatory sulfate reduction, producing sulfide and bicarbonate alkalinity in the process. The sulfide reacts with various cations to form relatively insoluble metal sulfides. Secondary metal removal processes include the formation of hydroxides, carbonates, and sorption mechanisms (Sheoran et al., 2010). The alkalinity produced during sulfate reduction increases the pH of the water. Passive versions of SRBRs primarily consist of a biodegradable organic media as the carbon source. The complex community of microbes within SRBRs include LIGNOCELLULOLYTIC bacteria responsible for the initial breakdown of lignocellulosic components such as hemicellulose, cellulose and lignin that provide more readily bioavailable carbon to fermenters and SRB. These microbial processes also create the anoxic environment essential for sulfate reduction.

A wide range of organic media have been evaluated in the literature for effectiveness in SRBRs, and identification of effective SRBR lignocellulosic media is critical for short- and long-term performance (Sheoran et al., 2010). Some characteristics of organic matter that are particularly important for SRBRs are organic fraction, nutrient content, and composition (Kuyucak and St-Germain, 1994; Sheoran et al., 2010; Cao et al., 2012). In this paper, we will discuss the characteristics of novel, regionally-available lignocellulosic media to identify candidates for potential use in large-scale applications. We collaborated with universities in the USA and Indonesia to conduct screenings of regionally-available SRBR media for potential use in large-scale SRBRs. Results stemming from these screenings can provide insights into the type of lignocellulosic media with potential for sustaining essential SRBR microbial processes in short- or long-term operation.

Methods

This paper summarizes three separate but complementary laboratory-scale evaluations of potential SRBR media. An initial screening of a range of regionally-available organic substrates was conducted in the USA and Indonesia using laboratory-scale SRBRs and synthetic MIW. Organic substrates evaluated in the USA included coconut (*Cocos nucifera*) wood and husk, common reed (*Phragmites* sp.), date palm (*Phoenix dactylifera*) wood, merbau/ironwood (*Intsia* sp.) wood, and corn (*Zea mays*) stalk. Substrates were individually screened. Six SRBRs were evaluated using a 50:50 mixture of either coconut husk and palm wood or coconut husk and ironwood. Substrates individually evaluated at the Institut Teknologi Bandung (ITB), Indonesia, included merbau/ironwood (*Intsia* sp.) sawdust, rice husk, cassava (*Manihot esculenta*) tuber, sweet potato (*Ipomoea batatas*), corn (*Zea mays*) stalk, vegetable waste, and king grass (*Pennisetum* sp.). These substrates were screened for their ability to support sulfate reduction as indicated by changes in oxidation-reduction potential (ORP), dissolved oxygen (DO), and pH. The SRBRs operated at ITB were also evaluated for metal removal and sulfate-reduction rates. Finally, four SRBRs were evaluated at Arizona State University (ASU), USA, using a mixture of 30% limestone and 70% spent brewing grains or sugarcane (*Saccharum* sp.) bagasse, by-products from the beer brewing and sugar industries, respectively. Water chemistry parameters such as pH, ORP, and DO were measured throughout operation. In addition, metal removal, sulfate reduction, and available volatile fatty acid (VFA) concentrations were also measured. The lignocellulosic composition (pre- and post-study) of the changes in available hemicellulose, cellulose, and lignin were evaluated, including an analysis of the available microbial community capable of degrading lignocellulosic material.

Feed solution

Synthetic feed solutions (Tables 1 and 2) were used for the laboratory-scale SRBR screening projects, and their composition is loosely based on actual MIW chemistry. The feed solution in Table 1 also mimics water that has received limestone pre-treatment to remove Al and Fe and increase pH. The SRBR laboratory-scale studies conducted at ASU used a synthetic feed solution containing the properties listed in Table 2.

Table 1: Synthetic MIW chemistry used for SRBR substrate screening

		Feed solution	**Chemicals required per 1 L deionized water**
pH (s.u.)		4.5 – 5.0	
Sulfate (mg/L)		235	
Metals (mg/L)	Cu	100	386 mg $CuSO_4 \cdot 5H_2O$
	Mn	13	38 mg $MnSO_4 \cdot H_2O$
	Zn	40	199 mg $ZnSO_4 \cdot 7H_2O$

Table 2: Synthetic MIW chemistry used for SRBRs in the ASU laboratory-scale study

		Feed solution	**Chemicals required per 1 L deionized water**
pH (s.u.)		2.6	
Sulfate (mg/L)		500	
Metals (mg/L)	Cd	0.1	0.3 mg $CdSO_4$
	Co	0.02	0.07 mg $CoCl_2 \cdot 6H_2O$
	Cu	0.7	1.8 $CuCl_2 \cdot 5H_2O$
	Fe	59	290 mg $Fe_2(SO_4)_3 \cdot H_2O$ 100 mg $Fe(SO_4) \cdot H_2O$
	Ni	0.01	0.04 mg $NiSO_4$
	Pb	0.04	0.15 mg $PbCl_2$
	Zn	57	175 mg $ZnCl_2$

Laboratory-scale SRBRs

SRBRs were filled with individual organic substrates to assess their capability to support sulfate-reducing bacteria and sulfate reduction. Limestone chips and/or pellets (30% dry wt.) were also mixed into the substrate to help neutralize MIW acidity while the sulfate-reduction activity ramped up. Once the SRBR reaches steady-state, then bicarbonate alkalinity generation is sufficient to neutralize influent acidity. A small amount of cow manure (1% dry wt.) was added as an inoculum in some SRBRs, while others were inoculated with the SRB *Citrobacter freundii*. The SRBRs operated at ITB also included a small amount of compost as an inoculant. Organic substrates evaluated were identified following a desk-top screening of regionally-available plant species, agricultural by-products, and local cultural knowledge. Organic materials were then gathered locally from a variety of locations, chopped into smaller sizes (2 to 6 cm), and dried to constant temperature prior to use.

In the studies conducted at ASU, two types of inocula were used: one was 25 ml of an enrichment culture grown for one month on the respective substrate and sulfate-rich medium. The other was 125 ml of anaerobic digester sludge from the Mesa Northwest Water Reclamation Plant, a local municipal wastewater treatment plant in Mesa, Arizona. The spent brewing grains were gathered from San Tan Brewery, a Phoenix-area brewery, and the sugarcane bagasse was obtained from Cajun Sugar Company in New Iberia, Louisiana. The organic substrates were mixed in a 7 to 3 ratio of organic substrate and limestone by weight, and then packed into the SRBRs.

Laboratory-scale SRBRs were fabricated using PVC columns having approximate dimensions of 10 cm in diameter and 117 cm tall. The base of the column was capped with a standard PVC pipe cap, which is tapped in the center to thread in a drain valve assembly. A plastic mesh screen was placed in the base of the column prior to filling with substrates to prevent contents from obstructing the drain valve. Columns were filled from bottom to top, first with 10 cm-depth of pea gravel for drainage, followed by 91 cm-depth of substrate (Figure 1). The mass of substrates used to fill the SRBRs was recorded to quantify sulfate reduction rates on a mass basis. Water level within SRBR columns was maintained at 5 cm above the top of substrate during operation. The top of the SRBRs was capped with a rubber lid to prevent oxygen intrusion. The SRBR columns were operated in continuous, down-flow mode with feed solution introduced through the cap at the top of the column. Flow rates varied among projects, ranging from 0.6 to 2 L/d and controlled using peristaltic pumps. The length of operation varied from approximately 60 to 130 days depending on the project.

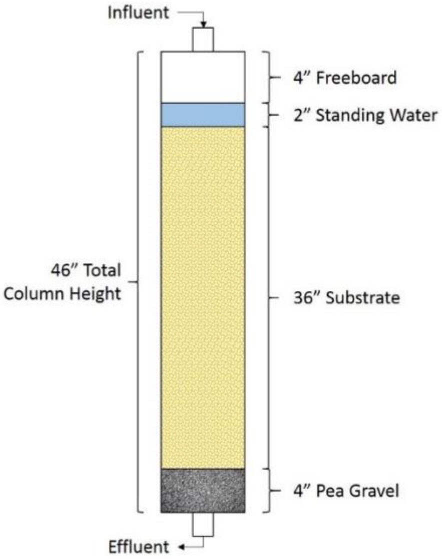

Figure 1: Laboratory-scale SRBR column schematic

Water quality monitoring

During dissimilatory sulfate reduction by SRBs, hydrogen ions are consumed, and bicarbonate alkalinity is produced. These reactions are only possible in an anoxic and reducing environment. Therefore, changes in redox conditions within SRBRs may be used as evidence for sulfate reduction. Aqueous samples were collected on a weekly basis. Physico-chemical parameters measured varied from project to project but included pH and ORP, at a minimum. Optimal conditions for SRBs to thrive and reduce sulfate include a pH in the range of 5 to 8 s.u. and ORP in the range of –100 to –300 mV (Sheoran et al., 2010). Dissolved oxygen (DO), electrical conductance (EC), and temperature was also recorded for some SRBRs. Analysis for total and dissolved metals was conducted at the outset to check for elements leaching out of the substrates. Weekly analysis of solely Cu, Mn, and Zn on both total and filtered samples occurred after the columns were no longer leaching other metals. Sulfate, free sulfide, and alkalinity/acidity were quantified weekly in some SRBRs to assess the extent of sulfate reduction. For the ASU SRBRs, a measurement for pH, ORP, and DO were collected at least twice a week and the analysis of sulfate, sulfide, and metals such as Cd, Co, Ni, Pb, Fe, Cu, and Zn, were conducted weekly. A weekly quantification of VFAs was analyzed using high performance liquid chromatography (HPLC) and included analysis of formic, acetic, propionic, butyric, valeric, and caproic acids.

Lignocellulosic and microbial composition analysis

Hemicellulose, cellulose, and lignin were characterized for the ASU laboratory-scale studies. Samples of the organic material analyzed were taken before the start of SRBR operation and after completion of the trials. Substrates samples from three equidistant locations (top to bottom) of each duplicate SRBR were retrieved for lignocellulosic and microbial analysis. Lignocellulosic analysis was characterized using an ANKOM Technology A2000 fiber analyzer. DNA extractions were performed for each sample using a DNeasy PowerFood Microbial Kit from Qiagen as directed by the protocol. After DNA extraction, the samples were sent for high throughput DNA sequencing at the Center for Fundamental and Applied Microbiomics at the ASU KED Genomics Core Facility. A Quantitative Insights into Microbial Ecology (QIIME 2) pipeline was used to assign taxonomy for the amplicon sequence variants (ASVs) using the SILVA database (Bolyen et al., 2019; Glöckner et al., 2017; Quast et al., 2012; Yarza et al., 2014; Yilmaz et al., 2014). For the ASU study, select genera of microbes known to have lignocellulytic activity were specifically identified.

Results and discussion

SRBR substrate screening

As expected, results varied among the organic materials evaluated (Table 3). SRBRs filled with coconut husk or merbau/ironwood (*Intsia* sp.) failed to achieve reducing conditions after 15 weeks of operation, with ORP remaining > 0 mV. The pH did increase between 0.3 and 1.0 s.u. but that was most likely due to the added limestone. All SRBRs containing mixtures that included ironwood failed to exhibit reducing conditions even after 15 to 27 weeks of operation, suggesting that the *Intsia* sp. used contains phytocompounds that grant it anti-microbial and/or anti-mold properties (cf. Reinprecht et al., 2020).

The coconut husk was, however, able to support reducing conditions when used in a mixture with date palm wood. These SRBRs achieved reducing conditions (ORP < −200 mV) within 2 to 4 weeks and maintained the reducing environment for at least 22 weeks, exhibiting an average ORP of −222 mV. This observation suggests that coconut husk does not directly inhibit SRBs but perhaps did not contain sufficient readily available organic carbon to support the necessary microbial communities, which was provided by date palm wood. However, coconut husk has been documented to inhibit common human oral microbial pathogens (Jose et al., 2014), as well as other microbes (e.g., Viju et al., 2013). Coconut palm wood also failed to support reducing conditions, though ORP did decline towards 0 mV at the end of 10 weeks of operation. Alternatively, *Phragmites* and corn stalk supported reducing conditions within 2 and 5 weeks, respectively, of start-up and maintained conditions throughout the 23 weeks of operation with a mean ORP of −184 and −173 mV, respectively. The SRBRs supporting sulfate reduction also exhibited the largest increases in pH, providing evidence of bicarbonate alkalinity production. The SRBRs with date palm, *Phragmites*, and corn stalk showed an increase in pH from 5.3 s.u. in the synthetic MIW to 6.3-6.6 s.u. The increase in pH was even more pronounced in the SRBRs with strongly reducing conditions (e.g., the date palm wood mixtures), which exhibited effluent pH ranging from 6.4-6.9 s.u. These results from this screening indicate that coconut husk, date palm, *Phragmites*, and corn stalk should be retained for further consideration.

Table 3: SRBR substrates screened in the USA. Mean effluent ORP and pH are shown. Mean influent MIW ORP was 207 mV and pH was 5.3 s.u.

	Effluent	
Substrate	**ORP (mV)**	**pH (s.u.)**
Coconut shells	112	5.4
Phragmites	–184	6.4
Date palm	–232	6.6
Merbau/Ironwood	65	6.2
Coconut palm	92	5.1
Corn stalk	–173	6.3

SRBRs evaluated at ITB containing locally-available substrates – sweet potato, corn stalk, vegetable waste, or king grass – all supported reducing conditions in their respective SRBRs (Table 4), with effluent ORP ranging from –16 to –572 mV during the 60-day trial. Vegetable waste and king grass SRBRs exhibited the most strongly reducing conditions (ORP = –429 and –572 mV, respectively). Alternatively, SRBRs containing rice husk and cassava tubers exhibited the lowest effluent sulfate concentrations, decreasing from 347 mg/L to < 30 mg/L by the end of a 28-day trial, despite exhibiting weakly or moderately oxidizing conditions (ORP = 0 and 206 mV, respectively). Sulfate reduction has also been observed in other SRBRs despite effluent ORP values > 0 mV. This is because effluent values may not accurately reflect water quality in microhabitats within the SRBR substrate matrix. SRBRs with cassava tubers and sweet potato exhibited decreases in pH to 4.0 s.u., possibly due to their naturally-occurring cyanide (Padmaja, 1995). During the final 4 weeks of the ~10-week trials, SRBRs containing merbau sawdust, rice husk, cassava, sweet potato, corn stalk, vegetable waste, or king grass removed 84 to 98% of Cu and 37 to 90% of Zn. The generally lower removal of Zn is not surprising since Zn particulates are relatively small and often are not fully filtered out by SRBR substrates. The ability of some substrates to remove metals despite not supporting a strongly reducing environment, such as cassava, suggests that mechanisms other than sulfide formation (e.g., adsorption, carbonate formation) are also acting on the cations within SRBRs. Combing ORP, pH, and metal removal results to infer the degree of sulfate reduction suggests that merbau, rice husk, sweet potato, corn stalk, and king grass were the best candidates to be retained for further consideration.

Table 4: SRBR substrates screened at ITB. Mean effluent water quality parameters during final four weeks of SRBR operation are shown

				Copper		Zinc	
	Eh	pH (s.u.)	Sulfate (mg/L)	Cu (mg/L)	Removal	Zn (mg/L)	Removal
Merbau sawdust	64	8.1	9	4.3	97%	8.04	89%
Rice husk	0	7.6	30	7.5	94%	7.28	90%
Cassava tuber	206	4.0	20	13.7	90%	18.52	75%
Sweet potato	−16	4.1	157	7.7	96%	41.2	44%
Corn stalk	−102	6.1	176	4.2	98%	34.3	53%
Vegetable waste	−429	6.7	238	6.4	96%	33.1	55%
King grass	−572	7.8	211	28.4	84%	46.3	37%

SRBR substrate and lignocellulolytic microbial community characterization

The spent brewing grains and sugarcane bagasse SRBRs evaluated at ASU were operated for a total of 135 days. The spent brewing grains and sugarcane bagasse SRBRs began operation at a 3-day hydraulic retention time (HRT) on day 50. SRBRs containing spent brewing grains continued at a 3-day HRT until the end of operation; however, the sugarcane bagasse SRBRs maintained the 3-day HRT from day 50 to 100 (additional details can be found in Miranda et al., 2022). The HRT for the sugarcane bagasse SRBRs was then increased to 6 days until the end of operation. SRBR performance was the greatest during the 3-day HRT and the average effluent water chemistry, sulfate, and total VFAs are presented in Table 5. The pH, ORP, and DO values during this time were well within the values needed for sulfate reduction to take place. Sulfate reduction rate during the 3-day HRT was 92% for the spent brewing grains SRBRs and 17% for the sugarcane bagasse SRBRs.

A possible explanation for the observed difference in sulfate reduction between the two substrates stems from the differences in concentration of available VFAs, which is partly determined by the lignocellulosic material utilized. Sulfate-reducing bacteria are ubiquitous in their ability to utilize carbon sources, which are commonly sugars and VFAs derived from the breakdown of lignocellulosic material. During the 3-day HRT, VFAs found in the effluent of the spent brewing grains SRBRs included acetic, propionic, butyric, valeric, and caproic acids. Sulfate-reducing bacteria can utilize acetic, propionic, and butyric acids as carbon sources for energy (Liamleam and Annachhatre, 2007). VFAs were not quantifiable in the sugarcane bagasse SRBRs, suggesting there was minimal availability of VFAs for the microbial community. It was hypothesized that the sugarcane bagasse SRBR's flow rate (2 L/day) to achieve the 3-day HRT was too high (spent brewing grains had a 1 L/day flow rate to achieve the 3-day HRT). Therefore, the microbial community was suffering the effects of washout. Washout effects include the physical removal of biofilm formation and readily available carbon sources. For this reason, the flow rate for the sugarcane bagasse SRBRs was decreased, achieving an HRT of 6 days (1 L/day flow rate) from day 100 to day 135. However, this only increased the sulfate-reduction rates to an average of 27%.

Table 5: Average performance of duplicate SRBRs containing spent brewing grains and sugarcane bagasse during a 3-d HRT. VFAs = Volatile fatty acids, BDL= Below detection limit

	pH (s.u.)	ORP (mV)	DO (mg/L)	Sulfate (mg/L)	Total VFAs (mM)
Spent brewing grains	5.9	−260	1.3	41	20
Sugarcane bagasse	6.3	−100	2.5	414	BDL

SRBR removal of metals during the 3-day HRT are summarized in Table 6. Metals that had excellent removal in SRBRs containing spent brewing grains with ~95% removal or greater were Cd, Co, Cu Fe, and Zn. In the sugarcane bagasse SRBRs, metals with removal > 95% were Cd, Cu, Fe, and Zn. Spent brewing grains exhibited better metal removal than sugarcane bagasse, and this may be related to differences in sulfate reduction rates and VFAs produced within both types of SRBRs.

Table 6: Average concentration and removal of metals in duplicate SRBR effluents during the 3-d HRT. BDL = Below detection limit

	Spent brewing grains		Sugarcane bagasse	
Metal	Concentration (mg/L)	Removal	Concentration (mg/L)	Removal
Cd	BDL*	>99.5%	BDL*	>99.5%
Co	BDL*	>94.8%	0.004	75.2%
Cu	BDL*	>99.3%	0.006	99%
Fe	0.03	99.9%	1.4	97.6%
Ni	0.002	80%	0.004	56%
Pb	0.03	25%	0.008	78%
Zn	0.01	99.9%	2	96.5%

*Detection limits for Cd, Co, and Cu in mg/L were 0.0005, 0.001, and 0.005, respectively

Analysis of the lignocellulose composition and lignocellulolytic microbial genera present in the SRBRs gave insights into why there was higher availability of VFAs in the spent brewing grains SRBRs versus the sugarcane bagasse SRBRs. The lignocellulosic analysis of the organic material before and after operation and documented microbial genera are presented in Figure 2. The main difference between each organic substrate was in its composition. Spent brewing grains consisted primarily of hemicellulose (40%) and "other" (34%). Whereas sugarcane bagasse consisted primarily of cellulose (47%) with a higher lignin (17%) percentage compared to the spent brewing grains. In general, of the three types of fiber in lignocellulosic material, hemicellulose is more readily microbially-degraded than both cellulose and lignin, followed by cellulose (Shrestha et al., 2017). Lignin is the most difficult of the three for microbial degradation, and it is more readily degraded in an aerobic environment than in an anaerobic environment, although this is still a topic that is not well understood (Shrestha et al., 2017; Li et al., 2009). The "other" category is even more readily available for microbial fermentation, consisting of sugars, starches, other carbohydrates, proteins, and amino acids. At the conclusion of the 135-day trial, we observed a decrease in the spent brewing grains SRBRs in the amount of hemicellulose and "other" category (7% and 4 %, respectively), suggesting that these two types of carbon sources were utilized by the microbial community. In the sugarcane bagasse SRBRs, we observed a decrease in the hemicellulose and cellulose category (3% and 2%, respectively).

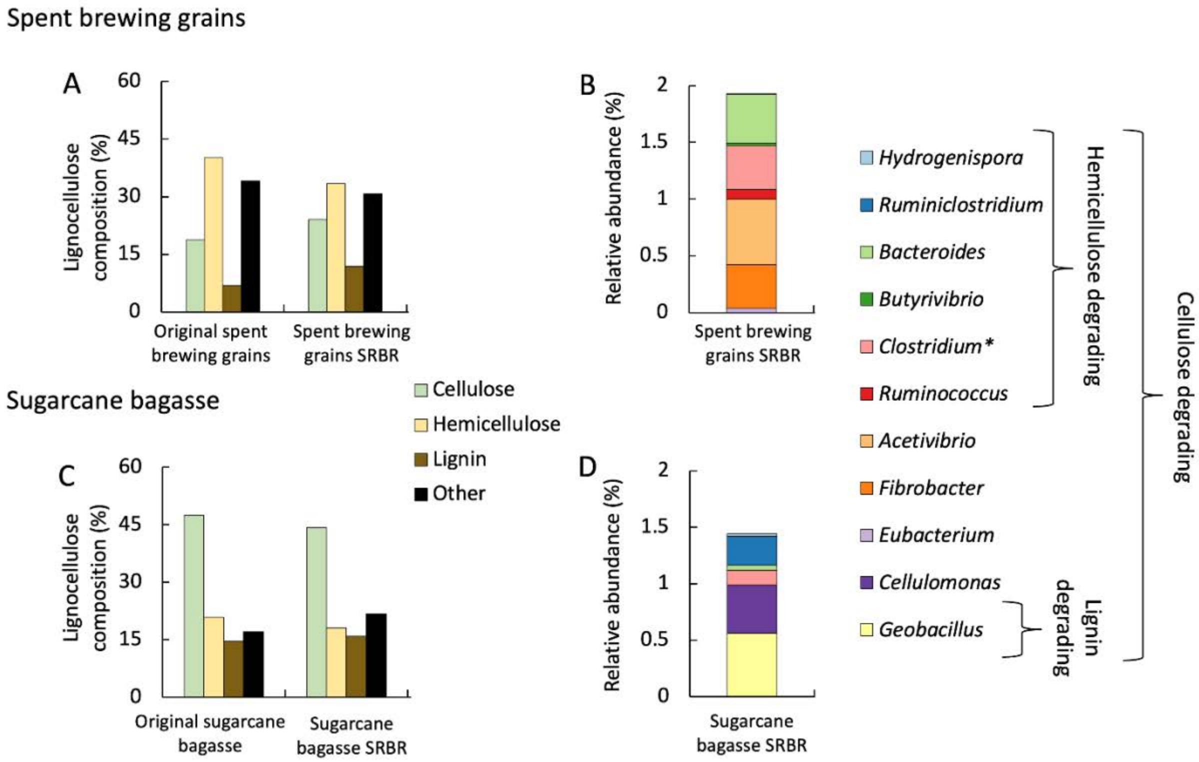

Figure 2: A-D Lignocellulose composition in SRBRs and selected genera containing lignocellulose -degrading species in SRBRs containing spent brewing grains (SBG) or sugarcane bagasse (SCB). The SRBR data are averages of duplicates

Panels B and D of Figure 2 show the lignocellulosic degrading microbial genera identified in each set of SRBRs. In the spent brewing grains SRBRs, *Bacteroides, Butyrivibrio, Clostridium, and Ruminococcus* containing species capable of degrading hemicellulose and cellulose (Brunecky et al., 2012; Shrestha et al., 2017, Tsavkelova and Netrusov, 2011) comprised about half of the total sequences of microbes available for lignocellulose degradation. *Acetivibrio*, *Fibrobacter* and *Eubacterium*, comprising the other half, are genera known to degrade cellulose (Shrestha et al., 2017). In the sugarcane bagasse SRBRs, *Hydrogenispora, Ruminiclostridium, Bacteroides,* and *Clostridium*, which are all capable of degrading hemicellulose or fermentation (Wu and Cheng, 2018; Xie et al., 2021; Shrestha et al., 2017; Tsavkelova and Netrusov, 2011), made up about a third of sequences of microbes with putative capabilities for lignocellulosic degradation, while *Cellulomonas* and *Geobacillus*, made up the remainder. Interestingly, *Geobacillus* has been shown to degrade lignin under oxic conditions but can also degrade cellulose (Meslé et al., 2022).

The difference in performance of the spent brewing grains and sugarcane bagasse can be attributed to the lignocellulose composition and the microbial community's ability to degrade the lignocellulose. In each set of SRBR before and after operation, the spent brewing grains showed larger decreases in hemicellulose, while sequences belonging to genera capable of hemicellulose degradation were also more abundant in the spent brewing grains SRBRs than in the sugarcane bagasse SRBRs. The higher percentage of hemicellulose present in the spent brewing grains could also explain the higher availability of VFAs promoting microbial growth and hence higher rates of sulfate reduction.

Conclusions

While SRBR technology has been in use for several decades, strategies remain for refining their design and improving performance. For example, designing passive SRBRs for application at mines around the globe to help remediate mining-influenced waters benefits from a more expanded view of the organic materials that can potentially be utilized. A wide variety of cellulosic and organic wastes, such as agricultural by-products or locally-available organic materials, have potential for use in passive SRBRs. Some of these have already been evaluated by others (e.g., see review by Sheoran et al., 2010), but various cellulosic and organic wastes remain to be evaluated. It is critical that these materials be capable of supporting the diverse array of microbial communities needed to optimize sulfate reduction without hindering them (e.g., via anti-microbial compounds) or inadvertently leaching additional metals into waters being treated. Designing SRBRs containing the organic substrates evaluated in this paper for long-term success will also benefit from a more critical assessment of what characteristics of the cellulosic and organic wastes influence SRBR microbial communities, and ultimately sulfate-reduction and metal removal performance. It may be beneficial to further test lignocellulosic organics high in hemicellulose such as the spent brewing grains for long-term microbial community support. Additionally, a combination of lignocellulosic materials high in hemicellulose and cellulose may be beneficial due to the differences in lignocellulosic microbial community composition supported by each to support long-term treatment system efficiency and performance. Additional analysis into these mechanisms and lingering questions would benefit the design, operation, and monitoring of full-scale SRBRs treating MIW.

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Biological Treatment of Uranium at the Historical Schwartzwalder Mine, Colorado, USA

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Abstract

The Schwartzwalder mine is a former underground uranium mine near Golden, Colorado, USA, that was dewatered and mined between ~1950 and 2000 and flooded with natural recharge thereafter. In 2013, the mine was dewatered to prevent seepage into Ralston Creek as the mine water contained uranium levels up to 26 mg/L. Biological in-situ treatment of the flooded mine workings ("mine pool") has been ongoing since 2013. This process involves the injection of soluble organic carbon into the mine pool, creating strongly reducing conditions that have resulted in 80 to 90% removal of uranium in-situ. This pre-treated mine pool water is pumped to an ex-situ reverse osmosis and ion exchange system prior to discharge to Ralston Creek. Although this system provides discharge water that meets local water quality guidelines (< 0.03 mg/L), continued active water treatment is not sustainable for final closure of the site.

Pilot-scale trials for semi-passive and passive biological uranium treatment via bioreactors and constructed wetland treatment systems (CWTS) at Schwartzwalder are ongoing to evaluate alternative long-term water treatment options that could achieve reclamation targets without perpetual active treatment. Bioreactors supplemented with synthetic iron sulfide and ethanol, or ethanol and elevated phosphate, demonstrated approximately 83% and 96% dissolved uranium removal, respectively. Consistent with this marked uranium removal, microbial community profiling of the bioreactor substrate identified genera with known uranium- and sulfate-reducing functionality, which comprised a significant fraction of the bacterial population. For the CWTS pilots, bulrush and water sedge plant species were tested for their ability to foster conditions that can sequester uranium from mine discharge water. Bulrush and water sedge systems treated uranium to 0.6 to 4.2 mg/L (93 to 29% removal) and 0.01 to 0.5 mg/L (> 99% to 93% removal), respectively, depending on the hydraulic residence time (HRT) of the CWTS. Water sedge systems treated to lower uranium concentrations than bulrush, including at a relatively short 5-day HRT. Such pilot-scale

testing suggests that a combination of passive and semi-passive biological treatment approaches may allow for reclamation and closure of the Schwartzwalder site.

Introduction

The historical Schwartzwalder uranium mine, located near Golden, Colorado, USA, was mined for approximately 50 years before closing in 2000. Following flooding, the mine workings contained elevated uranium concentrations (~ 26 mg/L) that require treatment to meet the existing discharge standard (0.03 mg/L). This is presently achieved by a reverse osmosis and ion exchange system; however, alternative (semi-) passive treatment options are desirable to facilitate closure and long-term management of the site. Many uranium-reducing bacteria (URB) couple the oxidation of organic matter to the reduction of hexavalent uranium, transforming it to its less soluble lower oxidation state (Newsome et al., 2014). Since 2013, this process has been promoted at the Schwartzwalder mine via periodic injection of soluble organic carbon (e.g., molasses, alcohol) to the flooded workings. While this resulted in a marked decline in dissolved uranium concentrations (80 to 90% removal; Harrington et al., 2015), further treatment of the mine discharge is required to meet the current discharge standard. This paper provides an overview of pilot study results from bioreactor and constructed wetland approaches designed to harness the activity of resident URB at the Schwartzwalder site to provide post-discharge treatment of uranium.

Methods

Pilot-scale semi-passive biochemical reactor

Three gravel-filled vertical upflow bioreactors (795 L capacity) were constructed at the site in 2020. One bioreactor (BCR-FeS) was pre-dosed with a slurry of Ferroblack®, a proprietary synthetic iron sulfide mineral, to evaluate its effect on shortened commissioning time and uranium treatment. Mine water was pumped into the bioreactors at a rate equivalent to a 7-day HRT, which transitioned to a 14-day HRT later in the pilot season. The influent water to BCR-FeS was amended with ethanol, nitrogen, and phosphate to stimulate microbial activity. A second bioreactor (BCR-PO_4) was amended with the same ethanol and nitrogen dose, but a higher phosphate target. A third control bioreactor (BCR-Control) received no carbon or nutrient amendment. Samples of effluent were collected periodically for water quality analysis.

Pilot-scale constructed wetland treatment system

Two series of constructed wetland treatment systems (CWTS) were constructed to evaluate its ability to sequester uranium. Both comprised a series of four cells filled with crushed stone, pea gravel, sand, and woodchips. One series was planted with bulrush and the other with water sedge. The CWTS matured through one growing season with periodic fertilizer and straw addition prior to the start of the pilot treatment program. To maintain healthy plants, the bulrush CWTS operated with a deeper water column (50 cm) than the water sedge (30 cm). Mine water was pumped into the first cell of each CWTS, with the subsequent three cells fed by gravity flow. Two flow rates were tested to evaluate a range of HRTs over the four cells in each series. Samples were collected from each cell outflow for water quality analysis.

Upon termination, the microbial community structure of the bioreactor and CWTS substrates was evaluated by 16S rRNA gene analysis.

Results and discussion

Bioreactor

Compared to the control in which uranium concentrations remained similar to the influent levels (6 to 7 mg/L), marked uranium removal was observed for the carbon-dosed bioreactors at both the 7- and 14-day HRT (Figure 1). The development of strongly reducing conditions was most rapid for BCR-FeS, evidenced by its low oxidation-reduction potential (ORP), resulting in sustained uranium removal for BCR-FeS throughout the pilot. Strongly reducing conditions developed in BCR-PO_4 operating at a 7-day HRT, coincident with a decline in uranium concentration (Figure 1). At the end of the 7-day HRT period, the uranium concentration in the BCR effluent was 1.1 and 0.75 mg/L for BCR-FeS and BCR-PO_4, respectively. This is equivalent to 83% (BCR-FeS) and 89% (BCR-PO_4) removal compared to the control. At a 14-day HRT, slightly lower uranium removal was noted for BCR-FeS (72%; 1.8 mg/L) with greater sequestration measured in BCR-PO_4 (96%; 0.25 mg/L) by the end of the test period. Although given the downward trend of uranium at the 7-day HRT in BCR-PO_4, it is unclear if the longer HRT was responsible for the improved uranium removal.

Given the carbon and nutrients supplied to BCR-FeS and BCR-PO_4, biological uranium reduction is anticipated to occur in both bioreactors. Indeed, microbial analysis identified bacteria with close relation to the *Desulfomicrobium* genus, known to host URBs, in both BCR-FeS and BCR-PO_4. Higher inferred abundance of URBs was measured for BCR-PO_4 relative to BCR-FeS, which may help explain the greater uranium removal observed. The addition of elevated phosphate to BCR-PO_4 may have changed the dominant speciation of dissolved uranium. PHREEQC modelling of the influent chemistry indicated the uranium was primarily present as ternary calcium-uranyl-carbonate species, which are slow to undergo microbial reduction (e.g., Ulrich et al., 2011). Under the high phosphate conditions present in BCR-PO_4, the dominant form of dissolved hexavalent uranium was a uranyl phosphate species that may be more amenable to bioreduction; however, there is uncertainty regarding the thermodynamic data that underpin the stability constants for such species (Wang et al., 2019). Regardless, while the BCR pilots suggest further significant uranium removal is feasible, treated concentrations remained at least one order of magnitude above the current site discharge standard (0.03 mg/L).

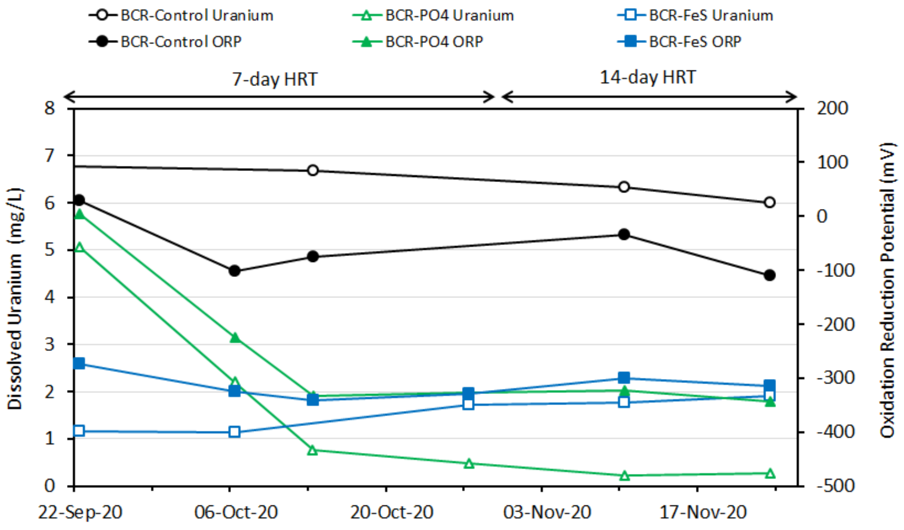

Figure 1: Change in dissolved uranium and ORP in bioreactor effluent during pilot study

Constructed wetland treatment system

Both the bulrush and water sedge CWTS exhibited significant uranium sequestration, particularly at longer HRT (Table 1). Under a 25-day HRT, the bulrush and water sedge CWTS achieved 93% and > 99% uranium removal, respectively (Table 1). Indeed, the uranium concentration in the water sedge CWTS discharge (0.01 mg/L) was below the 0.03 mg/L discharge standard. Lower uranium removal was observed at short HRT (5.4 day) for CWTS, although the water sedge showed markedly higher treatment (92%) than the bulrush (29%) CWTS. Both systems exhibited strongly reducing conditions throughout. Microbial community profiling indicated the presence of URB in both systems, with higher URB abundance in the water sedge CWTS consistent with the greater uranium removal observed for this system. The primary mechanism of uranium removal is likely microbial reduction of uranium, followed by precipitation as uraninite (UO_2) or non-crystalline forms of reduced uranium (Bernier-Latmani et al., 2010). Adsorption of uranium to the CWTS substrate may also play a role in the uranium sequestration observed (Bone et al., 2017; Wang et al., 2014).

Table 1: Uranium removal in CWTS at 5.4- and 25-day hydraulic residence time

	5.4-day HRT		**25-day HRT**	
CWTS plant type	Bulrush	Water sedge	Bulrush	Water sedge
Inflow uranium concentration (mg/L)	5.94	5.94	9.11	9.11
Outflow uranium concentration (mg/L)	4.23	0.50	0.64	0.01
Uranium removal	29%	92%	93%	>99%

Conclusion

The field pilots suggest that a water sedge-based CWTS may achieve the current site uranium discharge standard (0.03 mg/L), and full-scale CWTS evaluation is recommended. The BCRs demonstrated significant uranium sequestration and although they did not remove uranium to 0.03 mg/L, their role as a pre-treatment step to limit uranium loading to a downstream CWTS warrants further examination.

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Seven Years of PFAS Planning and Removal: Lessons Learned for the Mining Community

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are contaminants that have been detected in water supplies throughout the world. They have gained widespread public health attention and multiple regulatory agencies have implemented, or are in the process of implementing, limits for using these compounds and releasing them into the environment. This paper provides an overview of what PFAS are, where they can be present in mining environments, and how can they be treated. In addition, this presentation provides the lessons learned by the City of Issaquah, the first community to implement PFAS removal from groundwater. The City detected PFAS in 2015 at its 250 GPM (950 LPM) Well No. 4, the primary compound being PFOS; however, PFHxS, PFOA, and other PFAS were also present. PFOS was detected at concentrations as high as 600 ng/L, 8.5-times higher than the USEPA Lifetime Advisory Level of 70 ng/L for PFOS+PFOA and 40-times higher than the State of Washington's action level of 15 ng/L. The City immediately reviewed the situation and selected wellhead treatment for PFAS removal. Granular activated carbon (GAC) vessels were installed in lead/lag configuration, with more vessels planned for future expansions. The system was designed, permitted, constructed, and started up in 77 days. The facility started operations in June 2016.

At the time of writing, the system has been in continuous use for six years and is one of the longest continuously operating PFAS removal systems in the world. This paper discusses the operational surprises, challenges, and unintended consequences that the City has learned over this time. The lessons learned include much longer than estimated media life and lower operational costs, PFOS contamination of an adjacent and much larger Well No. 5 (1,250 GPM / 4,730 LPM), the media becoming radioactive despite the water having non-detectable radiation, ongoing bouts of biological growth, and ongoing issues with media disposal. Finally, additional PFAS have been detected due to transitioning to newer, more advanced analytical techniques.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are contaminants that have been detected in water supplies throughout the world. They were developed decades ago and began to enter commercial use in the late 1940s. These chemicals were incorporated into many products due to their unique chemical properties as lubricants and as water- and oil-repellents. Some of the industries using PFAS include mining production, automotive, aviation, aerospace and defense, biocides, cable and wiring, construction, electronics, energy, firefighting, food processing, household products, oil extraction, metal plating, medical articles, paper and packaging, semiconductors, textiles, leather goods, and apparel (OECD, 2013).

There are thousands of PFAS compounds, most of which are highly persistent, bioaccumulative, and toxic, and have been detected ubiquitously throughout the environment. PFAS are resistant to biological and thermal degradation. As a result, these human-made chemicals are expected to be detected for decades in the environment.

This paper describes what PFAS are and where PFAS can be found in the mining industry. In addition, this paper also presents the lessons learned from the City of Issaquah, Washington's, seven years of experience in dealing with these contaminants in their water supplies. The City has one of the longest continuously operating PFAS removal systems in the world, and the longest one in operation along the North American Pacific Coast.

What are PFAS?

PFAS are synthetic chemicals consisting of molecules with carbon-fluorine chains. These compounds exhibit strong and persistent surfactant qualities that have been used in multiple industries, including mining, as firefighting foams, foaming/frothing agents, wetting agents, and mist suppressants (Gluge et al., 2020).

Figure 1 shows the chemical structure of perfluorooctane sulfonic acid (PFOS), one of the most common PFAS compounds. Other common PFAS compounds are perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutane sulfonic acid (PFBS). The common feature of all these compounds is the presence of multiple carbon-fluorine bonds that provide the chemicals with their durable surfactant qualities. The differences between the compounds are the number of carbon atoms (i.e., length of molecule) and the type and number of additional functional groups at the end of each chain to provide additional properties that are beneficial to mining and other industries.

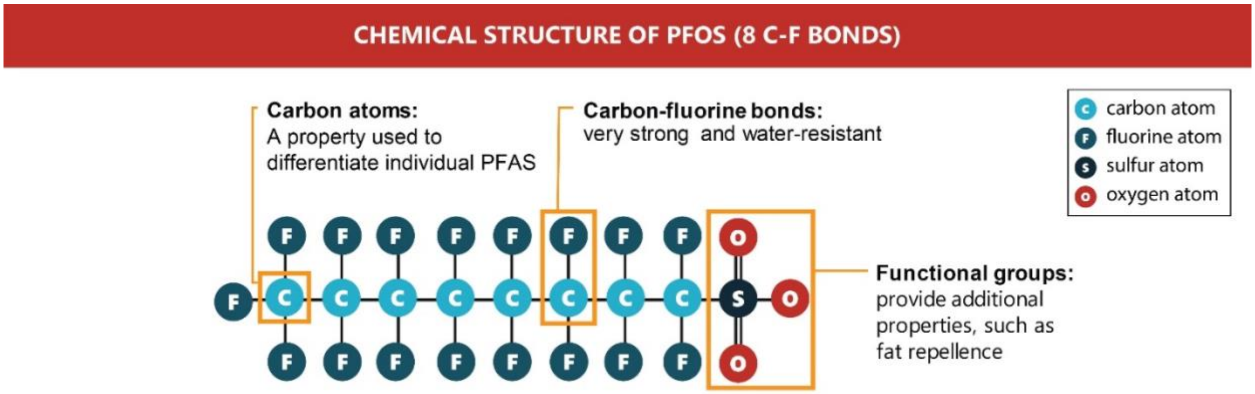

Figure 1: Chemical structure of PFOS, a common PFAS (Alito et al., 2020)

The durable physicochemical properties of PFAS that have made them useful and popular in industrial use have also resulted in negative impacts on the environment and human health (ATSDR, 2019; AWWA, 2020). Some PFAS either are, or degrade to, very persistent chemicals that accumulate in humans, animals, and the environment.

Their resistance to degradation, and high mobility in the environment mean that PFAS are now present throughout the world. Figure 2 is a conceptual diagram showing how these compounds move from various users and discharges to the environment and then back to urban areas.

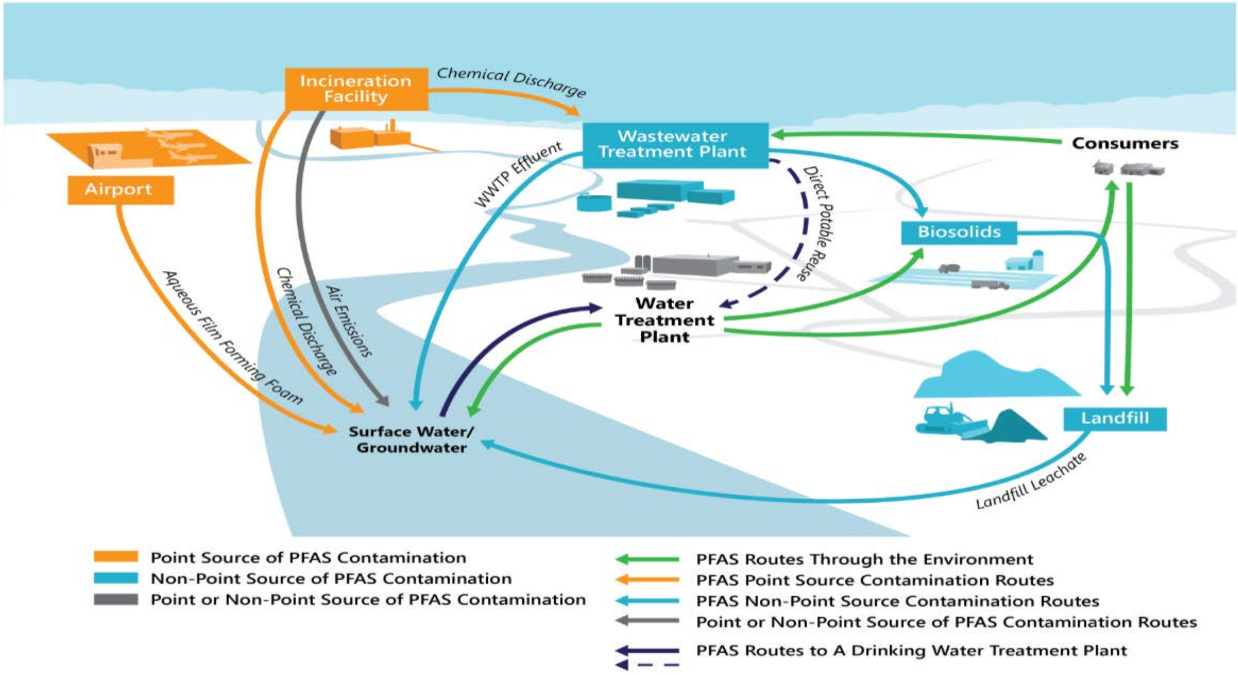

Figure 2: PFAS migration through the environment (Alito et al., 2020)

PFAS in mining

There are several uses of PFAS in the mining industry. These uses are summarized in Table 1. The surfactant qualities of PFAS have been utilized in ore processing (Gluge et al., 2020). They have been used to suppress sulfuric acid or cyanide misting when it is applied on leach piles to extract copper or gold. PFAS have also been added to sulfuric acid and cyanide to improve the wetting of ore piles for metal leaching. They are used in ore floating to create a stable aqueous foam that improves metal salt separation. Finally, given PFAS are persistent throughout the environment, PFAS at a mine may not have originated from mining operations, but could have been present as existing contamination in the mine's water supply. Use of this contaminated water has then spread PFAS throughout the operations.

Table 1: PFAS in mining operations

Ore processing	Other mining operations
Mist suppressing agent	Firefighting foam
Wetting agents	Hydraulic fluid additive
Flotation foaming agent	Biocide/herbicide
Existing contamination in supply water	Fire retardant clothing and fabric
	Oil/water repellant clothing and fabric
	Floor finishes and cleaning agents

PFAS are also found in other mining operations. Specifically, they are commonly used in firefighting foams, specifically aqueous film-forming foams (AFFFs) used to combat fuel fires. AFFFs are commonly stored at mines and used in actual firefighting situations as well as in practice drills. PFAS-laden AFFFs are one of the largest sources of PFAS in the world; their production has been stopped in the USA and Canada. Other PFAS uses include equipment hydraulic fluids, site biocides/herbicides, various types of clothing and fabrics, and even in cleaning materials used in indoor spaces.

Case study: City of Issaquah, Washington

The City of Issaquah, Washington, is a suburban community on the eastern outskirts of the Seattle metropolitan area. The City owns and operates their drinking water system and supplies water to approximately 43,000 people. Their water supplies consist of groundwater from four wells that the City owns; this is augmented with regional drinking water purchased from another agency. In 2013, groundwater treatment consisted of sodium hypochlorite addition for disinfection purposes and fluoride addition to match the fluoride concentrations in the purchased regional water.

The 1996 amendments to the federal Safe Drinking Water Act required the Environmental Protection Agency (EPA) to regularly monitor unregulated contaminants for potential future regulation. The third round of monitoring, the Third Unregulated Contaminant Monitoring Rule (UCMR3), was issued in 2012 and included several per- and polyfluoroalkyl substances (PFAS). The City was selected to sample their groundwaters and collected annual grab samples in 2013 to 2015. The sampling data submitted to EPA indicated that PFAS were found in high concentrations from water produced by the City's Gilman Well No. 4 (see Table 2).

Table 2: Gilman Well No. 4 PFAS concentrations reported for UCMR3

Year	PFOS (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFHxS (ng/L)	PFHpA (ng/L)	PFBS (ng/L)
2013	600	22	28	241	26	<9
2014	514	20	27	201	23	<9
2015	472	18	22	194	21	70

The EPA Provisional Health Advisory Limits were 200 ng/L for PFOS, 400 ng/L for PFOA, and no limits for the remaining compounds at the time of sampling. These advisory limits are voluntary and non-enforceable. In addition, data for UCMRs by definition are unregulated contaminants and the EPA did not inform the City that any additional actions had to be completed. The State of Washington had no adopted limits for PFAS at this time and did not comment on these results.

Multiple options were evaluated to manage the PFAS. These options and issues are summarized in Table 3. Review of these options led the City to select treatment as the preferred PFAS management option.

Table 3: PFAS management options

Management option	Advantages	Disadvantages
Abandon well	No capital costs	Potential loss of water rights. Purchased water is more expensive than groundwater, even with treatment. PFAS remains.
Blend PFAS concentrations down with other wells	Already in use at the time. Maintains water rights. Depletes PFAS plume. No change in operations.	Unable to reach Council directive to achieve non-detectable PFAS concentrations.
Pump water to adjacent Issaquah creek	Maintains water rights. No capital costs – use existing valving and piping. Depletes PFAS plume. Water augments low summertime flows and provides beneficial cooling.	Permitting a PFAS-laden discharge to sensitive fish habitat would take a long time, with no certainty that a permit would be issued. Purchased water is more expensive than groundwater, even with treatment.
Treatment	Maintains water rights. Depletes PFAS plume. Treated water still cheaper than purchased regional water.	Incurs capital costs. Higher annual operating costs. Change in well operations.

Table 4 presents a review of the treatment options. Given these issues, the City selected granular activated carbon (GAC) as the treatment option to purchase and install. This information was presented to City Council in February 2016 and Council authorized staff on March 21, 2016 to reach full-scale treatment as fast as possible.

Table 4: PFAS treatment options

Treatment option	Advantages	Disadvantages
Activated carbon absorption	No additional chemicals required. No repumping required. Effective PFAS removal. Compact outdoor design. Low capital costs.	Requires initial backwashing – wastewater management needed. Solid waste generation.
Ion exchange resin adsorption	No additional chemicals required. No repumping required. No initial backwashing required. Compact outdoor design. Low capital costs.	Very little published literature for PFAS removal at the time, and available data was inconclusive to achieving non-detectable concentrations. Solid waste generation.
Nanofiltration/ Reverse osmosis	Extensive literature demonstrating complete PFAS removal. Addresses other minor issues in groundwater quality (arsenic, manganese).	Requires repumping. Requires anti-scalant and cleaning chemicals. Requires building. Continuous liquid waste generation. Permeate requires post-treatment to minimize corrosion control issues. High capital costs.
Advanced UV/ peroxide oxidation	Does not generate a liquid or solid waste residual.	Requires peroxide storage. Requires building. High capital costs. Published literature shows only partial PFAS destruction.

The facility was fully commissioned and put into production on July 16, 2020, 77 calendar days after City Council authorization to begin design, and has been in daily operation since then. The only times the GAC system has not been in use are those hours in which the wells were offline due to lack of water demand and/or maintenance on the well pumps. Further investigations conducted after the system became operational determined that the PFAS were coming from a nearby firefighting training facility.

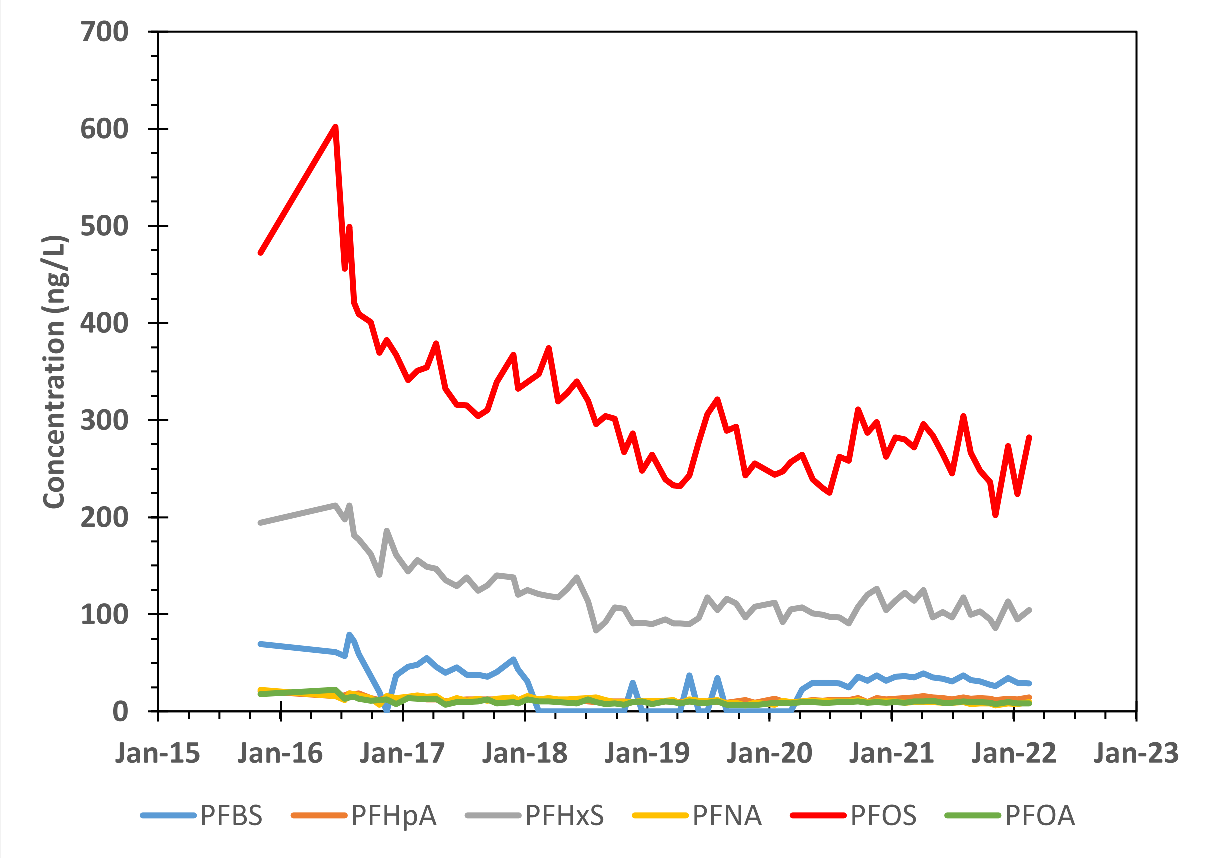

Figure 3: Gilman Well No. 4 raw water quality (full-scale)

The PFAS concentrations in Well No. 4 groundwater have slowly decreased over time as the well continues withdrawing water from the aquifer (see Figure 3 for all the data and Figure 4 for PFAS compounds found at lower concentrations). All water samples from the GAC system have found non-detectable concentrations for all six PFAS from the lag vessel outlet.

This is important as the EPA issued new guidance in November 2016, five months after the system became operational, that set the advisory limit to 70 ng/L for PFOS and PFOA combined. Similarly, the State of Washington issued regulations in 2021 that set individual PFOS and PFOA limits at 15 and 10 ng/L, respectively.

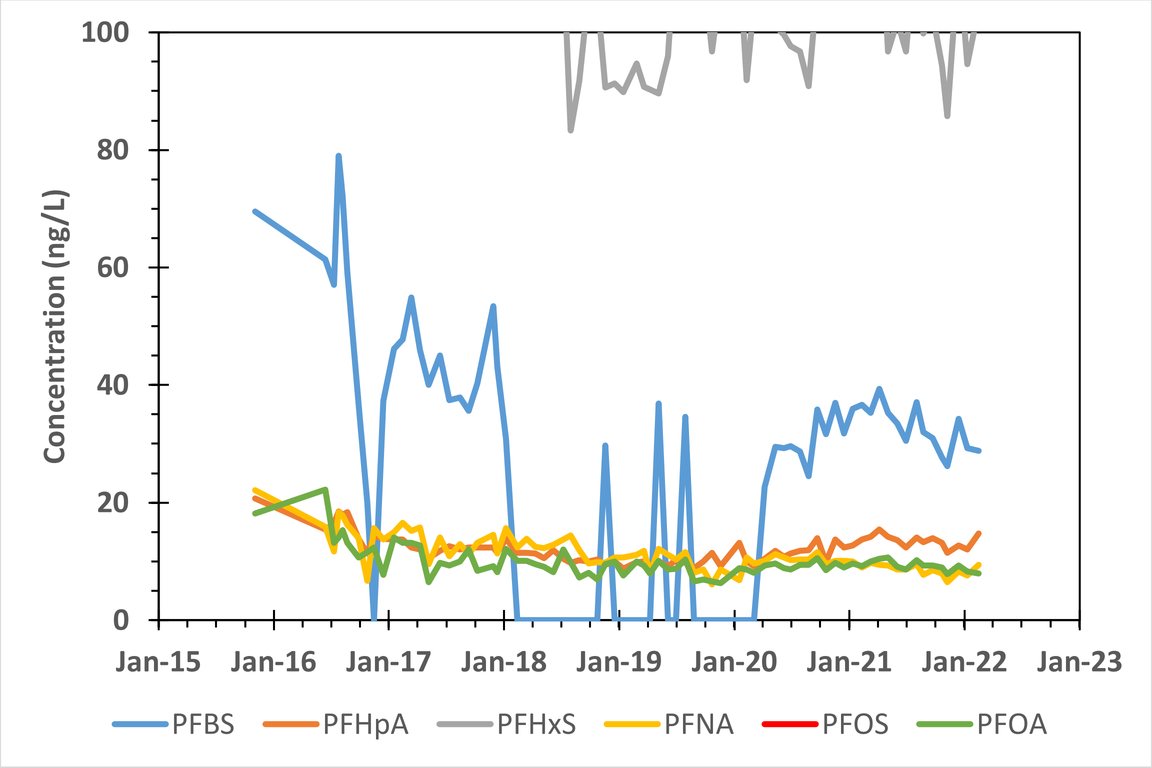

Figure 4: Gilman Well No. 4 raw water quality (reduced-scale)

The GAC media has been changed out once. The coconut media has now been removed and both vessels are filled with the agglomerated bituminous coal media. Table 5 shows a comparison of the media performance. These results have led to the City selecting the bituminous coal as the media for all subsequent replacements.

Table 5: Summary of GAC media performance

Parameter	Coconut media	Bituminous coal media
Dates in lead service	May 2016 to May 2017	May 2017 to present
Time in lead service (months)	11	54 and counting
Water processed (millions of gallons)	102	>463
Estimated PFAS sorbed (kg)	0.24	>1.18
Bed volumes to change-out	19,092	>86,600

Three operational challenges have arisen since this system started operations. The first is that bacterial growth was found on the GAC after six months of operation. This growth caused rapid headloss development. This issue was not identified earlier as the City had never experienced problems with bacteria due to the chlorine addition. However, the GAC system was installed prior to the chlorine addition feed point. GAC is frequently used as an engineered substrate for various purposefully designed and operated biofiltration processes, and the Gilman GAC system wound up being an inadvertent biological process. Laboratory analyses found that the bacteria were native iron bacteria that were using the GAC as substrate on which to grow, and utilizing the naturally occurring iron in the water. An evaluation was conducted to identify methods to manage this growth. Conversations with TIGG and Calgon Carbon indicated that suppression can be achieved by applying up to 1 mg/L chlorine onto the GAC. Further engineering analysis determined that the cost of purchasing additional equipment and repiping the system to provide chlorine prior to the GAC was prohibitive.

Instead, the City is backwashing the lead GAC vessel once per month to remove excess biological growth and reduce the system headloss. This process is not recommended by GAC vendors as it disrupts the mass transfer zone of the media and causes fully saturated GAC at the top of the media bed to intermix with GAC at the bottom of the bed that would be PFAS-free. The result is often early PFAS leakage from the GAC vessels. However, the City's experience after five continuous years of operation has not found such leakage occurring.

The second issue relates to the biogrowth-induced headloss development. The water main that Gilman Well No. 4 discharges into has an operating pressure of 110 psi. The clean filter headloss was 10 psi, so the pressure at the inlet side of the GAC is 120 psi. The original system was shipped with 125 psi rupture disks to protect the vessels with over-pressurization. These disks are the standard feature for these vessels. The biogrowth resulted in an additional headloss of up to 10 psi, resulting in feed pressures reaching 130 psi. The inlet rupture disk blew out at this pressure, causing water to pour out onto to the surrounding areas and causing a system shutdown so that staff had to replace the disk. After the disk ruptured a second time, staff replaced the device with a pressure relief valve and began closely monitoring headloss development. The lead vessel is backwashed just before the pressure relief valve would open.

The final issue relates to the disposal of the spent coconut GAC. The media vendor arranged final disposal of the spent media in California. During transit, the hauler entered a California Highway Patrol truck inspection station by the Oregon-California state line for routine inspection. The inspection indicated that the media was radioactive, and the shipment had to be stopped for further analysis. This issue caused City staff to exert considerable effort to make necessary arrangements for subsequent testing and verifications. The re-testing determined that the radioactivity was below regulated limits and the media could continue its transit to the final disposal site. The hauler was delayed for four days but the City was not fined.

The aftermath of the episode was an in-depth analysis for potential sources of radioactivity and how to manage it in the future. A sample of the groundwater and of the bituminous coal media in the lead vessel were sent for analysis. The data found that the groundwater had non-detectable concentrations of radionuclides and radiation. However, the media was found to contain appreciable amount of various radioactive elements.

The hypothesis is that non-detectable concentrations are not the same as zero concentrations. These potentially very low concentrations can add up to an appreciable total mass when there is a lot of water involved, such as it the case with the Gilman GAC system. In addition, conversations with Calgon Carbon have indicated that all types of GAC have demonstrated absorptive capacities for radionuclides. At the time of writing this paper, the author has sampled the existing media to determine its potential radionuclide content and its impact on final disposal options. This is a serious consideration as the bituminous coal in the lead vessel has now treated nearly four times the water of the coconut GAC that caused the initial concerns.

Conclusion

PFAS have become ubiquitous contaminants that are present throughout the economy, including the mining sector. PFAS's surfactant qualities provide multiple benefits in ore processing, firefighting, and other mine operations. However, this contaminant's persistence means that some mines may have potentially large PFAS concentrations.

There are several options to manage PFAS, such as abandoning the contaminated water supply, blending down the contamination, and treatment. The City of Issaquah explored these options and chose treatment. Treatment has successfully removed the PFAS for the past several years. We have gained considerable experience from it, including learning that:

- The GAC media has proven to be capable of reducing up to 600 ng/L of PFOS down to non-detectable concentrations.
- Bituminous coal carbon has a significantly larger sorption capacity for PFAS than coconut GAC.
- Unforeseen biological fouling caused excessive system headloss that resulted in equipment changes.

- The fouling also resulted in the City backwashing monthly, which is contrary to vendor recommendations. However, this action has not caused an issue with performance.
- The long operations have resulted in the media accumulating radionuclides, which is now an issue being reviewed to determine its impact on media disposal options, logistics, and ultimately costs.

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Accurately Forecasting the Extra Treatment Cost Associated with Removal of Lesser Regulated PFAS Species in Water

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Matilda Kearney, SciDev Water Services, Australia

Abstract

Per-and poly-fluoroalkyl substances (PFAS) are a group of recalcitrant, man-made, fluorinated molecules. PFAS contamination is commonly associated with aqueous film-forming foam (AFFF) manufacture and application. Since PFAS contamination was first discovered in water supplies, associated regulation has been constantly changing. Historically, the main molecules of concern were PFOS and PFOA, with PFHxS garnering more attention shortly after. It happens that these three molecules are considered long-chain PFAS molecules and as such are some of the easiest, and therefore cheapest, commonly encountered PFAS molecules to remove from water. However, thousands of other (some currently undetectable) PFAS molecules exist, many of which are currently less regulated, or unregulated. Regulation will continue to change as more research is done on the toxicity of individual molecules and associated families. As a complication, poorly understood and modelled degradation pathways exist for PFAS, meaning water that is free of specific molecules at the time of discharge may, in future, have detections. Regulators perceive this risk differently, and as such, human health and environmental guidelines differ drastically across local, state and national borders.

The global PFAS remediation market is estimated to be worth over $80 billion over the next five years (EBJ, 2019), with the Australian Defence Force spending over $505 million on their PFAS contamination response since 2015 (ADF, 2021). For the mining and infrastructure sectors, PFAS remediation is often triggered by new developments requiring environmental impact assessments or investigation into water reuse, discharge and dewatering activities. These sectors find themselves operating across multiple regulatory environments and, as a result, managing legacy PFAS contamination (usually a cocktail of both regulated and less/unregulated PFAS molecules) in significantly different ways. The risk associated with the discharge of water contaminated with less/unregulated variants is typically well quantified by legal and environmental departments, but to implement successful long-term PFAS remediation strategies, management teams also need the extra cost to be quantified.

The most common technologies for ex-situ remediation of PFAS-contaminated water is the use of both adsorptive filter media such as Granular Activated Carbon (GAC) and ion exchange (IX) media in a conventional water treatment plant (WTP). This research investigates long-term breakthrough trends for PFAS families and individual PFAS molecules at different stages of treatment within PFAS WTPs. Total oxidizable precursors (TOPA) and carboxylic acids families are the focus, with data sets gathered from two different industrial scale WTPs designed, built, and operating in Australia. Despite both WTPs utilizing adsorptive media and IX media as the primary treatment technology, each WTP is significantly different (low versus high flowrate, heavy versus trace influent contamination). However, similar trends of breakthroughs, and therefore cost increases, to manage lesser/unregulated PFAS molecules can be seen.

The first case study is a historical fire training ground operational from 1973 to 2015, when it was closed for remediation. This site was typical of hotspot/source contamination, with surface water concentration levels ranging to as high as 600 µg/L for sum of PFAS, and 685 µg/L for TOPA. The historical use of old-age AFFFs resulted in the majority of the PFAS compounds being in the sulfonic acid family, with 50.88% being (n:2) fluorotelomer sulfonic acids, 32.54% being sulfonic acids, 16.57% being in the carboxylic acid family, and only 0.01% being sulfonamides.

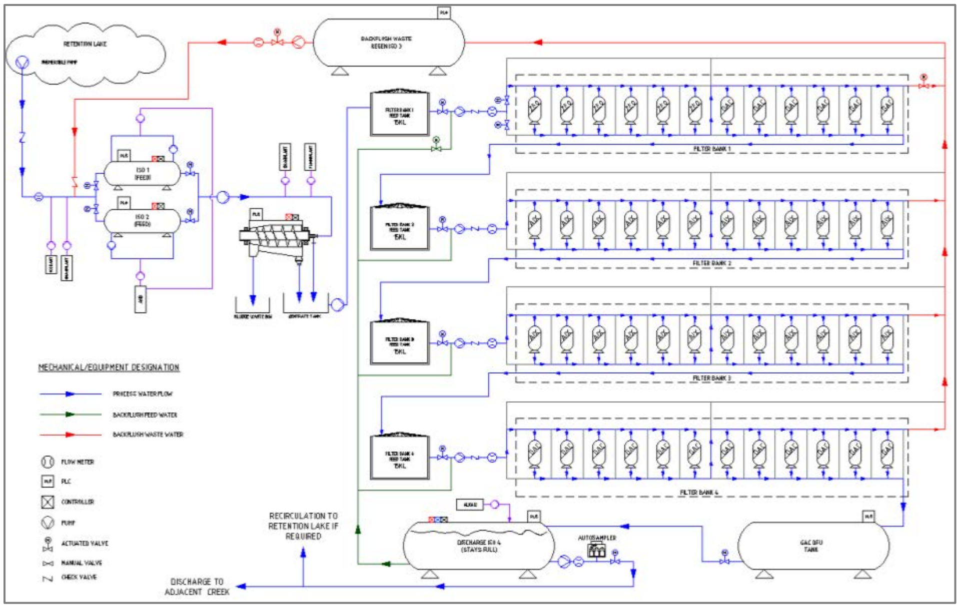

Figure 1: Block flow diagram of the case study 01 water treatment plant

Despite the national guidelines only regulating PFOS, PFOA and PFHxS, the Environmental Protection Licence (EPL) issued by the Environmental Protection Authority (EPA) required the treated water to be below 0.002 µg/L for all PFAS molecules and TOPA that can be determined in Australian National Association of Testing Authorities (NATA) accredited laboratories. The WTP for this project operated at a flow rate of 5.8 L/s with a maximum instantaneous flow rate of 8 L/s and treated around 80

ML of contaminated surface water on-site over a 12-month period. A block flow diagram outlining the WTP process flow can be seen in Figure 1.

The regulated PFAS molecules (PFOA, PFHxS and PFOS) at this site were removed entirely from the process water after filter bank 02, as seen in Figure 2. If this site was regulated in accordance with the national guidelines, we could remove every treatment stage after filter bank 02 and could most likely replace four of the AIX filters in filter bank 02 with granular activated carbon (GAC), which is a significantly cheaper adsorptive media. This simplification of the process flow would result in cost savings of over $460,000 in the initial procurement alone for this project. To compare the cost of design, procurement, installation, commissioning, operation, maintenance and then demobilization post completion of the project, the cost of this project was $0.054/L of water treated. Whereas the cost to treat to only the regulated PFAS compounds would only be $0.045/L of water treated.

The GAC from filter bank 01 was replaced after 8,000 bed volumes (BV) of water were treated (as can be seen from the drop in influent concentration to filter bank 02 below) and the IX media in filter bank 02 was showing evidence of dumping short-chain carboxylic acids after 11,000 BV. Assuming 65% recovery of IX media capacity after caustic brine regeneration and two successful regenerations before requiring new IX media, if this project was to continue long-term (1,000 ML) the cost for each system would be adjusted to $0.0365/L for the treatment of regulated PFAS compounds, and $0.0378/L for the treatment of full-suite PFAS and TOPA compounds. This would show a much lower disparity than the short-term treatment costs.

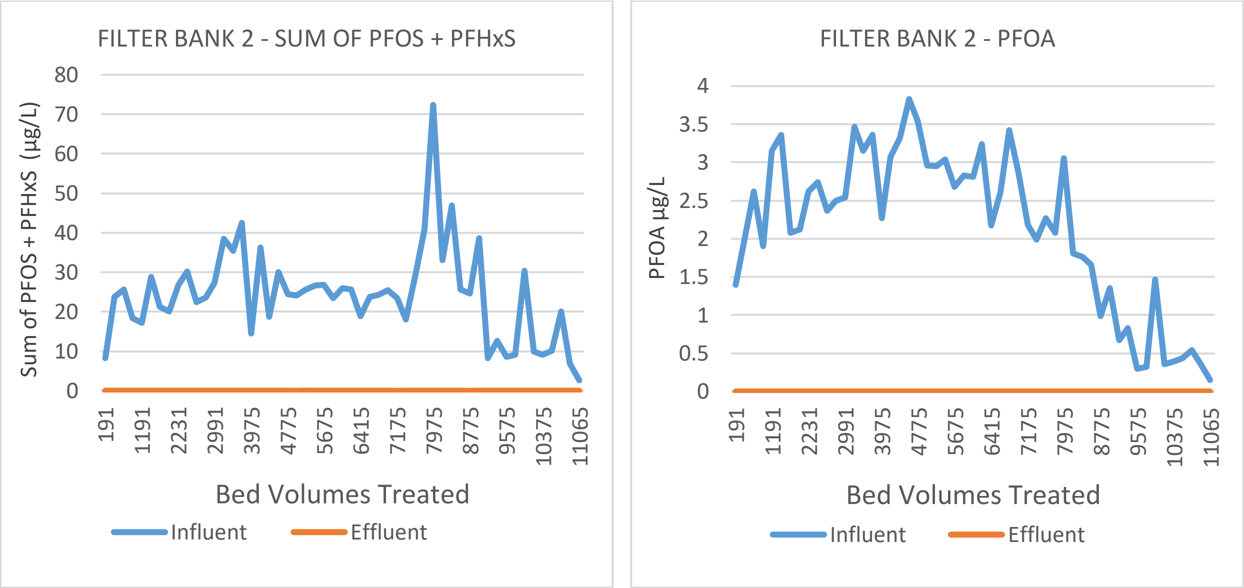

Figure 2: Sum of PFOS and PFHxS, and PFOA from filter bank 02

The second case study is a mine site located in Australia with no evidence of source contamination, and with only low-level PFAS concentrations present in surface water runoff. However, due to the site being situated in a drinking water catchment, the WTP was required to remove PFAS contamination down to below super ultra-trace (SUT) levels (below 0.0002 µg/L) for all 28 PFAS compounds. This criterion guarantees adherence to the 99th percentile level of ecological protection under the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for discharge to the environment. The WTP operates at a flow rate of 20 L/s with a maximum instantaneous flow rate of 29 L/s, and has treated 355 ML of contaminated surface water over the last 16 months. A block flow diagram outlining the WTP process flow can be seen in Figure 3.

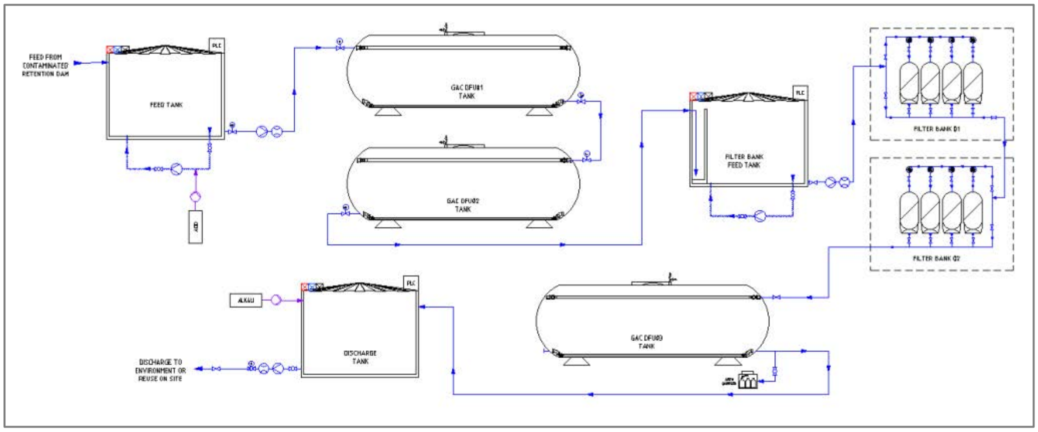

Figure 3: Block flow diagram of the case study 02 water treatment plant

The sum of PFAS influent concentration for this project is quite low, with an average concentration of 0.36 µg/L. However, the distribution of PFAS compounds makes the treatment much more complex, with 43.20% of the PFAS compounds being in the carboxylic acid family, 56.37% being (n:2) fluorotelomer sulfonic acids, and 0.43% being sulfonic acids. In addition, with the majority of the carboxylic acids present having 7 carbons or less (98.49% of carboxylic acids present), the removal of these short-chain compounds down to a SUT via GAC adsorption alone would be incredibly difficult, even with large volumes of media.

Results show that regulated PFAS molecules at this site are removed to below SUT levels after filter bank 01. However, the majority of these compounds are removed in earlier stages, with 88% of the removal occurring in the DFU01 and DFU02. At the time this paper was written, filter bank 01 had not discharged any regulated PFAS molecules after 355 ML of treatment. However, unregulated molecules started to break through filter bank 01 after 140 ML of treatment and from filter bank 02 after 270 ML, with the WTP currently offline for the replacement of all filter media in order to continue treating all PFAS down to SUT.

If this project only required treatment of regulated compounds to super ultra-trace levels, not only could we remove every treatment stage after filter bank 01, but we wouldn't need to replace any media, or at least not the AIX resin, for roughly another 50 to 70 ML. The simplification of the process alone would result in a cost-saving of over $327,00.00 in initial procurement. The overall cost of this project so far has been $0.008/L of water treated compared to $0.007/L to treat only the regulated compounds down to SUT. Comparing treatment models with long-term treatment (1,000 ML) the costs would be adjusted to $0.0078/L for the treatment of full-suite PFAS and $0.0061/L for the treatment of regulated compounds.

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Chapter 4:

Closure Water Management

A Tiered Approach to the Successful Construction of a Sulfate-Rich Water Passive Treatment System

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Abstract

A passive sulfate reduction system with iron scrubbers was identified as the most viable option for the treatment of elevated sulfate within leachate from an old landfill, and bench-scale trials were established in 2019 at the site to test the theory. This included the use of biochemical reactors (BCR) with different proportions of wood chips, straw, manure, limestone, and biochar to culture sulfate-reducing bacteria. In addition the concept of "bugs on booze" was trialled, using fixed bed anaerobic bioreactors (FBAR), in which alcohol is added to enhance the sulfate-reducer activity. In total three BCRs and two FBARs were set up for this stage of the assessment. The resulting treated leachate was then passed through different iron media types (haematite, magnetite, and iron filings) and sand filters to remove sulfide/free sulfur generated by the bacteria, with an aerobic wetland used to polish the effluent.

The success of the bench-scale project led to a pilot-scale system being constructed and monitored in the spring of 2020, the results of which confirmed the success of the bench-scale testing and provided useful insights into management of the system. This latest paper updates the project and provides a summary of the full-scale system that is being constructed in 2022, and demonstrates the final tier of the successful application of the innovative system.

Introduction

SLR Consulting (SLR) was appointed by British Gypsum (Saint-Gobain Construction Products UK Ltd trading as British Gypsum) to investigate options for the treatment of leachate emanating from an old landfill disposal site at their property in East Sussex. The options analysis undertaken by SLR highlighted a passive treatment option for the removal of the sulfate to below discharge standards. This was identified as a potential option, but it required treatability/feasibility testing. The concept involved the use of naturally occurring material containing sulfate-reducing bacteria to remove the sulfate, with the resulting dissolved sulfide in the water being "scrubbed" by a filter. An aerobic wetland would then be used to polish any final effluent before it was discharged. Full details of the bench and pilot scale can be reviewed in a paper presented in 2021 (Robinson et al., 2021), although a summary is presented below.

The treatment process summary

The design of a treatment system should be based on the results of a "staged process" of bench- and pilot-scale testing. Typically flow rates of c. 5 to 10 mL/min or less are termed a "bench-scale" study, while a "pilot-scale" study is one that would treat about 4 L/min or more. Bench-scale testing is an effective way to advance a project toward full-scale implementation while gaining useful knowledge about appropriate media, reaction rates, and functionality that increase confidence and overall effectiveness. The typical passive biological treatment process for sulfate reduction utilizes an anaerobic biochemical reactor or BCR. While BCRs receiving mining impacted water (MIW) may be configured as "up-flow" or "down-flow", experience has shown that up-flow BCRs are better than down-flow BCRs in treating sulfate-rich and metal-poor leachates.

The organic substrate comprises hard wood chips, limestone, straw, and biochar in varying proportions. To provide the naturally occurring sulfate-reducing bacteria, inoculum 0.1% animal manure is added. The bacteria consume the sulfate in the influent leachate and produce sulfide:

$$SO_4^{2-} + 2\ CH_2O = H_2S + 2\ HCO_3^{-}$$

The lack of suitable metals in the site discharge required a metal ion addition to passively sequester the sulfide generated through the sulfate-reduction process. The dissolved sulfide will precipitate as an insoluble metal sulfide or potentially as free sulfur. At the site, iron was added at bench scale via a treatment substrate such that the following reaction (through precipitation of dissolved iron or on metal iron surfaces), in the substrate will occur, shown simplistically below:

$$Fe^{2+} + S^{2-} \rightarrow FeS$$

This metal can be either in the zero-valent state such as scrap iron, or as an oxide. However, care in media selection is warranted. The effluent is then directed to a passive oxidation wetland.

This aerobic polishing wetland (APW), a lined shallow pond filled with soil and locally harvested or cultivated vegetation, is used to re-aerate the anoxic effluent from the BCR.

Bench-scale set up

To test the theory of a passive wetland treatment solution, a bench-scale system was set up at the site to run for 20 weeks. The bench-scale system comprised:

- 3 Biochemical Reactors (BCRs) – pump fed, each filled with a different test mixture comprising different proportions of manure, wood chips, hay, limestone, and biochar.
- 3 Sulfide Scrubbers (SCR), each filled with a different test mixture comprising magnetite, hematite, and iron filings.
- 3 Aerobic Polishing Wetland (APW) cells planted with wetland plants from the site; and
- 2 Fixed Bed Anaerobic Bioreactors (FBAR) with 2 Sulfide Scrubbers, Aeration Tub and Settlement Tub.

As part of the treatability, it was also decided to consider the use of a hybrid-passive approach, which involves the addition of a soluble form of hydrocarbon, in the form of alcohol, to increase the metabolic rate of the bacteria. To enable this a fixed bed anaerobic reactor (FBAR) was used, in which small quantities of ethanol were added to a small system to provide a food source for the bacteria. The reasoning was that with a more soluble food source, the bacteria will consume more of the sulfate, and hence less area will be needed for the treatment at pilot and full scale.

BCRs and SCRs 1 – 3

FBARs, SCRs and aeration

Aerobic polishing wetland

Figure 1: Bench-scale test set up

Monitoring and results

The system was monitored for a variety of analytes along with the flows throughout the system. Weekly field-based monitoring of pH, redox, and conductivity was undertaken, along with sulfate, sulfide, nitrate, calcium, and magnesium. At monthly intervals, phosphate, alkalinity, hardness, iron, nickel, zinc, and total organic carbon (TOC) was analyzed. The flows through the reactor were typically 6 L/d for the BCRs and 25 L/d for the FBARs. The latter was also reduced at the end of the treatment to be closer to the BCR flow rate, in order to act as a comparison. The monitoring of the system was undertaken at weekly intervals, when the redox and pH of the various components, coupled with the flow rates, were recorded. Samples were analyzed at an offsite UKAS (United Kingdom Accreditation Service) accredited laboratory for sulfate and other constituents. The results of the treatability study are shown in Figures 2 to 5.

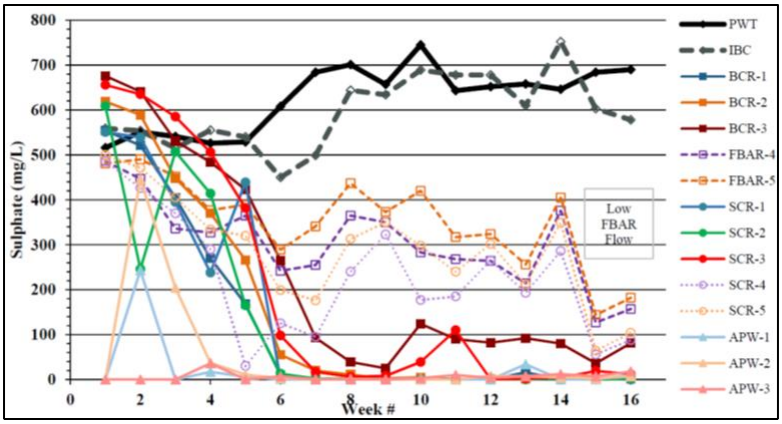

Figure 2: Sulfate concentrations

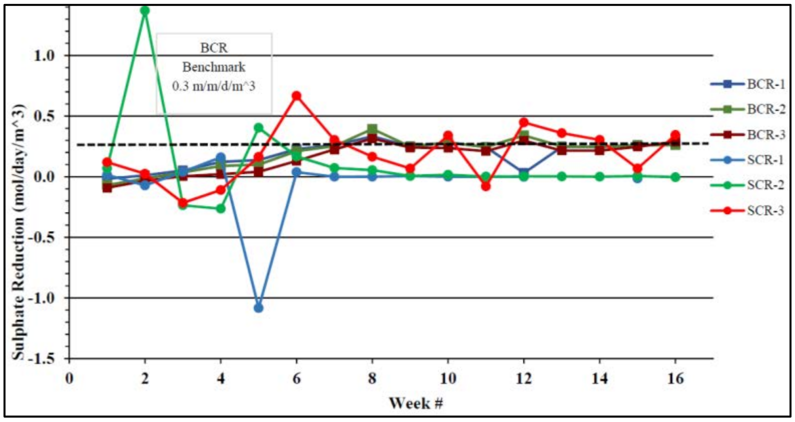

Figure 3: BCR sulfate reduction rate

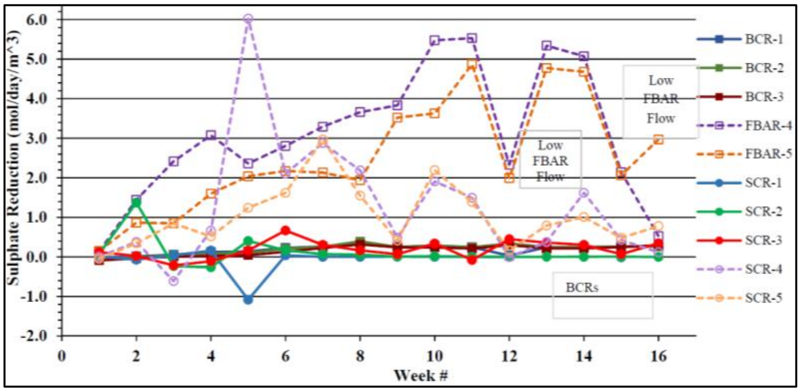

Figure 4: FBAR and BCR sulfate reduction rate

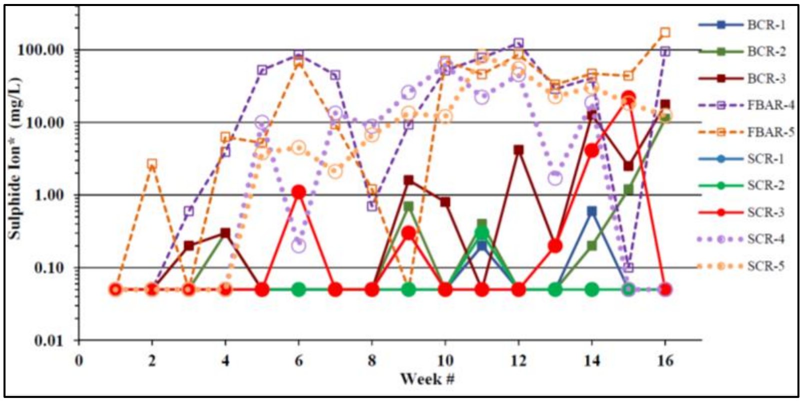

Figure 5: Sulfide concentrations

The bench-scale test results indicated that both BCR and FBAR treatment will produce an effluent that would meet a 250 mg/L sulfate discharge limit. In mine water treatment systems, sulfate reduction rates typically range from 0.1 to 0.3 moles/m^3 substrate/day. The rates for this study are shown to be at the upper end of this range. In addition, the FBAR rate of sulfate reduction was about 15 times that of the BCR reduction rate. Consequently, the media volume required to accomplish this with a BCR will be about 15 times greater than for the media volume for an FBAR with an identical treatment capacity. The land area footprint required for an FBAR treatment unit would therefore also be 15 times smaller than that required for a BCR. However, the FBAR process will require the delivery of a steady and reliable supply of food, such as alcohol, as a microbial nutrient.

The passive BCR process does not require the addition of nutrients, such as alcohol, and therefore is seen as a more practical solution at the site. The scrubbers appeared to sequester sulfide ion present in the BCR and FBAR effluents, although it was also clear that free sulfur was being precipitated in the outfall from the anaerobic systems. The bench scrubbers that received the FBAR effluents proved to be undersized. The aerobic wetland system was effective in removing the iron leached from the scrubbers and did have a positive impact on the organic carbon that came through the system. The results of the bench-scale testing were very encouraging. This has led to the design and development of a pilot-scale system at the site.

Pilot-scale testing

The success of the bench-scale trials led to the design and installation of a pilot-scale system on the site in the spring of 2020. The purpose of the system was to confirm the success of the bench-scale study by using the sulfate removal coefficients and preferred media option. The latter comprised mixing of wood chips, biochar, limestone, wheat straw, bench-scale organic material, and goat manure inoculum.

The desired flow being introduced into the system was 0.5 L/min and above, and there was no addition of alcohol as a nutrient. Review of the bench-scale testing showed that free sulfur precipitation dominated and hence the iron scrubbers were not required, although sand filters were included. The pilot-scale system had the original orientation of sequential treatment, although three biochemical reactors were established, such that variety in flow rate and other parameters can be used to test the system. To construct the pilot plant, shipping containers were used for the three BCRs. These were lined with insulation on the base and sides, which also prevented leaks, and reinforced such that they could hold the substrate and the water.

Sampling ports were established such that different horizons in the units could be analyzed if required. The aerobic polishing reed beds for the removal of BOD (biochemical oxygen demand)/TOC were designed with baffles to lengthen the flow path in the wetland. The piping allows for the later addition of an iron-based sulfide-sequestering unit, should monitoring indicate that sulfide is leaving the system at concentrations which are unsustainable from an environmental perspective.

The pilot system was commissioned in the spring of 2020, before the COVID-19 pandemic, and monitoring has been conducted since then by a skeleton staff on site. Sampling points included redox zone depth measurement in the anaerobic material, along with the treatment zones at various locations along the system.

Figure 6: Passive treatment pilot plant from right to left (feed tank; BCR1, 2, 3, 4; reed bed (APW) 1, 2, discharge holding pond showing purple/white bacteria)

The results of the ongoing monitoring indicate good sulfate removal, with no sulfide detectable in the effluent. Free sulfur, which has the potential to oxidize and release stored sulfur as sulfate, has been identified in the system, although during the spring and summer there was no evidence that this had occurred.

Elemental sulfur may be the primary product of sulfate reduction in the BCRs. Evidence includes the white cloudiness in the BCR effluents, white deposits in the wetland influent zones, and the purple tinge (likely the bacteria *Chromatium sp.* and *Chlorobium sp.*) in the final pond influent zone (Figure 8). Purple sulfur bacteria produce elemental sulfur as part of their life cycle. Thus far, the pilot cell is confirming the results of the bench-scale testing, with the latest influent sulfate of c. 800 mg/L being reduced to c. 100 mg/L in the effluent, thus providing robust design data for the full-scale system.

In the winter months the treatment efficiency decreased; this is believed to be due to temperature reduction and potential free sulfur re-oxidation. This temperature dependency is a relatively well-known phenomenon with passive systems, with sulfate-reduction rates improving in spring and some months. This aspect of the pilot scheme has been very useful in guiding potential management changes, which may need to be included in winter months to maintain the same reduction in sulfate.

Notwithstanding, the performance of the BCRs decreased over the winter months, and this was investigated. The monitoring showed some interesting changes in redox and TOC in the leachate entering the treatment system. It was postulated that the influent leachate TOC "food" that is digestible will sustain the BCR performance; however, when this food is reduced quickly in the influent leachate, the whole biosystem in the BCRs is essentially put into starvation mode, with knock-on lower sulfate-reduction rates. This provided very useful information, as it might suggest soluble organic matter amendment (as used in the bench-scale testing) may be required during the winter months if the sulfate treatment is shown to fall below established permit conditions.

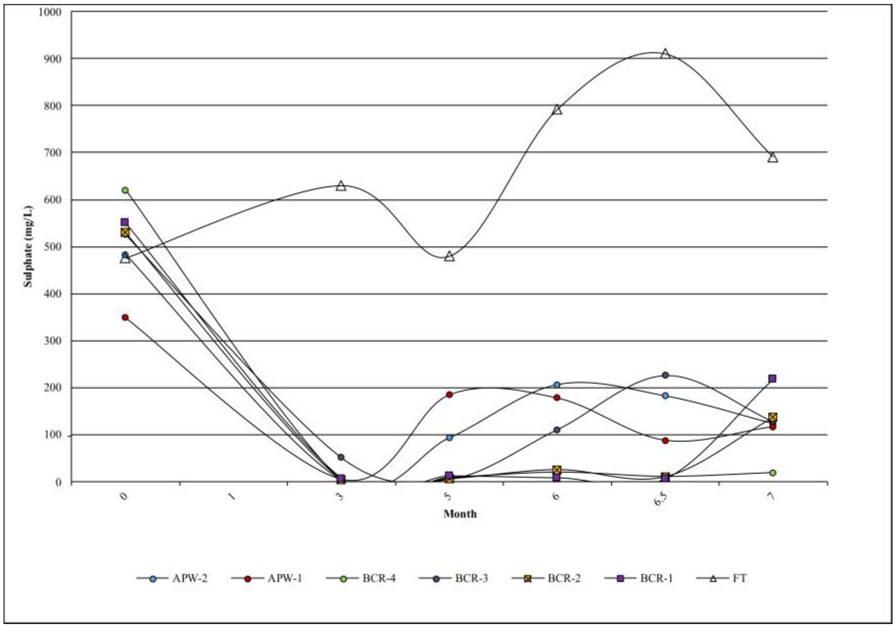

Figure 7: Example of sulfate treatment from the pilot plant operation

The pilot system operated until Jan 2022, and planning permission for the full-sale system was received in late 2021. The design layout of the full-scale system is shown below.

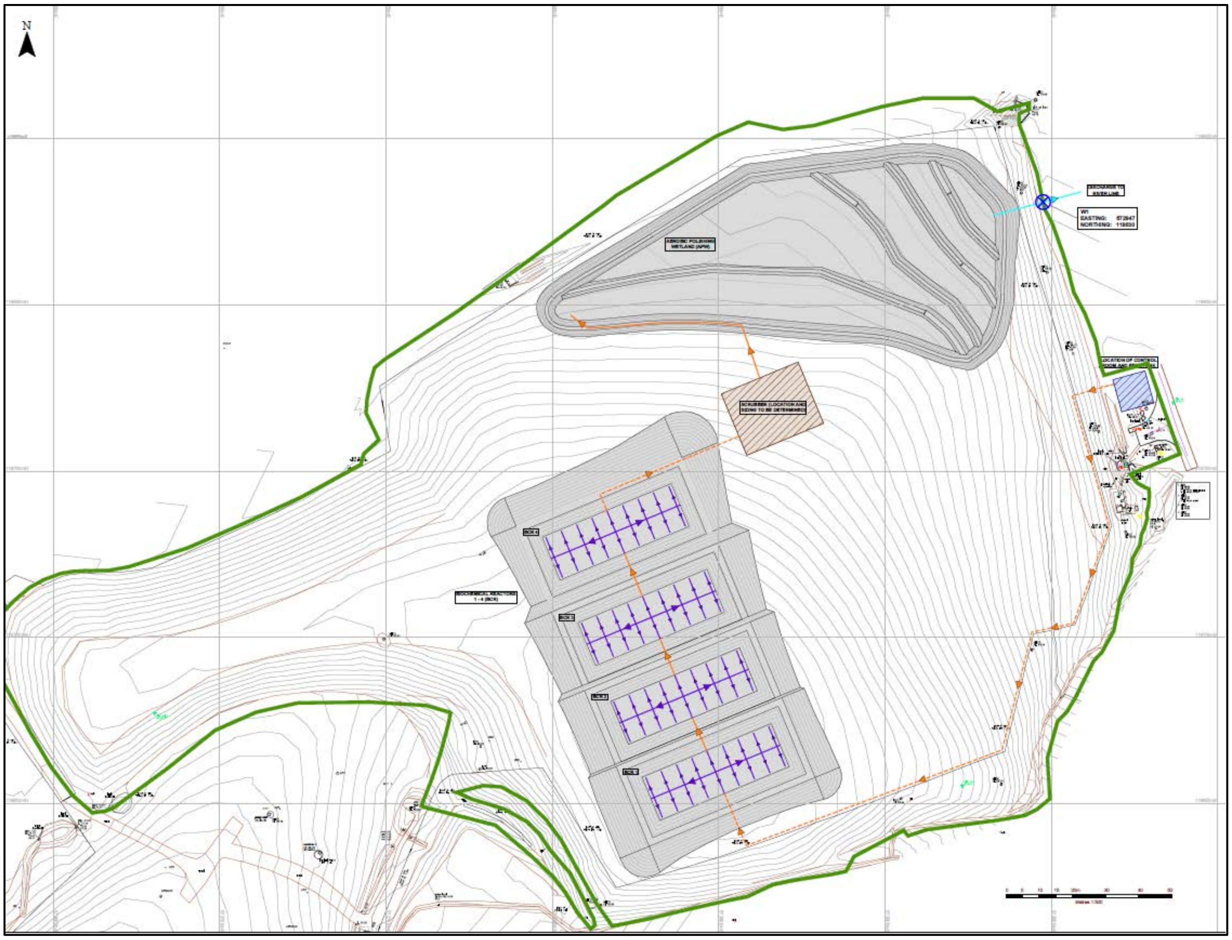

Figure 8: Proposed layout of full-scale system

It was decided to construct the system atop an old landfill at the site. Therefore, additional geotechnical assessments were made regarding the stability of the ground and the potential impact on leachate generation from the additional loading. Given this was an innovative system, the Environment Agency (UK regulatory) required additional information regarding the design and longevity of such systems. Construction of the system is planned for the summer, and the result of the initial work will be presented at the conference.

Acknowledgements

The authors would like to thank Saint-Gobain for giving permission to prepare this paper and embracing an innovative technology for sulfate treatment. We thank Jim and Lee at Linkan Engineering for their continued support on the project, along with the dedicated project team from Saint-Gobain and SLR.

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The State of “Zero Liquid Discharge”

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Abstract

As environmental and sustainability concerns continue to drive corporate decision-making, and effluent discharge criteria continue to become stricter, water management on mining sites has become increasingly crucial to the bottom line. To meet newer, stricter effluent standards, many companies have investigated “zero liquid discharge”, or ZLD, as a way of meeting those criteria and creating a reusable water source for other mining needs. But what is ZLD and is it really necessary?

The concept of ZLD is a misnomer. Every ZLD technology has a waste stream, and each waste stream contains some amount of “liquid discharge”, and the capital cost and operating cost of the technology depends directly on how close to zero liquid is contained in the waste stream. And these costs can be staggering. So, it is crucial that owners understand when a ZLD-type technology is required, and more importantly, when it is overkill. This paper will investigate this question and give an in-depth example showing how innovative process design can avoid a ZLD project in favour of targeted contaminant removal.

When ZLD is determined to be necessary, there are several different available technologies, with new technologies emerging every year. These technologies can come in many forms, from passive evaporation, thermal treatment, membranes, solidification, to other innovative technologies. This paper will review these different types of ZLD technologies and discuss the advantages and disadvantages of each. It will also include a case study of a thermal ZLD application with Class 3 estimates of three different variations on the level of ZLD. Finally, it is also important to understand the residuals management and handling considerations from different ZLD processes. This paper will review different residuals management considerations such as incineration, landfills, hauling logistics, and hazardous constituents.

Introduction

Zero liquid discharge (ZLD) was originally developed for the power industry to minimize the impact of increased salinity in the Colorado River and other arid environment water bodies. Recently, ZLD equipment represents a capital investment of $100 to 200 million annually (Weimer, 2015) and growing. The drivers for ZLD systems include strict environmental regulations, high costs associated with wastewater disposal, freshwater scarcity, and a public demand for "sustainable" water use. All of these drivers are continuing to be more pronounced each year; hence the increased focus on ZLD. Many industrial users benefit from the implementation of ZLD by receiving drastically shorter permit review periods, availability of high quality reuse water and a reduction in fresh water demand to the facility.

While ZLD systems can offer benefits, the drawbacks are often prohibitive. ZLD systems include many different unit processes, which make them complicated and difficult to operate. Many are highly energy-intensive, and if a waste heat stream is not readily available, they can be cost-prohibitive to operate. As the dissolved solids in the water are concentrated through the ZLD process, both corrosivity and scaling potential become important to consider in material selection of the unit processes. The metal alloys necessary to handle the corrosive nature of concentrated salts make the capital cost of the equipment prohibitive. For this multitude of reasons, high capital costs and operating costs of ZLD systems often make them impractical.

An additional consideration that is often overlooked with ZLD, is the waste stream. Every "zero liquid discharge" solution has a waste stream, and most of them contain some amount of liquid in the waste. Often the waste from a ZLD is an extremely concentrated brine (~60% solids) or even crystallized salt (85–95% solids), that when placed in a landfill immediately re-solubilizes to form a concentrated brine leachate that is very difficult to handle. The transportation of brine requires either corrosion-resistant pumps or contained tanker trucks, and in the transportation of crystalized salts it is difficult to avoid any moisture, which can re-solubilize the salt. Some waste materials may contain radioactive contaminants that require the entire waste stream to be disposed of as a hazardous waste. When evaluating ZLD options, it is critical to consider the environmental impact and disposal costs associated with that method of ZLD.

The challenges associated with ZLD have driven considerable research into more efficient, less expensive ZLD alternatives, several of which will be discussed in this review. However, the least costly alternative is always to avoid ZLD if possible. This paper will review ways of avoiding ZLD if possible; and if not possible, evaluate several different ZLD alternatives, comparing the advantages and disadvantages of each alternative.

Avoiding ZLD – selective contaminant removal

In many instances, ZLD is investigated because discharge regulations are strict for a particular contaminant that may be difficult to treat using conventional treatment approaches. In these cases, many industries see ZLD as the only option to manage their wastewater stream. However, if a novel treatment approach is developed specifically for the removal of that contaminant, ZLD can be avoided altogether.

One typical example of such a contaminant is sulfate. Sulfate is difficult to remove from water because the solubility of sulfate is between 1,500 and 2,000 mg/L, while regulations (when applicable) tend to limit sulfate to 250 to 500 mg/L. High-pressure membranes such as nanofiltration (NF) or reverse osmosis (RO) membranes are often evaluated for this situation, but because of the high potential for irreversible scaling from calcium sulfate in the concentrate stream, the membrane recovery cannot be run high enough to meet stringent discharge limits and membranes are not selected as the final solution. Figure 1 demonstrates the difficulty of using NF membranes to meet a discharge limit of 250 mg/L sulfate.

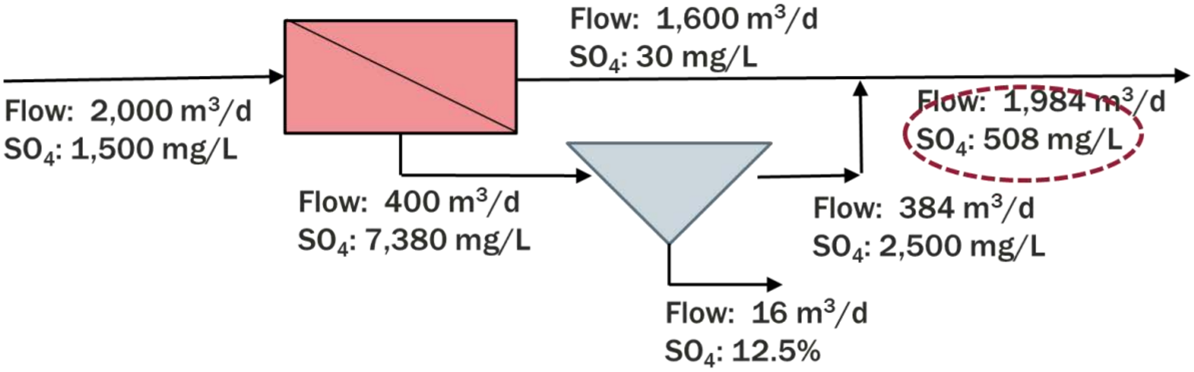


Figure 1: Example of NF membranes unable to achieve a sulfate limit of 250 mg/L

Figure 1 shows that even with a two-pass NF system, the treatment requirement of 250 mg/L cannot be achieved with a simple membrane design. This may lead one to think that ZLD is the best approach. However, if a treatment system is specifically designed to maximize sulfate removal, it is possible to achieve the treatment target with just a slight modification to the overall treatment system (see Figure 2).

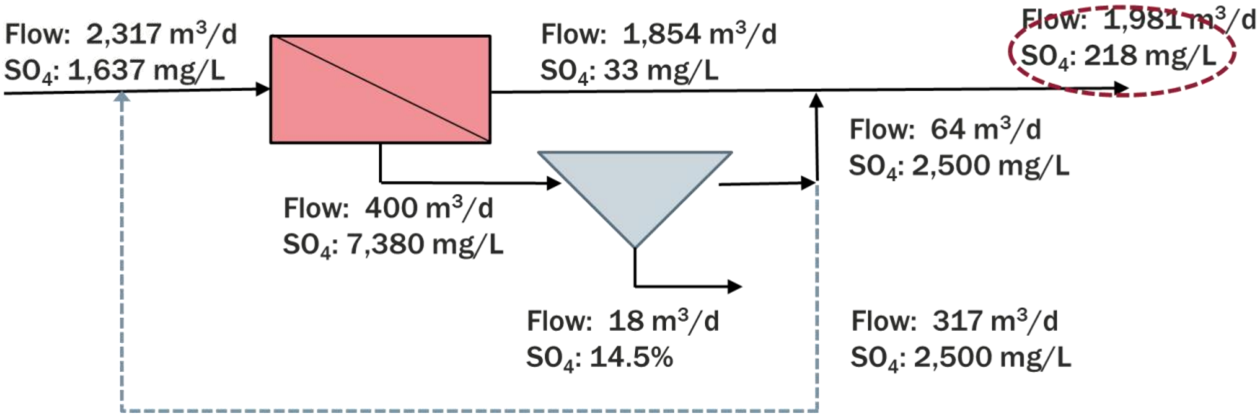


Figure 2: Membrane system enhancement to meet sulfate limit of 250 mg/L

Avoiding ZLD – other potential methods

In certain scenarios water treatment using membranes or other advanced treatment systems may produce effluent water quality capable of meeting water reuse or discharge requirements, but leave a concentrated waste stream that cannot be discharged or landfilled. In these cases there are a number of potential methods of disposing of concentrated waste that do not require a ZLD solution. The following lists some of those potential disposal methods:

- **Open mining pits or underground mine workings** – this option depends on many different aspects of the mine site, including the type of geology, location of groundwater table, mining plan, and other site-specific environmental concerns.
- **Deep well injection** – obtaining Underground Injection Control (UIC) Class I waste disposal well permits can be challenging in many locations due to concerns of enhanced earthquake activity, environmental concerns, and/or a lack of viable locations for these wells. If a business can obtain an injection well permit, this option often has reasonable capital and operating costs and can be an attractive disposal option.
- **Land application** – many mining sites have the ability to use waste water for dust control on roads. Some locations may also be able to use excess water for irrigation, or dispose of it through infiltration basins.
- **Ice dams** – in some cold-weather climates concentrated brine can be sprayed in layers that freeze during the winter. When ice melts, the water flows away leaving the solids and other contaminants in place (LUT, 2015). This method obviously requires a particular climate and is an emerging technology; however, it is an energy-efficient, low capital cost possibility.

Methods of zero liquid discharge

When ZLD is unavoidable, it is critical to thoroughly review all of the potential options to find the best alternative for each particular application. There are dozens of potential ZLD options, and this review paper will examine the following ZLD themes:

- passive evaporation;
- thermal evaporation;
- membranes; and
- solidification.

Each of these four ZLD themes will be discussed in more detail in the following sections.

Passive evaporation

Passive evaporation uses shallow, lined ponds to utilize areas of low humidity to evaporate water. These systems are typically installed in the southwest of the USA, where the climate is very dry and land area is plentiful. Design criteria for such a treatment system is for a climate with less than 0.3 meters (12 inches) of rainfall per year and where the evaporation rate is 1.0 meters (40 inches) per year or higher. The land area required is directly related to both the annual rainfall and the evaporation rate.

Evaporation ponds can be either lined or unlined. Depending on the contaminants present in the water or proximity to groundwater tables, regulations may require the ponds to be lined to prevent solids migration into the groundwater. In some instances, the cost of lining the pond is offset with an increased evaporation rate from solar radiation bouncing off the liner. Another method to increase the evaporation rate is to add dark-colored dyes to the water to absorb more solar radiation. It is also possible to increase the evaporation rate by installing a forced evaporation system that pumps water through spray nozzles, which create aerosol droplets with a high amount of surface area. This increased surface area allows much faster evaporation with a relatively low energy demand.

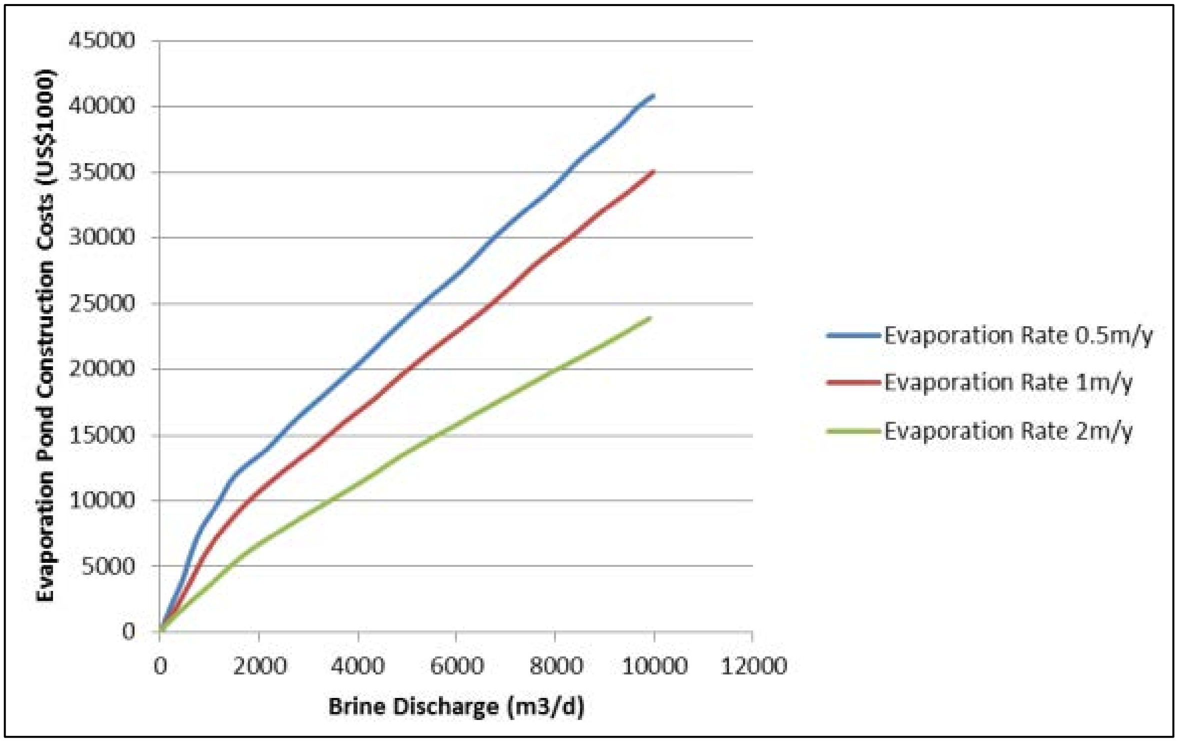


Figure 3: Construction cost of evaporation ponds (Lenntech, 2022)

One clear advantage of using evaporation ponds for ZLD is that the resulting solids do not require any direct solids handling as the solids remain in the evaporation pond. The final state of the solids is typically a salt slurry, because as the water evaporates and the solids continue to concentrate in the remaining liquid, the evaporation rate decreases due to the increased salinity. Final closure of the evaporation pond would include significant earthworks to cap the pond.

Table 1 contains a summary of the advantages and disadvantages of passive evaporation.

Table 1: Advantages and disadvantages of passive evaporation

Advantages	Disadvantages
Low OpEx (operating expenses)	Geographically/climate constrained
Relatively low CapEx (capital expenses) when compared to other ZLD alternatives	Large land area required
Low residuals handling, transportation, and disposal	Creates legacy residuals remaining in the lined ponds
Nearly zero greenhouse gas footprint	Highly visible
	Not applicable for reuse as the water cannot be recovered

Thermal evaporation

Thermal evaporation is the most commonly used form of ZLD because it is applicable in any climate or geography, it creates a nearly pure water for reuse, and it has a relatively small footprint compared to other ZLD technologies. Thermal evaporation typically has three main unit processes to achieve a true zero liquid discharge.

- falling film evaporator or brine concentrator;
- brine crystallizer; and
- solids centrifuge.

For a thermal ZLD system, incoming wastewater is pumped through a heat exchanger that uses pure water distillate to preheat the wastewater before entering the evaporator. The falling film evaporator is the most energy efficient evaporator available and is shown in the schematic in Figure 4. The system operates by pumping the brine solution to the top of a tall tower. The brine then falls through the inside of heat exchange tubes with compressed water vapour on the outside of the tubes. As the liquid falls down the tubes, a portion of the liquid evaporates with the remaining concentrated liquid falling back into the evaporator sump to be pump back to the top again.

The evaporated water from the tubes is sent to a mechanical vapor compressor, which slightly compresses the water vapour and pumps it to the shell side of the falling film evaporator tubes. A brine concentrator operates at up to 60% solids in the brine, which offers a significant volume reduction at a relatively low energy input. Falling film evaporators utilizing mechanical vapour compressors operate between 20–39 kWh_e/m^3 of distillate (Mickley, 2008).

For some projects, users simply implement the evaporator portion of the ZLD system and send the concentrated brine to smaller evaporation ponds.

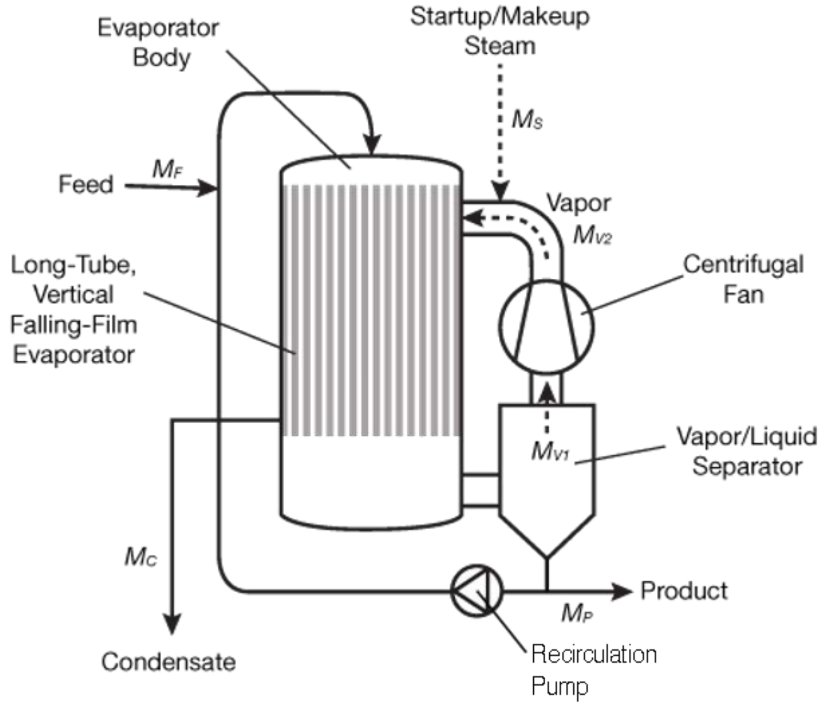


Figure 4: Falling film evaporator using mechanical vapour recompression

For projects that require complete ZLD, the concentrated brine would be pumped to a brine crystallizer, which heats the brine solution to near its boiling point as it is pumped into the crystallizer tank where the liquid flashes. The distillate from the flashing is collected, used in the heat exchanger to heat the incoming concentrated brine, and is collected and reused. As the liquid flashes, salts crystallize out of solution and are collected in the bottom of the crystallizer. The solids are then dewatered through a centrifuge and recovered in a 95–98% solid product. Crystallizers require significantly more energy than evaporators, requiring 52 to 66 kWh_e/m^3 of distillate (Mickley, 2008).

The brine in the crystallizer is around 80–90% salt solids, and this highly concentrated salt solution is extremely corrosive. Crystallizers must be constructed out of highly corrosion-resistant materials such as titanium, which significantly increases the capital cost of the vessels when compared to even 316 stainless steel. Similarly to the crystallizer, the centrifuge, the pumps and all piping must also be constructed of corrosion-resistant and heat-resistant material. The materials of construction make these unit processes extremely expensive capital costs, and also extremely expensive for on-going maintenance and spare parts as everything is custom-fabricated.

Table 2 contains a summary of the advantages and disadvantages of thermal evaporation.

Table 2: Advantages and disadvantages of thermal evaporation

Advantages	Disadvantages
True ZLD application if crystallizer is implemented as part of the thermal ZLD	High CapEx and OpEx
Small footprint	Complicated operation
“Dry” solids can be transported	Materials of construction incompatibilities
Pure water for reuse	Residuals management, disposal of large mass of solids
	High greenhouse gas footprint

Membranes for ZLD

Improvements in membrane technology have allowed membrane systems to approach ZLD. These “minimal liquid discharge” (MLD) systems are popular for minimizing liquid wastes because they operate with relatively low energy requirements and have a small system footprint. There are several types of MLD membrane configurations that utilize enhanced RO membrane system designs, including:

- **2 and 3 stage RO**: several RO stages can obtain water recovery up to 90%. Typically these systems require aggressive pretreatment to remove scaling potential in the membranes and significant chemical antiscalant and cleaning treatments.
- **Ultra-high-pressure RO**: utilizing pressures between 80 and 125 bar (1,200 to 1,800 psi) can concentrate solids up to the osmotic pressure of the salts, in the neighbourhood of 130,000 mg/L total dissolved solids in the concentrate.
- **Closed-circuit RO**: this type of RO system design utilizes a concentrate line recirculation in a semi-batch process to maximize water recovery, which can obtain 90–95% water recovery in many instances. Figure 5 shows a schematic of a closed-circuit RO, courtesy of Dupont’s (n.d.) website (DesaliTec).

Another type of membrane that can be used to concentrate contaminants and create a clean reusable permeate is forward osmosis (FO). FO is an emerging technology that has been under development for decades. The process uses a “draw solution”, usually an amine/carbon dioxide-based liquid to draw pure water from a brine, using the osmotic pressure of the brine solution to push the clean water through the FO membrane into the draw solution (see Figure 6). The pure water is then recovered from the draw solution by vaporizing the NH_3/CO_2 draw solution (and subsequently recovering that solution) and leaving pure water for potential reuse.

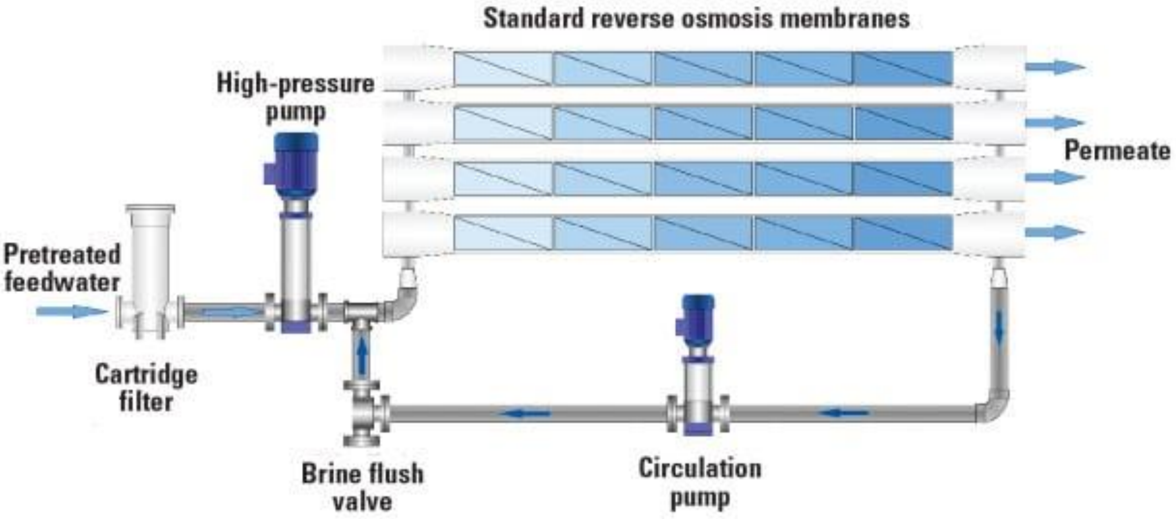
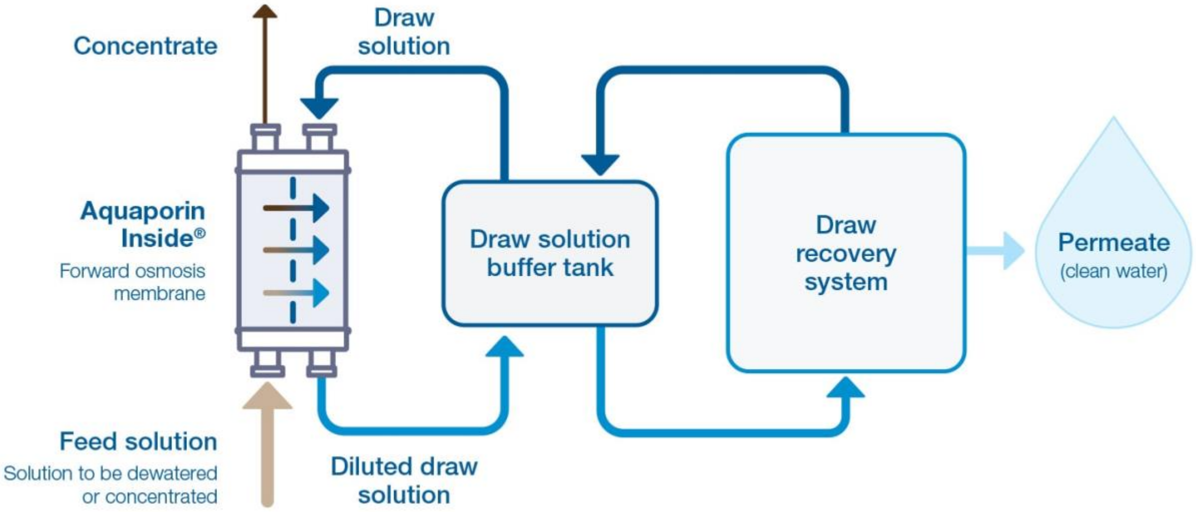


Figure 5: Closed-circuit RO



schematic

Figure 6: Forward osmosis schematic, courtesy of Aquaporin

Forward osmosis has been shown to achieve a concentrate stream that is 200,000 to 230,000 mg/L total dissolved solids (TDS), while modelling showed it would be capable of doing so utilizing only 21 kWh/m^3 of produced water (McGinnis et al., 2012).

Table 3 summarizes the advantages and disadvantages of FO when applied to MLD.

Table 3: Advantages and disadvantages of forward osmosis

Advantages	Disadvantages
Operates at low pressure	Like other membrane alternatives, not a true ZLD solution; still has a brine waste stream to manage
Small footprint	High CapEx
Capable of concentrating past osmotic pressure which can be upward of 230,000 mg/L TDS	Emerging membrane technology
Lower fouling propensity than conventional RO	Few full-scale applications
Relatively low greenhouse gas contribution	

Solidification

Solidification is a ZLD alternative where a brine solution, perhaps from an RO membrane system, is mixed with an absorptive additive such as fly ash to create a thick slurry that can harden, encapsulating the contaminants into a solid state. In order to get the slurry to harden properly, it is ideal to have a 1:1 ratio of brine to fly ash on a weight basis. This approach to ZLD has been recently adopted at power plants around North America to deal with coal combustion residuals, and has been shown as an effective way of closing waste ponds. It is particularly attractive at power plants because there is a readily available source of fly ash. A few mining sites have been able to mix concentrated brine solutions in with the tailings waste, especially as mines move toward paste and filtered tailings.

Solidification of residuals is an attractive option if the cementation source is readily availabl, because the contaminates are immobilized in the solid matrix and do not leach back out of solution. Therefore, solidification is a permanent disposal solution for hazardous contaminants. However, if a source of fly ash and/or cement is not readily available, the option would be cost-prohibitive.

Table 4: Advantages and disadvantages of solidification

Advantages	Disadvantages
Dual disposal method for power plants with coal combustion residuals	Requires vast land resources
Permanent residuals management	Requires fly ash amendment
Low CapEx	Difficult to maintain concrete in slurry piping
No significant greenhouse gas contribution	

Conclusion

Zero liquid discharge is somewhat of a misnomer as all technologies have a waste stream that have some amount of liquid entrained in that waste stream. The cost of ZLD systems is related to many factors including the location of the facility and the type of contaminants that need to be removed, and the moisture content of the waste stream. Typically, the lower the moisture content the more expensive the operating cost of the ZLD system. The lowest cost option is always to avoid ZLD if possible.

If ZLD is required there are several alternatives available that depend on the location of the facility, the discharge requirements, availability of thermal energy sources, availability of land, and other site-specific factors. Each system has its advantages and disadvantages, and there is no correct solution for every application. It is critical to thoroughly vet each ZLD for the particular factors at each application, and it is recommended to engage knowledgeable consultants to assist in the selection of the best ZLD solution.

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Quellaveco Mine Water Supply, a Stewardship Approach

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Abstract

In 2022 Anglo American will bring the Quellaveco mine online, culminating a four-year construction project and almost twenty-year journey from concept to development. Quellaveco is a world-class copper supply mine that will be an engine for the Peruvian economy for the next 30 years. The project is located in the valley of the Asana River, Moquegua River basin, in Southern Peru at an elevation of about 3,500 m. It has 7.6 million tons of reserves that will be mined as an open pit, initially at a rate of 127.5 ktpd. The region is mostly arid with a wet area developing above elevation 3,500 m.

In 2011 Quellaveco began an 18-month consultation in which Peruvian stakeholders from 31 local authorities and institutions, alongside representatives of the Moquegua community, gathered with Quellaveco representatives in dialogue tables. The aim was to define how Quellaveco could best contribute to the long-term sustainable development of Moquegua, and delegates succeeded in agreeing to 26 detailed and specific commitments related to water management, environmental care, and social investment. Among the agreements are limiting impacts downstream, and a water supply system that will serve the communities of Moquegua and Arequipa by addressing their needs, while meeting the demands of the project for process water.

The open pit and waste dump are located in the valley of the Asana River. Two dams and a 7.5 km diversion tunnel serve to convey the Asana River through the mine and limit impacts to downstream users.

The project requires a make-up water supply of up to 700 L/s. Approximately 80% will be provided from the Titire River, Tambo River basin, via a run-of-river intake, pump station, and a 95 km long, 24" to 28" diameter pipeline. The Titire River is a naturally contaminated stream with high metal concentrations, low pH, and high TDS. It lowers the water quality in the lower Tambo River, mainly during the dry season, with high metal concentrations such as boron and arsenic. This affects the raising of crops and cattle in a large irrigation and farm area in the lower Tambo basin, Arequipa Region. Removing bad quality water from the Titire River will diminish the negative impacts downstream.

The other component of the water supply system, which complements the Titire River intake, is a 41 m RCC dam on the Vizcachas River, Tambo River basin, with a multi-purpose, multi-year regulation reservoir capacity of 60 Mm^3. This source of good water quality will supply approximately 20% of the project make-up water, but it will also regulate and supply water for a delayed expansion of a large irrigation project in the Moquegua Region. In addition, the Vizcachas reservoir will provide extra flow during the dry season to improve water quality downstream. More importantly, it will release an equivalent amount of the water withdrawn from the Titire River during the dry season. This is essentially a swap of bad quality water from the Titire River for good quality water from the Vizcachas River during the dry season, benefiting the irrigation scheme in the lower Tambo basin.

Introduction

The mining industry must address critical challenges of safety, productivity, and the way land, energy and water are used in a changing social and climate environment. But it is about more than just the work the industry does and the footprint it leaves. Mining is part of the local people's lives, and they rightly expect the mining industry to make a positive contribution to socio-economic development in a sustainable way by reducing its environmental footprint and supporting biodiversity. In order to succeed, any mining activity requires the support and involvement of local communities and stakeholders.

Based on this context and understanding, Anglo American has developed a Sustainable Mining Plan that applies to all its operations and is built around three major areas or Global Sustainability Pillars:

1. **Healthy Environment.** Maintaining a healthy environment by creating water-less, carbon, neutral mines and delivering positive biodiversity outcomes covering three key areas: biodiversity, climate change, and water usage.
2. **Thriving Communities.** Building thriving communities with better health, education and levels of employment by working with local governments, community leaders, and NGOs to contribute to community needs: from housing and infrastructure to healthcare, education and recreation.
3. **Trusted Corporate Leaders.** Developing trust as a corporate leader, providing ethical value chains and improved accountability to the communities we work with.

These Pillars have a set of Global Stretch Goals associated with each of them, designed to challenge us to lead and innovate, and to deliver them between now and 2030.

Complementing the Global Sustainability Pillars, and at the heart of the Sustainable Mining Plan, is the Collaborative Regional Development, Anglo American model for providing long-term sustainable development opportunities to the regions around the operations. This approach starts by identifying socio-economic development opportunities with the greatest potential in a region via spatial planning and analysis. This creates the catalyst for partnerships with a broad range of stakeholders including community representatives, businesses and entrepreneurs, government, academics, and NGOs. Understanding the site context and listening to stakeholders is the way to stay ahead of evolving trends and provide the solutions to societal expectations around sustainable development.

The implementation of a Sustainable Mining Plan approach similar to the one described above has been key in the success of the Quellaveco Project development. The Project is in a water-stressed area and water is a competitive resource for local users.

Quellaveco in context

Peru is the world's second largest copper producer with 2.2 Mt or 11% of the world's production in 2020, behind Chile with 5.7 Mt or 29% of the world's production in 2020. By comparison, Canada is the 11th largest world copper producer with 0.6 Mt or 3% of the world's production in 2020. British Columbia is Canada's largest producer with 0.3 Mt or 54% of the country's production. Mining accounts for approximately 60% of Peruvian exports and 10% of the GDP, with the southern region of the country producing 60% of the country's copper.

Quellaveco is a porphyry copper and molybdenum deposit located at an elevation of about 3,500 m in the valley of the Asana River, Moquegua River basin, in Southern Peru (Figure 1), approximately 37 km northeast of the City of Moquegua, Moquegua Region. The project is owned 60% by Anglo American and 40% by Mitsubishi, with a total capital investment of nearly USD 5.3 B.

The Quellaveco mine ore reserves have been estimated at approximately 1.3 Bt, containing 7.6 Mt of copper (0.57%). This ranks as one of the largest undeveloped deposits in the world. It will be mined during the 30 years of operation as an open pit, initially at a rate of 127.5 ktpd via conventional crushing, grinding and flotation technology. The first production is planned for 2022, followed by a ramp-up during 2023. The average copper production rate is estimated at 0.3 Mtpa for the first 10 years, adding about 14% to the yearly Peruvian copper production based on 2020 figures. Therefore, the Quellaveco project will be a major contributor to Peru and in particular to the Moquegua Region (population of about 175,000 people), as during operations the project will employ a permanent workforce of approximately 2,500 people, mainly locals.

Figure 1: Quellaveco project location

The Quellaveco main process facilities include the pit and primary crusher, located in the Asana River valley together with the waste dump; the Papujune beneficiation plant, located in the Papujune Creek; and the Cortadera tailings storage facility, located in the Cortadera Creek, Locumba River basin, approximately 16 km from the Papujune plant. The concentrate will be transported by trucks to the port of Enersur in Ilo City, and will then be shipped by ocean to destination smelters (Figure 2).

Quellaveco will supply its make-up water requirements from two complementary sources, via a run-of-river intake in the Titire River and from the Vizcachas Dam in the Vizcachas River, both located in the Tambo River basin, and conveyed to the project area via a 95 km long pipeline (Figure 2).

Quellaveco is quite a spread-out project geographically, with facilities located in three main different river basins (Tambo River, Moquegua River and Locumba River) and, politically, in two different Regions of the country (Moquegua and Arequipa Regions). It is notable that the limits of the Regions do not coincide with the river basin areas, i.e., some of the river basins are shared by more than one Region (Figure 2), making the administration of the water resources more involved since the Regions are competing for the same water resources and are not necessarily in agreement on water management, as described below. This situation substantially increased the challenge and the dedicated efforts required during the negotiations with project stakeholders.

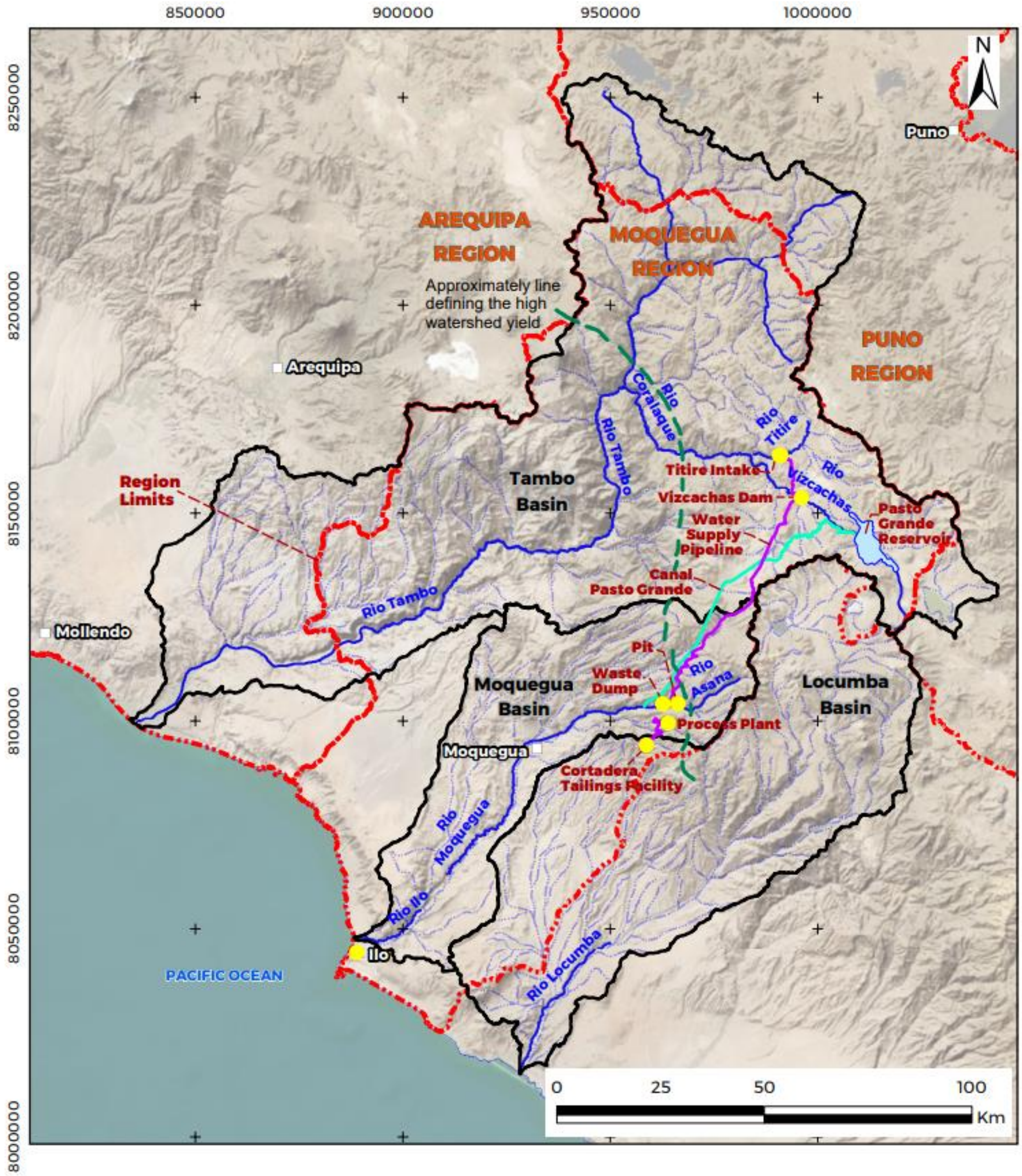


Figure 2: Quellaveco facilities location and regional setting

The region where the Quellaveco project is located is mostly arid with a wet area developing above an elevation of 3,500 m where annual precipitation is greater than 300 mm, and negligible below elevation 1,200 m, with an area of low precipitation in between.

The Tambo River is the most important watershed in the region. It has a watershed area of 13,022 km^2 with an average elevation of 3,300 m, reaching a maximum elevation of over 5,500 m. Based on gauged flows from 1991 to 2018 (Santa Rosa Station, located in the lower part of the river at 205 m elevation) the annual average flow is 28 m^3/s or 883 Mm^3, with a monthly average of about 97 m^3/s in February and decreasing to approximately 6 m^3/s in October. About 75% of the annual volume is concentrated between January and April, decreasing to about 9% during the dry season that occurs from September to December.

An important irrigation area of over 9,800 Ha has developed in the lower the Tambo basin. There are no important dams in the Tambo River watershed to help regulate the basin flows, except for the Pasto Grande Dam in the Vizcachas River, with a maximum capacity of 200 Mm^3 and in operation since 1989. However, this dam diverts the waters to the Moquegua River via the Pasto Grande canal (Figure 2), as it belongs to the Proyecto Especial Regional Pasto Grande (PERPG), an ambitious irrigation project still under development. This project is supported by the government with the goal of sequentially developing various irrigation areas in the arid Moquegua Region covering over 6,400 Ha.

The lower Tambo irrigation system experiences a water deficit during the dry season due to the sharp seasonality of the river and lack of infrastructure to help regulate the flows. The lower Tambo water users raised concerns that the PERPG project water diversion decreased both water availability and quality, the latter due to high metal concentrations, in particular boron and arsenic affecting crops and cattle raising. In response, the PERPG implemented a compensation by releasing water from the Pasto Grande reservoir. However, in turn, the Moquegua Region users claimed that this compensation is delaying the completion of the PERPG objectives, which is well behind its original schedule. The water deficit in the lower Tambo can be reduced or even eliminated with the construction of infrastructure to regulate the Tambo River basin. Several dam sites have been investigated under government sponsorship to regulate the Tambo River flows, for instance Paltiture and Huayrondo, but none have reached an advance staged of design.

Water stewardship philosophy

Social and permitting comments and process

Initial investigations identified the Chilota groundwater resources as a sustainable source to supply the 700 L/s required by the Quellaveco project. The groundwater aquifer is in the Chilota River basin near the confluence with the Vizcachas River. However, this groundwater option was strongly opposed by local communities, and in February 2004 the Regional government officially denied the use of groundwater by Quellaveco. Therefore, Anglo American had to look for an alternative water source to supply the project.

The replacement of the groundwater source led to an intense engineering investigation program to assess various surface water options and strategies within the frame of the Anglo American Sustainable Mining Plan and Stewardship program. In 2011 the Moquegua Regional government facilitated the establishment of dialogue tables with the primary objective of finding a way to resolve the social conflict generated by the project and to secure a water licence for its operation.

Three working groups were set up for the dialogue tables: a Water Resources Committee, an Environmental Committee, and a Social Responsibility Committee. All three groups were composed of representatives of public institutions, communities, and Anglo American. The groups met on a regular basis with support from technical experts, NGOs, and consulting firms who, as guests, supported and commented on the implementation of the studies.

The dialogue table was a lengthy process that took 18 months of consultation. Peruvian stakeholders from 31 local authorities and institutions, alongside representatives of the Moquegua community, gathered with Quellaveco representatives to define how Quellaveco could best contribute to the long-term sustainable development of Moquegua and at the same time benefit the Arequipa Region. The outcome of the negotiations was an agreement that included 26 detailed and specific commitments related to water management, environmental care, and social investment.

The dialogue table process was a success that allowed Anglo American to obtain approval and permits for the Quellaveco proposed water supply system. At the same time, Anglo American is perceived locally as a key player as a job provider and, also, as an important contributor to the regional planning of agriculture that is the main activity in the Region.

In 2014, the United Nations Development Program (UNDP) summarized the Quellaveco experience as follows: “The Moquegua discussion table has not only contributed to establishing social peace in the region; it has also promoted democratic governance based on dialogue, active listening, the continuous exercise of inclusion, consensus building and the definition of a common work agenda for sustainable development. Thanks to this experience, an objective has been achieved: sustainable investment in the environment focused on social responsibility, investment in basic infrastructure and social development.”

In summary, Anglo American has adopted an especially engaged approach to the Quellaveco water management since 2011, including the initial negotiation at the dialogue table, permitting, design process, and construction. Water management has guided most major aspects of the mine design, and continued participation by local representatives has established trust and engagement in the surrounding communities that has helped produce an innovative mine that respects and makes the best use of the most valuable resource in the region, water.

Quellaveco water solution and commitments

Following the denial of groundwater use as a source of make-up water supply for the Quellaveco project, and in light of the existing water management conflict in the Tambo River basin, the proposed water supply solution to the dialogue table was to use two complementary sources: Titire River via a run-of-river intake and the Vizcachas Dam in the Vizcachas River (Figure 3).

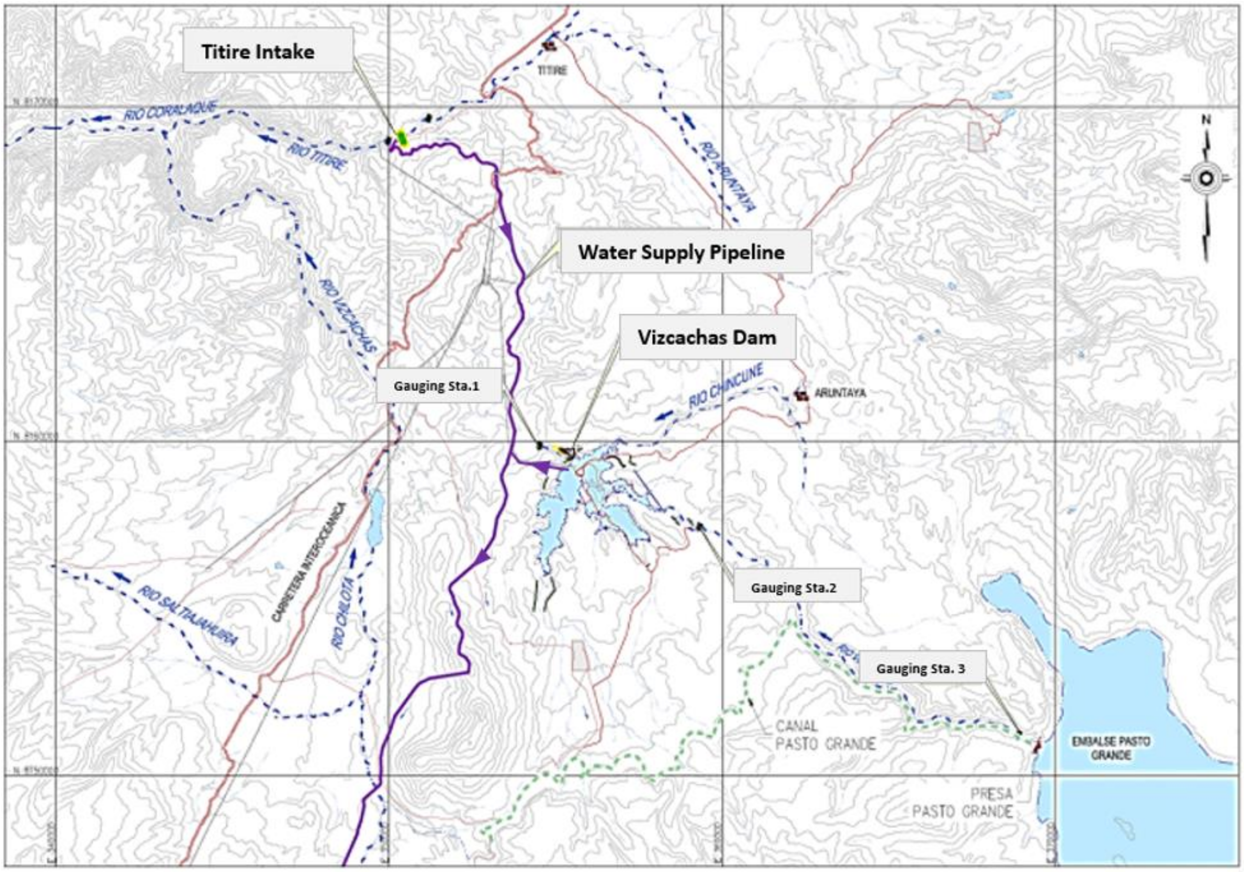


Figure 3: Quellaveco water supply arrangement

The strategy behind this arrangement is as follows:

1. The Titire River is a naturally contaminated stream due to geothermal activity with high metal concentrations, low pH, and high TDS, that lowers the water quality in the lower Tambo River, mainly during the dry season, with high metal concentrations such as boron and arsenic. This affects the raising of crops and cattle in the large irrigation and farm area in the lower Tambo basin, Arequipa Region. Removing bad quality water from the Titire River will diminish the negative impacts downstream.
2. The dam on the Vizcachas River was conceived as a multipurpose, multiyear regulation reservoir with a capacity of 60 Mm^3. This source of good water quality will:
    a. Supply the project make-up water, 4.8 Mm^3/yr.

b. Maintain an ecological flow, equivalent to 4.74 Mm^3/yr or 150 L/s.

c. Regulate and supply water for the delayed expansion of the PERPG irrigation project in the Moquegua Region, equivalent to 6.81 Mm^3/yr, or 650 L/s from September to December.

d. Provide extra flow during the dry season, on top of the ecological flow, to improve water quality in the lower Tambo, equivalent to 1.65 Mm^3, or 157 L/s from September to December.

e. Release an equivalent amount of the water withdrawn from the Titire River during the dry season, estimated at 3.84 Mm^3. This is essentially a swap of bad quality water from the Titire River for good quality water from the Vizcachas River during the dry season, benefiting the irrigation scheme in the lower Tambo basin.

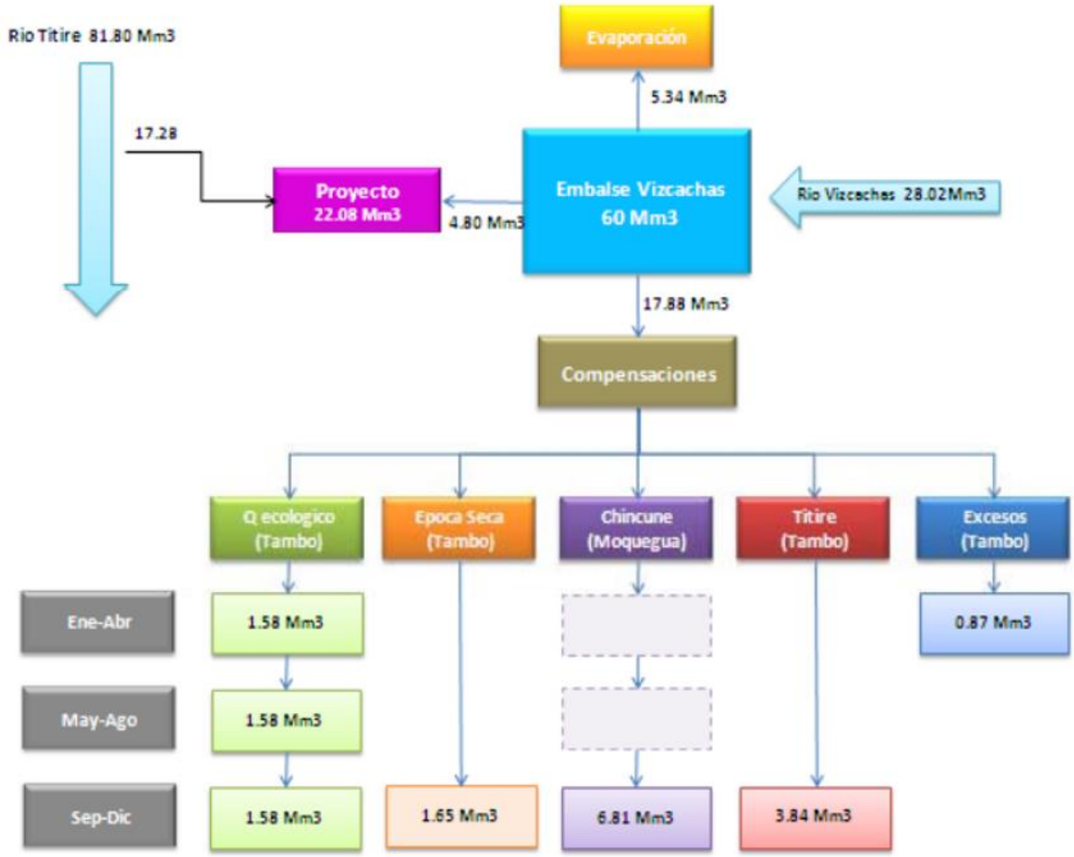


Figure 4: Quellaveco water balance

With this water supply arrangement, the project will supply approximately 80% of the make-up water using the contaminated waters from the Titire River and 20% from the Vizcachas River. A stochastic water balance model in the GoldSim platform was set up to simulate the Titire and Vizcachas Rivers and the project demand for the 30 years of the mine operation. The block diagram in Figure 4 is a summary of the water balance model.

The water supply arrangement satisfies three of the most important agreements regarding water management that involved the design and construction complex infrastructure:

1. **Asana River water protection**. The protection and conservation of the Asana River water in terms of quantity and quality is one of the most important commitments. This river provides critical agricultural and domestic water inputs to the Moquegua Region. The Quellaveco pit, waste dump, and primary crusher are located in the Asana Valley. Based on this commitment, Quellaveco designed and constructed a 7.8 km diversion tunnel that bypasses the Asana River through the mine, plus a dam located downstream of the disturbed area that is intended to control and divert all contact water generated by rainfall and runoff.
2. **Moquegua Region benefits.** The Vizcachas Dam will regulate the flow of the Vizcachas River, guaranteeing a volume of 6.81 Mm^3/yr from the rights PERPG has on the Chincune River, a tributary of the Vizcachas waters.
3. **Arequipa Region benefits.** The Arequipa Region will benefit from the interchange of fresh water from the Vizcachas Dam and contaminated water from Titire River plus the release of water during the dry season. It is notable that the water supply to the Quellaveco project has the lowest priority of all releases from the Vizcachas Dam.

Besides the agreements, Anglo American is continuing investigations to reduce water consumption. One example is the evaluation of a coarse particle recovery (CPR) plant, a breakthrough technology that has the potential to increase throughput and productivity, while reducing the production of traditional tailings and reducing overall water consumption. This initiative is in an advanced stage.

Quellaveco water system engineering

Asana River protection

The Quellaveco ore body is situated in the Asana River valley, where the pit will be developed. The waste dump and primary crusher are located downstream of the pit. The Asana River valley is the greatest area disturbed by the Quellaveco project (Figure 5).

Based on social input and permitting strategy, a basic premise for development of the mine was the long-term protection of the Asana river, which is one of the primary tributaries to the Moquegua River. The commitment of Quellaveco is to maintain the river flow, and also the natural quality of the river. This required the implementation of complex infrastructure with innovative concepts to move the project forward through permitting and operational phases.

The Asana River protection comprises the Asana River intake, diversion tunnel, and a control dam downstream of the mining area.

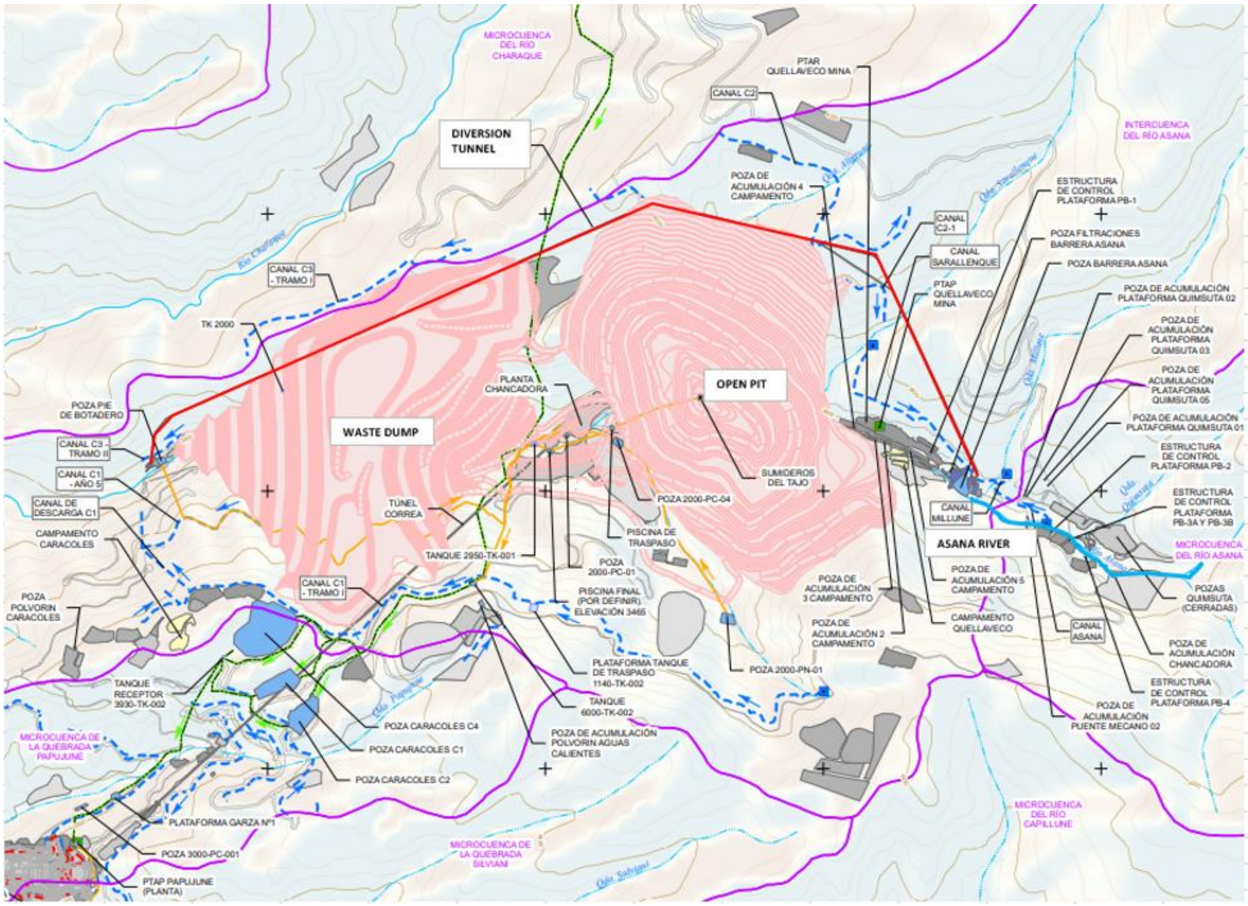


Figure 5: Pit, waste dump and primary crusher areas in the Asana River valley

The Asana intake and conveyance structures are designed to collect and channelize normal river flows during operation through the diversion tunnel structure. The intake consists of an ogee weir and sedimentation structure that is designed to manage flows up to the 1:100 return period event.

Normal and extraordinary flows captured by the Asana intake structures are transmitted through the channel workings to the diversion tunnel. The diversion consists of 7.8 km of drill and blast tunnel workings that receive ordinary and extraordinary flows from the Asana intake and Asana diversion, respectively (Figures 6 and 7).

The Asana diversion tunnel is constructed to operate during the entire mine operation and the period during which the river will be “relocated” to its permanent location during mine closure. The tunnel averages 5.2 m wide and is constructed with two concrete lined channels for low flow and high flow. It is designed to pass an event associated with a 1:1000-year return period.

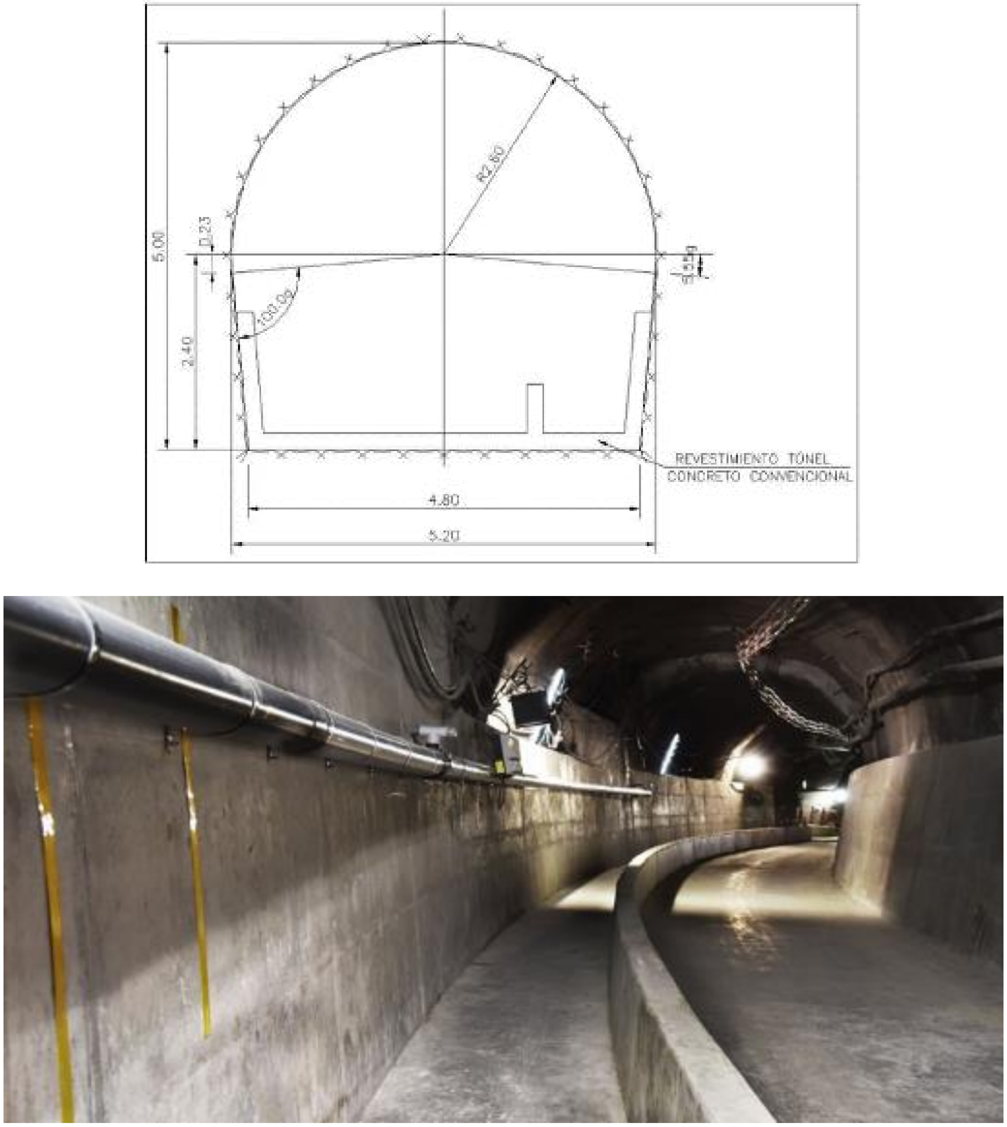


Figure 6: Asana diversion cross-section tunnel

Flows that bypass the Asana intake in extraordinary events, or results of channel/intake blockages, are captured in the impoundment of the Asana barrier (Figure 8). The barrier consists of a 45 m hardfill gravity dam with symmetrical upstream/downstream faces and a 214 m long crest that is 6 m wide. The barrier is sized to contain an extraordinary event with a return period of up to 1:1,000 years with a blocked diversion structure. Seepage is controlled by redundant systems, which include embedded waterstops and an upstream Carpi membrane at each expansion joint between the six monoliths. In the unlikely event that the maximum capacity of the impoundment is exceeded in one or subsequent events, the structure is protected by a reinforced concrete spillway capable of managing the flows associated with a 1:5,000 year event.

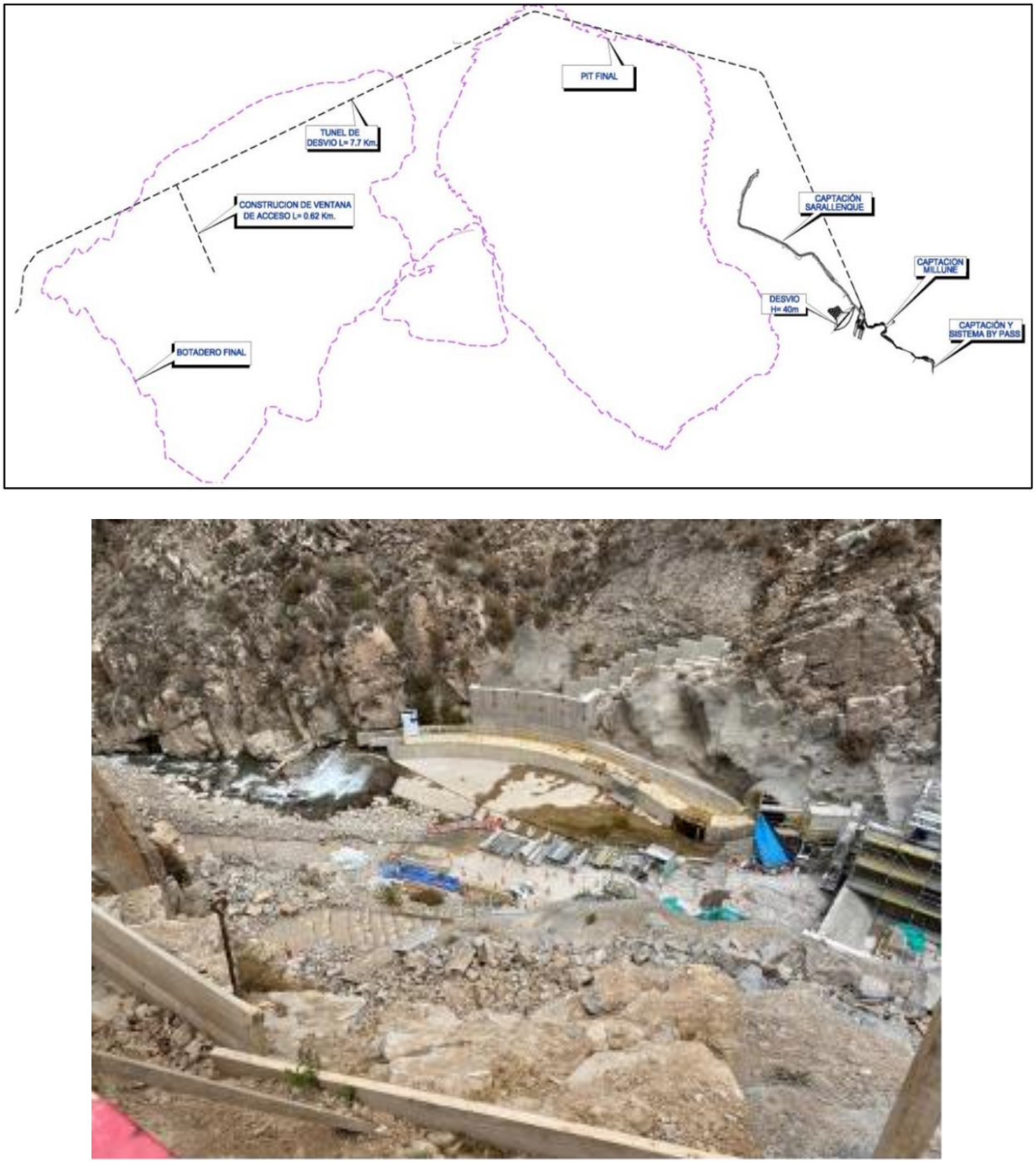
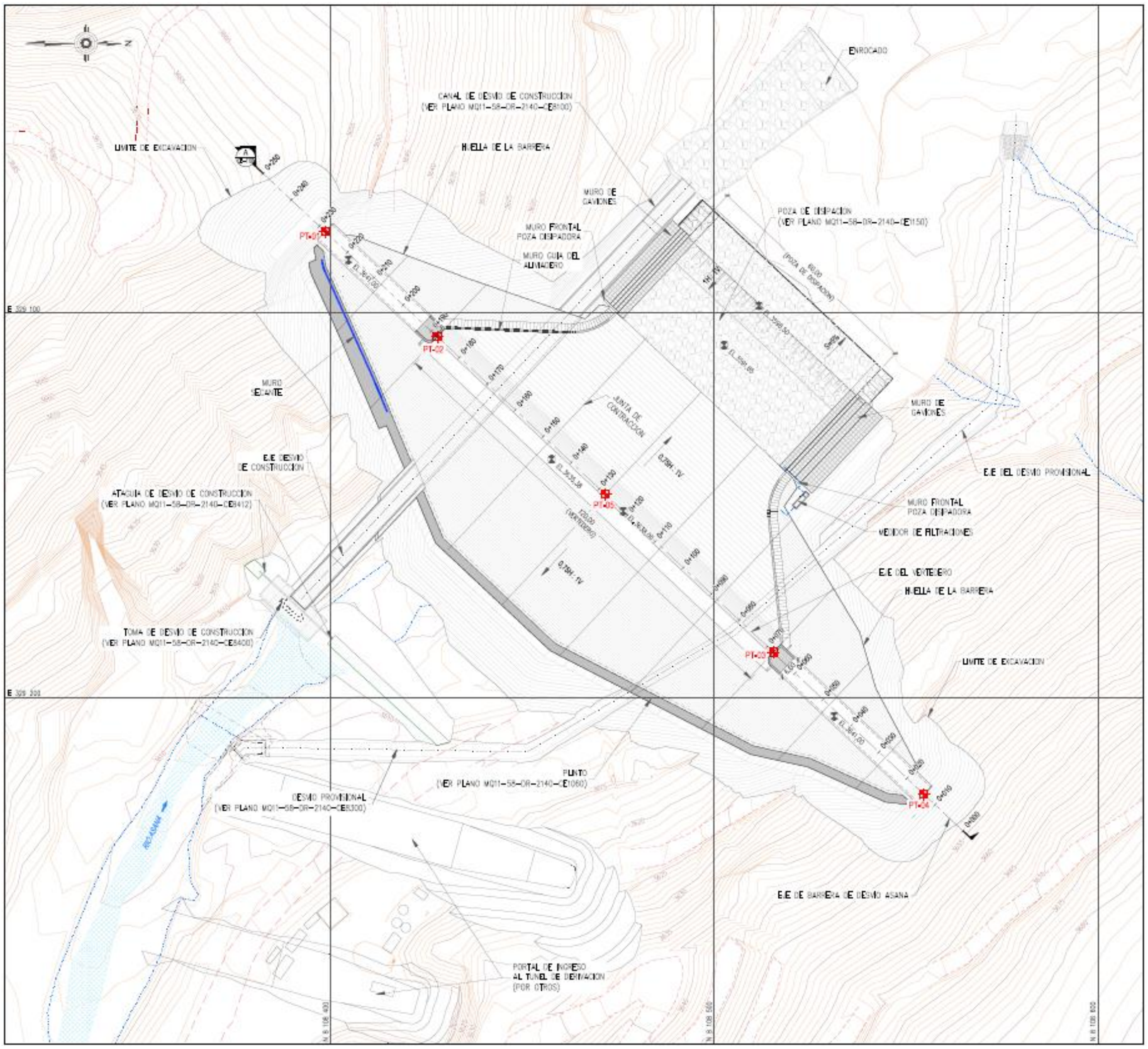


Figure 7: Asana diversion tunnel layout and exit

A control dam was constructed downstream of the Asana River disturbed area to contain contact water against potential downstream discharge. The control dam is a roller-compacted concrete (RCC) gravity dam with a maximum height of 34.5 m, a crest width of 6.6 m, and a length of 67.4 m. The upstream slope is

0.15H:1V and the downstream slope is a stepped spillway with a slope of 0.75H:1V. The spillway has a capacity of 160 m^3/s corresponding to a flow of 1:5,000 years (Figure 9).

The dam can contain a flood of 95,000 m^3 that corresponds to a return period of 100-years. It is worth noting that the first three years of operation are the more critical as floods are reduced as the waste dump advances. For instance, at year two of operations the 95,000 m^3 are equivalent to a return period of a 200-year flood.



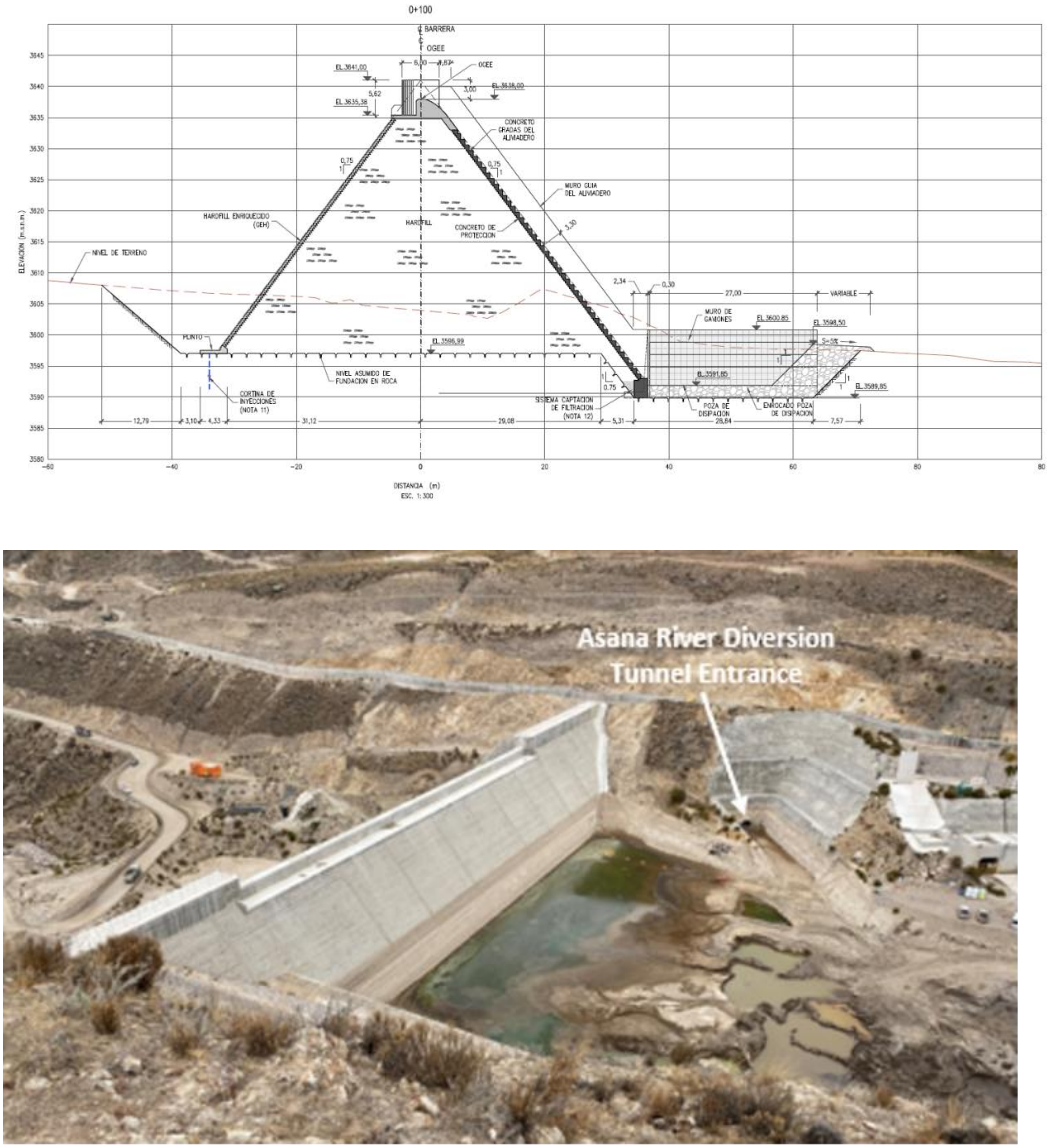
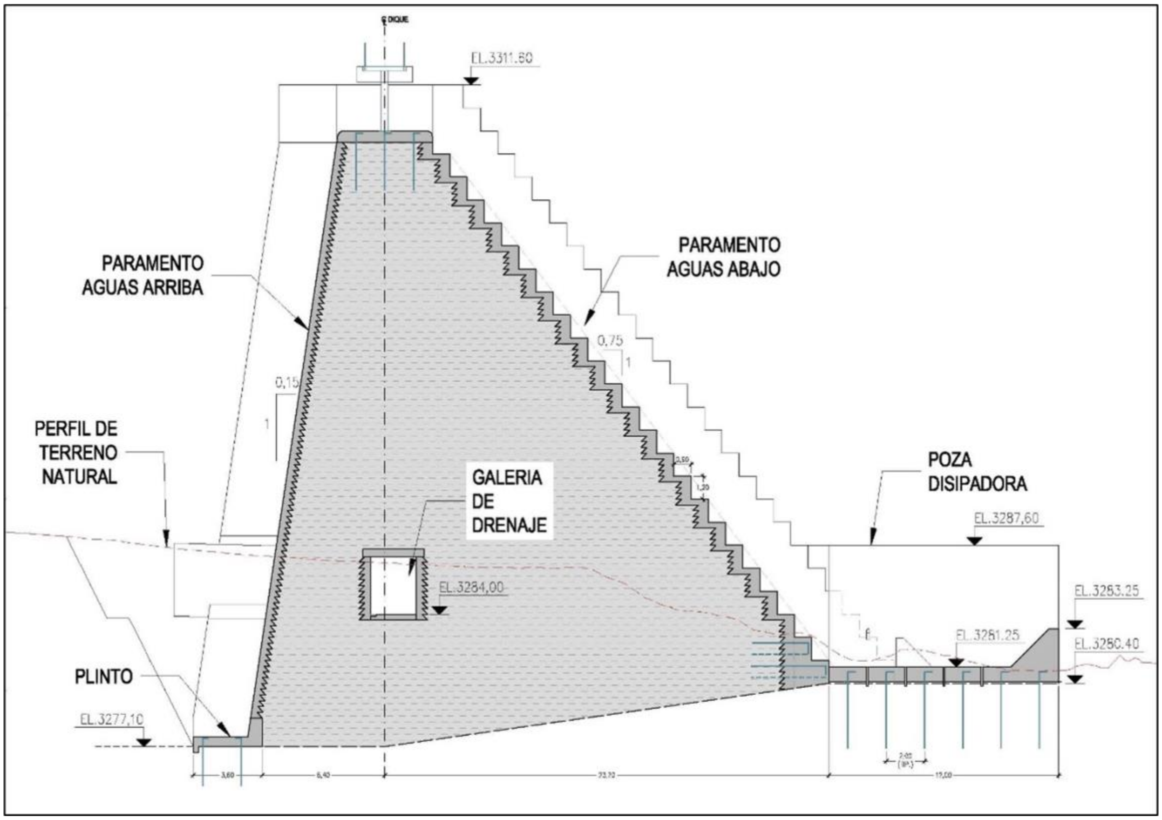


Figure 8: Asana barrier and tunnel intake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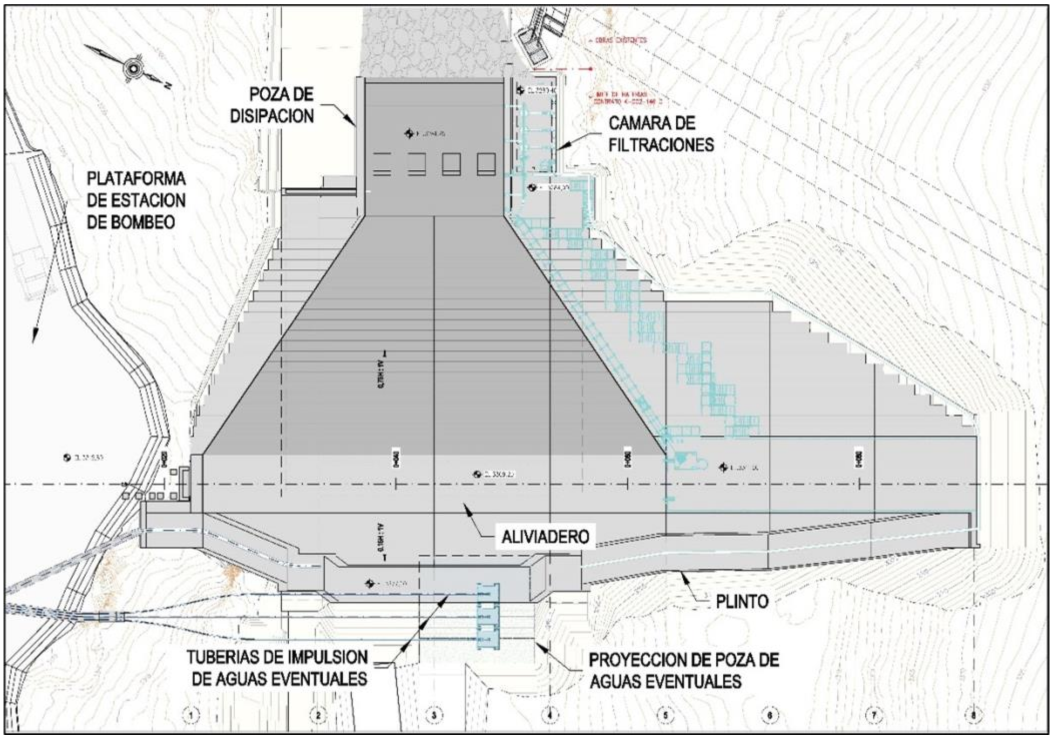
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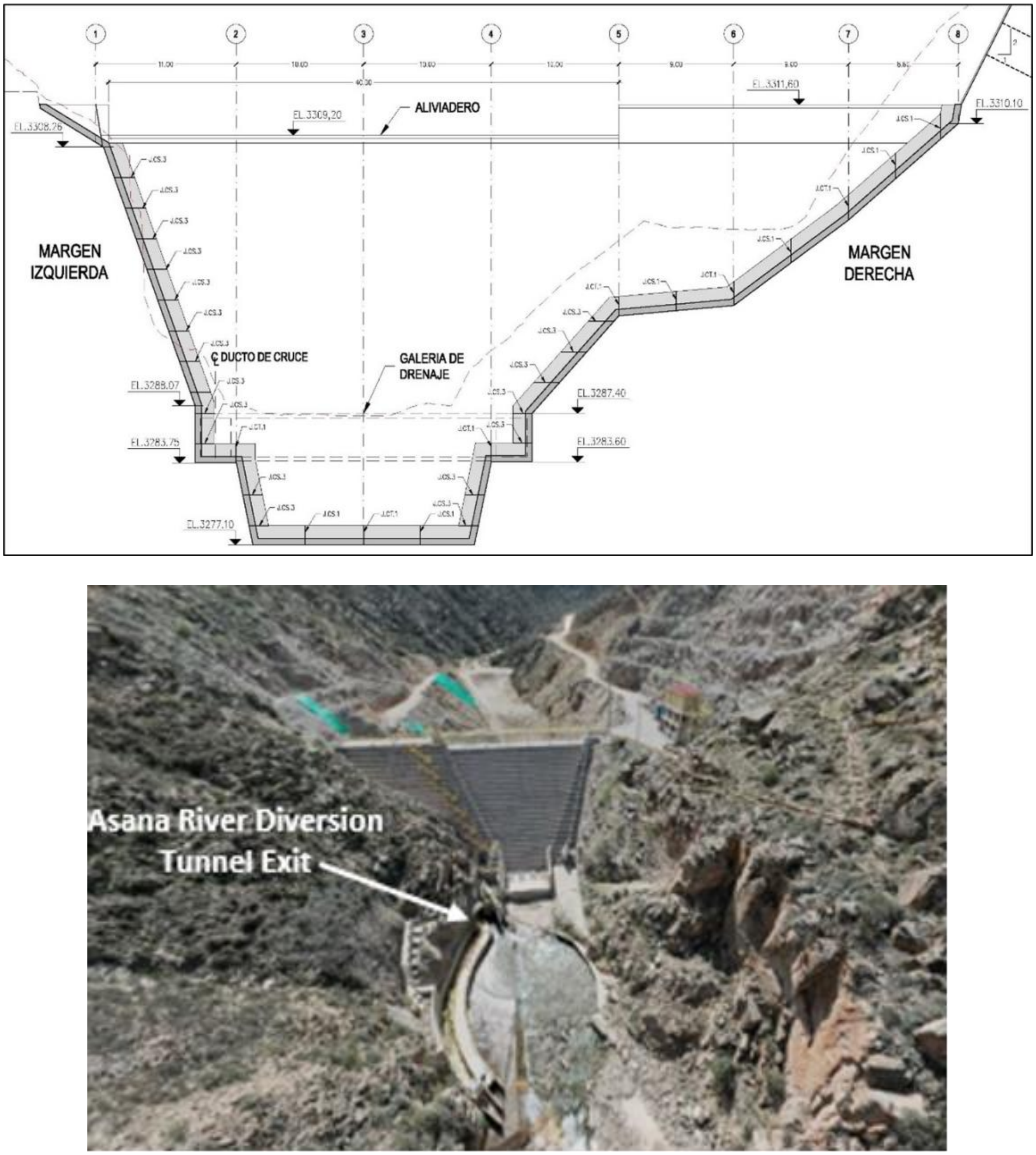

Figure 9: Asana River downstream control dam

Titire intake and water pipeline

The Titire River is naturally contaminated from geothermal activity in the region and shows especially high levels of boron and arsenic, along with other contaminates, which has an adverse effect on the water quality downstream. It has an average annual flow of about 2,600 L/s and will be the main water supply for the Quellaveco project via a run-of-river intake providing approximately 80% of the required demand.

The Titire intake is located in the Titire River about 7.8 km upstream of the confluence with the Vizcachas River at an elevation of 4,325 m (Figure 3).

The intake includes the intake structure, sedimentation structure, pumping system, and an overflow ogee weir (Figures 10 and 11).

The ogee weir consists of a fixed part and a mobile part. The mobile part has two radial gates for regulation of the water level at the entrance of the intake, which are fully open only during extreme events. The fixed part of the ogee weir has been designed for a flow of 362 L/s corresponding to a 100-year return period.

The intake structure has been designed for a maximum flow of 800 L/s, of which 100 L/s will be used in the sedimentation structure to get rid of sediment, and 700 L/s will be used to supply the project.

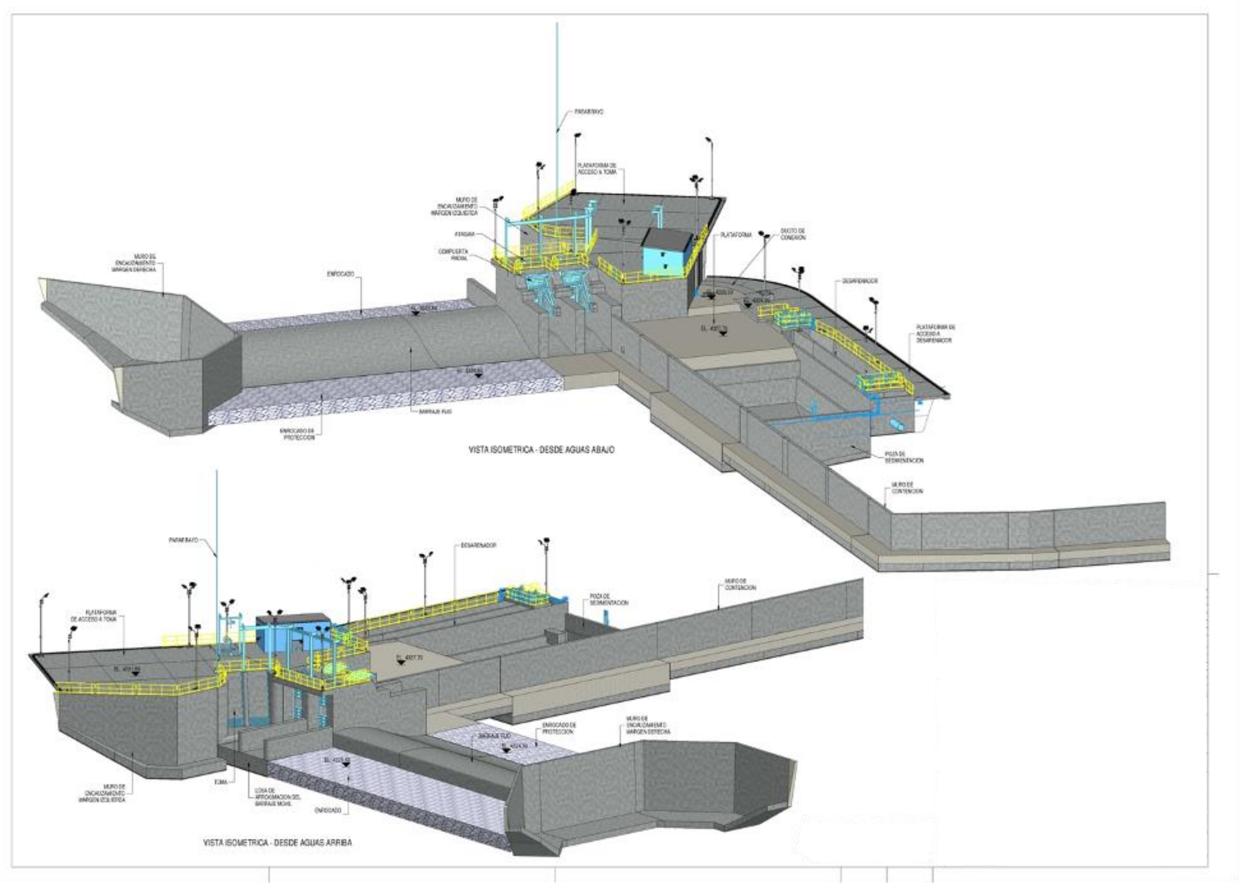

Figure 10: Titire intake 3D view

Figure 11: Titire intake

One gate regulates the intake flow to ensure that no more than 800 L/s is captured. The intake gate is automatically operated based on the signal of a radar flowmeter installed downstream of the gate. The flow passes through the sedimentation structure before reaching the pumping station (Figure 12).

The sedimentation structure has been designed to trap 80% of particles greater than 0.2 mm, avoiding any discharge of water with sediment downstream, in order to comply with environmental permits. The structure consists of two compartments, each with full capacity to convey 800 L/s, and can be used independently or together. In the latter case the efficiency to trap the 0.2 mm particles reaches 100% (Figure 12).

The inflow to the sediments compartments is controlled by flat gates. Flow with sediment will be regularly flushed out to a sediment collection pond by opening the flushing gate. Sediments will be cleaned up periodically with a submerged pump and transported by truck to the mine area at an estimated rate of 420 m^3/yr.

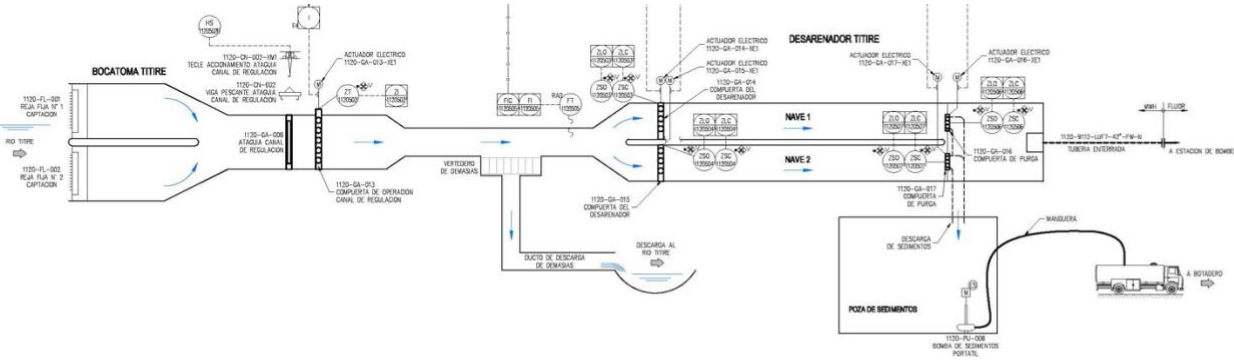

Figure 12: Titire intake schematic

The flow that passes the sedimentation structure is sent to a pumping station and conveyed to the mine area via a 95 km long, 24" to 28" diameter pipeline (Figures 2 and 3). If the Titire River cannot cope with the 700 L/s, then the Vizcachas reservoir will complement the flows, irrespective of the time of the year.

Vizcachas Dam

The Vizcachas Dam is located in the high mountain region at approximately 4,350 m elevation and approximately 65 km from the Quellaveco mine property. The dam receives the runoff from a 230.4 km^2 watershed that is drained by four rivers, Vizcachas, Chincune, Calasaya and Huilaque, yielding a total mean annual runoff of approximately 28 Mm^3 (Figure 13). The Vizcachas reservoir (Figure 14) has been designed as a multiyear facility with a capacity of 60 Mm^3, i.e. over double that of the mean annual runoff, thus requiring several wet years to be filled up. Volumes exceeding 28 Mm^3 are kept in the reservoir and released during dry years. At the same time, the reservoir is multipurpose as it will supply flow for several different needs at different times of the year, besides the project water demand.

The Vizcachas reservoir is a secondary water supply for the Quellaveco project, providing approximately 20% of the required demand.

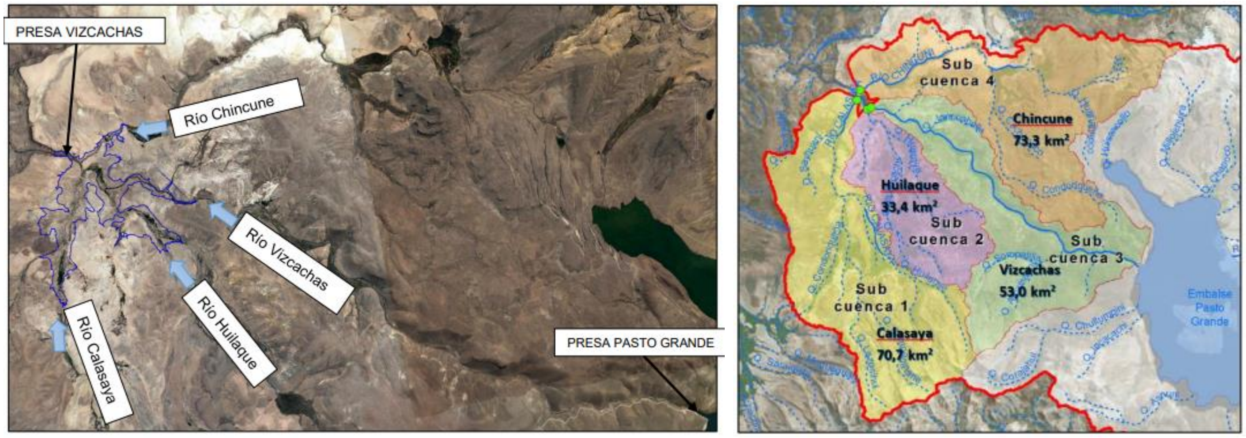

Figure 13: Vizcachas watershed

Figure 14: Vizcachas reservoir

The Vizcachas Dam is a roller-compacted concrete (RCC) gravity dam that stands approximately 50 m high at the critical section. The crest of the dam is 7 m wide and approximately 2 km long with a vertical upstream slope.

Seepage within the structure is controlled by a redundant system, which includes embedded waterstops at all expansion joints and a full faced upstream liner. In addition, water filtering into the structure is captured by two seepage collection galleries that capture and measure flows into the dam structure as part of an on-going monitoring program. The structure is protected by a reinforced stepped spillway with a slope of 0.8H:1V capable of managing flows associated with the 1:10,000-year return event estimated as 252 m^3/s (Figure 15).

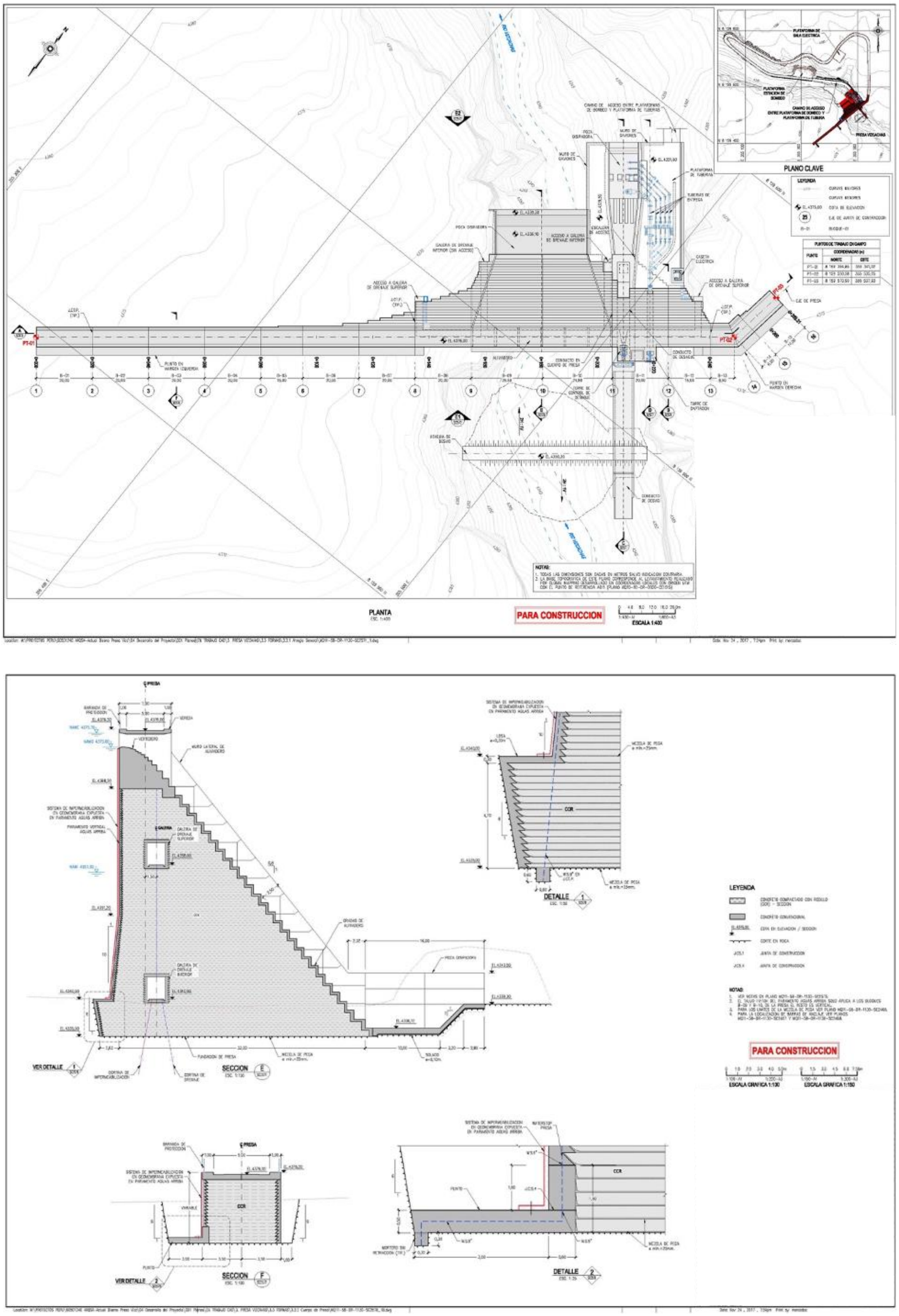

Figure 15: Vizcachas Dam plant view and vertical cross-section

The dam has been designed with a low-level outlet that allows the reservoir to be emptied when necessary (Figure 16).

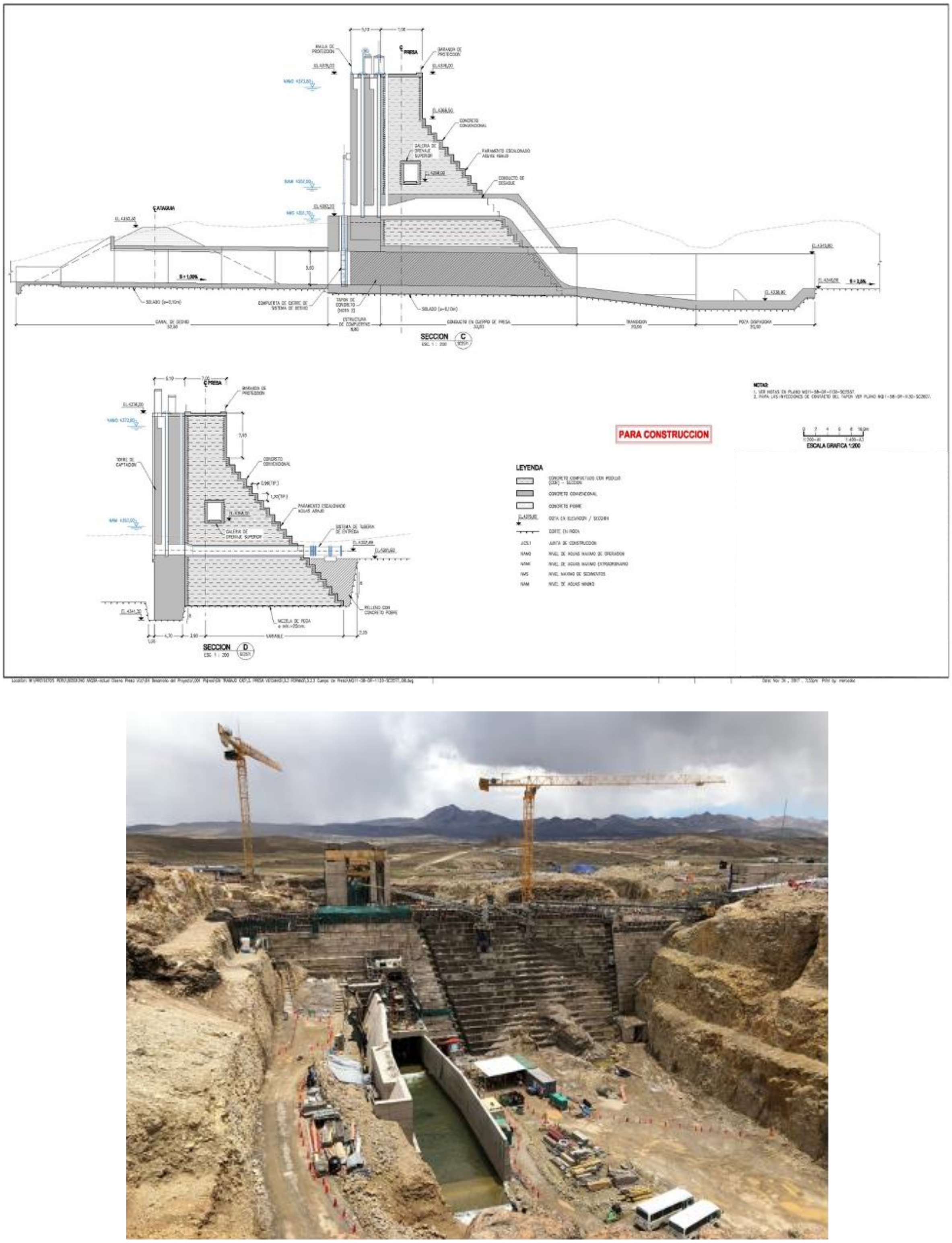

Figure 16: Vizcachas Dam lo- level outlet and stepped spillway

The flows allocated to several purposes will be supplied via a main 54" steel horizontal pipeline that has a maximum capacity of 6.2 m^3/s. The pipe branches into 6 pipes (Figure 17) to supply the different allocations as follows:

- **Pipeline 1:** 30" HDPE pipe, mostly buried, that supplies the Quellaveco water demand, up to 700 L/s.
- **Pipeline 2:** 18" steel pipe that compensates for the water taken by Quellaveco from the Titire River during the dry season of September to December, up to 700 L/s in case all the water is taken from the Titire River.
- **Pipeline 3:** 14" steel pipe that provides the extra flow during the dry season of September to December, 157 L/s.
- **Pipeline 4:** 18" steel pipe that provides the flow required by the PERPG irrigation project, 651 L/s from September to December.
- **Pipeline 5:** 10" steel pipe that provides the ecological flow, 150 L/s all year round.
- **Pipeline 6:** 48" steel pipe that provides the flow released from the Pasto Grande reservoir. Designed for up to 4.4 m^3/s. In case this flow is surpassed, the flow will be released by the low-level outlet.

All pipes are gauged with magnetic flowmeters and controlled by valves. Pipeline 1, which supplies the flow to the Quellaveco project, goes to a pump station, and the rest to the spillway stilling basin and is discharged downstream.

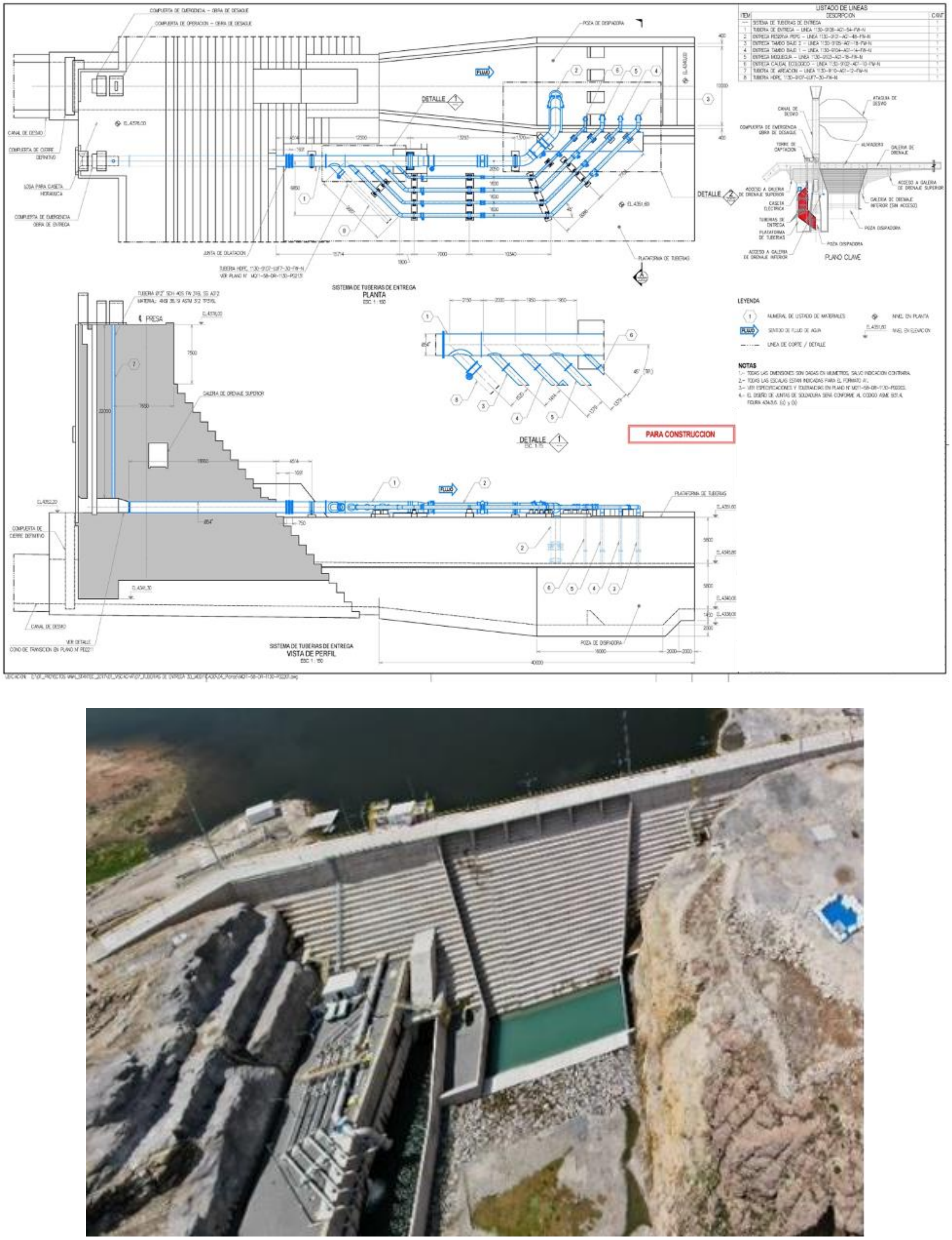

Figure 17: The Vizcachas Dam water supply

Conclusion

The mining industry by its nature directly affects two of the most essential resources we depend on: land and water. Therefore, there is a natural tendency to perceive mining activities as an intrusive and, by extension, non-environmentally friendly business. However, mining is part of society, and mining products are indispensable to sustain the current standard of living. At the same time, society rightly expects the mining industry to make a positive contribution to socio-economic development in a sustainable way by reducing its environmental footprint and supporting biodiversity.

Dialogue and consensus among stakeholders are the most powerful tools to overcome this dichotomy of the mining industry. How to articulate and implement the strategy is the key question. The Quellaveco case has been an example. After a long journey of negotiations, the Quellaveco project successfully secured, with the agreement of all stakeholders, the construction and operational permits and the make-up water required for its operation in a stressed water region with existing strong local conflicts over water resources management between the Regions of Moquegua and Arequipa, with which the Quellaveco project interacts.

The conflict over water resources management by the two Regions was taken by the Anglo American team as an opportunity to achieve success. An especially engaged approach to the Quellaveco water management strategy was adopted, aiming to reconcile the differences between the two Regions by organizing and participating in dialogue tables facilitated by the Moquegua regional government, supported by a solid engineering concept and design that is favourable for both Regions. Water management has guided most major aspects of the mine design, and continued participation by local representatives has established trust and engagement in the surrounding communities that has helped produce an innovative mine that respects and makes the best use of the most valuable resource in the region, water.

Given the success of the dialogue table as an enabler to the Quellaveco project and a means of bringing progress to the communities, it should be recognized that new community expectations will arise triggered by each step of the mining cycle (exploration, design, construction, operation, expansion, and closure). These inherently introduce challenges, together with socio-economic changes and unfavourable climatic conditions. To overcome these new challenges the communities and stakeholder strategy must be dynamic and adaptative to continually reinforce the relationships.

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A Tale of Two Treatment Systems: Evaluation of Active and Passive Treatment Strategies for a Legacy Mine

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Abstract

It is infrequent that the treatment possibilities for a given water chemistry and flow rate include both passive and active technologies. Usually, the solute concentrations and flow rate are too high for a passive system or too low for an active system. However, on occasion, the situation arises in which both passive and active processes are potentially viable treatment options. This is the case for a water source in the western United States where both active and passive pilot-scale systems were built and operated side-by-side in the field to assess their viability at treating historical mine seepage and identifying design criteria for potential full-scale implementation. The active treatment system consisted of equipment housed within a semi-trailer and utilized a high-density sludge (HDS) process, which traditionally uses calcium hydroxide reagent to raise the pH of the feed solution in order to precipitate dissolved metals. The HDS process was configurable as a single- or two-stage system depending on treatment goals.

The passive bioremediation system was partially housed in a mobile 40-foot shipping container installed at the site. The bioremediation system consisted of three stages: limestone pre-treatment, primary treatment via sulfate-reducing biochemical reactors, and secondary-treatment via treatment wetlands.

The active treatment system with two-stages achieved potential discharge limits for the primary water quality standards (WQSs). The bioremediation system achieved most, but not all, potential primary WQSs during the test period, and strategies for improving performance were identified. The results for each treatment system are discussed and compared to provide insights into which system might be better suited for this application.

Introduction

Various water technologies and strategies exist for treating mine-influenced waters, and treatment systems can generally be categorized as either active or passive. Active treatment requires daily operational input from staff in the form of process review, set point changes, maintenance, and other. Most active treatment requires chemical addition and mixing in reactors. Active treatment systems can typically handle changes in feed chemistry and flowrates. Passive systems usually rely on natural biological, geochemical, or physical processes to improve water quality. Passive treatment strategies are typically chosen for historical or remote mines because they do not generally use electricity, they operate by gravity feed, and typically require less operation, maintenance, and monitoring. The choice between active or passive strategies is critical for meeting treatment goals.

There are various factors influencing whether active or passive systems should be selected. Selection depends on considerations such as water treatment goals, regulatory requirements, flow rates, mass loading of metals requiring treatment, availability of land for a treatment system, and cost-effectiveness. Rarely does an opportunity present itself to simultaneously evaluate active and passive treatment systems side-by-side. This paper summarizes such an opportunity at a historical mine site in the Rocky Mountains of the western United States of America. The historical mine workings produce mine drainage, surface decant water, and mine tailings toe drainage. Mine drainage flow rates vary extensively over the course of the year due to precipitation, primarily as snow. Several retention, settling, and surge ponds are maintained onsite to accommodate higher flows during the spring runoff, and a water treatment plant (WTP) has been in operation at the site for over 40 years. Due to the age of the WTP, along with the type of treatment process in place, new treatment strategies are being evaluated, including an alternative passive treatment option for some of the water that requires treatment.

Two simultaneous pilot-scale evaluations were conducted at the site in 2019. The waters targeted for treatment are characterized by a low pH, as well as elevated levels of sulfate and several metals such as aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn). Other considerations include arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and nickel (Ni), according to potential discharge WQSs. The active treatment system consisted of calcium hydroxide addition in one- or two-stage high density sludge (HDS) reactors to precipitate metals.

The passive treatment system consisted of a biologically-based (hereafter referred to as bioremediation) treatment system consisting of three stages: neutralization pre-treatment, primary treatment biochemical reactors, and post-treatment wetlands. The principal design objectives of the evaluations were:

1. to optimize the treatment system components under local environmental conditions;
2. to evaluate the performance of locally-available bioreactor substrate materials and treatment wetland plants; and
3. to provide design data for potential future implementation of full-scale treatment.

Background

High-density sludge

High-density sludge is a traditional active treatment technology that uses a hydroxide reagent (typically calcium) to raise the pH of the feed solution in order to precipitate the dissolved metals in water. Depending on the targeted metals to precipitate, oxidation of this solution is commonly required. The basic process flow of this system is pictured in Figure 1.

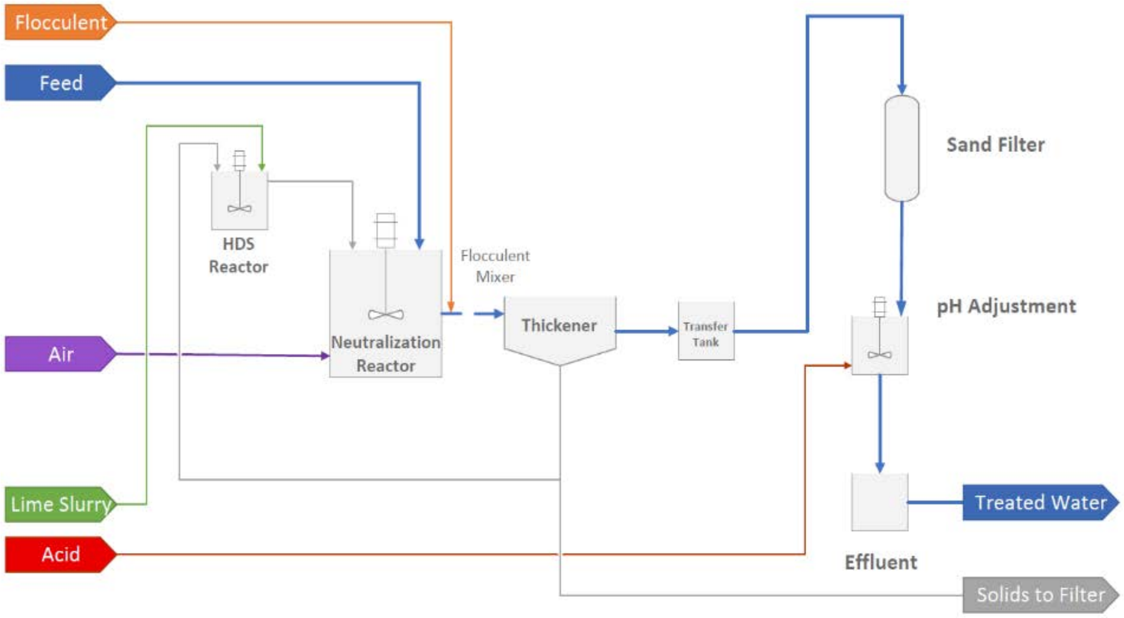

Figure 1: Single-stage HDS process flow diagram

Feed solution enters the neutralization reactor, where it is oxidized with air and mixed with a hydroxide/seed slurry. Solution then leaves the neutralization reactor, mixes with flocculant and is sent to a thickener for liquid solid separation. The clarified liquid overflows the thickener weir and moves on to fine solids removal, pH adjustment, and discharge. The solids settle in the thickener and are recycled to another tank (HDS reactor) where they are mixed with the hydroxide reagent. This step produces a "densifying" effect because hydroxide reagent coats the underflow or "seed" particle, which effectively removes waters of hydration and produces a denser sludge. As this hydroxide/reseed slurry is then mixed with the feed solution in the neutralization reactor it raises the pH in the reactor, causing dissolved metals to precipitate onto the densified particles compounding the effect. The hydroxide reagent addition is controlled by the pH of the neutralization reactor and is set based on the targeted metals to remove.

Bioremediation

The bioremediation treatment system consists of three stages, as shown in Figure 2. The first stage is a basic neutralization stage using limestone to increase pH and reduce acidity. Limestone is a relatively low-cost neutralizing agent that is safe and easy to use. Limestone pre-treatment is often preferred in systems that operate semi-passively as less maintenance is required compared to chemical dosing systems. While not a remote site, using limestone also negates the need to frequently transport potentially hazardous alkaline reagents to the site, and does not require additional equipment to operate a chemical dosing system. Increasing pH improves water quality by promoting the chemical precipitation of Al and Fe (oxy)hydroxides. Pre-treating the mining-influenced water (MIW) also helps support the biological organisms required for the second treatment stage.

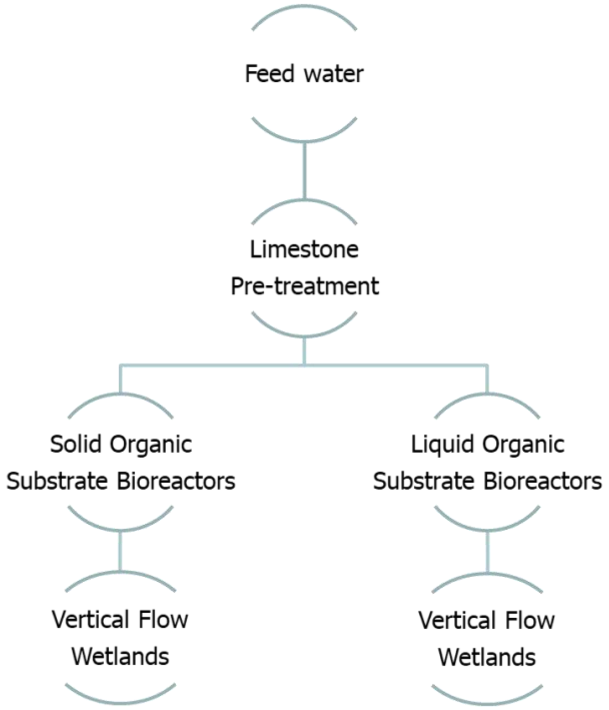

Figure 2: Three-stage bioremediation treatment process block flow diagram

Sulfate-reducing biochemical reactors (SRBRs) rely on a diverse assemblage of microbes to reduce sulfate to aqueous sulfide, which complexes with metal ions via precipitation as metal sulfides. Sulfate is reduced by sulfate-reducing bacteria while oxidizing an organic substrate. This evaluation compared the performance of two different substrates: a solid organic substrate and a liquid organic substrate. The solid substrate consisted of a mixture of readily available types of organic matter (wood chips, hay, and walnut shells). The liquid organic substrate was provided by a commercially available liquid carbohydrate-based product. The sulfate reduction process produces bicarbonate alkalinity, leading to additional metal removal at a higher pH.

The final treatment stage consists of vertical flow wetlands (VFWs) designed to promote oxic and aerobic conditions that increase dissolved oxygen, reduce biochemical oxygen demand (BOD), remove manganese as oxides, and filter out residual solids. Each treatment stage improves the pH of the MIW and adds buffering capacity to the final effluent water that can be beneficial for the receiving water. The post-treatment phase has the added benefit of improving the appearance of the landscape at the site.

Methods

High-density sludge

To perform the on-site HDS pilot, Freeport-McMoRan designed and constructed a portable pilot plant within a semi-trailer. The plant was configurable as a single- or two-stage system, with the option to run two single-stage tests congruently. Major equipment included: hose pumps, transfer tanks, solids reactors, thickeners, and a sand filter. All process equipment was housed within the trailer, with the exception of bulk reagent storage and potable water totes. Figure 3 shows an inside look of some of the equipment used in the pilot plant.

Figure 3: Two-stage HDS pilot plant

The trailer control system included a PLC, HMI, and a historian to trend and store key operating parameters over the course of the test work. The HDS control strategy was designed to be fully automated and operate the plant overnight without the need for night-shift intervention. Level indicators and switches monitored tank levels and triggered a safe shutdown of the plant if any plugging was detected. This level of automation minimized the chance of tank overflows, which preserved the integrity of the tests by limiting process upsets and solids lost into the secondary containment. The plant was designed with enough residence time in the reactors to test up to five gallons per minutes (gpm). Flocculant, chelate, and lime were all monitored and dosed as part of the control system. The primary control function was a neutralization reactor pH control loop in each stage, with a steady dosage of flocculant based on the feed flowrate. The solids recycle flowrate in each stage was varied to maintain a set point based on the solids sampling from the previous day, or current solids density as measured by a Marcy scale.

Whether the HDS process is configured as a single- or two-stage system depends on the targeted metals and level of removal for each. For the testing, dissolved Al was a key factor in determining the plant configuration. Since no final Al target had been determined at the time of the pilot, both single- and two-stage configurations were tested. Below are the configurations tested on-site:

- Single-stage HDS operated at a pH set point of 10.5.
- Single-stage HDS operated at a pH set point of 10.3.
- Single-stage HDS operated at a pH set point of 10.0.
- Two-stage HDS, stage 1 operated at a pH of 7.0, stage 2 operated at a pH of 10.5.
- Two-stage HDS, stage 1 operated at a pH of 7.0, stage 2 operated at a pH of 10.5 with chelate addition after stage 2.

Three different pH set points were chosen for single-stage operation to determine if pH solubility was a primary means of precipitation for aluminum. Aluminum is more soluble at higher and lower pH but less soluble in the near neutral range. Improved aluminum removal was expected with a lower pH setpoint. However, pH is also a significant driver for Mn removal. Optimum pH for abiotic Mn precipitation is around 10.5, so a balance between Al and Mn removal had to be achieved.

Bioremediation

The pre-treatment stage consisted of four 55-gallon drums filled with limestone (about 3-inch diameter) and connected in series. Due to the relatively low pH of the water to be treated and elevated levels of Al and Fe, a pre-treatment phase is needed to improve the water quality prior to contact with the sulfate-reducing bacteria. From the dissolution of calcium carbonate ($CaCO_3$), calcium ions are formed along with bicarbonate. This increases pH and allows the formation of low solubility metal hydroxides. Above a pH of 3.4, ferric Fe readily forms insoluble Fe hydroxides. Above a pH of 5.6, Al begins forming insoluble Al hydroxides. These solids were encouraged to settle out with the limestone and immediately after the limestone beds within a 55-gallon barrel settling tank. This reduces the suspended solids load that could enter the primary treatment and cause plugging issues.

The primary treatment stage for MIW is the SRBR. Sulfate reduction by bacteria produces sulfide ions along with additional alkalinity. Free sulfide combines with metals susceptible to sulfide precipitation (e.g., Fe, Cu, Zn, and Cd). These sulfides are relatively insoluble at circum-neutral pH. The additional alkalinity promotes increases in pH and further removal of metals, such as aluminum, that form insoluble hydroxide precipitates. The sulfate-reducing bioreactors were constructed using 120-gallon tanks (Figure 4). Two organic substrates were used as the source of organic carbon: a solid organic substrate (SOS) and a liquid organic substate (LOS). In this pilot plant, the SOS contained a mixture of wood chips (39% wt), alfalfa hay (10% wt), pecan shells (20% wt), and limestone sand (29% wt). The latter was for additional neutralization capacity, particularly during start-up. The LOS was provided by dosing a non-reactive aggregate-filled reactor with MicroC® 1000 (EOSi, Pocasset, MA, USA), a proprietary carbohydrate-based liquid providing organic carbon.

Figure 4: Primary treatment sulfate-reducing bioreactors

The wetlands treatment stage was designed to polish SRBR effluent and improve water quality prior to discharge. A vertical flow wetland was selected for evaluation as the most likely to continue operating year-round in an extremely cold climate. In a vertical flow wetland, water is treated as it percolates downward through the root zone of plants and through the 24-inch-deep layered sand and gravel bed (Figure 5). The unsaturated sand and gravel promotes an aerobic environment that returns oxygen back to the SRBR effluent, which is anoxic. The microbial community and plants also consume the high organic load (i.e., BOD) present in SRBR effluent. While not listed as a primary WQS, it is indicated as a secondary standard for basic water quality. Mn-oxidizing bacteria then drive the biotically-mediated oxidation of Mn, which can occur much faster and at a lower pH (ca. 6.5) than abiotic Mn oxidation.

Water samples were routinely collected from each stage of the treatment system to monitor performance. Field chemistry parameters (pH, dissolved oxygen, electrical conductance, oxidation-reduction potential, and temperature) were recorded weekly. Aqueous samples were collected every two weeks for quantifying metals (total and dissolved), anions, and acidity/alkalinity. The evaluation was conducted from mid-July to late-October 2019, until freezing conditions impacted the operation of the pilot study.

Figure 5: Vertical flow wetland as the final treatment stage

Results

High-density sludge

Five different HDS configurations were completed on-site from September through November 2019. Each single-stage configuration had four days of sampling, while the two-stage configuration had six total days of sampling, four with chelate addition and two without. Given that the final water quality standards are yet to be determined, this pilot was judged by the lowest potential discharge limits available.

All the primary WQSs were met in each configuration with the exceptions of Cd and Al. As expected, neither the single- nor two-stage configurations alone achieved the lowest potential Cd target. Only the addition of the chelate to the second stage effluent, followed by filtration through a 0.45-micron filter, achieved a final effluent concentration significantly below the target. Chelate could be added to either the single- or two-stage configurations if needed. Also as expected, the Al target was only achieved in the two-stage configurations. The Al standard is important to understand, as it changes the scope of a future treatment system. Table 1 shows the results from the various configurations.

Table 1: HDS pilot test results summary

Test summary	Reactor 1 pH	Reactor 2 pH	Passing status for selected water quality standards					
			Al	Cd	Cu	Fe	Mn	Zn
1 Stage – pH 10.5	10.5	n/a	Fail	Fail	Pass	Pass	Pass	Pass
1 Stage – pH 10.5	10.3	n/a	Fail	Fail	Pass	Pass	Pass	Pass
1 Stage – pH 10.5	10.1	n/a	Fail	Fail	Pass	Pass	Pass	Pass
2 Stage without chelate	7	10.5	Pass	Fail	Pass	Pass	Pass	Pass
2 Stage with chelate	7	10.5	Pass	Pass	Pass	Pass	Pass	Pass

Bioremediation

Improvements in pH were observed at each stage of treatment, with a final effluent pH within WQSs. The pH increased from an average of 2.9 to an average of pH 6.4 following pre-treatment, and this level was maintained through the SRBRs. In addition to improving pH of the MIW, limestone pre-treatment is advantageous for removal of Al and Fe prior to the solution entering the SRBRs. This reduces plugging and subsequent flow restrictions through the SRBRs. Total recoverable Fe was removed 99%, while 44% of the Al was removed in pre-treatment. Al removal was lower than expected but continued to be removed further downstream in subsequent treatment phases.

Performance of the SRBRs met expectations up to the flow rate evaluated. As the bioreactors required an acclimatization period ranging from 30 to 75 days, the target flow rate was not achieved during this evaluation. Regardless, the SRBRs exhibited metal sulfide precipitation and alkalinity generation. Average metal removal rates were comparable between reactor types (i.e., LOS vs. SOS), with the exception of Al removal. The SOS reactor exhibited continual removal of Al, potentially due to more effective filtration of Al hydroxide particulates. Total Al concentrations in the SOS reactors continued to be removed below the pre-treatment effluent levels to just above the WQSs. LOS reactors did not appreciably remove additional aluminum and maintained levels approximately the same as the pre-treatment effluent level.

Total recoverable Fe levels exiting the SRBRs were slightly higher than the pre-treatment effluent levels, potentially due to release of Fe from the substrate materials, e.g., woodchips and sawdust or lava rock. Dissolved Cu concentrations were removed by both types of reactors below WQSs. The LOS reactors were able to achieve the low level nearly from start-up. As expected, Mn concentrations were relatively unchanged within the SRBRs because Mn does not typically precipitate in reducing environments. There was an initial decrease in SRBR Mn concentrations, likely due to adsorption of Mn with the organic matter or the formation of Mn carbonates, but this was not sustained and Mn returned to pre-treatment effluent levels. Zn levels were reduced by both types of SRBRs to levels just above WQSs. Dissolved Cd concentrations were similarly reduced by both reactor types to just below WQSs by the end of the evaluation.

The vertical flow wetlands provided final polishing to the effluent from the SRBRs and generally improved water quality. DO and pH were improved by the VFWs and increased to approximately 4 mg O_2 /L and pH 7.5, respectively. Oxidation-reduction potential (ORP) increased as it passed through the VFWs, indicating the desired shift from anoxic to oxic conditions necessary for Mn oxidation. With the exception of Fe and Mn, COCs were removed below the benchmarked WQSs. VFWs removed additional Al, Cd, and Zn below WQSs from the SRBR effluent. Fe was further removed by VFWs, but not consistently below WQSs. Mn removal rate was approximately 90%, but was not sufficient to achieve potential WQSs. Further removal would be expected as the wetland plant communities mature and develop a more extensive root zone and associated rhizosphere, but this had not occurred by the end of this test period. BOD, while not a specific WQS, was improved by the VFWs with an average of 86 to 89% of incoming BOD removed. The reduction of additional COCs through the VFWs supports the need for any potential large-scale treatment system to include a polishing step to achieve treatment below WQSs for discharge. However, any treatment wetland will require more time to mature to maximize the biological removal mechanisms targeted.

Conclusion

As expected, results from this side-by-side evaluation of MIW treatment strategies reinforce some of the widely recognized characteristic differences between active and passive treatment systems. The active treatment system using high-density sludge was able to meet the WQSs for aluminum, cadmium, copper, iron, manganese, and zinc during the relatively short evaluation period. Alternatively, the passive bioremediation system achieved WQSss only for aluminum, cadmium, and zinc, but not for copper, iron, and manganese. Relative to the active system, the bioreactors took longer to achieve the steady state conditions necessary for sulfate reduction, while the wetlands needed additional time to mature. Opportunities exist for improving the performance of the bioremediation system and they warrant further consideration. For example, careful selection of bioremediation substrates would mitigate the potential leaching of metals into the treated water. Ultimately, these two treatment strategies are not competing against each other, but rather should be viewed as complementary tools, each with their own ideal applications.

Optimizing Contact Water Treatment during the Lupin Mine Closure

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Extended abstract

Introduction

The Lupin Gold Mine (Lupin) is located approximately 285 km southeast of Kugluktuk, Nunavut, and is owned by Lupin Mines Incorporated (LMI). Lupin is a remote sub-arctic site that is situated in an area of continuous permafrost. In 2017, LMI decided to end their Care and Maintenance period and enter Active Closure. During active operation and every two to three years during Care and Maintenance activities, a slurry lime solution had been dosed into the tailings containment area (TCA) to raise the water pH from its tailings-impacted acidic condition and to precipitate metals to meet LMI's water license discharge requirements.

The TCA consists of three open-water bodies and five tailings cells. As part of the Active Closure works, LMI is tasked with covering the tailings cells with esker sand to stop oxidation of the underlying tailings. In order to place the cover effectively, standing water on the uncovered portions of the cells must be removed. The acidic cell water is pumped to the first of the three disconnected water bodies, where it passes through a serious of syphons and two additional water bodies, before being treated and discharged to the environment. Given the remoteness of the site, lime has typically been ordered in bulk and transported at the beginning of the season; it is very difficult to resupply once the treatment season has begun.

Although used historically at the site, lime has several limitations for use in the sub-arctic region, and Stantec was concerned that it might not be efficient enough to meet the schedule during accelerated treatment activities under Active Closure. Lime does not dissolve readily without sufficient heat and mixing, and the lime slurry can clog pumps and pipes due to the limited mixing and dosing equipment at the remote cold-climate site, resulting in constant flushing or low productivity treatment. In addition, lime does not leave any residual alkalinity in the treated water; as such the TCA water would become quite acidic between dosing regimes (approximately pH 5) due to the low residual alkalinity and buffering capacity in the treated water.

Based on Stantec's experience on other closure and mine water treatment projects, we investigated the use of soda ash in place of lime. Although soda ash is only half as concentrated a neutralizing agent as lime by weight, its increased solubility, residual alkalinity, and comparable price made it an attractive alternative to lime.

Bench-scale testing

Given that the bulk materials needed to be transported to Lupin on an ice road prior to the 2020 water treatment season, bench-scale testing had to be conducted in 2019 on site water to ensure suitability of soda ash treatment and quantify the amount of required soda ash. Samples of acidic site water were collected at the end of the 2019 summer season and taken to an accredited laboratory for titration to various pH endpoints with a representative soda ash solution.

Based on the results of the titrations and site bathymetric survey (for volumetric estimate), a quantity of soda ash plus contingency was ordered and transported to the site during the winter of 2019/2020 via ice road during the closure fleet mobilization.

Existing treatment retrofit and additional treatment location

Under historical Care and Maintenance, dosing of the lime slurry had taken place at one location. This involved pumping untreated water to a mixing vat where lime was introduced, creating a dosing batch over a period of hours. Once the slurry reached the desired consistency, it was released back to the water body receiving treatment through a perforated line. Given the relatively low solubility of lime at typical site temperatures, water treatment under Care and Maintenance was a time-consuming and personnel-intensive process.

Once the switch was made to soda ash, mixing dosing batches now took minutes instead of hours. The soda ash was mechanically introduced to the dosing vat in one-ton mega-bags; previously, 50-lb lime back were added manually to the dosing vat. The reduced manpower requirements allowed the site dewatering contractor to commission a second upstream treatment location. The results of the bench-scale analyses were used to develop an inline dosing plan based on field measurements and adjustment. The second location dosed soda ash directly inline to the transfer syphon between water bodies, instead of only one location in the largest water body, greatly enhancing mixing and decreasing the need for additional water treatment at the downstream treatment location. Monitoring locations were established in the TCA waterbodies to inform dosing concentration and frequency of dosing and pumping activities.

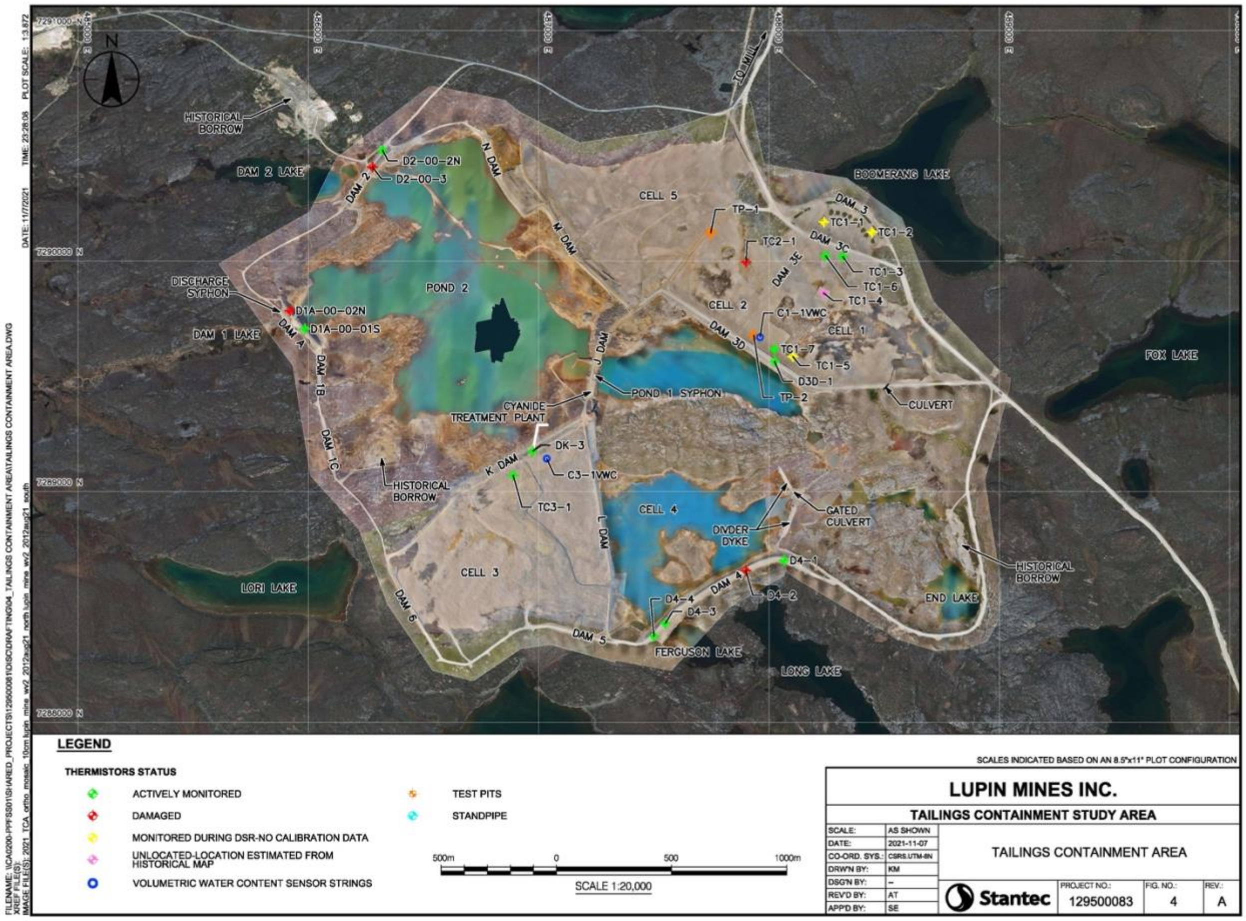

Figure 1: Map showing tailings containment study area

In-situ treatment and monitoring

Once the transfer, inline dosing, and environmental discharge were complete, there was still acidic contact water in the upstream water bodies that was at too low an elevation to be accessible with the syphon transfer system. For those isolated waterbodies, the second treatment location was retrofitted to dose a soda ash solution directly into the waterbodies, rather than having to move that water through the transfer/treatment system. By leaving the upgradient waterbodies at a neutral pH, the impact that upgradient drainage will have on downgradient pH values should be decreased. This hypothesis will be confirmed during freshet sampling in 2022. This upgradient treatment is referred to as in-situ treatment, to differentiate it from the batch dosing and transfer system used for primary water treatment.

After the in-situ treatment was complete, the site entered two years of monitoring to observe if the TCA pH values will remain consistent over time. If they do, then the site may be cleared for passive environmental discharge at the end of the monitoring season. The residual alkalinity from the soda ash treatment should be more effective in buffering the treated water against future pH reductions. This hypothesis was evidenced during freshet 2021, when the TCA pH was more than a full order of magnitude (>pH 6) higher than during previous freshets, which reduced the cost and time associated with yearly treatment.

2022 Closure activities

Water treatment is not expected in 2022 as the inline dosing and in-situ treatment should have left the TCA waterbodies at the required pH values at the end of 2021. Water sampling activities will occur during freshet 2022 to observe if pH values remained consistent with those observed at the end of 2021. Contingency neutralizing agent has been left onsite, should future water treatment be required.

Conclusion

Although Lupin had been using lime slurry successfully for neutralization of acidic water for decades, concerns were raised that the treatment system was not robust enough to meet the requirements of the aggressive Active Closure schedule. Initially, we investigated the retrofitting or replacement of equipment to increase the efficiency of the lime treatment, but ultimately a change in neutralizing agent was selected. Through applied scientific investigation, we were able to demonstrate to the client and the regulatory agencies that the change in neutralizing agent would improve the ease of treatment operation and increase the treatment efficiency, without any associated decrease in treatment effectiveness. Once the water treatment process was simplified, site personnel were free to complete other closure works.

LMI has been using the new soda ash treatment system for two years with significantly increased efficiency, reduced dosing time, and fewer operational challenges, and has successfully discharged millions of cubic meters of treated water to the environment since the change. The residual alkalinity left in the TCA water after treatment has raised the yearly freshet pH more than a full order of magnitude (>pH 6) vs. previous years, which has reduced the cost and time associated with yearly treatment.

Acknowledgements

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Chapter 5:

Water and Tailings Management

Review of Internet-of-Things Enabled Monitoring Systems for Tailings Storage Facilities

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Abstract

Water quality and geotechnical monitoring instruments have long-established designs that have become the backbone of monitoring. In recent years, advances in battery technology, radio communications, microprocessors, and telecommunications have enabled the Internet of things to become an important part of water quality and geotechnical monitoring in and around tailings storage facilities. The introduction of several protocols such as LoRa, ZigBee, or mesh-based TCP have increased the connectivity of instruments from individually programmed point-to-point communications to fully integrated systems. Several parameters have to be optimized concurrently to design robust Internet-of-things (IoT) systems. Despite the opportunities offered by these new developments, a compromise has to be reached between radio functionalities such as bandwidth and response time, range, and power in order to fulfill the requirements of any given monitoring project. Radio range is proportional to the electrical power required by the radio modules, yet power consumption should be minimized in all situations as solar power is often the only option for systems that are remote and isolated. In addition to these core concerns, compatibility has to be met with a wide range of instrument signal types such as vibrating wire, thermistors, RS-485, SDi-12, 4-20 mA, and time-domain reflectometry. Expanded compatibility often demands more powerful microprocessor that increase the drain on the power supply of the system, and thus needs to be accounted for when designing the entire system.

IoT best practices such as interconnectivity and the possibility to bring disparate technologies into a single framework will be discussed. Other IoT practices such as self-configuration and intelligent monitoring will be discussed in the context of water quality monitoring on mining sites. In some circumstances, smart sensors that reconfigure automatically for high-speed acquisition under pre-defined conditions would take advantage of IoT practices, but at the expense of extra load on the microprocessor and power supply. The balancing act between processing, radio, and the power supply will be expanded

upon with experience drawn from several mines in northern and eastern Canada. These new IoT practices also lay the groundwork for future developments such as the use of machine learning and artificial intelligence for more proactive monitoring of assets.

Introduction

Unfortunate events in recent years have increased the general awareness of the issues posed by tailings and tailings dams. Several major failures have shown that deploying remote monitoring techniques improves safety by providing engineers and mining companies with relevant data. Industry 4.0 brings practices such as the Internet-of-things (IoT) paradigm into the monitoring of tailings storage facilities (TSF). The IoT is a set of methods in which devices are connected to a network automatically and with a unique identifier. In many industries, the IoT is successful as a way to collect data from monitoring points, instruments, and the status of machines and data logging systems. Geotechnical instruments have proven designs that have become the backbone of tailings storage facility (TSF) monitoring, but in recent years, advances in batteries, radio technologies, microprocessors, and telecommunications have enabled the IoT to become an important part of TSF monitoring.

IoT best practices such as interconnectivity and the possibility of bringing disparate technologies into a single framework will be explored. Other IoT practices such as self-configuration and intelligent monitoring will be discussed in various contexts. IoT practices also lay the groundwork for future developments such as the use of machine learning and artificial intelligence (AI) for more proactive monitoring of assets. This review will cover the benefits of IoT systems and how the different hardware and software layers are interconnected. It will compare the features of several manufacturers of IoT hardware for TSF.

IoT characteristics

Monitoring is an integral part of the culture surrounding TSF. Piezometers, water sampling, surveying, and more have been used consistently to ensure the durability and safety of tailings for decades. For some older facilities, instruments such as piezometers have been in use for decades. Bringing an IoT framework to this field is an evolution prompted by the decreasing costs and increasing power of microprocessors and radio communications (RF) modules. By attaching specific devices to the instruments, an already-existing network of instruments can be converted to an IoT system. In the context of TSF and environmental monitoring at large, an IoT system is a system that monitors and controls sensors over a wide area, with data connected remotely and centralized in a server.

Dynamic and self-adapting

Instruments should be able to adapt to changes in the environment. A typical example of this is that wireless systems should provide redundancy for both the instruments themselves as well as for communications.

Self-configuring

By correctly designing the IoT hardware and its data connectors, adding instruments should be standardized in such a way that minimal technical knowledge is required for the field staff.

Interoperability

In tailings and environmental monitoring, there are different manufacturers of sensors, data loggers, and instruments. An IoT system should accommodate many types of instruments and allow the instruments to interact as needed. At a higher level, using standard data connectors to move the data from the instrument to the database facilitates integration of any type of sensors into IoT-based monitoring systems.

Unique identity

Each instrument can and should have a unique identity built into the system. This acts as a redundancy comparing manually tracking instrument locations, installation parameters, serial numbers, and calibration factors.

Integration into larger data networks

An IoT system should be able to allow analysis and comparison of data from many different sources and sites. For instance, working on weather stations, ground-based radar, InSAR, and in-ground instruments can lead to insights that were previous unattainable.

Context awareness

Context varies little in TSF compared to other industries. A classic example would be vehicle trackers that are able to give the exact location of the equipment on a mine site and then enable security features automatically according to that information. TSF are stable over years if not decades, and this facet of IoT is not as relevant.

Intelligent *decision-making*

TSF monitoring systems should be able to lead to more intelligent decision-making by offering sizable amounts of data that can be used by engineers to build detailed models of their structure, and perform preventative maintenance as needed.

IOT architecture

Table 1 summarizes the structure of an IoT project as used in TSF. The instrument layer is the instrument itself. An in-depth analysis of instrument types and technologies is beyond the scope of this review, insofar as the instruments are largely decoupled from the IoT hardware, with one important caveat. Instruments that have been installed for years or decades should be possible to add to an IoT network by attaching the proper hardware to them. This is not a new industry starting from scratch; on the contrary, continuity with older monitoring programs is critical. Moreover, instruments are often installed in the ground, and as such cannot have any type of telemetry built-in. These two points are addressed at the node layer. It usually comprises a data logger, a radio module, and a power source. The edge layer collects data from the nodes and pushes it to a local network or to the internet. The management layer is a software layer that assists in the data and inventory management of the instruments and nodes. The application layer is where all data is aggregated and used for monitoring, modelling, and more. The layers are intended as a framework rather than a strict set of recommendations: for instance, the node and instruments can be built into a single device in the case of tiltmeters, or in other cases, the edge device and nodes are the same device.

Table 1: Examples of items that are part of each of the five layers of an IoT system for TSF

Instrument	Node	Edge device	Management	Application
Piezometers	Data logger	Cellular	Instrument inventory	Graphing
Total station	Radio module	Satellite	Data archiving	Automated reports
LIDAR		Gateway	Security	Data analysis
Inclinometers		Distributed gateways	Traceability	Specialized tools

Instruments and node layers

Instruments in TSF are often in remote locations with no external power and no network connection. The node layer is used to bridge the gap between the instruments and the network and databases. Nodes are network-enabled devices that can transmit readings over radio links, collect data from instruments, and in most cases locally store the data. They may use a variety of protocols such as ZigBee, LoRa, PakBus, and proprietary versions or implementations of each, as well as generic-purpose products such as Wi-Fi and LTE.

These protocols can be sorted into two broad families: star and mesh networks. Star topology relies on having a transmitter at each location that transfers directly to an edge device (see the following section), typically called a gateway (Figure 1 a). This link can be unidirectional (the instrument transmits its data on a schedule or when certain conditions are met) or bi-directional, in which polling and other operations can be initiated over the link. Star topology is simple to use, simple to understand, and to manage. However, star networks have a few constraints that should be taken into consideration. There is no way to reroute the data around obstacles should the topology of a site change. It is also not typically possible to extend the range by adding repeaters. However, the most commonly used technology for star networks, LoRa, has a range of up to 15 km, easily covering even the largest TSF.

In mesh networks (Figure 2 b), nodes can communicate with each other and transmit relay data between them and all the way up to the gateway or edge device. These networks are often self-healing: if the radio link between two specific nodes is broken, data can be automatically rerouted. The radio technology behind this is more complex than what is required for star networks, but mesh networks tend to be more resilient and have fewer points of failures than star networks.

Several manufacturers offer products that work under this principle to enable IoT practices. A comparison of the specifics of each technology can be found in Table 2. This list is not exhaustive and is only meant to be representative of the author’s professional experience working in North America.

The design of nodes has to balance several factors to be deployed successfully in TSF. It is critical that they transfer data over long distances with minimal battery requirements. Power draw can be influenced by radio power, radio duty cycle, power to the chip that reads the instruments, calculations that need to be done onboard, and ambient temperature. All manufacturers make some compromise between all of the above to offer products that are appropriate for TSF monitoring.

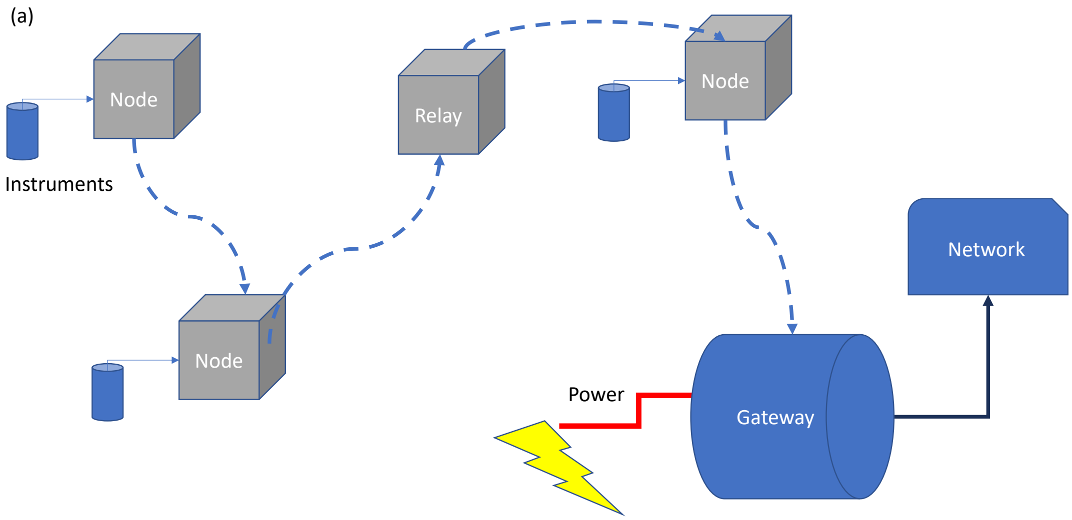

Figure 1 (a): Schematics of a star network

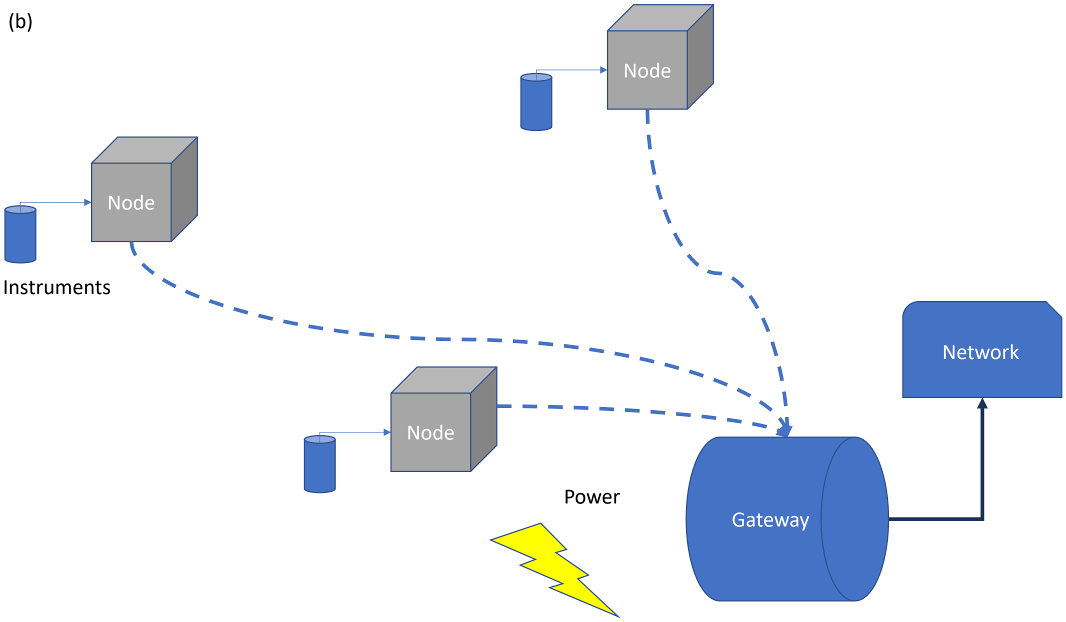

Figure 1 (b): Schematics of a mesh network

Table 2: Summary of key specifications of IoT node hardware for TSF

	Protocol	*Net. type*	*Self-healing*	*No. of hops*	*Range outdoor*	*Range indoor*	*Edge device*	*Instr. per node*	*Batt. life*
Ackcio	Mesh-LoRa	Mesh	Yes	>10	10 km	1 km	Prop. Gateway	1–8	10 yr.
Geokon	Mesh	Mesh	Yes	4	6 km	300 m	Prop. Gateway	1–8	1 yr.
Campbell Scientific	Pakbus	Cust.	N/A	>10*	40 km	1 km	Any	Many	1 yr.
Senceive	Prop. Mesh	Mesh	Yes	>25	500 m	200 m	Prop. Gateway	1–4	10 yr.
Sensemetrics	Prop.mesh	Mesh	Yes	?	12 km	1 km	Each node	Many	Solar
Worldsensing	LoRa	Star	Yes*	N/A	15 km	1 km	Prop. Gateway	1–5	10 yr.

* Limited by end-user programming

Delving in specifics of each technology is beyond the scope of this paper, but a few key differences are highlighted in this section. All products are compatible with vibrating wire instruments such as piezometers. All but Geokon’s Geonet are compatible with analog output instrument such as barometers or temperature sensors. Digital instruments are on a case-by-case basis for each instrument for every manufacturer, as the drivers have to be programmed on demand.

Ackcio

The gateway synchronizes the mesh network and offers an ethernet connection, a Wi-Fi connection, and a cellular network connection. The self-healing mesh network appears to work best in constrained areas such as underground mines, as opposed to open-air TSF. This product's strength is its compatibility with a large number of digital instruments from all leading manufacturers.

Geokon

Gekon's Geonet product deploys a mesh network with a limited range and a limited number of hops compared to other options such as Ackcio and Senceive. They are compatible with vibrating wire instruments and Geokon digital instruments. The gateway synchronizes the network and can be configured to contain a cellular modem with either an LTE-M or 3G connection. The limited compatibility with instruments from other manufacturers can make it a less desirable choice for systems with digital instruments or legacy instruments from other suppliers.

Campbell Scientific

Campbell Scientific is lagging behind their competitors to introduce fully integrated IoT solutions. However, the PakBus radio technology (Campbell's proprietary protocol) is flexible and can be made to work as a mesh network. The loggers are completely customizable and programmable, allowing for compatibility with all types of instruments available on the market. Campbell Scientific loggers now include built-in data connectors to interface their internal memory into IoT databases. These products are often the most cost-effective approach when a large number of instruments is to be connected to a single location. Most other systems discussed here can only accommodate a few instruments per node, whereas Campbell Scientific loggers can be easily expanded to read hundreds of instruments.

Senceive

Senceive's line of products offers the most robust mesh network in terms of range, number of hops, number of nodes, and stability of the products discussed in this review. They offer compatibility with vibrating wire and analog instruments, but have limited compatibility with digital instruments. The nodes have a long battery life. Of the products discussed here, they are the only ones that do not have memory backup on the nodes themselves. This sets up the gateway as a single point of failure, but several gateways can be deployed at once as backups with automatic rollovers.

Sensemetrics

The nodes (Threads) are all gateways with an ethernet connection that can also communicate with each other with a mesh network architecture. Each Thread is compatible with most digital instruments and analog instruments. They also offer a Strand product that is designed to exclusively read vibrating wire instruments, and which connects in a star pattern to individual Threads.

It is also the only system discussed in this review that has a proprietary cloud platform for configuration and management of the loggers and instruments. The battery life of individual Threads is low (in the order of weeks), and they typically require a solar panel for continuous operations.

Worldsensing

Worldsensing products (Loadsensing) work on a purely star network (LoRa) with a very long radio range. The nodes require little power and have a battery life of years or more. Nodes are compatible with vibrating wire instruments, analog instruments, and a select number of digital instruments.

Edge devices layer

An Edge devices layer comprises the devices that connect the local IoT network to the internet. In other industries, instruments themselves have their own connectivity, but the lack of local networks and power supplies on TSF makes the direct connection of each instrument impossible. Many products, such as Senceive, Worldsensing, Ackcio, and others use a gateway that acts both as the collection point for the local IoT network and as a connection point to the internet.

Other products, such as Sensemetrics' Threads, distribute the edge connectivity with each Thread being a data logger, radio transmitter, and internet connection point. This gives the most flexibility and redundancy, but increases operation costs. It is usually preferable to have fewer edge devices that aggregate data from several nodes due to the extra cost and power requirements incurred by cellular modems, built-in or external.

In a few cases, the instruments themselves connect to the internet or a local server, but this is unusual in tailings monitoring. Cellular modems are commonly built-in into strong motion sensors or seismographs. The typically large amount of data generated by this type of instrument makes it impractical to transmit measurements over local radio links.

Management layer

The management layer is both a benefit and a core component of an IoT system. In TSF and geotechnical monitoring, the standard is to know exactly why an instrument should be at a given location, what is expected to be learned from it, and how to handle its data. Even with these widespread precautions, it is not rare for practitioners to lose track of the instrument inventory or of historical data, or to ignore data. Large mining companies are showing interest in fully automating their monitoring systems in tailings across the world. This compounds the aforementioned data and instrument management issues as tens or hundreds of sites will be managed concurrently by small off-site teams.

The management layer can be split in two main categories: off-the-shelf specialized software and generic IoT platforms. Specialized platforms are usually designed from the ground up to be used specifically with geotechnical instruments. They include software such as Vista Data Vision's VDV or Canary System's Multilogger or Trimble's T4D. They include tools that are made to specifically integrate data from text files as generated by commonly used loggers and edge devices, as well as direct, custom-made connections to many of the same devices. Furthermore, they offer an application layer that contains tools typically used for TSF, such as displacement graphs (used with inclinometers), geo-localization of instruments and integration of weather station data. This category of software has the advantage of being simple to use and is often the best solution for small operations that cannot invest in setting up their own IoT infrastructure. This software tends however to be more closed-off, making the export of data to other tools more complicated than the software included in the next category.

The second category includes software that are first and foremost IoT platforms, but that can be adapted for TSF and the mining industry at large. At its core, the IoT platform should act as a bridge that connects the edge devices or nodes into a database. There are however hundreds of IoT management platforms, and each extend into data collection and into applications to varying degrees, and each offer functionalities that are relevant for specific industries. The database then becomes the central repository of instruments, instrument definitions, loggers, nodes, and the raw data. This database itself is where software such as business intelligence software collect data and information for advanced analysis. Examples of software that fill this management layer to control the instruments and consign data include OSisoft's Pi, Inductive Automation's Ignition, Google's IoT core, thingsboard.io, and Microsoft's Azure IoT.

Whichever software or IoT platform is selected, it should help with several key concerns of TSF monitoring. Inventory management of both instruments and nodes is a challenge for long-term monitoring. In TSF monitoring projects that last decades, there may be handoffs between engineering teams, contractors, or mine operators. A properly set-up management layer will ensure that each instrument exists as an entity with all its relevant information attached to it, such as installation, the installation date, instrument name, serial number, and more.

Similarly, long-term management of data can be made a lot more resilient. The authors have worked with mining operations that had decades worth of data lost because they were improperly stored in text files or Excel spreadsheets. Similarly, there have been cases where the exact process by which the calculated values were reached was lost, making it nearly impossible to re-analyze data or re-use it in more up-to-date models. Historically, instruments data has been collected manually and stored first on paper and then on computers in a completely ad hoc process. However, properly storing the data in a secure database, along with a long-term management plan for said database, is now feasible to prevent data loss or degradation over time. Using a generic IoT platform creates a database with which other IoT platforms could interact and more importantly, from which a database can be extracted and backed up at any moment.

Similarly, the management layer should give end-users an overview of the current status of the instruments network with real-time updates of parameters such as battery levels, uptime, crashes, data losses, etc. This leverages the advantages of using an IoT framework by lowering the risks of data loss due to hardware failure or communications issues.

Application layer

The foundation of the application layer can be the user interface of off-the-shelf products, as described in the previous section, or the software used to extract and analyze data from the database generated by an IoT platform. Commonly found functions such as graphing of historical data or report generation data have been introduced for TSF specifically over a decade ago by software companies such as Vista Data Vision or GeoExplorer and are standard in any modern business intelligence or analytics software.

Some commonly-used instruments require specific tools for plotting and interpreting data. In-place inclinometers and manual inclinometer probes have notoriously tricky data to analyze, which cannot be displayed accurately on regular time graphs. Distributed monitoring such as ground-based radar and total stations also require specialized tools for plotting. The application layer chosen for an IoT system should include the necessary tools for the instruments of a given TSF monitoring plan. Off-the-shelf platforms usually contain them as one of their selling points.

Because Industry 4.0 offers a more direct integration of geotechnical data, functions often found in manufacturing and utilities are now recommended to be added to TSF monitoring systems. Any complete IoT system should offer real-time alarms on readings, trends, and data loss. An alarm log should also be tied in and should be accessible for future reference.

Data distribution and control over access rights is another key component of the application layer: the exact views, graphs, or reports available for each user and stakeholder and can be tailored according to the needs of each.

The application layer encompasses emerging technologies such as machine learning and artificial intelligence. Access to large data sets is necessary to train most machine learning and AI algorithms, and the IoT will finally generate the amount of data needed. Training a machine-learning algorithm requires both success and failure states; engineers work tirelessly at preventing failure states, so datasets for these are currently limited. However, as more IoT systems are built and more researchers pool their data, more complete models of TSFs should eventually be developed.

Conclusion

The IoT and Industry 4.0 are trends in TSF monitoring that are going to change the face of the industry. They open the door to automated monitoring of the TSF themselves, but also of the instruments, data loggers, and data quality. This review has given an overview of what an IoT system for TSF should look like. A growing number of providers offer hardware compatible with instruments such as vibrating wire piezometers and in-place inclinometers. The hardware now offers standardized data exports, making their data available online for management and analysis. The hardware is the first component forming the basis of the various layers of an IoT system, as the nodes transform the instruments into IoT points of data collection. Through the integration of large amounts of data from the hardware and instruments, the management layer opens up possibilities that were not usually seen in previous iterations of monitoring plans, such as long-term resiliency of the data, real-time alarms, inventory management, and distribution of the data. These tools are really what set IoT systems apart, and what will help to usher in a new era of TSF monitoring.

Painted into a Regulatory Corner: Next Steps for Oilsands Closure Planning

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Abstract

The Athabasca oilsands region in Alberta, Canada, has been a primary economic driver for the country for decades. While production continues at an increasing rate with decreasing emissions per barrel, legacy producers are fast approaching the point where major tailings storage facility assets will need to be reclaimed. Past reclamation research programs have provided a rich dataset on technical aspects of optimizing landforms, cover system configurations, and re-establishing functional ecosystems. Thus, it is not a matter of scientific and engineering uncertainty that makes oilsands reclamation difficult. Rather, it is a matter of policy, legislation, and regulations that may preclude successful reclamation of tailings assets in the region.

The pathway towards reclamation certification of tailings ponds has not been tested. The intent of this paper is to propose new approaches for satisfactory reclamation outcomes in the region. By taking a realistic approach to examining the challenges faced by oilsands producers, we can begin to develop ways to achieve satisfactory outcomes for all stakeholders.

Introduction

Mining has been underway in the Athabasca oilsands region north of Fort McMurray, Alberta, Canada, since the 1960s. As legacy operators near the end of the approved Life of Mine (LOM), the focus on assets such as tailings ponds and the water stored within them necessarily turns to reclamation. Oilsands operators have consistently communicated that the goal for reclamation in the region is to return the land to a self-sustaining, locally common, boreal forest ecosystem. The return to a boreal forest ecosystem where an oilsands mine once existed is the expectation of the Alberta Energy Regulator (AER) and stakeholders, and represents the currently permitted condition.

Investors in oilsands operations are increasingly looking for concrete action on sustainability commitments, such as recently stated goals of being carbon neutral. At the same time, operators have a stated objective of returning investment on shareholder capital. It will be increasingly difficult for operators to satisfy both the aims of shareholder returns and achieving net-zero carbon emissions, while also maintaining closure liabilities. Investors will place their money where they feel there will be a return, and if closure liabilities are not reduced via reclamation activities, the impetus for investment is lost. Thus, operators have both financial, regulatory, and reputational obligations to satisfy when being induced to undertake closure operations.

Technical scientific and engineering aspects of oilsands reclamation are well understood and have been the subject of extensive research for decades. Furthermore, there is extensive technical guidance available around cover system design, landform optimization, and the establishment of functional ecosystems. However, the challenge associated with achieving successful reclamation is not simply a technical matter. Rather, the challenge lies in the interlacing of policy, legislation, and regulations that govern the process of lease relinquishment for mining operations. While the expectation for reclamation is to have a lease relinquished to the Crown, achieving the permitted closure vision for many operators is dependent on receiving reclamation certification for each asset on site. The process for receiving reclamation certification has not been tested in the oilsands for a tailings storage facility.

To date, a reclamation certificate has not been granted to a conventional tailings facility containing large volumes of water and flowable tailings behind a dam. Oilsands producers are largely at a point where a decision must be made regarding the preferred path toward closure to begin implementation of closure plans in the coming years. Committing to the current path towards achieving reclamation certification is untested and may prove challenging. Conversely, an alternative land use scenario, or implications for an element of long-term care, may not be feasible from the perspective of stakeholder expectations, irrespective of whether the closure outcomes are improved. Decades of expectations from oilsands stakeholders as to what successful closure looks like, may be difficult to reverse.

The problem

Investment in oilsands producers will flow to where there can be a reasonable expectation of return on investment. If oilsands operators are to offer a return to shareholders on their capital investment, while simultaneously upholding sustainability commitments, then major liabilities – in this case closure liabilities – must be acted upon with commitment. Demonstrating a reduction in closure liabilities will be a signal to shareholders that operators are serious about following through on sustainability commitments, thus providing confidence for further investment.

Investment will flow to operators that demonstrate serious commitment to sustainability goals and follow through on closure commitments. Following through on closure commitments also presumes that the pathway to achieving closure is well known and has a reasonable chance of success. However, this may not always be the case, and presents an additional challenge that must be considered.

Regulatory overlap

Many tailings storage facilities (TSFs) in the Athabasca oilsands region are nearing the end of their design service life. Oilsands operators are legally obligated under EPEA (Environmental Protection and Enhancement Act) to pursue reclamation certification as part of closure operations, with the intention of relinquishing the oilsands lease back to the Crown. The expectation from many stakeholders has been that the land once used for mining will be returned to a state that closely resembles the pre-existing state, making oilsands mining a temporary use.

An ostensibly well-defined process exists that outlines how an oilsands lease could be returned to the Crown (Figure 1). This process is familiar to oilsands operators and guides the current planning approach to closure in the industry.

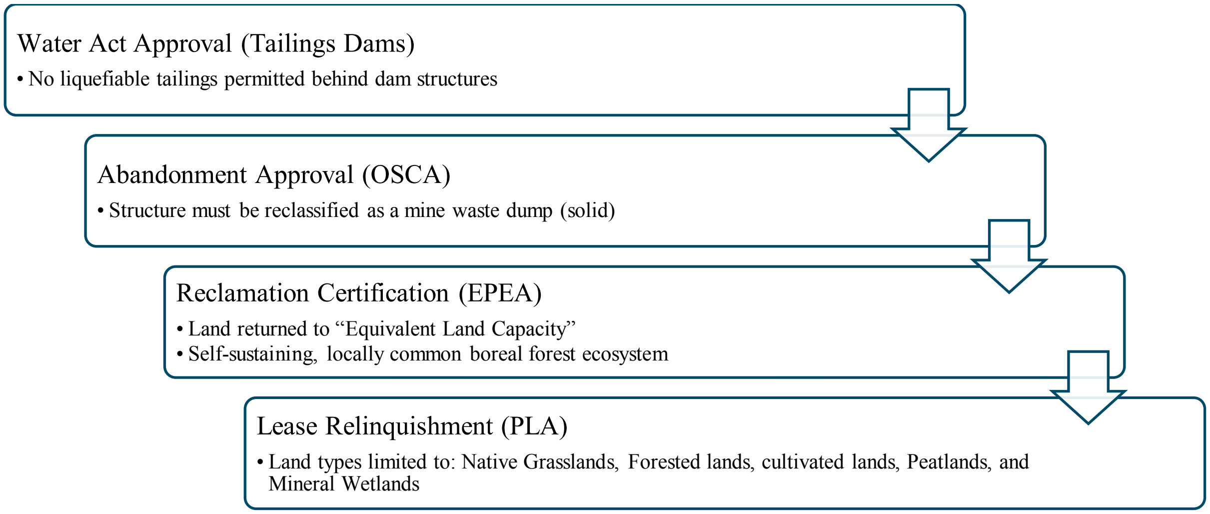

Figure 1: Regulatory overview

The first step towards relinquishment begins with the Water Act (Government of Alberta, 2020) and the updated *Manual 019 – Decommissioning, Closure, and Abandonment of Dams at Energy Projects* – published by the Alberta Energy Regulator (AER) in 2020. Manual 019 requires that a tailings dam be delicensed to meet the conditions of closure. Delicensing dam structures ties into the Canadian Dam Association (CDA) criteria identifying when a dam is no longer classified as such (CDA, 2014); that is, when there is no liquefiable material behind the dam. Allowing tailings dams to drain and consolidate naturally may take decades or centuries and could still result in quantities of material that may be considered flowable. Natural settlement of tailings within the facilities likely requires timelines that could be considered de facto long-term care, a state that is in contravention of EPEA approvals for these facilities.

Manual 019 identifies that oilsands tailings facilities are expected to be permanent structures on the landscape and must be designed to be physically stable in perpetuity. Irrespective of this design criterion, a TSF must have its contents rendered non-flowable through removal of entrained pore water to receive reclamation certification, as part of the process outlined in Figure 1. Once the water is removed and tailings material within a dam is rendered non-flowable, the structure can be classified as a solid waste structure rather than a dam as part of the Oil Sands Conservation Act (OSCA). This allows the former TSF to be reclassified and regulated as a mine waste dump.

An abandonment approval for a mine waste dump issued under OSCA is the next step in the process. The abandonment approval confirms that the structure will be geotechnically stable and will not require continued maintenance. The criteria for receiving the abandonment approval may require an indeterminate time to verify.

Application for a reclamation certification under EPEA points toward the regulatory endpoint for the leaseholder. The application can be made once the chemical, ecological, and social concerns associated with the facility are addressed. The most important aspect of reclamation certification under EPEA is the requirement to demonstrate Equivalent Land Capability (ELC). The Conservation and Reclamation (C&R) Regulation under EPEA defines ELC as the ability to support various land uses following reclamation in a fashion that is similar, but not necessarily identical, to what existed prior to mining. It is under C&R that the commonly understood objective of achieving a locally common, self-sustaining boreal forest for oilsands sites is found.

Closure incentives

The fundamental reason any mine will undertake closure activities is to reduce a liability. Oilsands operators have a legal obligation under EPEA to pursue reclamation certification. The Mine Financial Security Program (MFSP) is a financial mechanism for the AER to recover prospective costs for closure if an operator abandons the asset prior to achieving reclamation certification. Thus, an oilsands operator retains both a legal and financial liability that will induce the company to undertake closure operations.

There are four security deposits under MFSP, with the most relevant instrument being the Operating Life Deposit (OLD). Provisions for the OLD begin 15 years prior to the end of mine life (EOM) and must be fully funded based on the approved MFSP calculations with six years of reserves remaining. Legacy operators in the region are quickly approaching the point where the OLD must be fully funded to meet this commitment. Given the size of mining assets on the operator’s leases, MFSP obligations represent a non-trivial percentage of their total market capitalization. Thus, there is a strong financial incentive to undertake progressive closure operations, exactly as the policy has intended.

The Water Act

While the process to delicense a tailings dam and move towards closure of tailings structures begins with the Water Act, in fact this policy comes into play much earlier in the life on oilsands tailings dams. Under current regulatory regimes, there is a lack of defined criteria for water release in the oilsands. While the

Alberta Tier 1 Soil and Groundwater Remediation Guidelines provide well-defined metrics for release over myriad land use characterizations, the AER and Alberta Environment and Parks (AEP) have not specified release quality metrics for oilsands operators.

Much of the challenge surrounding oilsands closure relate to the requirement to store water on-site. Storage and recycling of process water in lieu of treatment and release leads to hypersalination, further exacerbating an existing environmental liability. Storage of water in TSFs increases the risk classification for tailings dams on-site.

Were water treatment completed and release allowed, the geotechnical stability and safety of these TSFs would improve dramatically, reducing the risk of catastrophic failures and the inadvertent release of tailings to the Athabasca in the exceedingly unlikely event of an embankment failure. Furthermore, many challenges related to closure arise due to storage requirements of water and the timing of reclamation. Having the option to release treated process water would set off a chain of timing events that would immediately accelerate closure timelines.

Policy solutions

The physical scale of the oilsands reflects the scale of the challenges facing the oilsands industry with respect to how water is dealt with in closure. Myriad financial, environmental, and legal issues overlap with societal expectations, investor pressure, and corporate reputation. Despite challenges in conducting closure operations, there are policy solutions with the potential to address perceived barriers to achieving closure objectives. The current regulatory regime seems to let perfect be the enemy of the good, and the following policy suggestions are offered to build momentum in the industry.

It must be noted that in proposing the following policy solutions, the intent is not to minimize objections, ignore concerns, or advocate for lower standards on behalf of oilsands operators. The attention called here is especially true for the very real and present concerns that local Indigenous communities have with respect to the environmental effect of the oilsands on downstream communities. Any changes to current regulations must be made with the free, prior, and informed consent of the Indigenous communities that will be affected. The following is simply offered for consideration by all affected stakeholders on how to progress closure in the oilsands region. The important decisions involving and made by Indigenous communities are outside the scope of this paper.

Develop performance-based criteria

The Alberta Tier 1 Soil and Groundwater Remediation Guidelines and the AEP Environmental Quality Guidelines for Alberta Surface Waters exist to protect important receptors, including aquatic life, agricultural use, and recreational use. These guidelines do not consider antecedent environmental conditions, such as the hypersaline groundwater in the Athabasca Oilsands region or the presence of petroleum hydrocarbon compounds in the Athabasca River from natural oil seeps along the banks.

If oilsands operators were permitted to release water to the Athabasca River from tailings pond supernatant, utilizing performance-based guidelines at downstream monitoring points, cumulative effects from release by multiple operators could be coordinated without negatively impacting the downstream ecosystem. However, the management of cumulative effects in this way requires a level of coordination that may not be possible, and if implemented may still require significant "guess and check" with respect to release in order to capture appropriate volumes over multiple operators.

Allow water release

While the decision on whether to release water to the Athabasca River carries with it important social implications, the technical matter of water treatment is straightforward. Water treatment and release to major receptors is a widely accepted practice in many industrial, municipal, and mining contexts worldwide. The technical ability to treat water to a level of quality such that it would meet applicable guidelines is currently available.

With influence from operators, it is possible that the case could be made to the AER and AEP that water meeting the Alberta Surface Water Quality Guidelines, or the Alberta Tier 1 Soil and Groundwater Remediation Guidelines. is acceptable for release to the Athabasca River. However, this requires a regulator and stakeholders that are amenable to allowing release under stringent release guidelines, as there has currently been no permitted release.

Consider long-term care

Much of the problem with oilsands reclamation surrounds timelines. Much of the water entrained in tailings storage facilities will naturally drain, allowing the system to consolidate, given sufficient time periods. In other words, under a long-term care scenario, closure could proceed exactly as promised. Long-term care models exist and have ample historical precedent. There are many examples of successful long-term care of closed mines in Canada, and the model could be adapted to the oilsands. While public perception may be that long-term care is synonymous with "walk away", the reality is that with a risk-based monitoring approach, long-term care is a perfectly feasible means of managing environmental liability.

A risk-based approach can be implemented to estimate the level of remediation and associated costs at oilsands sites, as well as considerations for long-term management and funding. The process for long-term care with respect to the evaluation of potential sites and planning for long-term management includes completion of a detailed site assessment and characterization, followed by a comprehensive and accurate risk analysis process. Following a risk analysis, estimation of activities and costs for remediation and long-term management are completed, based on the identified risks and objectives.

In the case of limited or incomplete data available to characterize the current site hazards and risks, a site investigation and data-acquisition program can be developed. Detailed site assessment is required to assess public safety and ecological risk to inform remediation and long-term management decisions. Once sufficient information is available to inform discussion, a comprehensive and accurate risk analysis process should be completed to determine the level of remediation required. This analysis will also be required to estimate the cost of long-term management to ensure that costs are not significantly underestimated. Conversely, there is a chance that precluding a risk assessment may result in expenditure without justification.

By adopting a risk-based long-term care model, sites can be adaptively managed while granting public access to areas where the owner still retains liability. In this way, the objectives of closure are largely retained, while not imposing onerous costs to artificially accelerate a process that is otherwise expected to take decades or centuries.

Conclusion

Investors are increasingly demanding demonstrable and measurable action on sustainability initiatives from oilsands owners. To deliver on their sustainability commitments, oilsands companies must manage liabilities, thus ensuring there is a steady return on capital. The primary liability facing oilsands owners is in closure, specifically the enormous volumes of water entrained in tailings facilities, and the associated reclamation costs. Thus, it is a financial, legal, and reputational imperative for oilsands operators to expeditiously advance closure.

Despite the importance of advancing closure, there are regulatory challenges that make the process less than straightforward. While a pathway exists on paper, that path to closure has not been tested on a large scale in the oilsands. The untested process is especially true for tailings storage facilities. Thus, the regulatory outcome for closure may not be exactly as once envisioned and communicated to stakeholders.

The widely communicated closure goal of returning the oilsands region to a locally common, self-sustaining boreal forest ecosystem may be both difficult to achieve, and no longer the optimal outcome. Fortunately, alternative closure end states exist, and have historical precedent. Allowing alternative end land uses, permitting water release, applying an institutional control program, and facilitating long-term care are all examples of how closure objectives can be satisfied within realistic timeframes. By exploring and implementing realistic alternatives, the oilsands industry can be a major player in facilitating a sustainable transition following the end of operations.

Market Viable Products from Mine Tailings

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Abstract

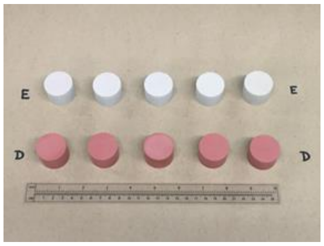
Market Viable Products (MVP) will reduce the volume of mine tailings left behind as a waste after copper is extracted from ore. The tailings are initially in the form of slurry, along with mine waters at 50% composition by mass. The slurry is deposited at the mine tailing's impoundment, and the water is decanted in a pond and reused within the mining process. Utilizing MVPs to reduce the tailing's impoundment could present a solution for lifecycle operation with potential environmental, social, and economic impacts. Multiple MVPs may need to be considered to consume the large volumes of tailings stored in the impoundments.

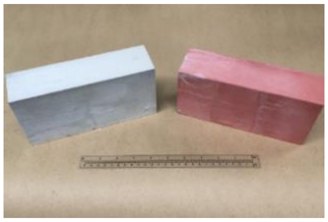
This paper summarizes studies conducted with Freeport-McMoRan Inc. (Freeport) mine tailings over the last fifteen years. The studies were conducted in collaboration with technology partners, and also used internal resources. Some of the studies listed here are in the proof-of-concept stage, while others are completed. The primary goal of these studies was to evaluate the feasibility of making MVP from mine tailings. The products evaluated included bricks, formed products, fiberglass, glass, acid-resistant concrete, aggregate media, ceramic tile, and insulation/coatings materials. The focus for each product is on markets and competition, customer demand, unit cost, percent of tailings utilized within the product, capital/operational cost, and carbon footprint. The goal is to have a clear understanding of the end applications and the pro and cons associated with each product. At the end of the study, all products will be ranked in terms of potential and suggested future implementation to reduce tailings inventories and associated liabilities. Each mine site has deposited tailings that could be utilized for MVP, if successful.

Formed products

Sixty tons of tailings from the Sierrita mine were used to produce a large batch of bricks in Germany. The bricks were steam cured with sand-lime composition. Four different element sizes were produced. Efflorescence of alkali salts was observed on some of the brick surfaces. Additional measures might be required such as coatings, plasters, and paints if the bricks are exposed to contact with water. The bricks were excellent for noise and heat insulation. In addition, the unit cost of manufacturing the bricks was competitive with clay bricks and cinder bricks. These Sierrita bricks are used at the Freeport corporate office as a decorative material in elevator banks. Picture of the bricks are shown on the right.

Brixx





The Brixx study was conducted with Pittsburgh Minerals and Environmental Technology (PMET) as a technology partner. Tailings material from the Sierrita, Henderson, Climax, and Grasberg mines were used at different times over the last fifteen years. A small batch demonstration project produced bricks in various colours. PMET patent technology was used to convert the tailings into bricks. In general, the process was comprised of two phases.

In Phase I, tailings characterization and small-scale sample prep took place. The small samples consisted of mixing lime, water, and tailings to uniform slurry and then pressing the mixture to form shapes at forming pressures of 5,000 psi, 7,500 psi and 10,000 psi. The shape was then cured in an autoclave for six to eight hours with saturated steam.

Full scale products were made in Phase II. The produced formed product met the ASTM C-73 standards for severe application. It also passed the analysis of the Toxicity Characteristics Leaching Procedure (TCLP) for leaching of RCRA metals. Some of the parameters evaluated in the study were: tailings mineralogy; matrix of various mixes; mechanical properties; water absorption; TCLP analysis; and financial evaluation for full-scale production.

The operating cost of production was favourable. Capital cost was not estimated. Approximately 7 pounds of tailings will be consumed for each brick produced.

Geopolymer

A study was conducted in 2013 with The University of Arizona, Civil Engineering Department as technology partner. Freeport tailings from the Sierrita mine were provided for the proof-of-concept phase. Batch-scale tests were conducted to produce formed product based on geopolymerization. In addition, aluminium sludge was also provided from the mine site and added to adjust Si/Al and Na/Al ratios and enhance the geopolymerization process. Aluminium sludge was produced in a High Density Sludge (HDS) water treatment process evaluation as part of the mine closure study. A matrix using different compositions was used to achieve the optimum mixture. The effects of different factors including activator concentration, water/solid ratio, and curing time and temperature on compressive strength, water absorption, durability (freeze/thaw), and environmental feasibility were studied. The product passed a TCLP analysis as part of the environmental evaluation.

Batch-scale tests produced 30 bricks that met the American Society for Testing and Materials (ASTM) standards. Moreover, commercial evaluation for six million bricks per year plant production was conducted with total capital and operating cost of $2.66 million. The sales price per brick was $0.50 and was competitive with other formed products during the 2013 evaluation.

Acid-resistant concrete

This study is in the proof-of-concept phase with The University of Arizona, Civil Engineering Department as technology partner. The objective is to develop a method for producing acid-resistant concrete from mine tailings and aluminium sludge by using the innovative geopolymerization technology. Different solutions will be used as the activator under different conditions. A matrix using various parameters will be developed to outline the optimum mixture. After the “recipe” is developed, technical and economic analyses will be performed for the MVP.

Insulation/fillers

This study is to be conducted with the Arizona State University (ASU) as Freeport’s technology partner; specifically, the Center for Bio-mediated and Bio-inspired Geotechnics (CBBG). A series of laboratory-scale tests will be conducted to evaluate the potential for combinations of mine tailings and binder-forming additives selected by CBBG to achieve desirable fresh and hardened properties of cementitious materials.

The materials will be used in applications including coatings or sprays, grouts, and “just-add-water” products. The objective is to maximize the percentage of tailings used in the product. Specific properties will be evaluated for coatings and sprays, as well as grouts/mortars. A matrix will be developed with additives at different percentages to achieve the desired properties. In addition, field-scale tests will be developed, as well as verification/validation studies for materials belonging to the coatings and grout/mortar classes. Tailings from two different mine sites were initially screened for the study and deemed feasible.

Ceramic tiles

A series of testwork will be conducted by our technology partner, IntoCeramics, to produce ceramic tiles from tailings. This will be a proof-of-concept study using Freeport mine tailings, but the technology is somewhat established with a variety of waste products having been used as feed source by IntoCeramics in the past. The feed material will be evaluated to determine the process characteristics. The next step will focus on forming five 4 inch × 4 inch ceramic tiles. Other raw materials will be added to achieve the desired characteristics. The sample will then go through a series of processing steps such as heating, cooling, and annealing, as deemed necessary. The physical properties of the ceramic tiles will be tested for strength-Modulus of Rupture (MOR), water absorption, and TCLP leaching for the RCRA 8 metals. Other shapes and products could be considered, if feasible.

Fiberglass

The scope of this study is to produce fiberglass from tailings and is to be conducted by Nomad Fabrication LLC under a non-disclosure agreement. In phase one, the study will focus on the proof-of-concept where glasses will be produced from silicas and alumina, directly as fiberglass alternatives or composited with cured resins. This phase will capture tailings characterization, thermal evaluation, formulation of the "recipe," and the business case for the specific recipe. This would be considered the base case.

If successful, a bench -op test and full-scale plant production will follow. The concept is to grade the end-result glass filaments and introduce these to commercial supply chains, as well as to investigate premise-fabrication to manufacture roving, matting, or chopped products. The study will evaluate a matrix to be used in creating the "recipe" with a wider spectrum of commercial applications. The "recipe" will be tested in its flexibility for production of MVPs, with some products reaching the mass consumer but others having specialty applications.

The goal is to determine the limiting ingredients and their cut-off range for MVP production. At present, the study is being conducted at an external facility, with the option to be moved in-house.

Glass

The goal of this study is to make glass from tailings. The scope of work is being formulated for proof-of-concept. The process flow diagram is in development and is being evaluated in-house with major process steps including melting, spinning, shaping, cooling, testing, and packing. A wide range of MVPs could be made based on the specifications and end applications. The tailings sample used for the study was from the Henderson mine and contained 58% quartz (SiO_2).

Eight grades with commercially available glass fibres are available, ranging from 52% to 75% quartz. Each grade corresponds to a different application, with the most widely used type having 63% to 72% quartz (Type-A). Other grades such as S grade and AR glass will have a higher market price, but must have 0 to 18% of zirconium dioxide (ZrO_2). Recycled glass, such as cullet, can be used to enhance the quartz percentage in the feed. Other ingredients are required to change the physical, chemical, and mechanical properties of the final product for specific applications. Due to the COVID-19 pandemic, the current glass production has decreased, but it is expected to reach over $150 billion in 2024.

Sandblasting media

This study is being conducted by US Minerals, and it is in the initial screening phase of characterization of physical properties. The goal is to use tailings material as feed to produce aggregate blasting media. Tailings from two different mine sites were provided for the evaluation, and the results are pending. Potential end applications for the media are in steel fabrication, offshore oil drilling, blasting, painting contractors, ship building and repair, petrochemical, and refining contractors. At present, US Minerals is producing a variety of grades and aggregate materials as coal slag, iron silicate (copper slag), and specialty abrasives.

If the MVPs are successful, the value addition will have a major economic, social, and environmental impact, not just for Freeport-McMoRan but for the global mining industry as well. This “cradle to grave” approach will drive the leading edge of innovation and positive global prospective for the mining industry.

Quantifying Flood-Induced Risk to Tailings Embankment Stability: Avoiding the Alarmist Model

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Abstract

A 60-year-old closed tailings storage facility (TSF) in a semi-arid climate was re-evaluated for embankment slope stability. The TSF has not completely drained down, and contains perched saturation of a low-lying area of the pre-TSF topography, which may impact slope stability. Compounding the problem is the formation of a large lake at the beach of the TSF following flood events, and occasional flooding of a creek near the toe of the TSF embankment. These flooding events lead to temporary recharge of the aquifer beneath the TSF and potential rise of the water table to the bottom of the TSF.

The geotechnical design of buttress support for the TSF by another consultant assumed a worst-case scenario of a 20-foot rise in water levels within the TSF near the embankment, an assumption that was challenged by the TSF owners. In addition, fluxes that needed to be accommodated by buttress underdrains were uncertain. However, it was difficult to objectively come up with a reasonably conservative model to guide the design, as opposed to an unrealistically conservative model that would suggest the need for further buttress reinforcement and investment based on an unlikely scenario.

To aid in this decision, SRK constructed a cross-sectional model of the TSF and underlying aquifer, deliberately designed to be a light-weight model that would accommodate uncertainty analysis. The model was run thousands of times in order to explore a wide range of hydraulic parameter values. Acknowledging that a model is not an exact replica of reality, each model run was ranked based on its ability to match historical data (previous flooding events), thus allowing the modellers to constrain the range of reasonable hydraulic parameter values. Then, the model was run again multiple times in predictive mode, this time adding duration of flooding events to the parameter space. The probability of future flood events to cause a water level rise of 20 ft was then explored in the context of the best-performing models in terms of historical matching, as opposed to an arbitrary assumption of a “worst case” around a single “calibrated” model. Considering parameter configurations that reasonably matched historical data, only one predictive

scenario resulted in exceedance of the threshold 20 ft water level rise. Under the predictive model assumptions, buttress underdrain fluxes of up to 800 gpm were calculated.

Introduction

The structural stability of tailings storage facilities (TSFs) – or lack thereof – has been of concern for decades (e.g., Rico et al, 2008). TSF dam failures have been increasing in recent years (Islam and Murakami, 2021). This paper focuses on an inactive TSF in the semi-arid southwest of the United States. A seasonal lake forms on top of the TSF following intense storm events, which in turn recharges groundwater below the tailings, and to a lesser extent the TSF itself. Such recharge events cause groundwater levels to temporarily rise below the TSF.

Unrelated to the seasonal lake, a consulting company was retained by the TSF owners to design a buttress to support the TSF embankment, which was originally built using the upstream construction method with an overall embankment slope of approximately 2H:1V. One of the buttress design assumptions was the ability of the buttress to withstand pore pressure increases below the embankment crest of up to 20 feet. Pore pressure increases were envisioned as resulting either from rising groundwater levels to the bottom of the TSF, or from increased saturation within the TSF. SRK Consulting, Inc. (SRK) was asked to provide hydrological analysis to test the adequacy of the pressure increase assumption.

This paper presents the methodology, assumptions, and development of a groundwater model to test hydrological conditions at the TSF. The modelling work was done in three stages:

1. Construction and calibration of a deterministic-calibrated 2D model.
2. Exploration of model parameter space using a stochastic Monte Carlo approach.
3. Execution of stochastic predictive simulations, making use of a subset of the models from the previous step that produced reasonable calibration to available data.

Site description

The TSF was built in the late 1920s and filled with tailings slurry over the course of approximately 30 years. Despite the TSF being inactive during the past 60 years, routine and high-resolution water level monitoring have only begun in the past several years. The hydrological and hydrogeological conditions described in the following subsections are therefore largely derived from these observations.

Hydrological conditions

Two major dry watersheds upstream of the TSF have a combined drainage area of 7.4 square miles and produce significant runoff only during large storm events. These runoff events result in the formation of a temporary lake on top of the tailings. The extent and height of the lake are controlled by a spillway, which would discharge excess water to a dry gulch downstream of the TSF. The seasonal lake water is not otherwise actively managed (i.e., lake water is not removed by pumping). The maximum possible footprint of the temporary lake is shown in Figure 1.

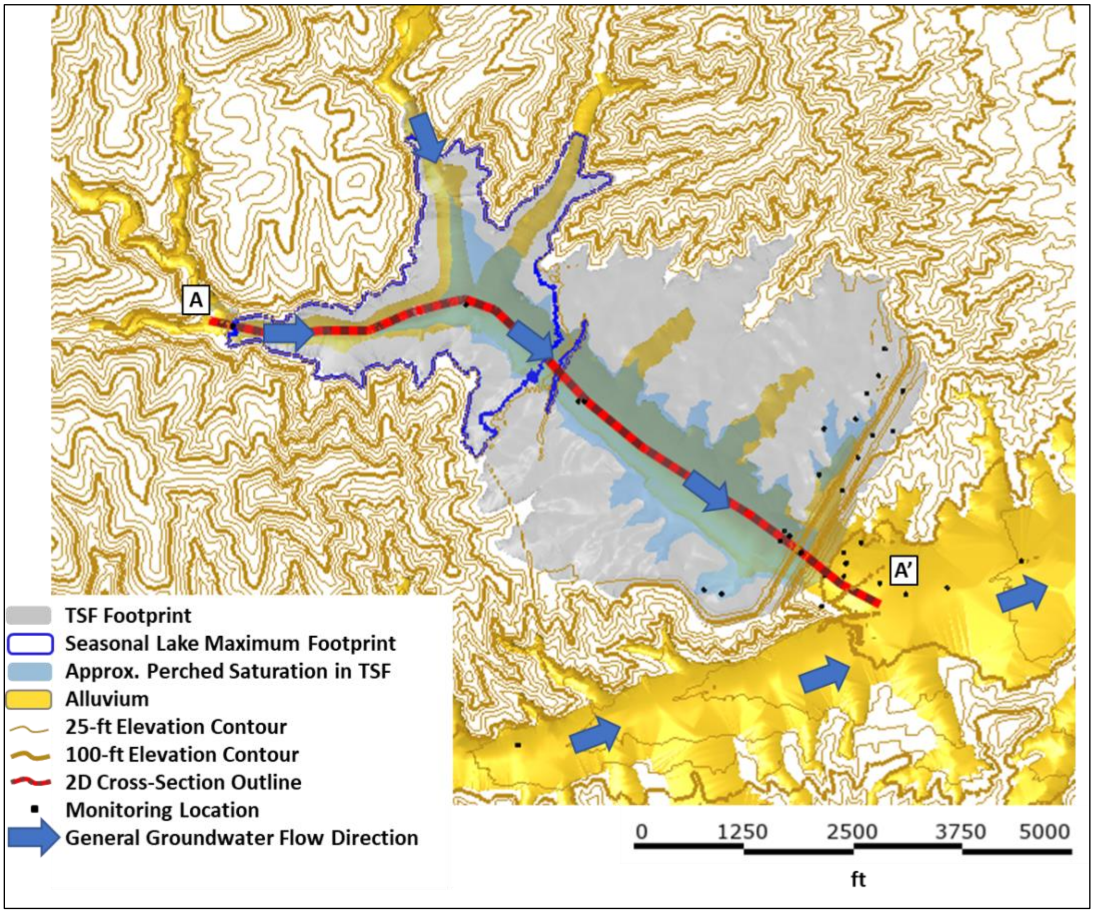

Figure 1: Site layout

Figure 2 presents the lake elevation record for the period of 2017 to 2021. This record was constructed from direct measurements and processing of satellite imagery. Figure 2 also shows the storm event precipitation record for the vicinity of the TSF. Storm events that resulted in floods that led to formation or expansion of the lake are highlighted. Overall, four distinct flooding events were observed between 2017 and the middle of 2021. Analysis of historical satellite data dating back to 1984 (not shown) revealed that repeating flood events in consecutive years, leading to the formation of the lake, are not uncommon. However, flooding did not occur between 2010 and 2017.

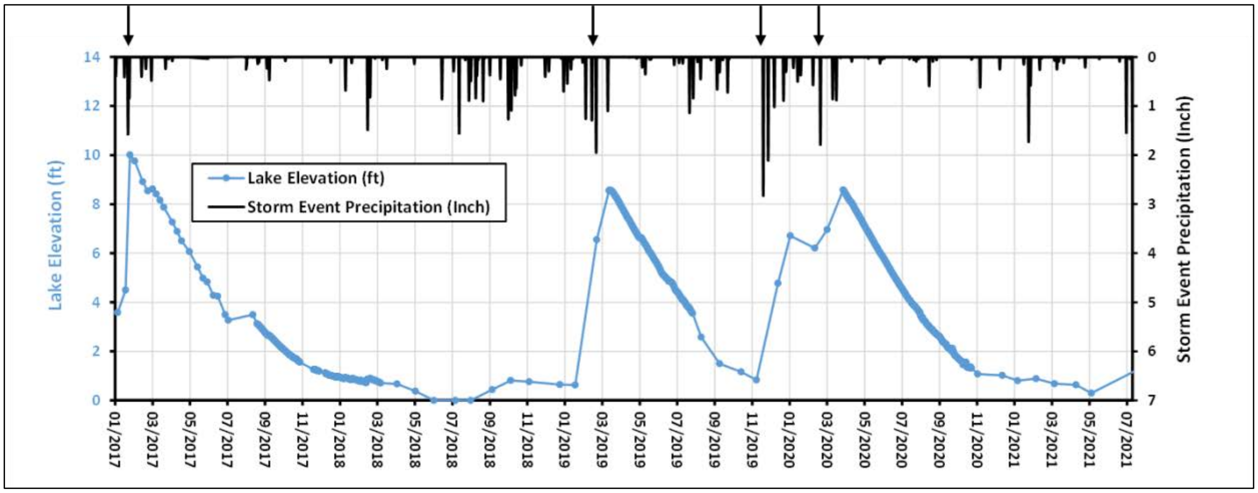

Figure 2: Lake elevations and storm precipitation events (arrows point to storm events that resulted in flooding events)

Hydrogeological conditions

The TSF was constructed primarily over Cenozoic-age, cemented conglomerate, and partially over recent, unconsolidated alluvium filling topographic lows (Figure 3). The alluvium thickness ranges from 0 to 80 ft below the TSF and is up to 100 ft thick downgradient of it (Figure 3). Cone penetration tests revealed that the contact between the TSF and the underlying alluvium tends to have a higher degree of fine particle size. Direct observations from sonic drilling cores have shown that this contact has a distinct black colour, likely due to mineral precipitation of manganese oxides.

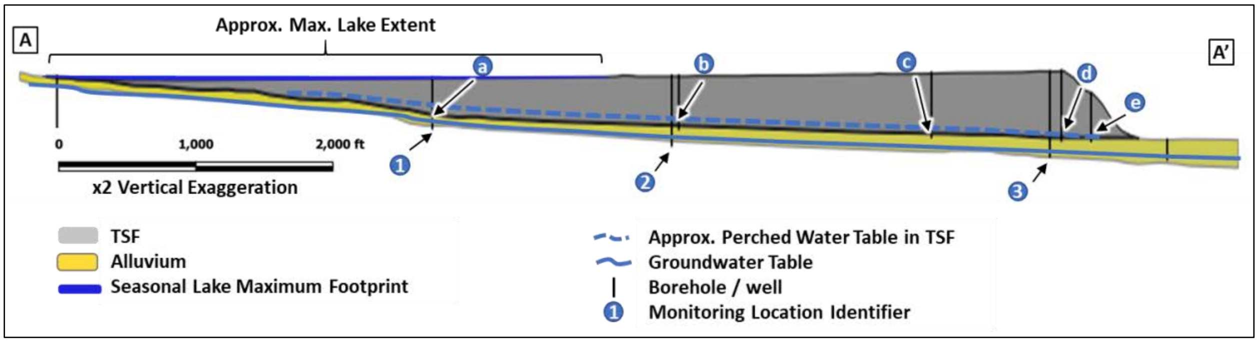

Figure 3: TSF cross-section

A perched water table exists within the TSF (see Figure 1 for plan view, Figure 3 for cross-section) with saturated thickness of up to 30 ft. The perched water levels are declining (draining down) at rates ranging from 0.2 to 0.4 ft/ year (Figure 4). One monitoring location within the lake footprint (labelled "a" in Figure 3 and Figure 4), has shown a steady increase in water levels since 2018, on the order of 3.5 ft, likely a delayed and subdued response to the repeating flood events described earlier. The remaining perched-saturation monitoring locations within the tailings show no response to flooding or storm events.

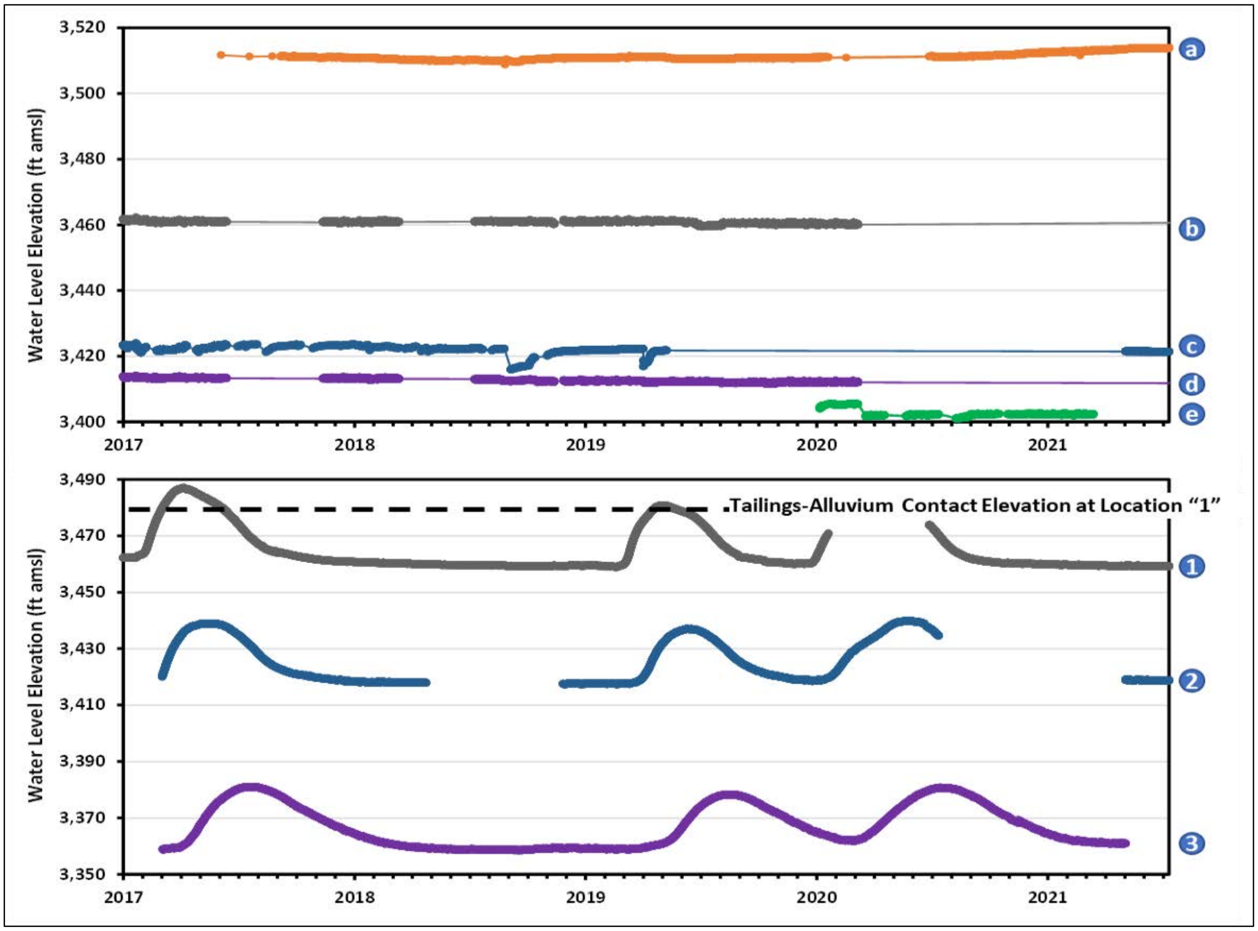

Figure 4: Measured perched water levels in the TSF (upper plot) and groundwater levels (lower plot) (see Figure 3 for location identifiers)

Under base flow conditions, the groundwater table is found 20 to 40 ft below the bottom of the TSF, the latter value representing conditions near the TSF embankment. Following flood events, the water table in the alluvium mounds below the TSF. A mounding wave with an amplitude of approximately 25 ft propagates from the upgradient portion of the TSF, in the alluvium along the axis of the pre-TSF natural channel towards the embankment (Figure 4).

Model construction and calibration

Simulations of the hydrological system's response to hydraulic stresses – both past and predictive – were carried out using the finite-element code FEFLOW (DHI, Version 7.4). The two-dimensional (2D) model domain followed the cross-sectional path A- A' shown in Figure 1. Richard's equation for unsaturated water flow (Richards, 1931), in tandem with the modified van Genuchten retention curve model (Schaap and Van Genuchten, 2006), were used to accurately simulate saturation and de-saturation of the various hydrogeological units during and after flood events, respectfully.

Simulated hydrogeologic units

The model initially included the three major hydrogeological units discussed earlier: the TSF as a single hydrogeological unit, the alluvium, and the cemented conglomerate. However, during model calibration it became apparent that additional sub-units were required to allow reasonable reproduction of measured water level data (Figure 5). These sub-units included :

- A low-permeability, 5-foot-thick layer at the interface between the TSF and the underlying alluvium.
- A wedge-shaped zone carved out of the upgradient, thinned portion of the tailings, representing recent flood sediments at the lake-alluvium contact.
- A near-surface sub-unit within the lake footprint over the TSF, representing a playa-type hard-pan ("crust") observed at the surface.
- The alluvial unit was subdivided into two sub-units, upstream and downstream, to allow flexibility in modeling calibration and account for potential facies change.

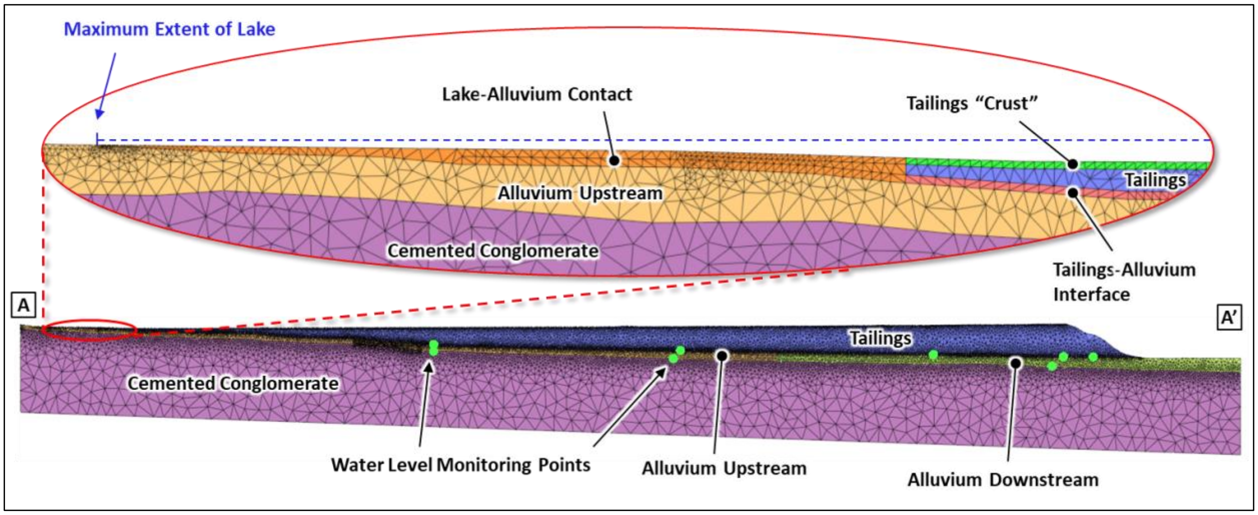

Figure 5: FEFLOW 2D model domain

Simulated boundary conditions

The contribution of the lake to recharge at the top of the model domain was simulated as a time-varying head boundary condition, corresponding to measured lake elevations. Constant-head boundary conditions were used at the upgradient and downgradient nodes to emulate baseline groundwater levels.

Deterministic model calibration results

Model calibration to observed water levels was done manually initially, and then automatically using PEST (Doherty, 2015). Plots of observed and simulated water levels in the TSF and in groundwater are provided in Figure 6.

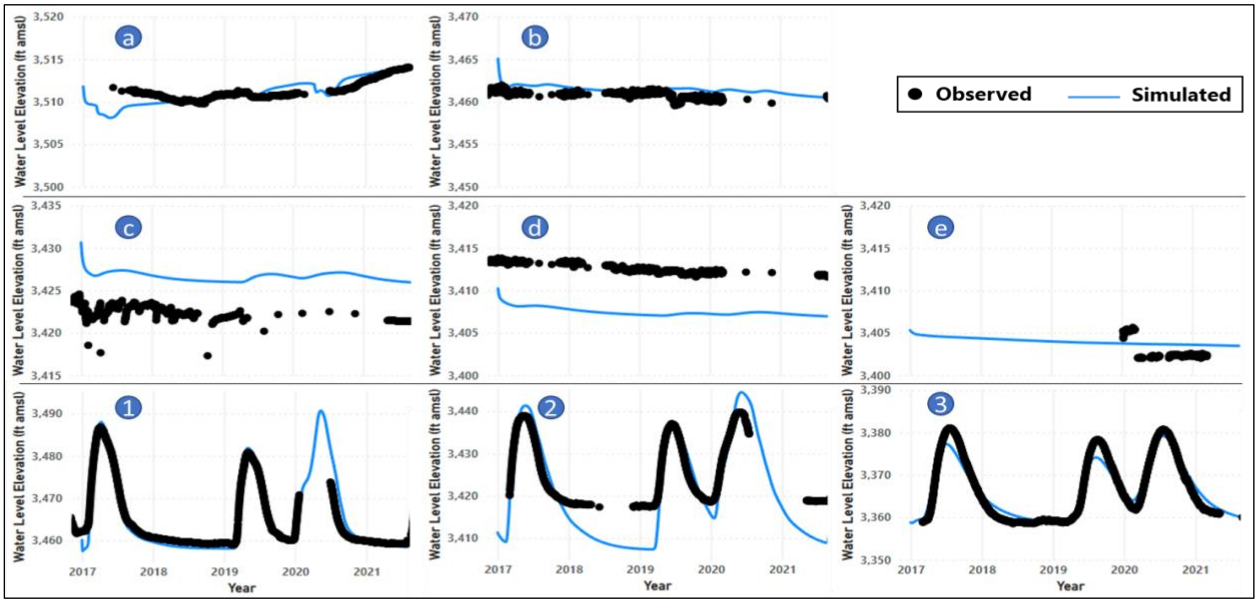

Figure 6: Observed and calibrated water levels in the deterministic model (see Figure 3 for monitoring location identification)

Overall, the deterministic 2D model reasonably reproduced observed water levels within the tailings and in the groundwater system. Key measures of adequate calibration were reproduction of the muted response of lake flooding onto location “a”, which is located within the footprint of the lake, and reproduction of the mounding amplitude and arrival time in location “3”, which is located below the embankment.

Monte-Carlo simulations

While the deterministic model proved useful, it was acknowledged that various hydraulic parameter combinations could result in similarly well-calibrated models, particularly given the inherent non-linearity of unsaturated flow equations used. Moreover, the main objective of the modelling work was to generate predictions of system behaviour to future hydraulic stresses, to guide TSF buttress construction. The complex influence of various model parameters on model results meant that it was difficult to tease a **reasonable** “worst case” of parameter value combination. *In other words, one could parameterize a model so that prediction outcomes would suggest a worrisome or even catastrophic outcome, yet this prediction would be considered overly-conservative, to the point of unrealistic. Such an ill-constrained prediction could result in unnecessary allocation of resources to address a problem that is unlikely to exist.* For these reasons, a stochastic Monte Carlo approach was taken.

The Monte Carlo method is decades old (Metropolis and Ulam, 1949), but often proves too costly or time consuming to be applied to complex numerical groundwater models. The computational demand was a key consideration in the construction of a relatively simple 2D model. It was better to have a simple model that could be explored for its “incorrectness”, than a complex model that would not necessarily provide more information due to a lack of real-world data. The 2D model was run multiple times to create unique model realizations, where in each realization a random value was assigned to hydraulic parameters within constraints that were in line with the conceptual site model. Then, only hydraulic parameter value combinations that resulted in a reasonable reproduction of historical water level data were considered in the predictive simulations.

We acknowledge the problematic subjectivity of the term “reasonable” in this context; however, the perception and acceptance of risk is also subjective. The methodology described here allowed us to convey model results to the TSF owners in terms of standard goodness-of-fit statistical measures, and in turn allowed the owners to accept or reject a certain level or risk associated with the predictive simulations.

Monte Carlo methodology

The Monte Carlo simulations were done in two stages, a “pre-calibration” stage and a “prediction” stage. Initial conditions, boundary conditions, and simulation time of the pre-calibration stochastic simulations were similar to those of the deterministic calibration model. Overall, 14,984 simulations, with randomly-generated hydraulic parameter values, were executed, and the assigned values were recorded. Given limited field data for the various parameters, a uniform distribution of parameter space was used for random sampling. To ease the computational burden, the 10 least-sensitive parameters – as calculated by PEST during the deterministic calibration – were excluded from perturbation and their values held constant from the deterministic calibrated model.

The results of the pre-calibration simulations were compiled, and goodness-of-fit statistics were calculated for each model realization. Due to the greater interest in the behaviour of the groundwater system below the TSF embankment and the immediate effect of the seasonal lake on recharge to the TSF, greater weight was assigned to groundwater level observations there (Locations “a” and “3” in Figure 3). A common calibration metric of normalized root mean square error (NRMSE) was used as the measure of goodness-of-fit. All model executions and post-processing were done via python scripts.

The predictive simulations used the same model domain design and hydrogeological units as the pre-calibration simulations, but with a few modifications to boundary conditions (Figure 7):

- The alluvial aquifer downgradient of the TSF was conservatively assumed to be saturated up to the ground surface, controlled by a constant-head downgradient boundary condition. This assumption was analogous to a series of wet years recharging the alluvial aquifer downgradient of the TSF to the fullest, a phenomenon observed in historical data, although typically short term.

- A seepage face boundary condition was applied to the face of the embankment and along the ground surface below the eventual footprint of the buttress. The seepage face boundary was analogous to the presence of a planned drainage system below the proposed buttress.
- The seasonal lake was assumed to be at maximum capacity for a duration of one year. This conservative hydraulic stress was analogous to a potential series of flood events.

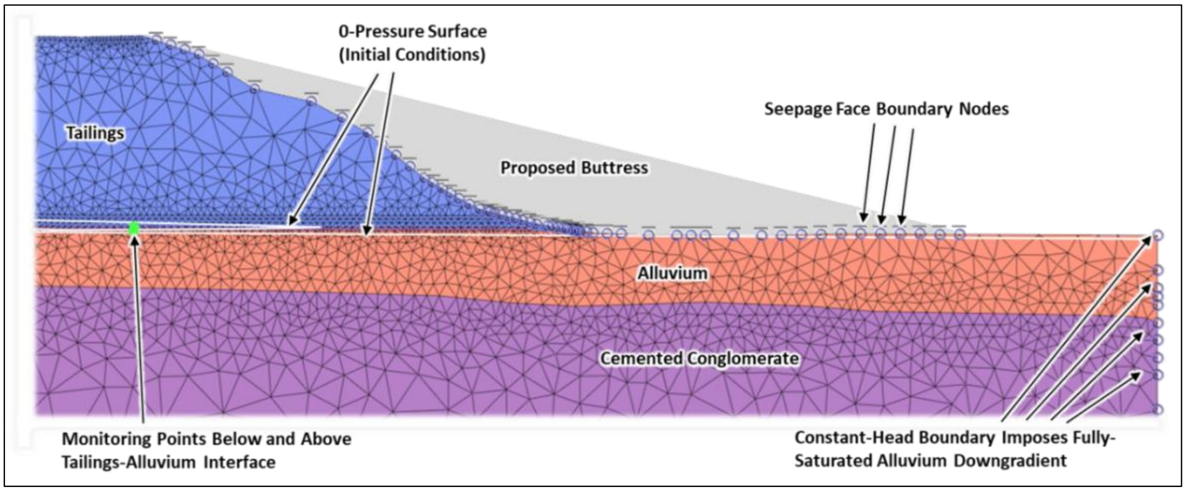

Figure 7: Initial and boundary conditions for the predictive Monte Carlo simulations (the proposed buttress was not simulated)

The predictive simulations were run for a duration of 10 years. Hypothetical observation points were added below the crest of the embankment (Figure 7), at the contact between the tailings and the alluvium and 5 ft above this contact (i.e., below and above the low-conductivity layer that is present between the tailings and the alluvium).

Monte Carlo simulation results

The pre-calibration Monte Carlo simulation were classified based on goodness-of-fit to observed water level data. Ensembles of Monte Carlo pre-calibration simulations that resulted in NRSME of 0 to 5% are presented in Figure 8. Of the 14,984 simulations, 214 unique parameter value combinations satisfied this metric. For demonstrative purposes, simulated water levels at location "a" within the 0-5% NRMSE range are compared to simulations with higher calculated NRSME for location "a" are presented in Figure 9.

Predicted water levels below and above the Tailings-Alluvium Interface, for the parameter value combinations that resulted in NRSME of 0-5%, are presented in Figure 10A. The maximum pressure increase at the bottom of the TSF embankment in the selected 319 simulations was 21 ft, in one scenario. Simulated fluxes across the seepage face that correspond to the planned under-buttress drains were converted from 2D to 3D volumetric fluxes by multiplying by an approximate alluvial channel width of 700 ft. These fluxes are presented in Figure 10B. The maximum calculated peak seepage rate was 820 gpm.

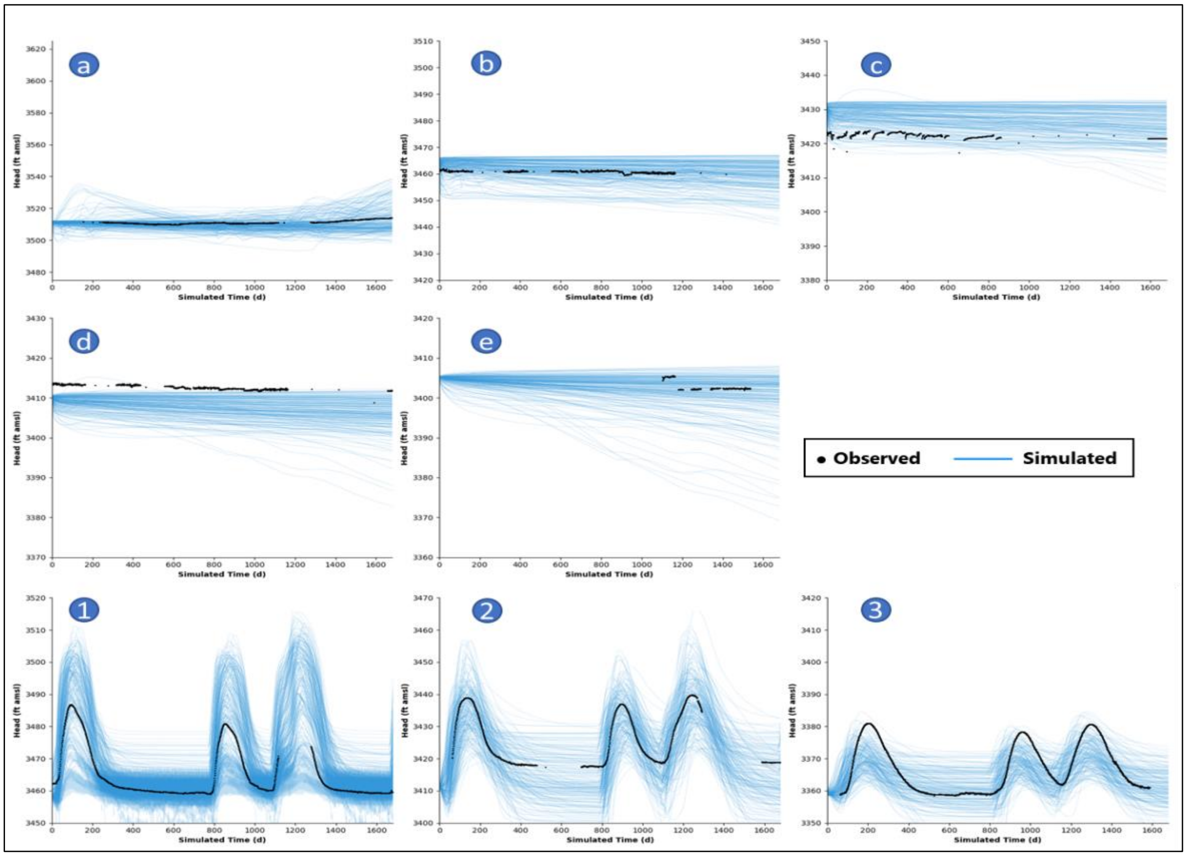

Figure 8: Monte Carlo water level ensemble of simulations with NRMSE of 0-5% (see Figure 3 for monitoring location identification)

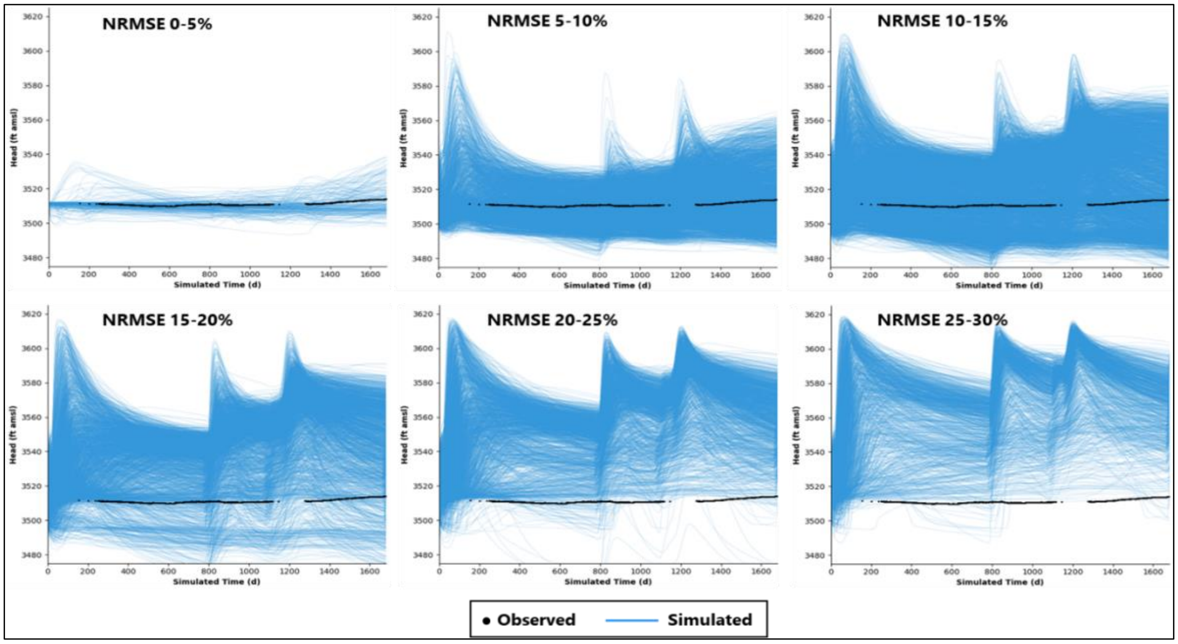

Figure 9: Comparison of pre-calibration Monte Carlo water level results for simulations with varying NRMSE values, monitoring location "a"

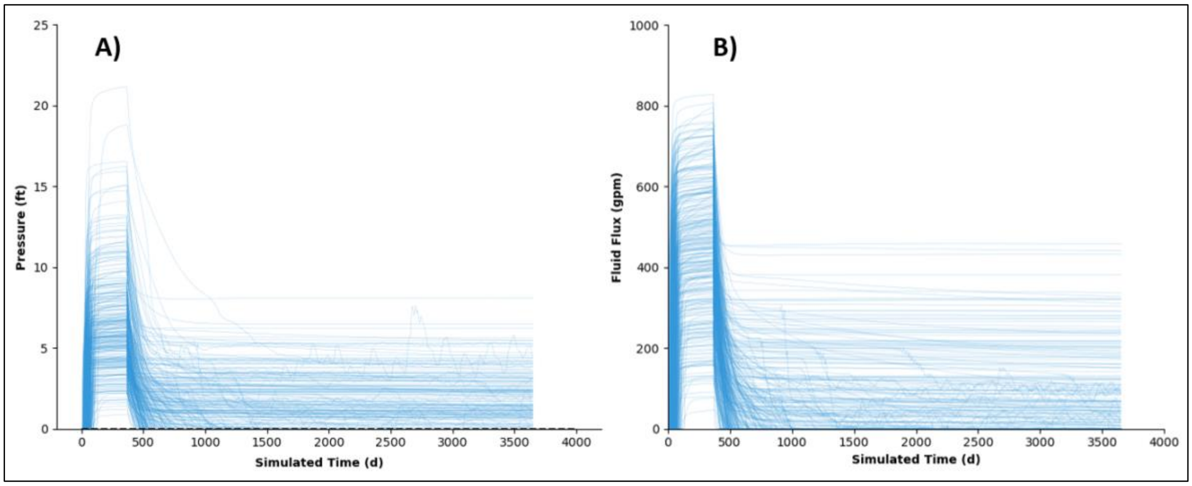

Figure 10: Results of the predictive Monte Carlo simulations (A) pressure increases below the embankment, B) volumetric fluxes reporting to the buttress underdrains)

Conclusion

A 2D groundwater model was constructed to represent and predict responses to hydraulic stresses at an inactive TSF, in support of the construction of a buttress intended to reinforce the embankment of the aging TSF. The main objective of the modelling work was two-fold: to predict pressure response below the existing embankment to a future flooding event, and to estimate peak fluxes of excess water to under-buttress drains in aid of drain design.

In this paper, we presented a methodology that incorporates several stages of numerical modelling:

- Deterministic model calibration to past observations. This step aided in establishing and refining a conceptual model for the site. The calibrated deterministic model was designed to be a rather simple, yet robust, model that would support stochastic modeling of the system in terms of run times.
- Stochastic pre-calibration Monte Carlo simulations. These Monte Carlo simulations explored deviations in hydraulic parameter values from those inferred by the deterministic calibration. An ensemble of model realizations that reasonably matched historical water level data was then re-used for predictive simulations.
- Stochastic predictive Monte Carlo simulations. The predictive models considered a single predictive scenario of flooding under conservative boundary condition assumptions. A subset of these predictive simulations, which implemented the same combinations of hydraulic parameter values as the best-calibrated pre-calibration runs, was considered for predictive analysis.

The methodology described above rules out a single model as a “best-calibrated model” that is then re-used to generate a single prediction. It embraces the notion that a model is an imperfect representation of reality, and that a single calibrated model hides biases resulting from a modeler's subjective decisions. Stochastic modelling enables exploration of multiple combinations of hydraulic parameter values that may result in multiple statistically similar acceptable models. Acceptance of a range of models for generation of predictions, which are guided by goodness-of-fit to historical data, constrains results of predictive models by eliminating models that are unlikely to be a reasonable representation of reality.

In this paper, a NRMSE statistic with a value range of 0 to 5% was discussed as an acceptable goodness-of-fit measure. The authors do not suggest that this NRMSE range, or even NRMSE itself as a statistical measure, are always adequate. Rather, it is expected for these statistical measures to be project-specific, debated, and accepted by various stakeholders. The perception of risk is a human trait, and we are guided by appetite to embrace risk or to discount it. However, the methodology described here sets the stage for debate, and in the authors' view allows stakeholders to be better informed of the risk they are willing to accept.

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Towards Autonomous Tailings and Pit Lake Monitoring with Amphibious Robots

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Abstract

Unmanned amphibious robots are being used for environmental monitoring of difficult conditions such as tailings deposits. The challenges of accessing difficult environments range from potentially unstable tailings beaches to shallow water deposits with obstacles, and navigating in these difficult conditions has been mitigated by using a screw-drive propulsion system. Amphibious screw-drive robots have been instrumented to operate either by remote control or autonomously. Current robotic work in tailings impoundments includes deployment of standard geotechnical equipment, such as cone penetrometers and vane shear tools to measure the shear strength of soft tailings, surface and subsurface sampling, installation of equipment and sensors, and deployment of ground penetrating radar and sonar systems. This paper first reviews the state-of-the-art robots for tailings monitoring, then discusses the gaps and challenges for full autonomy of tailings monitoring, provides the requirements for a completely autonomous system working on tailings ponds, and presents advances in the design of amphibious robots that can conduct autonomous bathymetry surveys and collect material samples. Bathymetry surveys are necessary to determine the sludge and water volume contained in ponds and to identify subsurface structures. Material samples are used to validate the measured mudline and pond bottom, study water chemistry, solids content, particle size distribution, and composition. Other sensors can be deployed to measure other water parameters in-situ such as dissolved oxygen. Different models of amphibious robots are described. A HELIX 25 robot was used to navigate a water capped deposit autonomously using RTK-GPS and on-board sensors. Bathymetric data was collected using a dual frequency transducer at 33 kHz and 200 kHz and shallow areas were investigated with a novel mechanical system, MANTA, for continuous measurement of shallow depths. A HELIX AR2 robot collected a range of samples at a distance over 2 km from the shore staging area. A HELIX Neptune rover was used to deploy in-situ instruments in inaccessible pit lakes and tailings storage facilities. The advantages over manual surveying and sampling are presented, including reduced cost and risk to human workers. Also, future opportunities for deploying robots in tailings are discussed.

Introduction

Autonomous robotic systems are playing a key role in the areas of environmental monitoring and site investigations. Autonomous robots are machines that can operate in dynamic environments, performing complex tasks and actions that take into account the results of previous operations, external inputs, and observations of their state and environment. Rather than having a single purpose or a predetermined range of activities such as traditional machines, autonomous systems adjust their actions and behaviours to the condition of their environment and their perception of their surroundings. Advances in on-board sensors, control systems, estimation methods, and artificial intelligence (AI), have enabled the development of very complex operations such as autonomous driving, autopilot systems, and autonomous exploration. (Green, 2012).

Autonomous systems are being integrated into every industry, including healthcare, defense, aerospace, transportation, and mining. The recent push of autonomous haul trucks has made the concept of autonomy familiar to the mining industry, with overall positive results. There are innumerable opportunities for research in the area of autonomous systems, such as interactions with humans, robustness to all extreme weather conditions, reliability of sensors and control methods, planning and perception algorithms, state estimation, visual navigation, machine learning, etc. These technologies allow autonomous robots to operate with different degrees of autonomy and make informed decisions quickly, efficiently, and with a high degree of accuracy in highly dynamic environments.

The key advantage of robotic systems is the ability to go places where people cannot. Robots can access areas that are too risky or costly for humans and human-crewed equipment, and perform complex tasks. The most extreme example is space exploration, where robots have been crucial to explore the surface of Mars (Knuth et al., 2012). On Earth, robots have been used to investigate areas that are too dangerous for people such as collapsed mines, caves, nuclear reactors, toxic sites, mine sites, etc. (Tsitsimpelis et al., 2019). Robots are typically instrumented with on-board sensors and payloads that have resulted in an unprecedented amount of collected data in harsh environments. These large datasets can be used to continuously improve the intelligence of autonomous systems by training new AIs, and can be used to find new relationships and correlations within the robot's operational environment that were unnoticeable before. The applications of aerial, marine, and ground robots are increasing every day as industry operators realize that they can use robotics to extend the capabilities of their current workforce.

While the general reception for autonomous robots in the industry has been positive, there are two main issues commonly discussed. First, the high costs of creating the technology may discourage some operators from investing in robotics development. Currently industry users, such as mining operators, prefer a services model to implement robotic solutions to their operations. In this case, the costs of development, implementation, and up-keep are offloaded to service providers and original equipment manufacturers. Robot developers are motivated to develop platforms that are sufficiently versatile and generalized. Open architectures and interfaces are common themes to make the robots easier to modify, customize, and adapt to deploy different payloads, sensors, and generally perform a large variety of tasks. High efficiencies and cost savings in development can be achieved by developing platforms that are modular, can be quickly adapted to address multiple and changing market needs, and are ready for redeployment and reuse.

Second, there are concerns that future autonomous systems may displace human workers. The concern is valid and there is no consensus on how society should respond to this concern. In the area of monitoring hazardous environments, robotic technologies have extended human capabilities, while keeping humans safe, rather than primarily replacing workers. Over the last few years, robotic systems have been proposed to aid human workers in collecting samples and estimating soil properties (Olmedo and Lipsett, 2016). Robotic systems have been used to collect samples that were off-limits to human crews.

Environmental monitoring and site investigations of remote and hazardous locations are challenges for the mining industry. Advances in robotic systems and remote sensing technologies can improve the extent and quality of studies conducted in challenging environments. In the past, site investigations were limited to areas that were accessible to human workers. Currently, robots are being used in previously-inaccessible areas such as unstable and intrafficable terrain, toxic areas, unstable tailings beaches, shallow water deposits with obstacles, pit lakes with rock fall hazards, etc. There is a global push to increase and improve monitoring activities in areas affected by mining operations, including tailings dams and impoundments to improve remediation efforts (Holm, 1993), environmental assessments (Plumlee et al., 1994), the performance of mining processes (Lipsett et al., 2014), and complying with legislative requirements (Wills and Finch, 2016).

This paper presents a brief review of the state of the art of robotic systems for environmental monitoring, and the gaps in the technology specific for monitoring tailings impoundments. Then, the latest developments in screw-drive amphibious robots are presented, highlighting some use-cases and real field applications. Finally, the paper discusses lessons learned and identifies opportunities for future work.

Robots for environmental monitoring and site investigation

A comprehensive review of the robotic systems for environmental monitoring has been compiled by Dunbabin and Marques (2012). Mobile platforms have been used to provide access to difficult locations by air, water, and ground. This section provides a general overview of the common capabilities in each area with a few examples.

Unmanned aerial vehicles

Unmanned aerial vehicles (UAVs) have been used for environmental monitoring, primarily for imaging, with some proof-of-concept payloads to collect soft soil samples (Olmedo and Lipsett, 2016). Aerial surveys with UAVs (Figure 1) are rapidly replacing traditional satellite imagery, providing faster deployment and data collection to produce geo-tagged 3D maps, digital terrain models, digital surface models, and contour lines. The mining industry has benefited from more accurate stockpile volume estimations and other accurate site measurements to determine berm heights, deposit boundaries, slopes, and elevation changes. UAV operations may sometimes be challenging in all weather conditions and in areas where there are regulated air spaces, such as close to an aerodrome or airport.

Figure 1: UAV conducting aerial measurements (Dronitech, 2019)

Unmanned surface vessels

Unmanned surface vessels (USVs) have been used in marine environments for many applications. USVs can carry single-beam sonars, multibeam sonars, side-scan sonars, and other instruments to map the depth and surface of the bottom of bodies of water and conduct efficient hydrographic surveys. Long range USVs may be deployed for several months at a time, using a combination of solar, wind, battery, and diesel energy. These systems can be used for sea-going research, security and defense applications, etc. There are several USVs manufacturers that provide off-the-shelf solutions for environmental monitoring of aquatic areas affected by mining operations. Examples of USVs for bathymetry with waypoint navigation are Z-boat 1800RP and Hydrone (Figure 2).

(a) Z-Boat 1800RP (Teledyne Marine USV, 2022) (b) Hydrone (SeaFloor Systems, 2022)

Figure 2: Examples of USV commercially available systems

Remotely operated vehicles and autonomous underwater vehicles

Underwater robotic platforms are generally categorized as remotely operated vehicles (ROVs) and autonomous underwater vehicles (AUVs). These have been used for monitoring underwater structures, inspection of wrecks and underwater industrial assets, manipulation of objects underwater, mapping the bottom of bodies of water and obstacles that may pose a danger to human vessels, etc. (Ludvigsen at al., 2017). Generally these robots carry sonars for object and bottom detection, lights and cameras for visual navigation and inspection, and manipulators such as claws. ROVs have been used in drilling for deep sea mining operations (Ludvigsen at al., 2017) There are commercial off-the-shelf solutions such as Teledyne's vLBV300-L (Figure 3) (Teledyne Marine ROV, 2022), that are typically used for inspection of oil and gas structures and pipe inspections.

Figure 3: vLBV300-L – SeaBotix ROV (Teledyne Marine ROV, 2022)

Ground unmanned vehicles

Ground unmanned vehicles (UGVs) been used for mapping underground mines that human workers cannot access (Coetzee et al., 2012; Green, 2012; Nüchter et al., 2004), and for other mining applications such as explosives handling, haulage, surveying, dozing, excavation, and drilling (Marshall et al., 2016). Some areas in tailings impoundments have been accessible for tracked and wheeled vehicles to collect samples (Figure 4) (Olmedo and Lipsett, 2016). In extraterrestrial site investigation missions, collecting and analyzing soil samples are critical tasks. Custom payloads for coring and drilling and sample-return have been developed, and are currently operational in several robots (Helmick et al., 2013).

Figure 4: RTC-II UGV drilling on an oil sands tailings deposit

Amphibious robots

Amphibious robots are required for areas that are inaccessible for USVs and UGVs, such as very shallow water, saturated soils, and lakes with underwater shallow obstacles, unstable tailings beaches, cohesive soils, etc. The typical environment of tailings impoundments is dynamic and variable. There can be areas that rapidly change from having a hard crust to being fully saturated soils with a water cap. Some amphibious equipment has been developed with buoyant wheels and tracks that can access materials with low bearing capacity, but may be prone to getting stuck in highly cohesive terrain and materials with high adhesion and shear thinning properties. Transition zones are particularly difficult for traditional wheeled, tracked vehicles, or vehicles with a hull.

An example of buoyant wheels is the hybrid robot used to investigate aquatic environments in the Amazon rainforest rivers (Freitas at al., 2011). Navigation of these difficult conditions has been mitigated by using a screw-drive propulsion system. Screw-drive robots consist of two or more counter-rotating pontoons with Archimedean screws (Group and Cole, 1961). This propulsion mechanism has been demonstrated over the last decades in a wide variety of applications and terrains, including marshes, swamps, open water, hard ground, saturated soils, and tailings deposits.

Figure 5: Screw-drive amphibious robot moving across a lake

Screw-drive robots for tailings monitoring

Amphibious screw-drive robots have been developed to address the need for unmanned all-terrain vehicles to deploy payloads and collect measurements in tailings deposits. Screw-drive robots close the gap between UGVs and USVs that are limited to hard ground and open water environments, and allow access to areas too dangerous for human workers. This section reviews the latest developments in screw-drive robots for bathymetry surveys, material sampling, in-situ material characterization, ice thickness measurements, and deployment of geotechnical tools.

Amphibious robots for bathymetric surveys

Bathymetric surveys are used to determine the sludge and water volume contained in tailings deposits and to identify subsurface structures or areas that require additional work such as dredging. Screw-driven amphibious robots have been instrumented to carry sensors for bathymetric surveys in challenging environments. Generally, screw-drive propulsion systems suffer from lesser energy efficiency than robot boats with a hull and thrusters, but excel at navigating in difficult deposits such as tailings ponds with saturated clays, underwater obstacles or islands, and shallow transition areas with minimal water cap, where traditional drone boats can get immobilized.

In addition, the hard and soft ground mobility capabilities of these amphibious robots allow them to traverse tailings beaches and reach open water without the need for a dock or other direct access.

HELIX 25, a robot developed for research of screw-drive propulsion systems, has been used to conduct bathymetric surveys in inaccessible locations for human workers. As shown in Figure 5, HELIX 25 has been deployed in mine pit lakes that have rock-fall hazards preventing human workers from reaching the water to deploy a USV or a human-crewed boat. HELIX 25 was able to roll across hard ground to reach the water within the hazard zone and drive into the water to collect depth measurements using a dual frequency transducer of 33 kHz and 200 kHz. HELIX 25 navigated the water-capped deposit autonomously using RTK-GPS and on-board sensors, and followed a predetermined waypoint path.

In very shallow areas, less than 30 cm deep, a novel mechanical system, MANTA, is used to continuously measure shallow depths. It consists of a tethered mass that is dragged behind the rover on the water-ground interface, and an electrical system to measure the position of the tethered mass.

Figure 6: HELIX 25 conducting a bathymetry survey in a pit-lake

HELIX Neptune, a commercially available platform, has also been deployed to conduct bathymetric surveys in hazardous locations. The robot was instrumented to operate either by remote operation or autonomously. With a payload capacity of approximately 100 kg, HELIX Neptune was built with a novel device to be able to move the sonar systems in and out of the water, allowing the rover to navigate in mud and sludge without risking the sensors. A suspension mechanism was incorporated to prevent damage to the sonar system if there were to be an impact with an undetectable underwater obstacle or with soft soils (Figure 7).

Figure 7: HELIX Neptune accessing a lake through vegetation

Water sampling and in-situ characterization

Areas affected by industrial mining operations need regular environmental monitoring. Water and sludge sampling and characterization are required to determine the effect of mining operations in water bodies, to monitor the performance of treatment processes, and to study water chemistry, solids content, particle size distribution, and composition. HELIX Neptune has been deployed to collect water samples from depths up to approximately 80 m in otherwise inaccessible pit lakes. The system consists of a winch system that can lower standard water samples such as a vertical Van Dorn sampler, and a triggering mechanism to release a standard trigger to activate the sampler when it reaches the desired point. The sampling operation can be remotely controlled, or conducted autonomously.

The same mechanisms that deploy water sampling tools can be used to deploy sludge samplers such as an Ekman grab sampler, and density plates to validate depth measurements with sonars. HELIX Neptune has deployed other commercially available sensor packages for in-situ water characterization studies and recorded measurements of temperature, conductivity, pH, dissolved oxygen, and sound velocity in water, etc. (Figure 8).

Figure 8: HELIX Neptune deployed in a pit-lake with YSI EXO Sonde

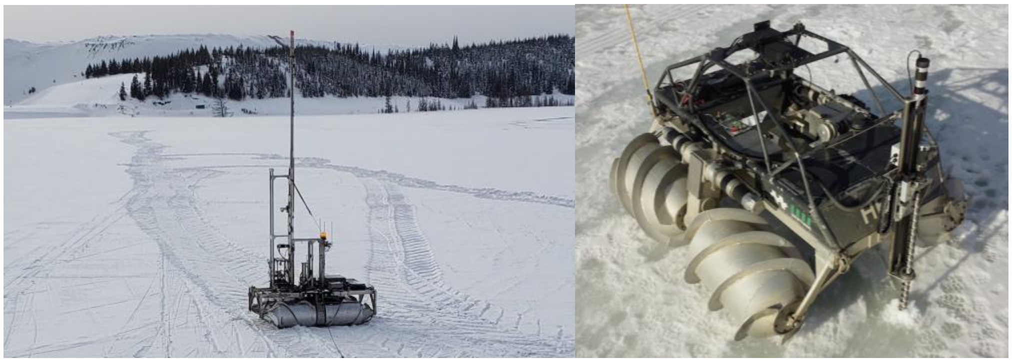
Robotic geotechnical surveys

Geotechnical surveys in tailings impoundments are critical to understand consolidation behaviours and determine the performance of treatment processes (Wills and Finch, 2019). HELIX AR2, a robot the size of a small car, has been designed to deploy geotechnical tools in difficult-to-access tailings storage facilities, such as oil sands tailings ponds, where the mature fine tailings and bitumen residues produce a terrain with the consistency of honey. HELIX AR2 has been used to deploy cone penetrometers of various sizes and digital vane shear tools up to a depth of 4 m (Figure 9). It has also been part of survey campaigns collecting piston samples to study the material composition, water content, particle size distribution, clay activity, and residual bitumen. The robot was able to collect up to 10 samples per trip, and was deployed approximately 2 km from the shore of the deposit. The current limitation of the rover is its mass and ability to reach larger depths. The 4 m maximum capacity is sufficient in some deposits, and has served as a proof of concept to demonstrate the benefits of using unmanned systems for geotechnical investigations, including the capability to reach previously inaccessible locations and reduce the cost and risk to human workers.

Figure 9: HELIX Neptune deployed in a pit-lake with YSI EXO Sonde

Ice depth measurements and winter operations

HELIX Neptune and HElIX AR2 have been deployed in winter conditions for determining the elevation and depth of water deposits with a frozen layer for water-balance studies. The rovers are instrumented with ice drills to be able to drill through the ice layer and deploy tools through the hole. A single beam sonar was deployed through the ice hole to determine the depth of the deposit (Figure 10). Other applications during the winter involve measuring ice thickness to determine if an ice road would be able to support the load of vehicles and such.



(a) **(b)**

Figure 10: (a) HELIX AR2 deployed on a frozen deposit, and (b) HELIX Neptune drilling through ice

Future work

The success of unmanned technologies motivates the continued research and development of robotic systems to access harsher and more demanding environments. Some opportunities for new robots include areas on tailings deposits with volatile atmospheres, in which all equipment needs to be intrinsically safe. Larger and heavier robotic platforms would allow the deployment of heavier tools and payloads, for example to reach drilling and sampling depths of 30 m or higher and to withstand contact reaction forces during these operations.

Conclusion

The role of autonomous robotic systems in tailings monitoring has increased. The gap between unmanned surface vessels and ground vehicles has been filled with amphibious screw-drive robots that can deploy tools and collect measurements in hazardous challenging terrains. These robots are being used to conduct bathymetric surveys and geotechnical investigations, and to collect water and materials samples while reducing costs and risk to human workers. Field work has demonstrated the benefits of these systems, and the results motivate future work focused on research and development to create larger and more capable rovers.

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