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TECHNICAL ARTICLE

Passive Treatment of Neutral Mine Drainage at a Metal Mine in New Zealand Using an Oxidizing System and Slag Leaching Bed

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Abstract Rehabilitation at a metal mine in New Zealand is complete with the exception of a 22 L/s discharge pumped from underground. The discharge has a pH of ≈6, alkalinity of ≈150 mg/L, dissolved oxygen (DO) <1 mg/L, elevated Fe and Mn, as well as elevated concentrations of Zn and As. Planning passive treatment was difficult because historical total Fe ranged from 20 to 200 mg/L, and Mn (11–22 mg/L) is soluble in the circumneutral pH range, due to conditions in the workings. Speciation analysis and modelling of the mine drainage chemistry indicated four factors were important for passive treatment design: (1) dissolved Fe is ≈20 mg/L and all is dissolved Fe(II); (2) Fe(II) concentration is stable because it is limited by saturation with respect to siderite ($FeCO_3$); (3) the remaining Fe is colloidal $Fe(OH)_3$ with a variable concentration; and (4) Mn is limited by saturation with respect to rhodochrosite ($MnCO_3$). Equilibrium of Fe and Mn with minerals means that dissolved concentrations have an upper limit and are relatively stable, allowing an optimized treatment system. A pilot-scale passive treatment system was installed that included an oxygenation cascade of drops through V-notch weirs, settling ponds, and a slag leaching bed. Oxidation of Fe(II) to Fe(III) was followed by precipitation and settling of $Fe(OH)_3$. Bicarbonate alkalinity in the mine drainage prevented acidification, and release of dissolved CO_2 caused the pH to increase slightly. Manganese was removed by precipitation (of carbonates, oxides or oxy-hydroxides) in the slag leaching bed at elevated pH and high DO. Zinc and As were removed by adsorption onto $Fe(OH)_3$. The oxygenation system removed 82–96 % of the Fe and 10 % of the Mn. The slag leaching bed removed 99 % of the remaining Mn.

Keywords Ferrous · Fe oxidation · Mn · Fe hydroxide · V-notch weir · Passive treatment · Slag leaching bed

Introduction

Contaminated mine drainage is a common issue associated with mining in New Zealand (Haffert and Craw 2010; Pope et al. 2010) and around the world (Plumlee and Logsdon 1999). Mining exposes minerals that are geochemically unstable at the Earth's surface and can cause the release of trace elements as well as acidity and salinity. Acid mine drainage (AMD) from coal mines in New Zealand has been investigated extensively (Alarcon 1997; Black et al. 2005; deJoux 2003; James 2003; Pope et al. 2006); however, contaminated mine drainage from metal mines can also be significant (Craw et al. 2005; Webster-Brown and Craw 2005).

Metal mines in the North Island of New Zealand are often hosted in volcanic systems, where the base metals and precious metals are primarily found in epithermal deposits. These deposits are formed by geothermal circulation of groundwater driven by heat from near-surface (≈1–3 km) magma. The ore mineralogy of these deposits often includes native gold or gold-silver electrum, and various sulphide minerals, such as pyrite (FeS_2), arsenopyrite (FeAsS), sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$).

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The alteration mineralogy includes various silicates, subeconomic concentrations of sulphide minerals, carbonates, and clay minerals (Berger and Bethke 1985; Henley et al. 1984). Mining epithermal deposits can cause contaminated mine drainage with low pH water and elevated trace elements, or neutral pH with elevated trace elements (such as As, Mn, and Zn), depending on the type and relative abundance of acid-forming and -neutralizing minerals.

AMD is usually treated with active or passive treatment systems (Skousen et al. 2000; Trumm 2010; Younger et al. 2002). Treatment techniques usually involve oxidation, pH adjustment, and precipitation and collection of oxides and hydroxides. With active treatment, these processes are mechanized, monitored in real time, and continually optimized. However, in passive treatment systems, there is less scope to modify or optimize chemical conditions during treatment. The challenges with passive treatment relate to establishment of geochemical conditions that immobilize the target metals or trace elements, ensuring that the reaction rates match the size of the system, and designing hydraulic residence times (HRT) that match the flow rates and treatment objectives.

We provide a case study from a precious metal mine in the North Island of New Zealand and discuss the design, installation, and operation of a passive treatment system trial to remove dissolved components to below discharge compliance limits. We used a cascade to oxygenate the anoxic AMD and to oxidise the reduced chemical species, followed by a slag leach bed for pH modification to remove Mn. Oxygenation cascades are commonly used in passive treatment systems, though their effectiveness is commonly assumed and seldom measured. Slag leaching beds are less commonly used; however, they are useful where chemical modification of mine drainage to $\text{pH} > 8$ is required because slag commonly contains CaO (Simmons et al. 2002; Skousen 2002; Ziemkiewicz and Skousen 1998). Peer-reviewed literature on the methods adopted for this treatment trial is not abundant; our objective was to thoroughly evaluate the treatment processes, identify the removal mechanisms, and measure their effectiveness.

Study Site

The study site is a closed epithermal gold mine located in the North Island of New Zealand. The mine operated in the late 1800s and early 1900s as a narrow vein underground operation, and more recently in the 1990s as a combined open-pit and underground operation. The geology includes hydrothermally altered andesite with a typical alteration mineral suite, including sulphide (sphalerite, galena, chalcopyrite), carbonate (calcite and rhodochrosite), and silicate (quartz, kaolinite, illite, smectite). During mining, a tailings dam was constructed to contain gold processing residues and sulphide-bearing waste rock. During rehabilitation and after closure, the waste rock dumps and tailings pond margins were reshaped and capped with non-acid generating material and topsoil. Landform rehabilitation and revegetation has been successful, and the tailings remain saturated to prevent oxidation (MacGillivray et al. 2001).

To prevent uncontrolled discharge of groundwater from underground workings into a nearby river, water is continuously pumped from the flooded underground workings at an average flow rate of 22 L/s and treated in an active treatment system prior to discharge. The water contains elevated concentrations of Fe and Mn with trace concentrations of Zn and As. At the time of sampling, the active treatment plant used lime addition only; however, the process currently uses hydrogen peroxide for oxidation, and lime and ferric salts for coagulation and precipitation of metals to achieve specified water quality targets (Boothroyd et al. 2005).

Since closure, the water chemistry from the underground workings has improved slightly. However, treatment is still required to achieve the water-quality targets. In the long term, passive treatment would be a more economical and sustainable solution than operation and maintenance of active treatment. This aim of this study was to identify, design, and test a passive treatment system for the site.

Mine Water Geochemical Interpretation

Prior to selection and design of an optimal passive treatment solution, the water quality data from the mine site were reviewed. The PHREEQC geochemical modelling program (Parkhurst and Appelo 1999) was used to identify aqueous species, determine mineral saturation relationships, and predict the impact of changes in water chemistry on the dissolved components present in the mine pool. This investigation guided the selection and design of different parts of a passive treatment system.

The water chemistry at the site has a moderate pH (5.8–6.3), a high buffering capacity (120–180 mg/L $CaCO_3$ equivalent), low dissolved oxygen (DO) (<1 mg/L), elevated SO_4^{2-}, hardness, Fe, Mn concentrations, and slightly elevated concentrations of Zn and As. The concentration of Fe within the old analytical data ranged between 20 and 200 mg/L (Fig. 1). The total Fe concentration varied due to the complex hydrogeological conditions in the underground workings and the pump rate used to control the water level in the mine. However, most analyses were completed on unfiltered samples and included particulate Fe. The few analyses available for dissolved Fe had concentrations between 20 and 25 mg/L. Mn concentrations ranged from 11 to 22 mg/L (Fig. 2).

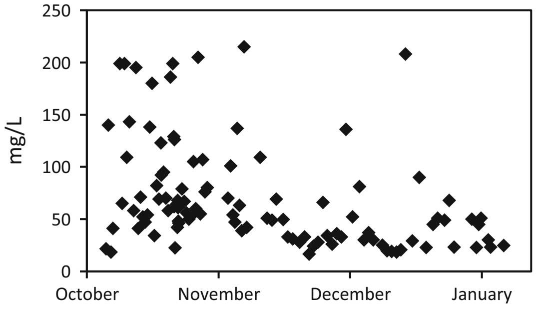

Fig. 1 Total Fe concentration changes with time in the mine pool

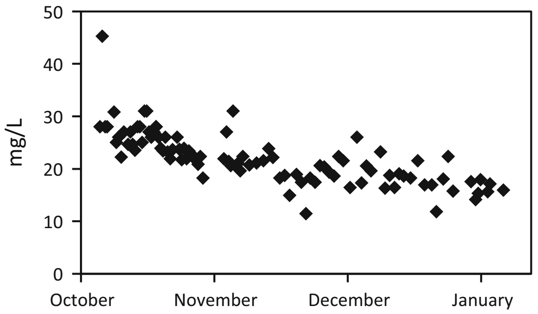

Fig. 2 Mn concentration changes with time in the mine pool

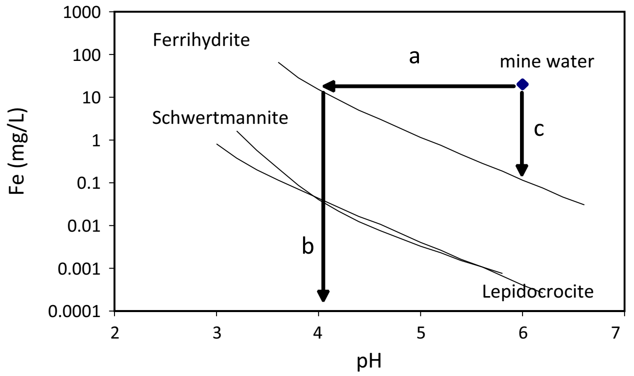

Fig. 3 Mine water plots as supersaturated with respect to common Fe(III) minerals, ferrihydrite and schwertmannite; therefore, the elevated Fe concentration is likely to be Fe(II)

Iron

Oxidized mine drainage systems attain equilibrium with respect to Fe(III) minerals, commonly ferrihydrite, schwertmannite, or similar minerals (Bigham et al. 1996). In these systems, elevated Fe(III) concentrations can only be maintained at low pH, and precipitation of Fe(III) minerals often buffers pH at $\approx$2.5–4 through Lewis acid reactions (Eq. 1). However, the mine pool has a pH about 6 and elevated dissolved Fe. If Fe in the mine pool was oxidized and present as dissolved Fe(III), the highest likely pH is <4 (Fig. 3, arrows a, b), assuming saturation with likely Fe(III) minerals. The highest dissolved Fe(III) concentration possible at the measured pH ($\approx$6) is <0.1 mg/L (Fig. 3, arrow c).

Table 1 Mineral saturation in the mine pool from PHREEQC geochemical modelling

Mineral	Formula	Saturation index
Manganite	$MnOOH$	−8.9
Hausmannite	Mn_3O_4	−23.1
Pyrolusite	MnO_2	−17.6
Pyrochroite	$MnOH_2$	−7
Rhodochrosite	$MnCO_3$	0.08
Siderite	$FeCO_3$	0.04

$$Fe(III) + 3H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+ \qquad (1)$$

These interpretations along with the low DO indicate that the aqueous chemistry of the mine pool is reduced. Assuming a dissolved Fe concentration of at least 20 mg/L, more than 99 % of the dissolved Fe must be Fe(II). In addition, Eh and pH measurements combined with thermodynamic data for Fe oxidation and reduction speciation indicate that most samples plot within the dissolved Fe(II) stability field (Supplemental Fig. 1). (Note: supplemental figures accompany the on-line version of this paper and can be downloaded for free.) Therefore field measurements of pH and Eh also indicate that dissolved Fe is mostly reduced in the mine water. Understanding Fe speciation in the mine pool is important because Fe oxidation is acid-neutralizing (Eq. 2), whereas precipitation of Fe(III) minerals contributes acidity (Eq. 1); therefore, Fe speciation influences treatment system design.

$$Fe(II) + \frac{1}{4}O_2 + H^+ = Fe(III) + \frac{1}{2}H_2O \qquad (2)$$

The results of the PHREEQC modelling show that the mine pool is about saturated with respect to siderite (Table 1), suggesting that the concentrations of dissolved Fe(II) are likely to remain stable at about 20 mg/L, or perhaps decrease through dilution.

Manganese

In general, mine drainage systems do not attain equilibrium with respect to Mn minerals because Mn is often present as a trace component. High Mn solubility over the common mine drainage pH range of 2–8 and typical Eh conditions often prevents equilibrium with respect to Mn minerals (Supplemental Fig. 2). However, modelling of the mine pool water indicated that Mn was roughly saturated with respect to rhodochrosite and undersaturated with respect to common Mn oxyhydroxide minerals (Table 1). Increasing pH oversaturates the mine drainage with respect to rhodochrosite, so $MnCO_3$ precipitation is favoured by increased pH. Comprehensive assessment of carbonate mineral saturation during mine pool water treatment is not possible because thermodynamic data is not available for minerals such as kutnahorite ($CaMn(CO_3)_2$), which has been found in mine drainage studies (Bamforth et al. 2006). However, increased pH will supersaturate the mine drainage chemistry with respect to Mn carbonates, oxides, and hydroxides, and if these minerals precipitate, the dissolved Mn concentration will decrease.

Passive Treatment System Design

The treatment approach selected for the site involved three steps: oxygenation; oxidation of Fe(II), and settling of $Fe(OH)_3$, with adsorption of some Mn, Zn, and As; and pH manipulation to precipitate Mn as carbonate, oxide, or oxyhydroxide minerals. Prior to construction of the trial system, a literature review was completed to determine optimal techniques to increase the DO to near-saturation, and to model Fe(II) oxidation kinetics at various pH values to determine the HRT required for oxidation of Fe(II) to Fe(III).

Oxygenation

In the mine pool, equilibrium with siderite and the reduced and anoxic nature of the water prevents oxidation of all of the Fe(II) to Fe(III). Addition of DO to the water after it is pumped from the workings will lead to precipitation and settling of $Fe(OH)_3$. Three factors are critical for Fe removal:

- Addition of sufficient DO,
- Reaction time for oxidation of Fe(II) to Fe(III), and
- Residence time for settling of $Fe(OH)_3$.

Stoichiometrically, each mole of Fe(II) oxidized to Fe(III) requires ¼ mole of O_2 (Eq. 2). Assuming a maximum concentration of 30 mg/L of Fe(II) (0.537 mmol/L) in the inlet to the oxygenation cascade, a maximum of 4.3 mg/L of DO (0.134 mmol/L) is necessary for complete oxidation to Fe(III). The reaction kinetics of Fe oxidation show that reaction rates are proportional to the DO content (Stumm and Morgan 1996); therefore, the system should be designed to increase the DO to near-saturation.

Equations for modelling oxygen transfer at cascades are typically based on weirs or other hydraulic structures rather than stepped cascade aerators (Koduri and Barkdoll 2003). A study of various weir configurations by Baylar and Bagatur (2000) found that the V-notch weir produces the greatest oxygen transfer and a drop height of 0.9 m entrains the greatest amount of air. Kim and Walters (2001) found that ideal tail-water depths are about 2/3 of the drop height and derived the following predictive equation for oxygen entrainment through V-notch weirs with specified drop heights and tail-water depths:

$$r_{20} = 1 + 0.453 F_J^{0.453} h^{1.117} \left(\frac{H}{h}\right)^{0.475} \tag{3}$$

where r_{20} is the DO deficit ratio at 20 °C, F_J is the jet Froude number, $[gh^3/(2q_J^2)]^{0.25}$ where $q_J =$ the jet unit discharge at the point of impact (m^2/s), and g is the gravity coefficient (9.8 m/s), $H =$ the tailwater depth, and $h =$ the fall height. Equation 3 was used to model the increase in DO for water from the mine pool as it passed through V-notch weirs. The DO concentration reached saturation after five drops through V-notch weirs with drop heights of 0.9 m into tailwater depths of 0.6 m; therefore, the trial passive treatment system was designed accordingly.

Fe(II) Oxidation and Precipitation

The reaction kinetics of Fe oxidation are strongly influenced by pH (Stumm and Morgan 1996). Rates of Fe(II) oxidation at pH 5, 6, and 6.5, and a constant DO content increases as pH increases (Fig. 4). The pH of the inlet water is approximately 6 and the DO content is typically <1 mg/L. At pH 6 and DO at saturation (10 mg/L), reaction kinetics indicate that 99 % of the Fe(II) will convert to Fe(III) within 48 h. Therefore, the passive treatment system was designed for an HRT of ≈ 48 h.

At pH 6, Fe(III) will not remain in solution but will precipitate as ferric hydroxide (Eq. 1). The overall reaction of oxidation of Fe(II) and precipitation as an hydroxide (Eqs. 1, 2) is acid producing; however, the molar balance of alkalinity in the water with the acid produced during $Fe(OH)_3$ precipitation indicates that there is excess alkalinity (30–100 mg/L $CaCO_3$ equivalent) in the mine water. Therefore, $Fe(OH)_3$ precipitation should not cause substantial pH reduction. Bench top trials on mine pool water of Fe(II) oxidation by agitation indicated a slight pH increase during oxidation and precipitation, presumably due to release of excess CO_2 from the mine water.

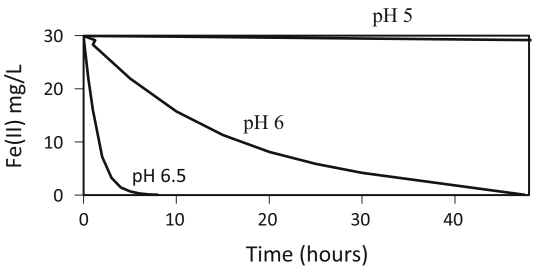

Fig. 4 Rate of oxidation of Fe(II) to Fe(III) at pH 5, pH 6, and pH 6.5 under a constant DO concentration of 10 mg/L

Following precipitation, the settling velocity of $Fe(OH)_3$ is difficult to predict because it depends on colloid aggregation as well as precipitation, so the settling rate was not used to determine the ideal HRT.

Mn Removal

The pH increase required to supersaturate the water with respect to Mn minerals cannot be achieved by addition of limestone or through the biogeochemical processes that are typically used in passive treatment of mine drainages. Several approaches were considered, including: use of cement kiln dust which contains calcium oxide; use of steel slag, which also contains calcium oxide and; use of pyrolusite, which could potentially trap Mn through auto-catalytic processes (Stumm and Morgan 1996). Steel slag was selected as the preferred reactive substrate to remove Mn because it is available in large quantities from the steel manufacturing industry in the North Island of New Zealand.

Methods

The trial passive treatment system consists of three parts: an oxygenation cascade, a series of settling ponds, and a steel slag leaching bed (Fig. 5).

Oxygenation Cascade and Settling Ponds

The oxidation system was constructed in two parts:

- Five drops through V-notch weirs at a design flow rate of 0.5 L/s.
- Five settling ponds, with two additional drops through V-notch weirs between the second and third settling ponds.

Water from the well head was diverted through a gate valve and a 40 mm alkathene pipe at a flow rate of 0.5 L/s to the start of the oxygenation cascade. Water passed from the 40 mm pipe into a 1.2 m long PVC pipe that was 150 mm in diameter. A V-notch was cut into the end cap of

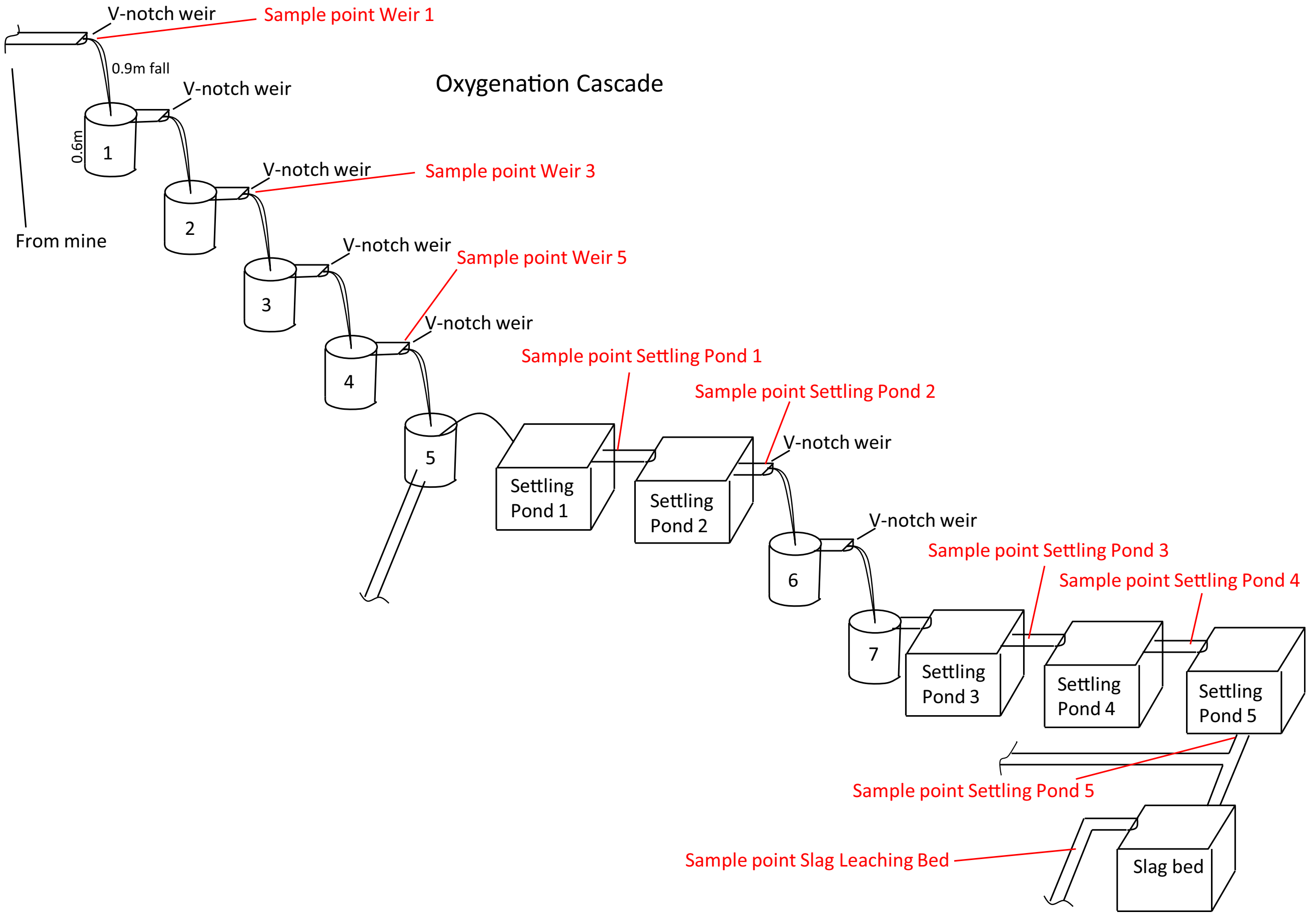

Fig. 5 Schematic of trial system

Fig. 6 First three V-notch weirs and barrels in the oxygenation cascade

the PVC pipe and the pipe was secured to four fencing standards so that there was a slight downstream slope to the pipe (Fig. 6). Water flowed out of the V-notch weir and dropped 0.9 m into a 0.6 m diameter and 0.95 m high barrel. A 40 mm outlet pipe was connected to the barrel at 0.6 m above the base of the barrel in order to maintain a tailwater depth of 0.6 m. This configuration is repeated for five drops through V-notch weirs into five barrels (weirs and barrels one to five). The total elevation drop from the first weir to the water surface in the fifth barrel was 5.5 m.

A small flow was diverted from the fifth barrel into the settling/reaction pond. Water from this barrel flowed into the first settling pond at a flow rate of 0.011 L/s through a siphon system using 4.8 mm clear Teflon tubing. To minimize build-up of Fe deposits in the siphon, an automatic flushing system was attached to the top of the siphon hose. The flushing system consists of a 40 mm pipe from barrel number four to a valve connected to the siphon hose (Fig. 7). The valve opened every three h for one min and water from barrel number four at a high hydraulic head flushed Fe precipitates out of both ends of the siphon hose. The remainder of the 0.5 L/s that flowed through weirs one to five of the oxygenation cascade was diverted to the active treatment plant.

Fig. 7 Weirs and barrel 5 in the oxygenation cascade showing the siphon hose between the barrel and settling pond 1 with attached automatic flushing valve

After the two settling ponds in series (settling ponds one and two), the 0.011 L/s flow passed through two additional V-notch weirs and barrels (weirs and barrels six and seven) with the same dimensions as the first five weirs, and then into three settling ponds in series (settling ponds three, four, and five). These final settling ponds were added partway through the trial period to add additional reaction and settling time.

Each settling pond was a clear plastic 1.12 m^2 tub that was 0.81 m deep. Three baffles were constructed in each tub to reduce short-circuiting of the water and to encourage settling of $Fe(OH)_3$. Water entered each tub at the top, flowed under the first baffle, over the second baffle, under the third baffle, and out near the top of the tub at the opposite end. The water from settling pond five passed through a gate valve to a slag leaching bed. Excess water not treated by the slag leaching bed was diverted through a T-junction to the active water treatment plant. All of the alkathene piping in the second part of the oxidation system and in the slag leaching bed system was 30 mm in diameter.

Once the oxygenation and oxidizing system was started, the site was visited weekly. Each time, field data were collected at each weir and at the outlet from each settling pond, flow rates were measured through the V-notch weirs and through the settling ponds, and samples were collected from the inlet to the system and at the outlet from each settling pond and laboratory-analysed for Ca, Fe, Mn (all both total and dissolved), sulphate, and alkalinity.

Slag Leaching Bed

After the $Fe(OH)_3$ is captured in the settling ponds, Mn could be removed by precipitation of Mn carbonates, oxides, or oxy-hydroxides at an elevated pH and high DO. Three factors are critical for Mn removal:

- Sufficient elevation of pH (>8),
- Introduction of DO after depletion during Fe oxidation, and
- Residence time for settling of precipitates.

A common problem with leaching beds used for treating AMD is the clogging of passages with precipitates, which decreases permeability, causes short circuiting or preferential flow, and therefore reduces residence time (Faulkner and Skousen 1994; Watzlaf and Hyman 1995). To overcome this problem, leach beds with horizontal flow during treatment and vertical flow during flushing are used (Hellier 1999). During normal operation, preferential horizontal pathways become established as precipitates build up. These preferential flow pathways are removed by rapid vertical flushing and the precipitates are dislodged and removed from the system. The horizontal flow—vertical flush concept was used in the construction of the slag leaching bed at this site.

The slag leaching bed was another clear 1.12 m^2 and 0.81 m deep plastic tub (Fig. 8). A gate valve was used to control the inflow. Water entered the unit through a 40 mm PVC header and two vertical inlet pipes. Each inlet pipe has three rows of 8 mm holes through which the water entered the pond. Two pipes on the opposite end of the leaching bed have identical holes through which the water left the unit. The water then flowed through a settling pond with baffles and then into the active treatment system. A single flushing pipe was installed at the base of the slag leaching bed with two rows of 8 mm holes for drainage. A ball valve in this pipe was closed during normal operation and open during flushing into the settling pond. The leaching bed was filled with steel slag generated from the electric arc furnace process at New Zealand Steel Limited. The slag contained approximately 15 % CaO and ranged in size from 20 to 60 mm.

Dissolution of the CaO present in the slag increased pH sufficiently to precipitate Mn oxide (MnO_2 or Mn_2O_3). If the water is oxygenated and in equilibrium with a Mn oxide, auto-catalytic oxidation of dissolved Mn can occur at the Mn mineral surface, which is favourable for increased precipitation of Mn oxide. The precipitate is trapped either within the slag bed or in the following settling pond. The residence time of the water through the bed can be varied to determine the relationship of residence time to effectiveness of Mn removal and pH increase.

Once the slag leaching bed was started, field data were collected weekly from the inlet and outlet, flow rates were measured, and samples were collected from the inlet and outlet and laboratory-analysed for Ca, Fe, Mn (all both total and dissolved), sulphate, and alkalinity.

Laboratory Analyses

Water samples were analysed at a commercial laboratory using atomic absorption spectrometry and ICP-MS by APHA method 3111-B for metals. Ion chromatography by APHA method 4500 was used for sulphate analysis. Alkalinity was completed at the laboratory by titration to pH 4.5 using an auto-titrator for alkalinity by APHA

Fig. 8 Slag leaching beds with inlet piping in foreground

method 2320-B (APHA 2005). Samples for dissolved metals were filtered to 0.45 µm by the laboratory and samples for total metals were digested prior to analysis.

Results

Inlet Water Chemistry

The pH of the inlet water to the treatment system ranged from 5.82 to 7.61. Alkalinity ranged from 113 to 161 mg/L (as $CaCO_3$ equivalent), with an average of 135 mg/L. The DO ranged from 0.45 to 1.13 mg/L, with an average of 0.68 mg/L.

Total Fe concentrations ranged from 4.9 to 28 mg/L, with an average of 16.7 mg/L. Between 75 and 100 % of the Fe was dissolved, ranging from 3.6 to 25 mg/L, with an average of 15.4 mg/L. It was assumed that the dissolved Fe was all Fe(II) and particulate Fe(III) represented the difference between total and dissolved Fe. Using this assumption, particulate Fe(III) ranged from 0 to 4.8 mg/L, averaging 1.4 mg/L. Mn ranged from 13 to 17.4 mg/L, averaging 14.7 mg/L. Over 95 % of the Mn was dissolved.

Oxygenation Cascade and Settling Ponds

The oxygenation cascade operated for 104 days. Flow rate through the V-notch weirs ranged between 0.15 and 0.48 L/s. DO concentrations increased through the five V-notch weirs to the following average concentrations: 6.1 mg/L after weir one, 8.9 mg/L after weir two, 9.3 mg/L after weir three, 9.6 mg/L after weir four, and 9.7 mg/L after weir five (Fig. 9).

The settling ponds operated for 90 days. Flow through the ponds ranged between 0.009 and 0.050 L/s, equating to HRTs between 30 and 160 h. As the water passed through the ponds, the DO decreased by an average of 2.54 mg/L, due to oxidation of Fe(II). Total and dissolved Fe concentrations decreased as the water passed through the settling ponds. Particulate Fe(III) showed a slight increase through the first pond and decreased substantially through the remaining ponds (Fig. 10). The pH consistently increased as the water passed through the ponds, with the increase ranging from 0.01 to 1.42, with the final pH at the end of the final settling pond spanning 6.83–7.66. The total Fe concentration at the outlet from the settling ponds averaged 1.9 mg/L, with only 0.03 mg/L of Fe(II). This equates to an average removal rate of 89 % of the total Fe.

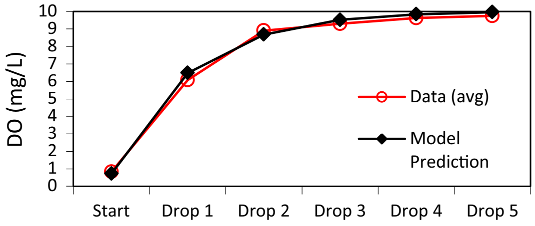

Fig. 9 Model and averaged measured values for oxygen transfer through cascade of V-notch weirs

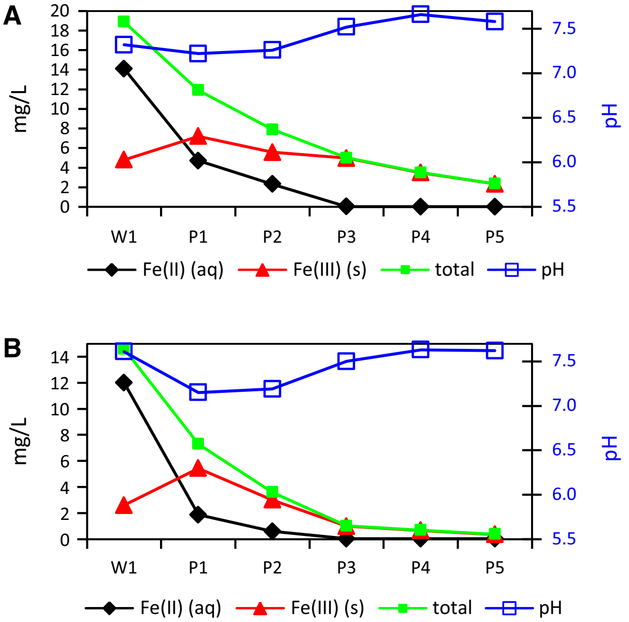

Fig. 10 Iron concentrations and pH through the oxidizing system. **a** HRT of 135 h; **b** HRT of 80 h. *W1* Weir 1, *P1* Pond 1; *P2* Pond 2, *P3* Pond 3, *P4* Pond 4, *P5* Pond 5

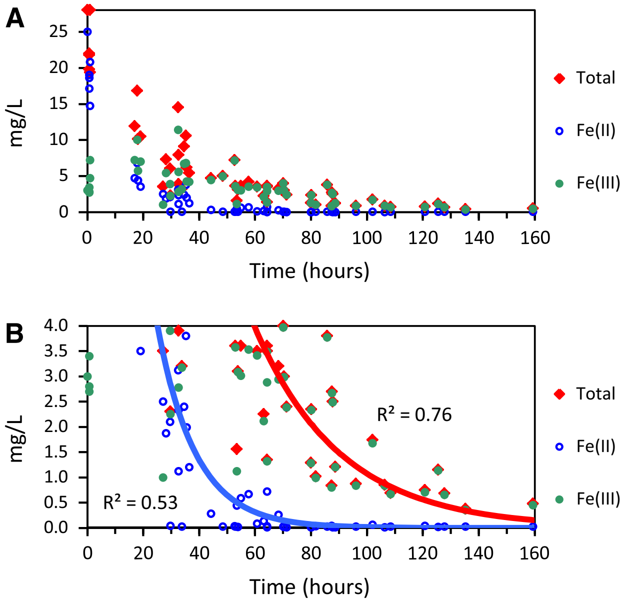

Fig. 11 Iron concentrations according to residence time in the oxidizing system. **a** All data shown; **b** Fe concentrations at or below 4 mg/L with curves fitted to Fe total and Fe(II) concentrations

The Fe concentrations for all sampling points are presented in Fig. 11. The concentrations are plotted according to the total HRT in the oxidation system at that point. Since data were collected after each settling pond over multiple dates and flow rates, oxidation of Fe(II) to Fe(III) and settling of $Fe(OH)_3$ can be compared to HRT. This data shows that at an HRT of 40 h, Fe(II) concentrations decreased to about 2 mg/L, and that at an HRT of 80 h, total Fe decreased to about 2 mg/L.

As the water passed through the settling ponds, Mn concentrations decreased to between 11.0 and 12.8 mg/L, with an average of 11.6 mg/L. Above HRTs of 80 h, Mn removal rates ranged from 7 to 20 %.

Slag Leaching Bed

The slag leaching bed operated for 60 days. Inlet water chemistry had a pH from 6.83 to 7.66, and 0.38 to 3.2 mg/L total Fe, with an average of 1.9 mg/L [only 1.6 % dissolved Fe(II); the remainder was particulate Fe(III)]. Mn ranged from 11.0 to 12.8 mg/L, with an average of 11.6 mg/L (88–100 % dissolved, with an average of 96 %). Flow rate through the slag leaching bed ranged between 0.0021 and 0.027 L/s, equating to residence times between 4 and 51 h.

The pH increased to between 8.1 and 11 in the outflow and was related to HRT; longer residence times had a higher pH outlet water. Alkalinity decreased and Ca concentrations increased through the slag leaching bed. The average alkalinity in the inlet water was 112.6 mg/L ($CaCO_3$) and the average in the outlet was 80.1 mg/L ($CaCO_3$). The average Ca in the inlet water was 233 mg/L and the average in the outlet was 261 mg/L (12 % increase).

Total Mn leaving the slag leaching bed was between 0.1 and 3.8 mg/L (70–99 % removal). At low concentrations (<1 mg/L), most of the Mn was particulate, whereas at high concentrations (>2 mg/L), most of the Mn leaving the system was dissolved (dissolved concentration ≈ total concentration). The amount of Mn removed by the slag leaching bed was proportional to HRT (Fig. 12). This trend has been modelled with an exponential curve to give an indication of Mn removal at untested intermediate residence times. However, the dataset is statistically small.

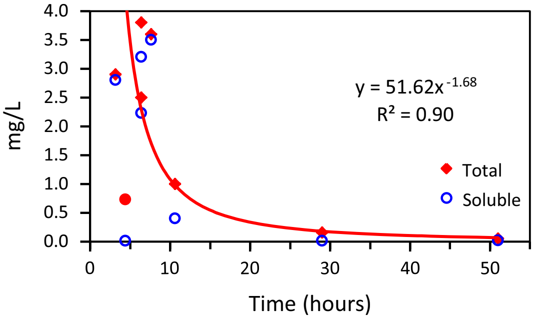

Fig. 12 Manganese removal according to HRT in the slag leaching bed

Discussion

The geochemical modelling completed prior to initiation of the field trial proved to be accurate and useful for interpretation of mine drainage chemistry and understanding the potential stability of the chemistry over time. These interpretations are important for optimal passive treatment system design. This work also shows that the models for oxygen entrainment through cascades, DO consumption during oxidation, and oxidation reaction kinetics accurately predicted treatment system performance.

Oxygenation Cascade and Settling Ponds

Cascades are known to be effective at entraining oxygen in water and increasing DO (Baylar and Bagatur 2000; Koduri and Barkdoll 2003). Our results show that a series of V-notch weirs effectively increased DO levels to near saturation. Comparison of the increase in DO through the cascade in this system closely matched the model by Kim and Walters (2001). The levels were only slightly less than the model predictions, and this is probably because some Fe(II) oxidation (and hence DO consumption) occurred in the barrels in the system.

The stoichiometric predictions for the amount of DO necessary to oxidize Fe(II) in the settling ponds can be compared to the actual decrease in DO through the ponds. The average Fe(II) concentration entering the ponds was 15.4 mg/L; Eq. 2 predicts 2.21 mg/L DO is required and the actual decrease in DO averaged 2.54. These closely-matched results suggest that using chemical equations to predict required DO for oxidation are useful when designing oxidation cascades for passive treatment systems.

The oxidation of Fe(II) and precipitation as an hydroxide (Eqs. 1, 2) is acid producing and should result in a drop in pH as the water passes through the settling ponds. However, adequate alkalinity and release of dissolved CO_2, contributed to stability of pH as the water passed through the settling ponds. This suggests that geochemical modelling can be conducted to determine the effect of alkalinity on pH changes during generation of proton acidity from oxidation and hydrolysis. Changes in pH caused by Fe(II) oxidation and CO_2 degassing as water flows down cascades has been observed in other mine drainage experiments (e.g. Geroni et al. 2012), with similar results to this study.

The oxidation rates are compared in Fig. 13 to Fe reaction kinetics (Stumm and Morgan 1996). Separate graphs are shown for different dates because the starting Fe(II) concentration varied. The measured oxidation rates closely follow the model predictions for pH 6.0 at a DO concentration of 10 mg/L. This analysis shows that Fe reaction kinetics for pH 6 and DO at saturation can be used to predict oxidation rates for Fe at this site, and potentially at other sites with similar chemistry.

There was significant removal of Mn in the $Fe(OH)_3$ settling ponds (up to 20 %), probably through adsorption onto the reactive surfaces of the ferric hydroxide precipitates (Rose and Cravotta 1998) rather than through precipitation of Mn oxides, which requires pH > 7.

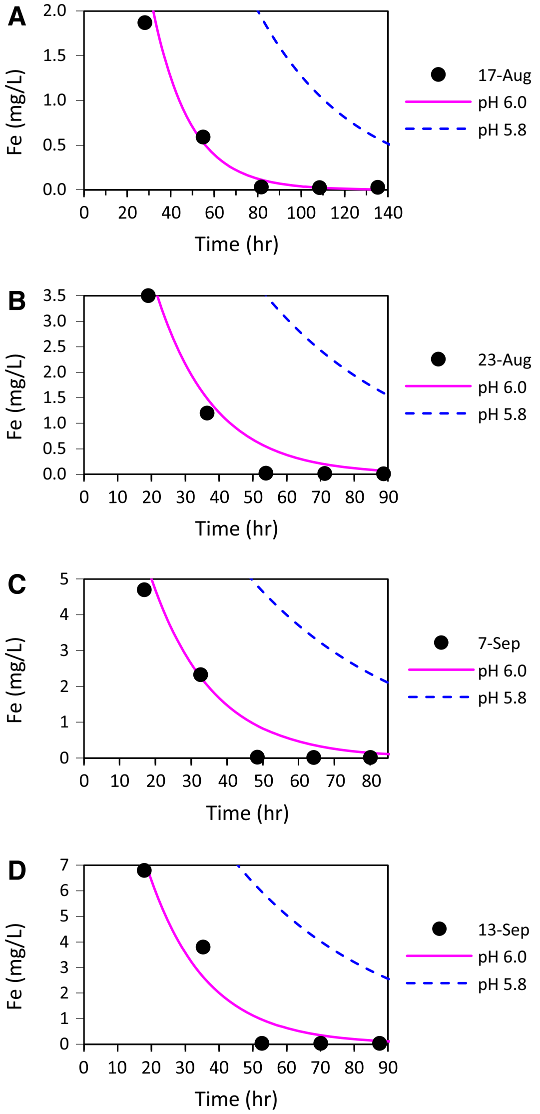

Fig. 13 Fe(II) oxidation rates predicted by reaction kinetics model compared to measured values in oxidizing system. **a** Data from 27 August; **b** data from 23 August; **c** data from 7 September; **d** data from 13 September

Slag Leaching Bed

The alkalinity decreased as mine drainage flowed through the slag leaching bed and pH increased. This indicates that alkalinity, which is mostly HCO_3^- between pH 6.5 and 9.5 and mostly CO_3^{2-} between pH 9.5 and 11, is consumed by the slag leaching bed, probably by carbonate precipitation.

There are several possible geochemical removal mechanisms for Mn under the conditions in the slag leaching bed. Two of the most likely mechanisms are precipitation as a complex carbonate, such as kutnahorite (Bamforth et al. 2006) or precipitation as a hydroxide (Stumm and Morgan 1996). It is possible that either or both mechanisms are reflected in the slag leach bed Mn removal data. Preliminary interpretation of our data indicates that there is bimodality in the dataset that suggests two processes: one at relatively short residence times (<10 h), which reduced the Mn concentration to between 2 and 4 mg/L, and a second at longer residence times (10–50 h), which continued to reduce the Mn concentration to between 1 and 0.1 mg/L. It is also possible that this data fits a trend (Fig. 14) and reflects precipitation kinetics of one process rather than bimodality caused by two processes. Additional study of Mn removal through slag leaching beds is required.

Molar balance of the Mn and HCO_3^- removed in the slag leaching bed indicates that complex Mn-bearing carbonate minerals precipitated. The ratio of Mn to HCO_3^- is close to either 1:2 or 1:3, suggesting that Mn is one of two cation components in the carbonate mineral. It is difficult to determine with certainty the other cationic component of these minerals, however, it is likely to be Ca because CaO is the component that dissolves to increase pH within slag leaching beds (Simmons et al. 2002). Therefore, it is likely that complex carbonate minerals such as $CaMn(CO_3)_2$ (kutnahorite) or $Ca_2Mn(CO_3)_3$ precipitated. Kutnahorite has been found in mine drainage remediation studies (Bamforth et al. 2006).

At longer residence times, another Mn removal process may also be operating to remove Mn to sub-mg/L concentrations. Conditions within the slag leaching bed favour

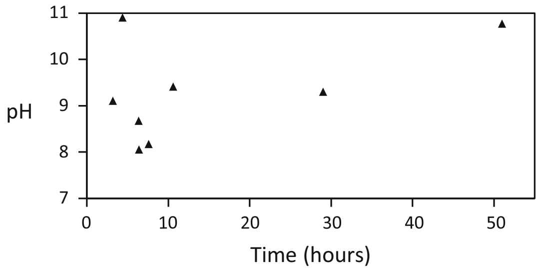

Fig. 14 The pH of discharge from slag leaching bed versus residence time

MnO_2 precipitation (Simmons et al. 2002), which requires oxidation of Mn(II) in solution to Mn(IV). This reaction is relatively slow, and therefore might require residence times of more than 10 h. The reaction can be catalysed by freshly precipitated MnO_2, making the reaction self-catalysing (autocatalytic; Stumm and Morgan 1996).

Conclusions

Geochemical analysis of mine drainage at a closed metal mine in New Zealand shows that the water is highly reduced, Fe(II) concentrations are limited by saturation with respect to siderite, and Mn concentrations are limited by saturation with respect to rhodochrosite. A passive treatment system was designed and constructed to remove Fe through oxygenation and settling of $Fe(OH)_3$ and remove Mn through formation of carbonates and/or oxides by pH adjustment. The system included an oxygenation cascade, settling ponds, and slag leaching bed.

The oxygenation cascade saturated the mine drainage with DO, and 40 h in the settling ponds lowered the dissolved Fe(II) to <2 mg/L. An additional 40 h of settling decreased total particulate Fe to <2 mg/L. Therefore, a residence time of 80 h for this part of the system was sufficient to meet site-specific discharge limits. Mn concentrations were reduced by up to 20 % in the oxygenation cascade and settling ponds through adsorption.

The slag leaching bed design successfully removed Mn. The Mn removal was accompanied by a reduction in HCO_3^- and an increase in pH. A residence time of 5–10 h in the slag leaching bed lowered Mn to between 2 and 4 mg/L; the residence time required to decrease Mn to <1 mg/L was 10–30 h. Mn removal is likely through carbonate precipitation, as $CaMn(CO_3)_2$ or $Ca_2Mn(CO_3)_3$. At long residence times (>10 h), Mn removal may also be occurring through MnO_2 (pyrolusite) precipitation.

The trial treatment system was established to complete proof of concept for passive treatment at a closed gold mine. The system successfully lowered Fe and Mn enough to meet site discharge criteria and removed other trace elements with elevated concentrations. Models for oxygen entrainment through cascades of V-notch weirs, models for DO consumption during oxidation, and modelling of oxidation reaction kinetics accurately predicted treatment system performance. This work also shows that sites in the North Island of New Zealand, where low-DO, Fe(II)-rich mine drainage with Mn can be common, can be effectively treated with an oxidizing system and slag leaching bed.

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