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TECHNICAL COMMUNICATION

Predicting Water Quality Trends in Lone Tree Pit Lake, Nevada (USA)

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Abstract

Lone Tree pit lake became acidic during groundwater recovery at a gold mine in Nevada. Alkalinity was added periodically to shift the lake to a neutral pH. Improved knowledge of the pit lake's sources of acidity was essential for water quality prediction. The primary source of acidity and metals at Lone Tree appears to be dissolution of chemical loads by groundwater flowing through sulfide-enriched rocks exposed in the highwall. About 60% of the highwall consisted of potentially acid-generating rock based on analysis of sulfur and carbon in blast-hole samples collected during mining. Analysis of acid ingress over time indicated that complete oxidation of about 2.3 m of highwall would account for the sulfate and acidity mass balance in the pit lake. In addition, the analysis showed that chemical loading stored in the submerged highwall was likely released over many years by influent groundwater. A synthetic rinsing curve was calibrated against measured water quality to simulate chemical releases from the weathered rock.

Keywords ARD · Mitigation · Wall rock · Geochemical modeling

Introduction

The Lone Tree gold mine, located 47 km east of Winnemucca, Nevada was mined from 1991 to 2006. The groundwater dewatering rate ranged from 630 to 3340 L/s. After dewatering ended in 2006, water levels recovered in the pit, from about 1100 m above mean sea level in late 2006 to 1310 m in November 2018. The Lone Tree pit lake currently contains about 78,100 million liters (ML) of water. Although pit water was initially circumneutral, acidic conditions developed by the second year of filling. State regulations required maintenance of a neutral pH in the lake, so alkaline amendments (slaked lime or trona) have been added to the lake since 2010. The purpose of this evaluation was to predict future water quality in the pit to guide continued water management obligations. Water quality has been monitored since the end of groundwater dewatering in 2006. Over 11 years, more than 100 monitoring events provide a detailed record of water quality evolution. Detailed examination of this record was the basis for improved understanding of the acidity-loading sources and for predicting future water quality trends.

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Description of the Lone Tree Pit Lake

Hydrologic Water Balance of Pit Water Recovery

Predicted groundwater recovery at Lone Tree was simulated with a regional groundwater model (Itasca 2018) that accounted for groundwater depressurization during mining, pit geometry, regional climate, and pumping of an adjacent well during the early stages of filling. The resulting predicted water levels (Fig. 1) track closely with the observed recovery. The groundwater model was used to predict Lone Tree pit gains and losses of water from groundwater inflow, precipitation, evaporation, highwall runoff, pumping, and seepage losses.

Water Quality Trends

Four stages of lake evolution and chemical management are illustrated by the pH trends at Lone Tree (Fig. 2) and the overall water quality (Table 1). The lake was initially circumneutral, from the first measurements in late 2006

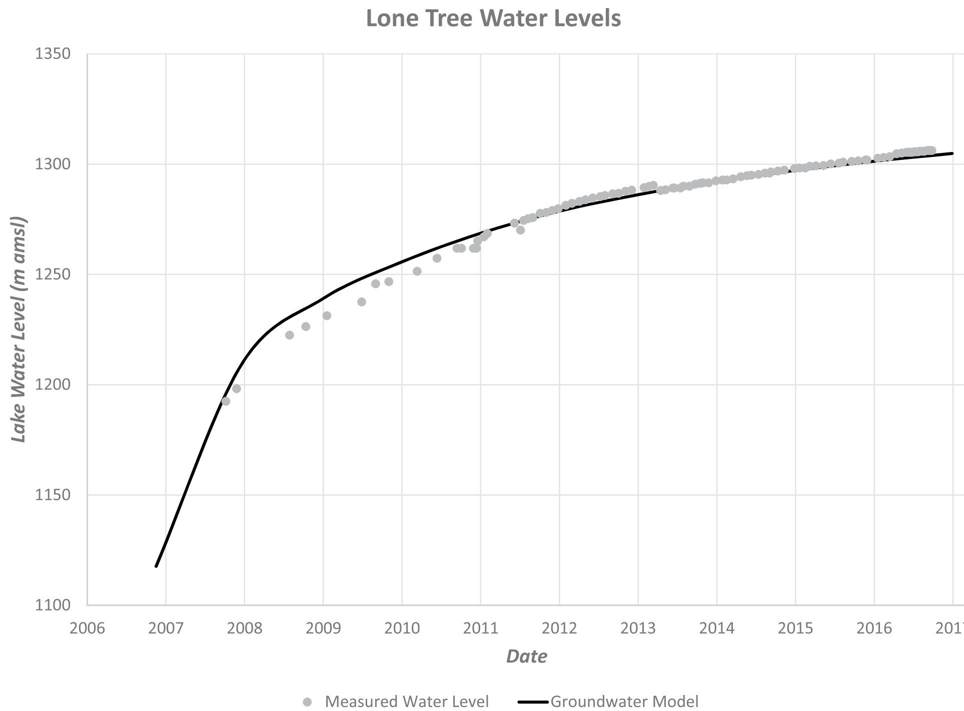

Fig. 1 Predicted and measured lake level recovery at Lone Tree

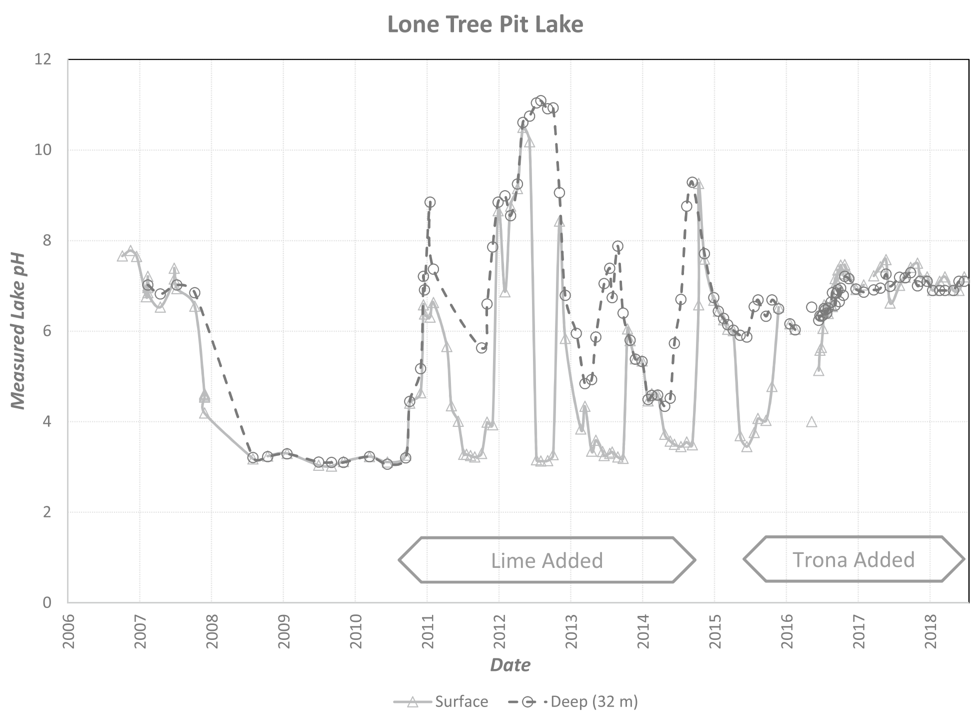

Fig. 2 Lone Tree pit lake pH near surface and at depth for 2006 to 2018

until late 2007. Then, the lake became increasingly acidic from late 2007 until late 2010, reaching a pH of 3.1. Slaked lime ($Ca(OH)_2$) was added to the lake from late 2010 until mid-2014. The surficial pH control was only partially successful using lime because during the lime addition, the pit lake surface layer would acidify during the summer and then a late fall turnover would mix the acidic surface water with more alkaline subsurface water, resulting in increased pH. This occurred because the lime slurry tended to sink below the surface layer. Conversely, the subsurface layer developed a pH that at times exceeded pH 10 during the summer, indicating over-liming. Newmont switched to trona ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$) addition in early 2015 because of its higher solubility, which

Table 1 Water quality in the Lone Tree pit lake representing different stages of water management

Constituent (mg/L)	Initial lake water	After acidification	With Lime neutralization	Re-acidification in summer	Trona addition
Collect date	11/28/2007	6/14/2010	11/5/2012	6/20/2013	6/13/2017
Bicarbonate	< 1.0	< 1.0	28.3	< 1.0	15.8
Alkalinity: carbonate (as CaCO3)	< 1.0	< 1.0	9.6	< 1.0	< 1.0
Alkalinity: total (as CaCO3)	5.2	< 1.0	37.9	< 1.0	15.8
Aluminum	2.6	57.7	0.89	13.8	1.35
Antimony	0.045	0.018	0.043	0.043	0.043
Arsenic	0.0055	0.065	0.13	0.09	0.12
Barium	0.067	0.049	0.021	0.015	0.033
Beryllium	< 0.002	0.0164	< 0.002	0.0055	< 0.002
Boron	0.76	0.96	0.65	0.74	0.83
Cadmium	0.013	0.1	< 0.002	0.013	0.0092
Calcium	118	324	657	582	435
Chloride	17.9	23.7	21.3	21.5	23.1
Chromium	< 0.006	0.028	< 0.006	0.012	< 0.006
Copper	0.07	1.4	< 0.01	0.63	0.075
Fluoride	3.62	8.99	3.9	4.46	1.79
Iron	< 0.06	24.1	0.957	7.32	2.87
Lead	< 0.003	0.00882	< 0.003	< 0.003	< 0.0075
Magnesium	30.4	75.8	6.7	36.3	66
Manganese	1.08	3.69	0.0276	0.945	1.45
Mercury	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002
Nickel	0.331	1.86	0.017	0.38	0.23
Nitrate plus nitrite as *N*	1.01	0.065	0.9	< 0.05	< 0.05
pH (S.U.)	5.55	3.11	8.84	3.29	6.66
Phosphorus	ND	< 0.05	< 0.05	< 0.05	< 0.05
Potassium	22	32.7	34.9	36.7	35
Selenium	< 0.003	0.0056	0.0045	< 0.003	< 0.040
Sodium	121	156	168	173	209
Sulfate	684	1890	2100	2150	1870
Thallium	0.033	0.044	0.0063	0.0088	< 0.015
Total Dissolved Solids	1000	2600	3020	2980	2670
Zinc	1.45	11.7	0.068	2.11	1.01

improved reaction with the surface layer in summer. By 2016, the pH was effectively controlled in both the surface and subsurface layers using trona. The pH trends illustrate the mixing dynamics of the lake, which makes pH control especially difficult with lime.

The initial 1.5 years of alkaline pH was unexpected, given the abundance of potentially acid generating (PAG) rock in the pit floor and along the lowest pit benches, and was attributed to a short-term reversal of groundwater gradients caused by rapid water level increases fed by the fracture-dominated groundwater system. This phenomenon likely delayed input of acidity from the weathered highwall until about 2008 when local groundwater gradients again directed groundwater flux through the weathered highwall and into the pit.

Acidification of the surface layer of the lake during summer was also unexpected. Regional groundwater enters the lake system at all levels of the 200 m deep pit lake, so it is curious that virtually all of the acidity conveyed in the groundwater would report to the surface layer. The apparent cause of this phenomenon was the high temperature of the geothermally-influenced groundwater (35–40 ℃), which causes it to be buoyant in the pit lake averaging 12.8 ℃. Satellite photos (Fig. 3 inset) show clear indication of plumes of acidic water entering the pit surface layer along fault and fracture intersections in the east highwall, where most of the groundwater is thought to enter the pit lake.

Temperature and redox profiles for the lake (Fig. 4) in 2017 show clear indications of seasonal stratification starting in March at a depth of 15 m, with the thermocline

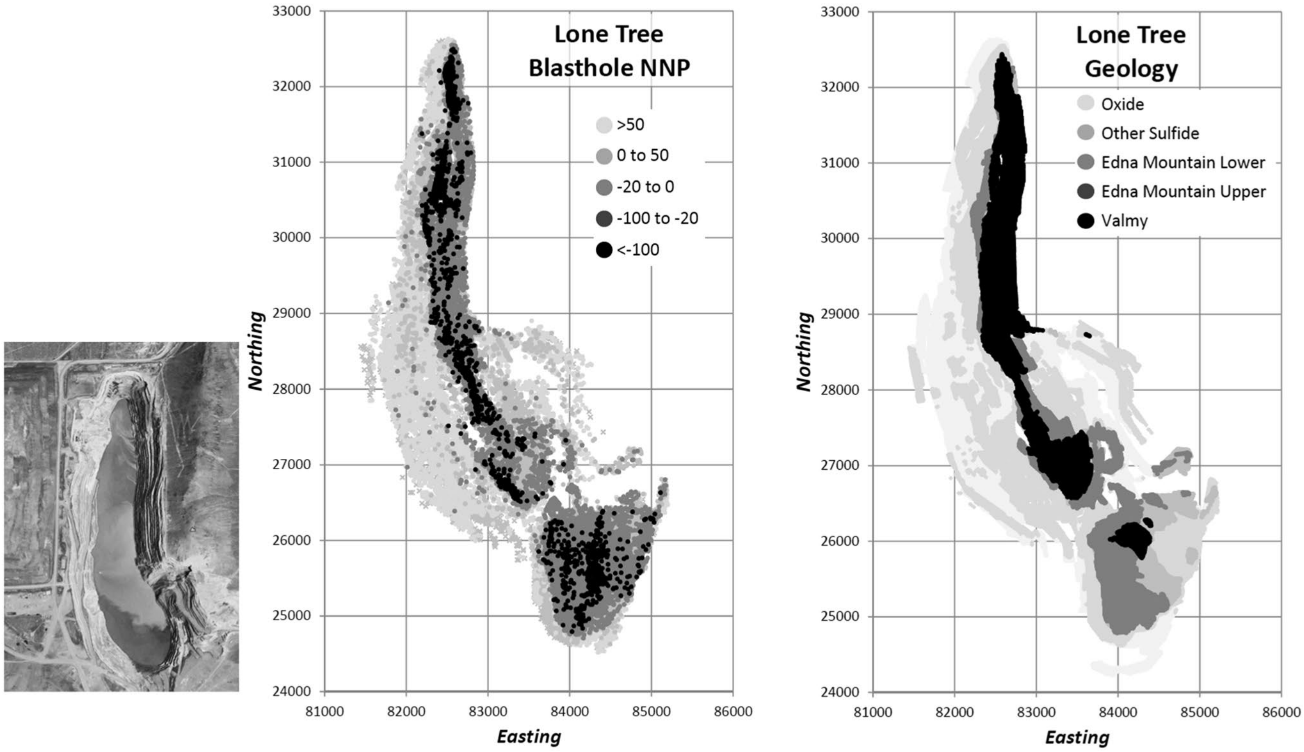

Fig. 3 Net neutralization potential in the Lone Tree highwall (left) and exposed rock units (right). Satellite photo of Lone Tree from September 2010 is lower left

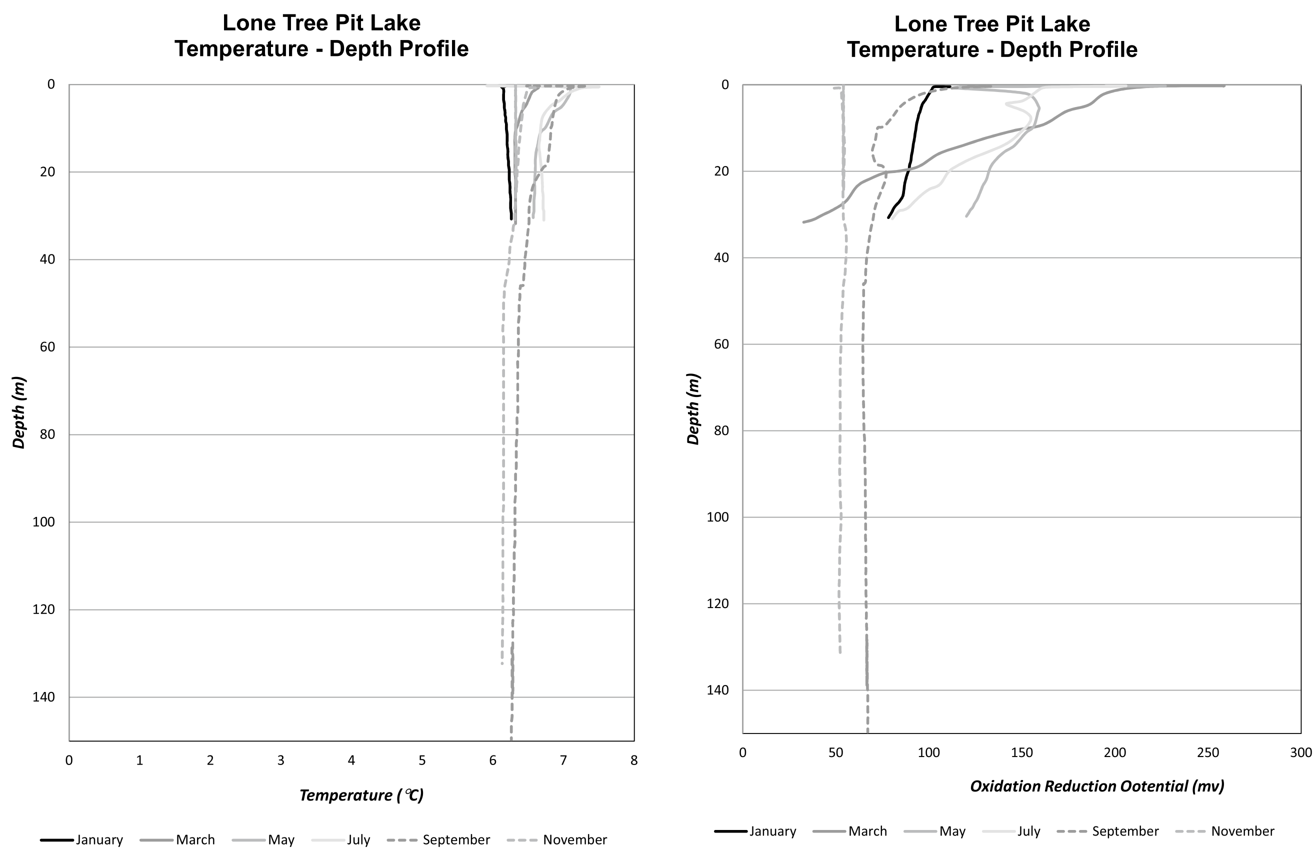

Fig. 4 Temperature (left) and redox (right) profiles in Lone Tree pit lake

deepening to 30 m by September. Despite the seasonal stratification, overturn of the lake has supplied the deeper layers with ample oxygen as redox remained between 50 and 200 mv at all depths for all dates. The pH of the water column remained uniformly between 6 and 6.5 during the entire 2017 monitoring period.

Geology of the Exposed Highwalls

The geology of the exposed bedrock in the highwalls (Fig. 3, right) shows generally older rocks in the east highwall and younger rocks in the west highwall, due in part to a series of north–south normal faults. The deepest portion of the pit exposes the Wayne Zone, which is an important ore host and was a conduit for mineralization of sedimentary rocks in the east highwall, principally the Valmy Fm. The Wayne Zone is highly mineralized and contains jarosite ($KFe_3(OH)_6(SO_4)_2$), alunite ($KAl_3(OH)_6(SO_4)_2$), goethite ($FeO(OH)$), and clay minerals. Primary rock units exposed in the Lone Tree pit include the Valmy, Edna Mountain, and Havallah formations. The Valmy formation overlies the late Ordovician Roberts Mountain thrust, which dates to the Antler Orogeny. The Valmy is a cherty quartzite containing abundant authigenic pyrite. Younger post-Antler rocks include the Permian Edna Mountain and Havallah formations. The Edna Mountain consists of weakly calcareous sandstone. The Havallah consists of deep ocean sediments accreted onto the plate margin, and consists of chert beds and basalts overlain by calcareous sandstone, shale, mudstone, sandy limestone, and conglomerate. Extensive mineralization is associated with the Wayne Zone, with the most prominent alteration found in the Valmy and Edna Mountain rocks (Bloomstein et al. 1993).

During mining, samples were collected from blast-hole cuttings for gold assays. Subsamples were also analyzed for pyritic sulfur and inorganic carbon using LECO thermal combustion analysis. Estimated acid neutralizing potential (ANP), acid generation potential (AGP) and net neutralization potential (NNP, as ANP minus AGP) were calculated from the blast-hole sulfur and carbon data (Fig. 3, left). Unoxidized Valmy and Lower Edna Mountain material account for about one-third of the submerged rocks in the highwall. The proportion of PAG rock, based on blast-hole data, was greater than 60% of the exposed rocks. Average total sulfur within the PAG zones was about 1.5% by weight.

Net Acid and Sulfate Ingress to the Pit

Water quality monitoring data and alkaline amendment addition rates were used to calculate the average quantity of acidity (as $CaCO_3$) that reached Lone Tree from 2007 to 2016 (Table 2). Since there was no direct measure of acidity entering the pit lake, the average acidity input was calculated by difference using the balance of measured alkalinity load changes in the lake from 2007 to 2017, measured inputs of alkaline reagents, and other gains and losses of alkalinity. In the early stages of filling, alkaline water (300 mg/L) was pumped to the Lone Tree pit lake from a nearby well (from mid-2007 to early 2012). Some groundwater seepage out of the lake occurred in response to pumping, which removed some acidity. These gains and losses were also considered. For the purposes of the acidity ingress calculations, lime efficiency was assumed to be 20%, while 100% trona efficiency was assumed. The average rate of acid ingress was 12 t/d. Acid ingress in 2017 was estimated by Newmont at 8.4 t/d, indicating that acid ingress may be gradually decreasing.

Table 2 Alkalinity and acidity balance for the Lone Tree pit lake

Acidity mass gains	Alkalinity input (t) as $CaCO_3$	Estimated efficiency (%)	Effective alkalinity (t) as $CaCO_3$
1. Alkalinity in Pit Lake 2007			0
2. Alkalinity in Pit Lake 2017[1]			3000
3. Lime added	67,000	20%	13,400
4. Trona added	9,000	100%	9000
5. Acidity removed due to seepage out of pit lake[2]	4,000	100%	4000
6. Alkalinity gained from water pumped into pit lake	16,000	100%	16,000
7. Net Alkalinity added to pit lake (sum lines 3–6)			42,400
Alkalinity consumed by acidic groundwater inflow to pit lake (line 7 minus 2)			39,400
Time of filling 2007–2017 (days)			3226
Average daily acidity gain (*t/d*) as $CaCO_3$			12
Sulfate mass gains			Sulfate mass (*t*)
Sulfate Mass (Dec 2011)[3]			102,000
Time of filling (2007–2017)			1398
Average daily sulfate gain (*t/d*)[4]			73

[1]43.2 mg/L alkalinity and 68,700 ML water

[2]Removal of acidity is equivalent to a gain in alkalinity

[3]2100 mg/L SO_4 and 53,470 ML water

[4]Ratio of acidity to sulfate gain is 17%

Sulfate gains in the pit lake were estimated by determining the sulfate load in 2011 and dividing by the number of days the lake was filling. Comparing the average acidity (12 t/d) and sulfate (73 t/d) ingress provides an important measure of the naturally-occurring neutralization within the Lone Tree system. Based on the stoichiometry of pyrite oxidation (Eq. 1), 2 mol of sulfate produced by pyrite oxidation should result in 2 mol of acidity as $CaCO_3$ (Eq. 2). As a result, the mass ratio between acidity as $CaCO_3$ (formula weight of 100 g/M) divided by sulfate (96 g/M) should be 1.04. The actual ratio at Lone Tree is 0.17, indicating that much of the acidity is being neutralized, either by alkalinity contained in a portion of the influent groundwater or by dissolution of carbonates or other minerals within the weathered rock zone.

$$FeS_2 + 15/4\, O_2 + 7/2\, H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (1)$$

$$4H^+ + 2CaCO_3 = 2CO_2 + 2\, H_2O + 2\, Ca^{2+} \quad (2)$$

Potential Mechanisms of Delivering Acidity to the Pit Lake

Alternative Chemical Release Models

Pit lake predictive models use widely varying assumptions about the interaction between groundwater and the weathered highwall. A common assumption used to predict pit lake water quality is that groundwater only removes accumulated chemical loads from the portion of the weathered highwall near the current lake surface (first flush model). The rate of chemical release from the active portion of the weathered highwall is often indexed to humidity cell tests. An alternative assumption about groundwater interaction with the highwall is that chemical release occurs from the entire submerged portion of the highwall. For the slow release model, the rate of chemical release is estimated from either an empirical rinsing curve based on column tests or a synthetic rinsing curve. The thickness of the weathered rock zone in the highwall is often based on a diffusion model (Davis et al. 1986).

The two different chemical release models yield different patterns of chemical loading over time. During early stages of pit lake recovery, water levels tend to increase rapidly, so initial chemical loading is much higher for the first flush model, while loading is higher in later stages for the slow release model.

Comparing Actual Sulfate Trends to Predicted Sulfate from First Flush Model

The first flush model was used to simulate sulfate inputs to the pit lake. Using the change in water level, the change in submerged highwall area was calculated for each year of filling. Next, the thickness of highwall that would need to oxidize to deliver the observed sulfate mass was calculated. During initial filling, sulfate could be accounted for with < 1 m of weathered highwall. However, more than 40 m of weathered highwall was needed to account for the sulfate mass increase by 2017. There is no plausible explanation for such widely varying depth of weathering between the lower and upper benches, so this model appears unsuitable to describe the chemical evolution at Lone Tree.

Comparing Actual Sulfate Trends To Predicted Sulfate From Slow Release Model

In the slow release model, the entire submerged highwall continues to contribute chemical mass until loads are fully rinsed from the highwall. The rate of delivery was based on a synthetic leaching curve for the weathered highwall. The model is based on an exponential decay curve of chemical mass with cumulative rinsing by groundwater (Eq. 3). The mathematical form of Eq. 3 facilitates calculating incremental loading as a function of groundwater flux. The synthetic rinsing curve was calibrated to humidity cell tests conducted on weathered rock samples from the Valmy formation (C (mg/L) = 10,000 for LS ≤ 1, $6216 \times e^{-0.057(LS)}$ for LS > 1). Both the timing and total mass of sulfate from humidity cells compared favorably with the synthetic model.

$$C = C_o \text{ for } LS \le N, = C_1 \times e^{-k(LS)} \text{ for } LS > N \quad (3)$$

where Co is first flush concentration, N is the duration of the first flush set at 1 pore volume in this model, C1 is the concentration after the first flush found through solving the exponential equation, k is a dimensionless coefficient for the decay curve, and LS is the pore volume of groundwater leached through the weathered rock (m^3 groundwater/m^3 rock).

The slow release model had a good fit to sulfate in years 2010 to 2016 but a poor fit during the initial years. The model over-predicted sulfate loading for the early stages of filling. The likely explanation for the poor fit, discussed previously, is that the pit lake initially filled faster than the regional groundwater system, causing chemical loading from the lower benches to be delayed. The model was adjusted by delaying 95% of the estimated 2007 loads and 25% of the 2008 loads until 2009 through 2011.

Predicted sulfate based on delayed loading showed improved agreement with measured sulfate and acidity trends (Fig. 5). The model mirrored the gradual increases in sulfate from 500 mg/L in late 2007 to over 2,000 mg/L by 2012. The model showed continuing increase in sulfate from 2012 to 2017, while measured sulfate declined slightly. Declining sulfate after 2012 was attributed to gypsum formation, which was not simulated in the mass balance model.

A sulfate balance for the highwall was developed by estimating the weathered highwall thickness (2.3 m) that provided the best fit to measured sulfate. This thickness is similar to but is at the upper range of weathered highwall thickness values based on the Davis Ritchie model. Figure 6

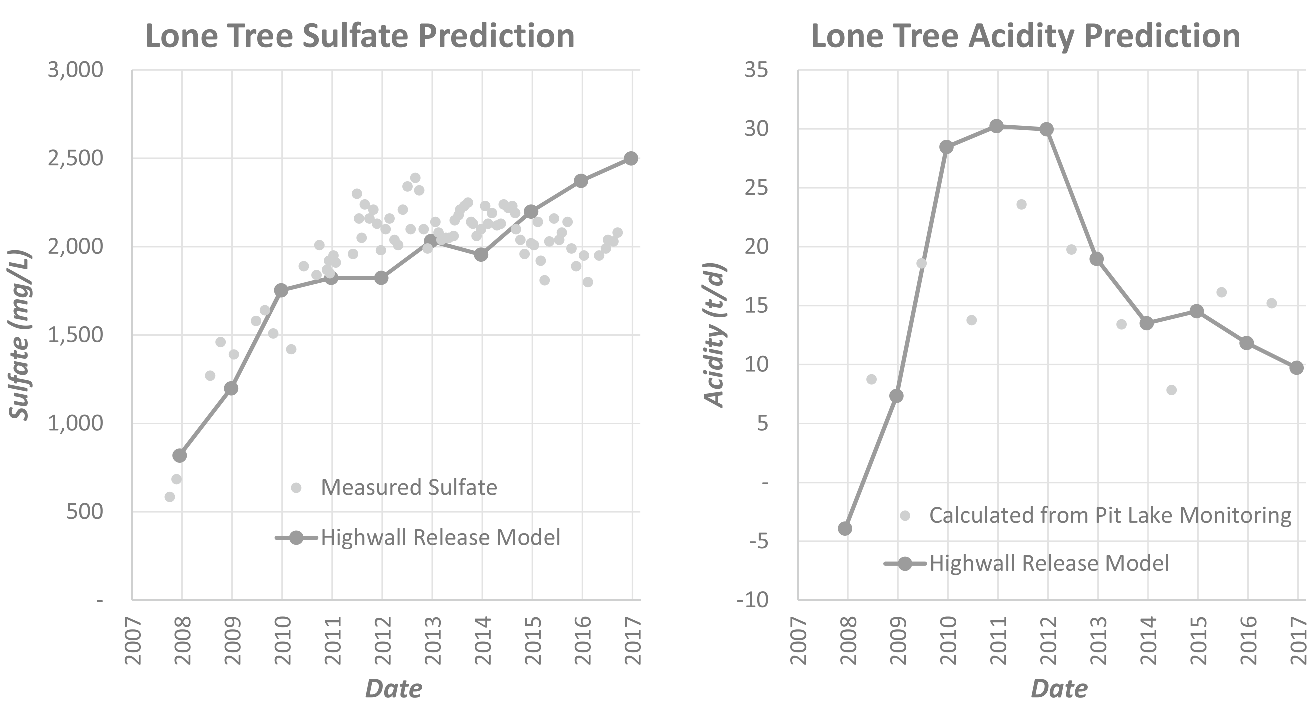

Fig. 5 Comparison of predicted and measured sulfate (left) and acid ingress (right)

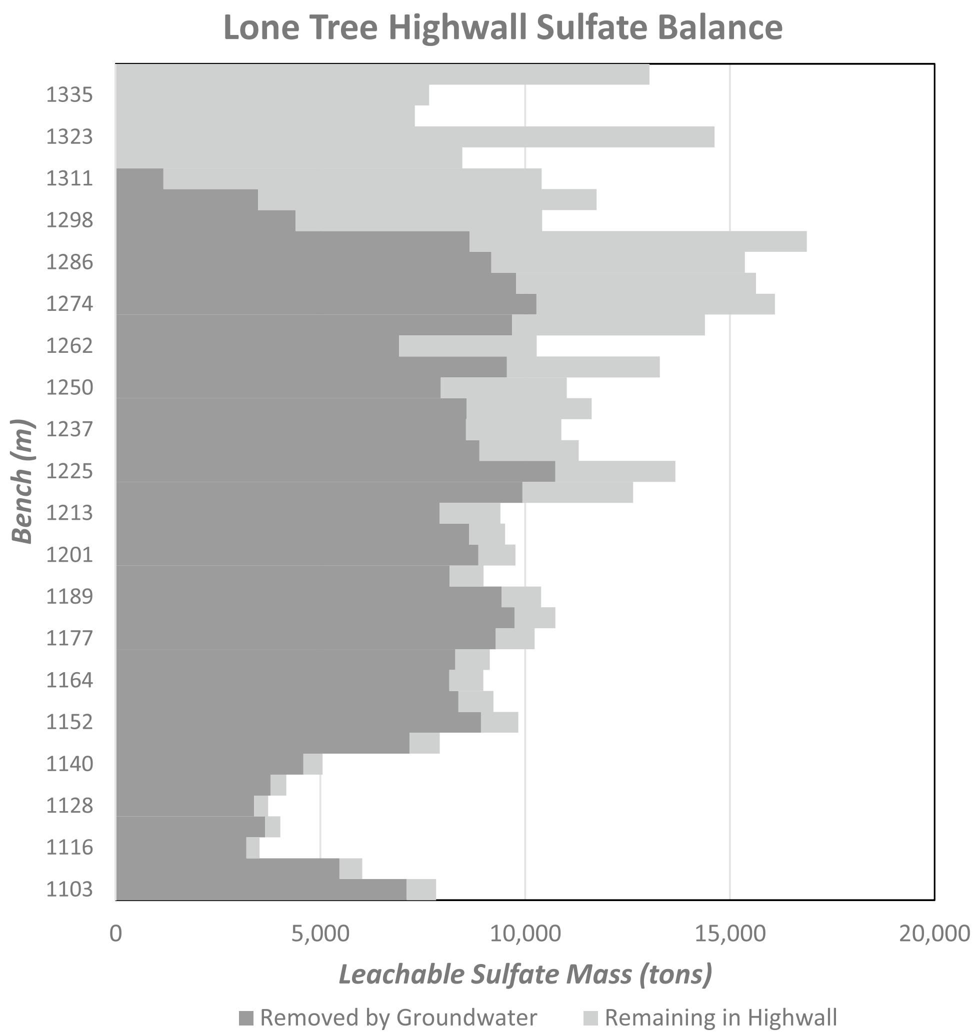

Fig. 6 Sulfate mass by bench shows amount rinsed into the lake by groundwater and proportion remaining in the weathered highwall

shows the balance of sulfate rinsed by groundwater into the pit lake and sulfate remaining in the highwall as of 2017 based on the sulfate balance predicted by Eq. 3.

The similarly calibrated acid ingress model showed good agreement to acid ingress based on pit lake water quality (Fig. 4). Predicted acid ingress showed relatively steep declines after 2011 (16 t/d) to 10 t/d by 2017. The gradual decline in estimated acid ingress is due to decreases in PAG rock in the upper highwall and gradual reduction in acidity as the submerged highwall is leached by groundwater. Overall, 65% of the sulfate mass was removed by 2018.

Predicting Metals in Lone Tree Pit Lake

The highwall slow release model used to simulate sulfate and acidity inputs to Lone Tree was next used to simulate key contaminants (aluminum, arsenic, iron, manganese, cadmium, copper, and zinc). A synthetic release curve (Eq. 3) was calibrated to the Valmy humidity cell tests in a similar fashion to sulfate. Predicted contaminant behavior was validated by comparing simulated and actual concentrations for a selected time period between seasonal turnover events from late 2012 to late 2013.

In late 2012, the lake surface layer had a neutral pH, a slightly positive net alkalinity, and low levels of metals. The lake surface layer gradually became more acidic, with increased metal concentrations over the ensuing 11 months. Based on the conceptual pit lake model, the acidification of the surface layer was caused by input of a mixture of acidic and alkaline groundwater to the surface layer. A lake turnover event in late 2013 caused the acidic shallow and alkaline deep layers to mix in early October 2013. This acidification process was simulated in PHREEQC (D'Appelo and Parkhurst 2013) by a series of mixing steps, starting with water from the epilimnion and then adding an appropriate volume of groundwater. Low temperature solids that could be expected to form in pit lakes were simulated as potential equilibrium phases (Eary 1999).

The initial epilimnion volume was modeled as 6857 ML and groundwater inputs of 118 L/s resulted in the addition of 3223 ML over 11 months, causing the surface layer to expand from 6.1 m to about 9.75 m in thickness. A mixture of 35% PAG-influenced groundwater and 65% background groundwater was found to provide the best fit to measured changes in metals and acidity over the calibration period.

Simulated input of combined PAG-influenced and background groundwater caused the surface layer to gradually acidify, similar to a titration reaction where acidic water is added to a system with initially alkaline conditions. The simulated change in pH and metal concentrations fit the measured trends in water quality closely. The agreement between simulated and observed acidity and metal concentrations was taken as confirmation that the gradual input of net acid groundwater, and the composition of the water predicted from the slow release model of chemical release from the highwall correctly simulated observed changes in water quality (Fig. 5).

Pro-Forma Water Quality Prediction

The calibrated pit lake model was used to perform several forward-looking water quality simulations. Starting with the Lone Tree pit water after the lake turned over in 2018, future water quality was simulated by adding the quantity of groundwater, rainfall, and evaporation predicted by Itasca (2018). The composition of the acidic groundwater was based on the slow release model. PHREEQC was calibrated as previously described. Water quality was predicted for 10 annual time steps. The three cases simulated included (1) continued trona addition, (2) slaked lime addition, and (3) no alkaline amendments.

Results of all three simulations for pH and dissolved iron (Fig. 6) show continuation of the alkaline lake pH if amendment addition continues at a diminishing rate that tracks the declining net acid input to the lake. Lake pH declines in about 1 year to 3 S.U. if amendments are not added. Dissolved iron and other metals remained low for the alkaline amendment cases, but iron increased almost linearly to 120 mg/L in 10 years if no alkalinity is added (Fig. 7, 8, 9).

Little change in Lone Tree water quality is expected over the next 10 years based on the pro-forma water quality model if alkaline amendments continue. Water would become

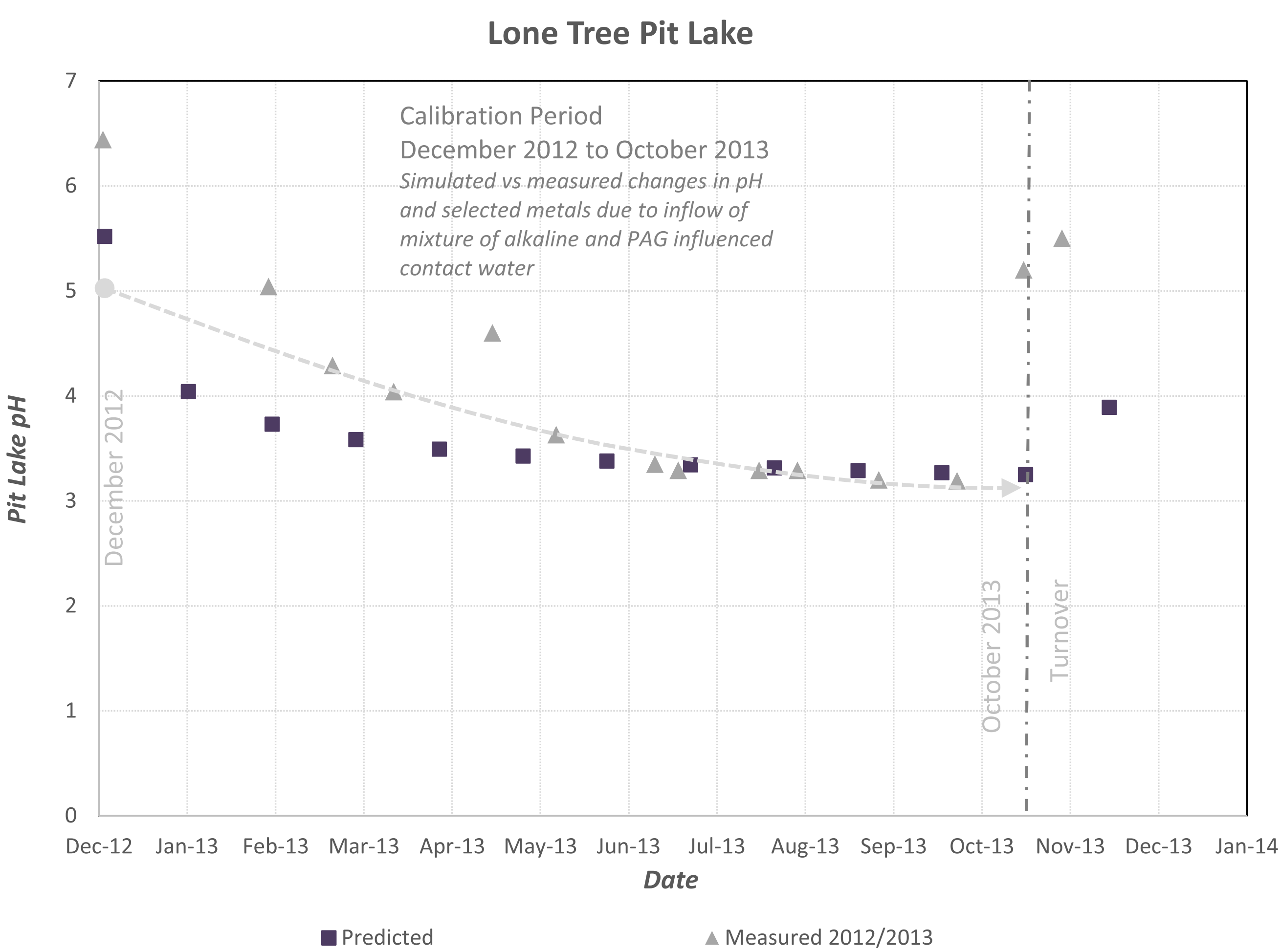

Fig. 7 Simulated versus measured pH in the Lone Tree pit lake for the 2012 to 2013 calibration period

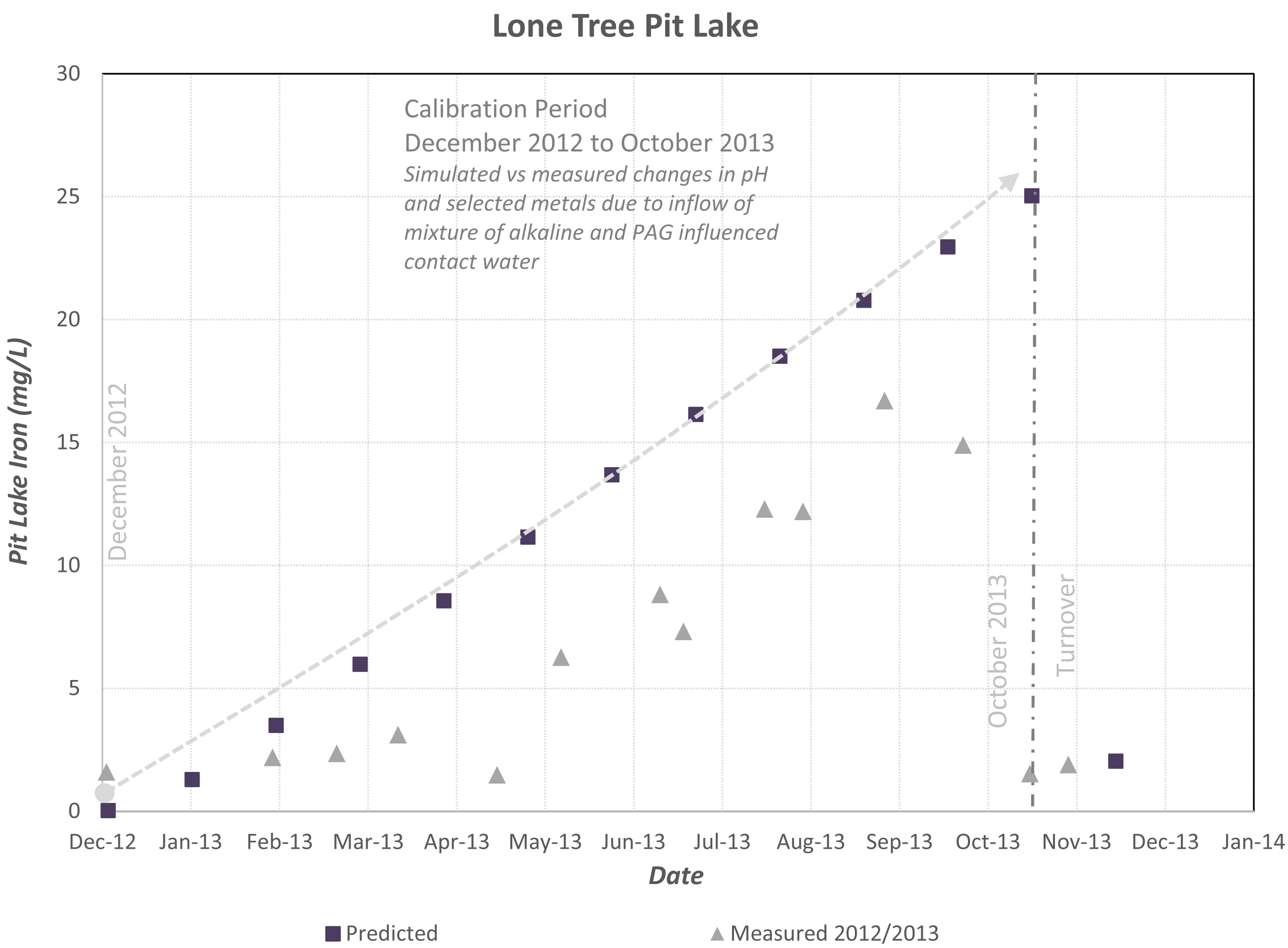

Fig. 8 Simulated versus measured dissolved iron in the Lone Tree pit lake for the 2012 to 2013 calibration period

gradually more acidic and higher in metals if amendments are suspended. The model predicts about 50% reduction in acid ingress from current levels over the 10 year period.

Measured constituent concentrations were less than the Nevada Division of Environmental Protection (NDEP) Profile III reference values for both 2018 measurements and for predicted 2028 pit water, assuming continued addition of lime or trona. NDEP reference values are an ecological risk screening level used for evaluating pit lakes.

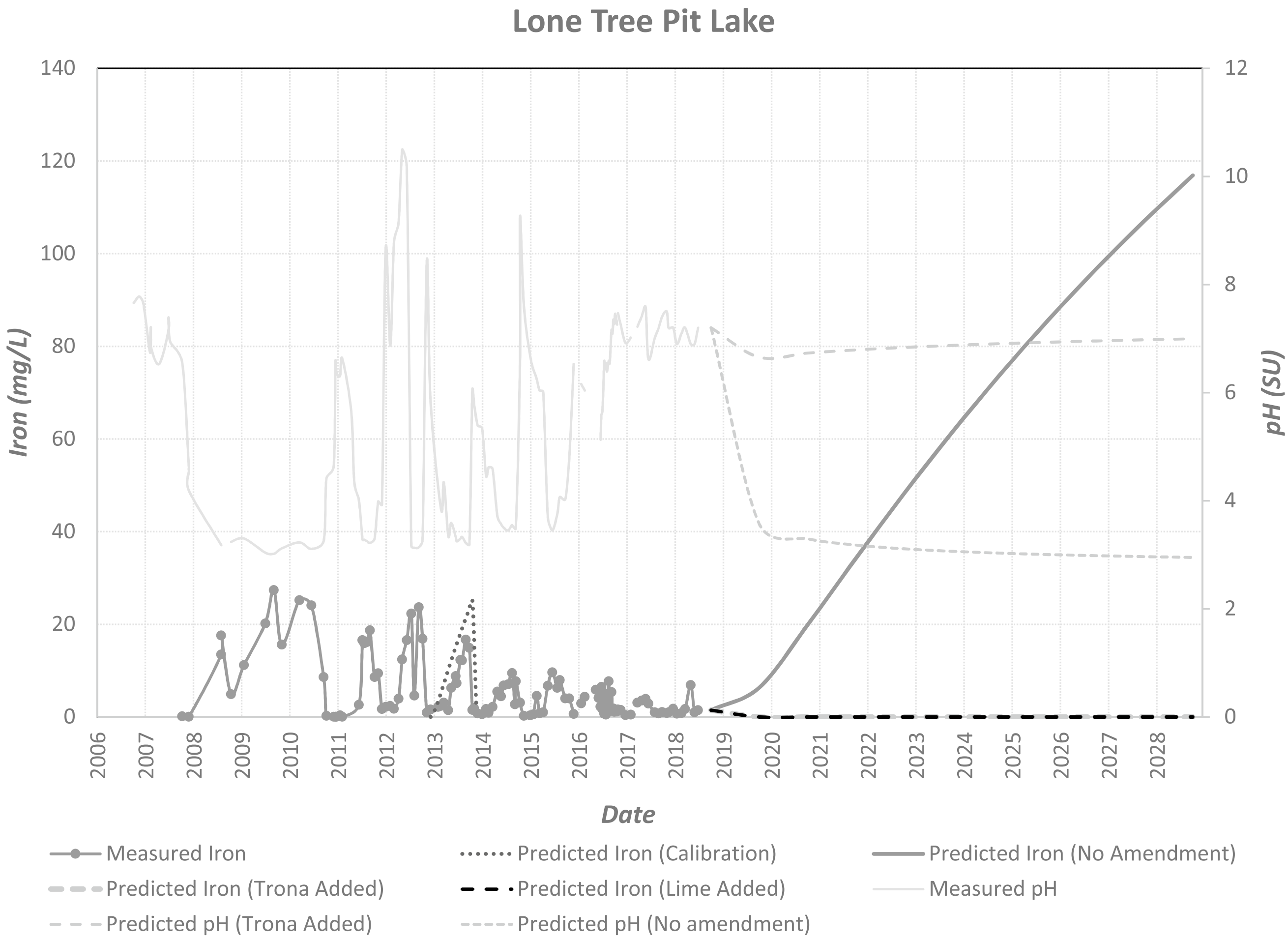

Fig. 9 Simulated pH and dissolved iron in the Lone Tree pit lake for 2018 to 2028

Conclusion

Water quality monitoring data from Lone Tree provided important insights into pit lake evolution. The mass balance trends for sulfate and acidity support a slow release model of chemical releases from the weathered highwall. In this conceptual model, chemical mass is slowly released from the entire submerged portion of the pit lake over many pore volumes of leaching by influent groundwater. A synthetic release curve that approximates the slow release was calibrated using leaching tests of weathered rock samples. A fully weathered highwall thickness of 2.3 m provided the best fit to the observed sulfate trends.

References

Bloomstein E, Braginton B, Owen R, Parratt R, Raabe K, Thompson W (1993) Geology and geochemistry of the lone tree gold deposit, Humboldt County, Nevada. Preprint 93–205. In: Annual Meeting of the Soc for Mining, Metallurgy, and Exploration

Davis GB, Doherty G, Ritchie AIM (1986) A model of oxidation in pyritic mine wastes: part 2: comparison of numerical and approximate solutions. Appl Math Model 10:323–329

Eary LE (1999) Geochemical and equilibrium trends in mine pit lakes. Appl Geochem 14:963–987

Itasca (2018) Update of the lone tree groundwater flow model and predictions of future pit-lake infilling. In: Technical memorandum to Newmont Mining (unpubl)

Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC version 3—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Techniques and Methods, book 6, ch A43, https://pubs.usgs.gov/tm/06/a43. Accessed July 2018