

Passive treatment of neutral mine drainage at a metal mine in New Zealand using an oxidising system and slag leaching bed¹

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ABSTRACT

Rehabilitation at a closed metal mine in New Zealand is complete with the exception of a consistent 20 L/s drainage from underground workings. The discharge has pH ~ 6, alkalinity ~150 ppm, dissolved oxygen (DO) <1 ppm and elevated Fe, Mn, As and Zn. Treatment difficulties are caused by a variable total Fe concentration (~20-200 ppm) and the highly soluble nature of Mn (15-22 ppm). Modelling indicates four factors important when considering remediation: (1) dissolved Fe is ~20 ppm and all is dissolved Fe(II), (2) Fe(II) is controlled by saturation with respect to siderite (FeCO₃), (3) remaining Fe is all colloidal Fe(OH)₃ and (4) Mn concentration is saturated with respect to rhodochrosite (MnCO₃). Equilibrium of Fe and Mn with minerals means that dissolved concentrations are stable and a treatment system can be optimised to the water chemistry. A pilot scale passive treatment system has been installed that includes an oxygenation cascade of drops through V-notch weirs, settling/reaction ponds and a slag leaching bed. The system treats Fe(II) by oxidation to Fe(III) followed by precipitation and settling of Fe(OH)₃. High alkalinity prevents acidification, and release of dissolved CO₂ causes the pH to increase. Manganese is removed by precipitation of Mn carbonates, oxides or oxy-hydroxides in the slag leaching bed at elevated pH and high DO. Zinc and As are removed through adsorption onto Fe(OH)₃. The oxygenation system removes 82-96% of the Fe, 10% of the Mn, 89% of the As, and 59% of the Zn. The slag leaching bed removes 99% of the remaining Mn.

Additional Key Words: manganese, arsenic, ferrous iron oxidation, iron hydroxide, adsorption, V-notch weir, metal mines.

INTRODUCTION

Contaminated mine drainage is a common issue associated with mining in New Zealand. In mining, large volumes of minerals that are unstable under surface conditions are exposed, resulting in increased oxidation of sulphides and release of trace elements. Secondary reactions between mine drainage and other rocks result in additional release of trace elements. Acid mine drainage (AMD) from coal mining in New Zealand has been investigated extensively (Alarcon, 1997; deJoux, 2003; James, 2003; Black et al., 2005; Pope et al., 2006); however, contaminated mine drainage from metal mines can also be significant (Craw et al., 2005).

¹ Paper presented at Securing the Future and 8th ICARD, June 23-26, 2009, Skellefteå, Sweden.

In this work, we interpret the geochemistry of drainage from a precious metal mine in New Zealand dominated by manganese and iron and install and operate a small-scale passive treatment system to remove contaminants to below discharge limits.

MINE WATER GEOCHEMICAL INTERPRETATION

The site is a closed metal mine in New Zealand which has a consistent flow of approximately 20 L/s pumped from flooded underground workings to prevent uncontrolled discharge through adits. The water chemistry has moderate pH (5.8 - 6.3) high buffering capacity (120-180 mg/L - CaCO₃ equiv), low DO (<1 mg/L), elevated SO₄²⁻, hardness, Fe, Mn, and trace amounts of Zn, and As. Treatment difficulties are caused by a variable total Fe concentration (20 - 200 mg/L) and the highly soluble nature of Mn; however, dissolved Fe concentration is fairly consistent (20 - 25 mg/L). Equilibrium geochemical modelling with PhreeqC indicates that the highest dissolved Fe(III) concentration possible at the measured pH (~6) is 0.1 ppm. Therefore, under the chemical conditions present at this site and assuming equilibrium, almost all (>99%) of the dissolved Fe must be Fe(II).

Manganese concentrations are about 11 to 22 mg/L. In general, AMD systems do not attain equilibrium with respect to Mn minerals because Mn is often present as a trace component. High solubility of Mn through common mine drainage pH ranges (2-8) and typical Eh conditions often prevents equilibrium with respect to Mn minerals. However, modelling solution chemistry with PhreeqC for this site indicates that Mn is saturated with respect to rhodochrosite (MnCO₃; SI = 0.08) and under-saturated with respect to common Mn oxyhydroxide minerals (SI = -7 to -23). Increasing pH over-saturates the mine drainage chemistry with respect to rhodochrosite, so MnCO₃ precipitation is favoured by pH increase. In addition, the mine pool is about saturated with respect to siderite, FeCO₃, assuming about 20 mg/L of dissolved Fe(II) (SI = 0.04).

Equilibrium of dissolved Fe and Mn concentrations with minerals means that dissolved concentrations are stable and a passive system can be optimised to the water chemistry.

METHODS

The treatment approach selected for this site involves oxygenation, oxidation of Fe(II) and settling of Fe(OH)₃ followed by pH manipulation to precipitate Mn carbonate, oxide or oxyhydroxide (Figure 1).

Oxygenation cascade and reaction/settling ponds

Addition of O₂ to the neutral mine drainage (NMD) 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).
- Residence time for settling of Fe(OH)₃.

The reaction kinetics of iron oxidation indicate that reaction rates are proportional to the DO content and strongly influenced by pH (Stumm and Morgan, 1996). The pH of the inlet is approximately 6 and the DO content is typically below 1 mg/L. At pH 6 but with saturated DO, reaction kinetics for Fe(II) to Fe(III) oxidation indicate 99% of Fe(II) will convert to Fe(III) within 48 hours (Stumm and Morgan, 1996).

The overall reaction of Fe(II) oxidation and Fe(III) precipitation as a hydroxide is acid producing; however, a comparison of alkalinity in the NMD with acid produced during

Fe(OH)₃ precipitation indicates that there is excess alkalinity (30-100 mg/L CaCO₃) in the mine water. Therefore Fe(OH)₃ precipitation should not cause substantial pH reduction.

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 found that the V-notch weir produces the greatest oxygen transfer and a drop height of 0.9 m entrains the greatest amount of oxygen (Baylar and Bagatur, 2000). Ideal tailwater depths are about 2/3 of the drop height (Kim and Walters, 2001). The trial oxygenation cascade uses 5 V-notch weirs with drop heights of 0.9 m into tailwater depths of 0.6 m and is based on empirical relationships from Kim and Walters (2001).

In summary, the oxidation system is constructed in two parts (Figure 1):

- 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 at a design flow rate of 0.011 L/s.

Once the oxidising system was started, site visits were conducted on a weekly basis. For each site visit, 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 and one time for Mg, Zn and As.

Slag leaching bed

The slag leaching bed is 1.12 m square and 0.81 m deep. Water enters the unit through a gate valve and flows horizontally through the bed. The water then flows through a settling pond with baffles and then out of the trial system. The leaching bed is filled with steel slag generated from the electric arc furnace process at New Zealand Steel Limited. The slag contains approximately 15% CaO and ranges in size from 20 to 60 mm; other major components include Fe, Mg, Si, Al and Mn in minerals such as wustite, larnite, hematite and gehlenite. 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, site visits were conducted on a weekly basis. For each visit, field data were collected from the inlet and outlet, flow rate was 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.

RESULTS AND DISCUSSION

Oxidation system

The oxidation system operated for 65 days. The flow rate through the weirs in the oxygenation cascade ranged between 0.15 to 0.48 L/s and the flow rate through the settling ponds ranged between 0.009 and 0.050 L/s. The site was visited eight times.

Iron

Comparison of the DO levels through the cascade of V-notch weirs with the model predictions shows that adequate DO for oxidation of Fe(II) is added through the cascade, and that the model by Kim and Walters (2001) accurately predicts oxygen transfer (Figure 2).

The model involves solving for r_{20} in $r_{20} = 1 + 0.453F_J^{0.453}h^{1.117}(H/h)^{0.475}$, where r_{20} = DO deficit ratio at 20°C, F_J = jet Froude number, H = tailwater depth, and h = fall height.

Total Fe in the untreated NMD ranged from 4.9 to 18.9 mg/L, with 75% to 100% consisting of dissolved Fe at pH 5.82 - 7.66. Modelling of Fe speciation indicates dissolved $Fe \approx Fe(II)(aq)$ with negligible dissolved $Fe(III)$. Almost all $Fe(III)$ is present as particulate $Fe(OH)_3(s)$. Dissolved and total Fe concentrations measured throughout the system and under varying flow conditions match with oxidation of dissolved $Fe(II)$ and settling of $Fe(OH)_3$ precipitates (Figure 3). As the $Fe(II)$ is oxidised, $Fe(III)$ concentrations rise through the first settling pond but then decline as $Fe(OH)_3$ settles out of solution. High alkalinity prevents acidification and release of dissolved CO_2 causes the pH to increase.

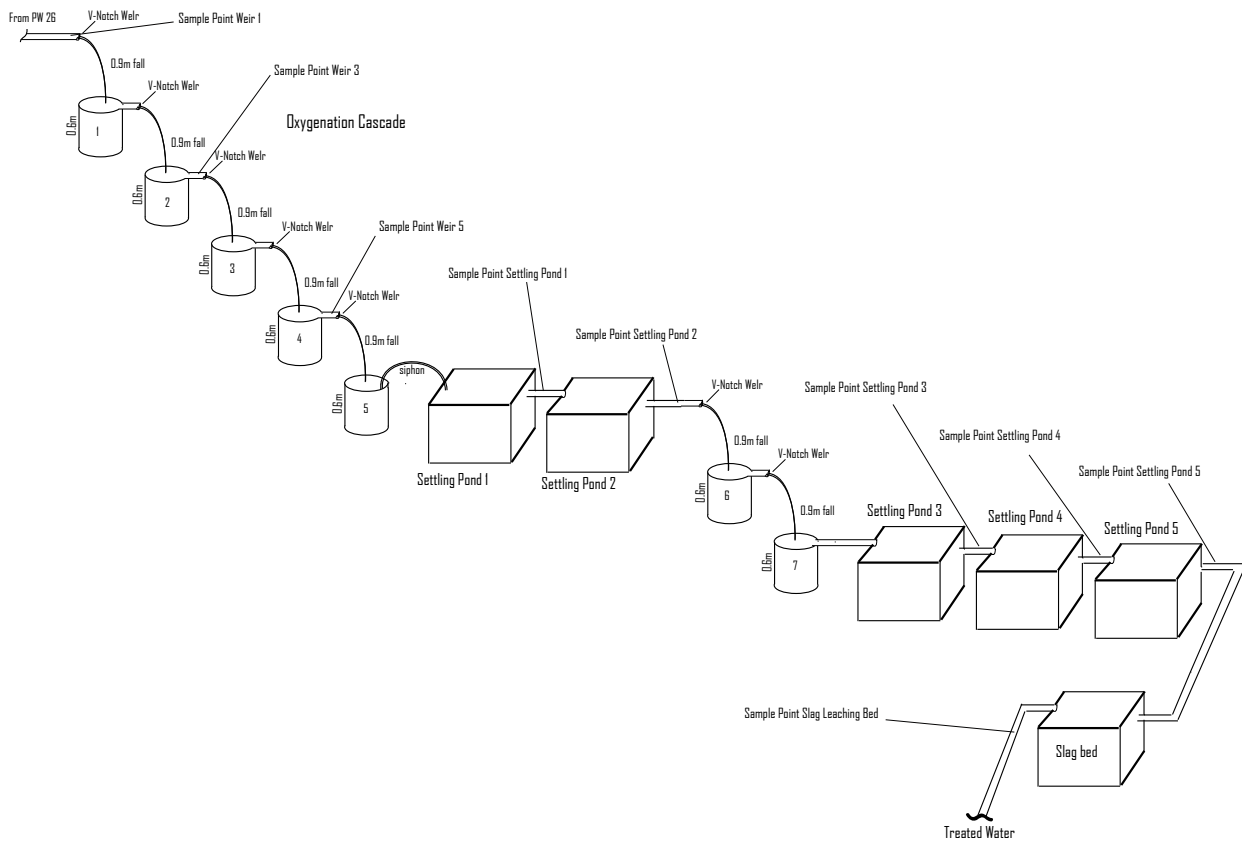


Figure 1. Schematic of trial system

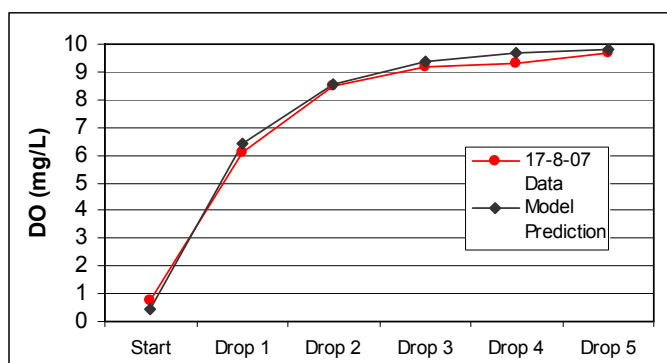


Figure 2. Model and measured values for oxygen transfer through cascade of triangular-notch weirs.

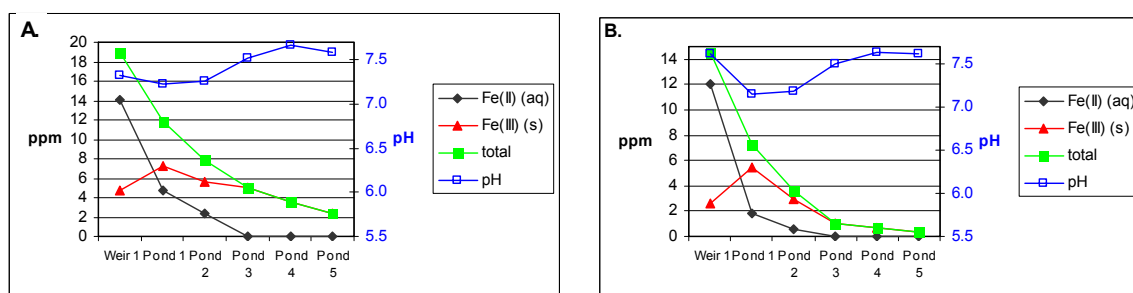


Figure 3. Iron concentrations and pH through the oxidising system. A. Data from 17 August 2007, total residence time in system 135 hours. B. Data from 7 September 2007, total residence time in system 80 hours.

The oxidation rates (the residence time vs. concentration of Fe(II) oxidised) are compared in Figure 4 to Fe reaction kinetics (Stumm and Morgan, 1996). The measured oxidation rates closely follow the model predictions for pH 6.0 at a DO concentration of 10 mg/L, although actual pH values for water in the system varied between 5.82 and 7.66. This analysis suggests that iron reaction kinetics for a pH 6 and DO of 10 mg/L can be used to predict oxidation rates for iron in the NMD at this site.

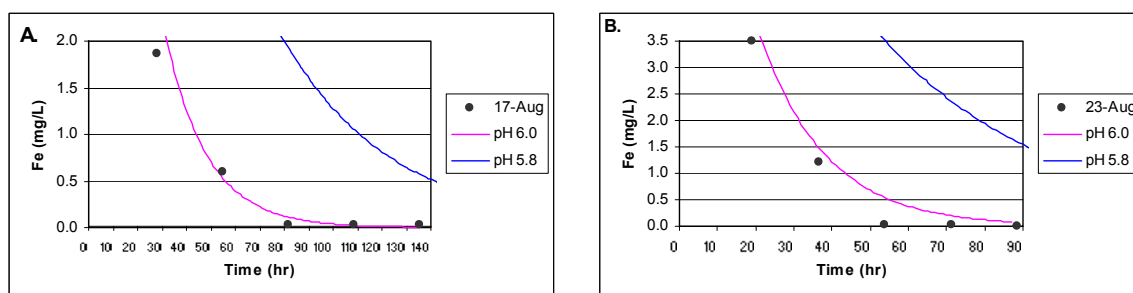


Figure 4. Fe(II) oxidation rates predicted by reaction kinetics model compared to recorded values in oxidising system. A. Data from 17 August 2007. B. Data from 23 August 2007. Results follow the pH 6.0 curve.

The Fe concentrations for all sampling points are presented in Figure 5. The concentrations are plotted according to the total residence time in the oxidation system at that point. For example, at a residence time of 60 hours and greater, all Fe concentrations were below 5 mg/L, and total Fe concentrations consisted predominantly of Fe(III).

Based on this data, it is recommended that residence times should exceed 80 hours to reduce Fe concentrations to below a resource consent level assigned to this site of 2 mg/L total Fe (dissolved + particulate).

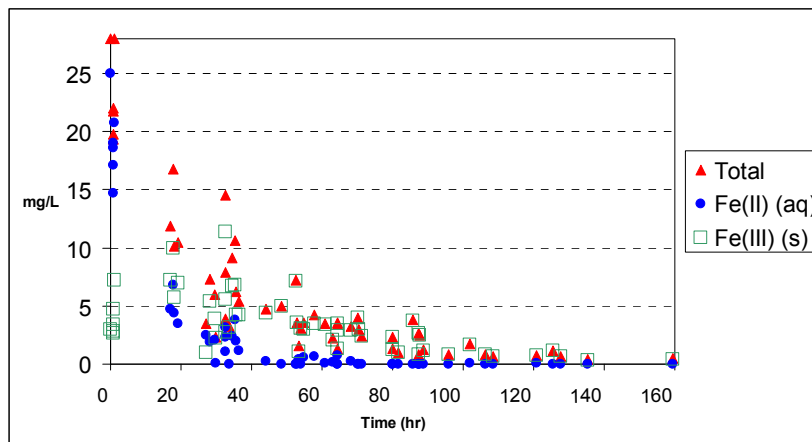


Figure 5. Iron concentrations according to residence time in the oxidising system.

Manganese, zinc, and arsenic

Total Mn concentrations in the untreated NMD ranged from 13.0 to 17.4 mg/L, and dropped to concentrations between 11.1 and 12.8 mg/L through the oxidising system. Above 80 hours residence, removal ranges from 7 to 20% and a fitted trend line predicts a removal of 11%. Manganese removal is likely through adsorption onto ferric hydroxide surfaces rather than through precipitation of Mn oxides. Total Zn concentrations (0.037 mg/L) dropped by 41% and total As concentrations (0.088 mg/L) dropped by 89% through the system. Zinc and As removal is likely through adsorption onto ferric hydroxide surfaces.

Slag leaching bed

The slag leaching bed was operated continuously for 51 days. The residence time in the bed ranged between 4 and 51 hours.

Aqueous manganese

Total Mn entering the slag leaching bed was between 11 and 13 mg/L and was 88 to 100% dissolved. Total Mn leaving the slag leaching bed was between 0.1 and 3.8 mg/L (70 - 99% removal). At low concentrations in the discharge (< 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 concentrations \approx total concentrations).

The amount of Mn removed by the slag leaching bed is proportional to residence time (Figure 6). This trend has been modelled with an exponential curve to give an indication of Mn removal at intermediate residence times that have not been tested. However, the dataset is small for treatment in a statistical manner. In addition, it is possible that there are multiple mechanisms for the removal of Mn.

pH, alkalinity and calcium

In general pH increased through the slag leaching bed from about 7.5 in the inflow to between 8 and 11 in the outflow and was proportional to the residence time in the slag leaching bed (Figure 7).

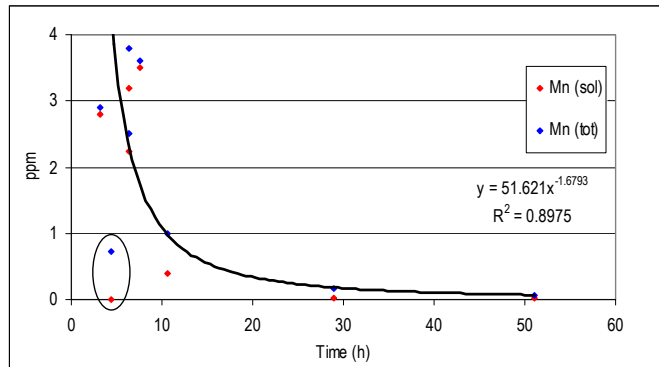


Figure 6. Mn removal vs. residence time in the slag leaching bed. Circled data points are outliers and residence time is uncertain for these points.

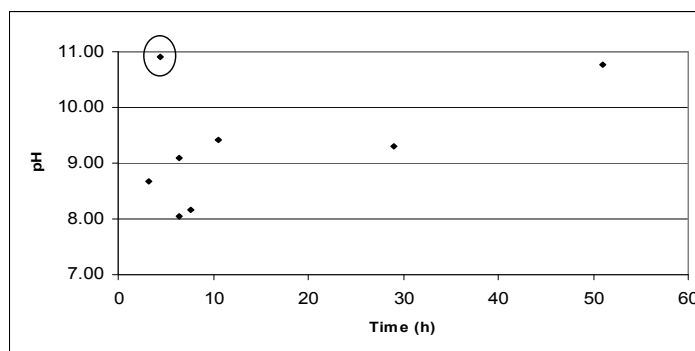


Figure 7. pH of discharge from slag leach bed vs. residence time in the slag leaching bed. Inflow – not shown - is about pH 7.5 for all samples. Circled data point is an outlier and residence time is uncertain for this point.

Despite the pH increase through the slag leaching bed, the alkalinity decreases as mine drainage flows through the slag leaching bed. 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.

Mechanisms of Mn removal

There are several possible geochemical removal mechanisms for Mn under the conditions present 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 Mn removal data for the slag leach beds. Speculative interpretation of our Mn removal data indicates that there is bimodality in the dataset that suggests two process; one at relatively short residence times (<10 hours) which reduces the Mn concentration to between 2 and 4 mg/L, and the second at longer residence times (10 to 50 hours) which continues to reduce the Mn concentration to between 1 and 0.1 mg/L. However, it is possible that this data fits a trend (Figure 7) 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 during operation of the slag leaching bed indicates that complex Mn bearing carbonate minerals precipitate. The ratio of Mn to

HCO₃ 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 reactive component that dissolves to increase pH within slag leaching beds. Therefore, it is likely complex carbonate minerals such as CaMn(CO₃)₂ (kutnahorite) or Ca₂Mn(CO₃)₃ precipitate and remove Mn from solution. 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 that removes Mn to sub-mg/L concentrations. Conditions within the slag leaching bed favour precipitation of MnO₂ (pyrolusite). This reaction requires oxidation of Mn(II) in solution to Mn(IV) and is often slow and therefore might require residence times of more than 10 hours to be effective. The reaction can be catalysed by formation of pyrolusite so that this reaction becomes self catalysing (autocatalytic; Stumm and Morgan, 1996).

CONCLUSIONS

Geochemical analysis of a NMD at a closed metal mine in New Zealand show that the NMD is highly reduced, Fe(II) concentrations are controlled by saturation with respect to siderite, and Mn concentrations are controlled 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 oxides by pH adjustment. The system included an oxygenation cascade, settling/reaction ponds and slag leaching bed.

The oxygenation cascade saturates the NMD with dissolved oxygen and 40 hours in the reaction/settling ponds is enough to lower the dissolved Fe(II) concentration to below 2 mg/L and an additional 40 hours settles total particulate Fe to below 2 mg/L. Therefore a residence time of 80 hours for this part of the system is recommended to meet discharge limits. Manganese, Zn, and As are reduced through the oxygenation cascade and settling/reaction pond through adsorption.

Results from the slag leaching bed indicate that the design is successful for Mn removal. In addition, Mn removal is accompanied by a reduction in the concentration of HCO₃ and an increase in pH. The residence time in the slag leaching bed required to remove Mn to between 2 and 4 mg/L is 5 to 10 hours and the residence time required to remove Mn to less than 1 mg/L is 10 to 30 hours. Manganese removal is likely through Mn/Ca carbonate precipitation, CaMn(CO₃)₂ (kutnahorite) or Ca₂Mn(CO₃)₃, and at the long residence times (> 10 hours) Mn removal may also be occurring through MnO₂ (pyrolusite) precipitation.

If scale up work is to be completed on the slag leaching bed it must be conducted with systematic laboratory based work to better characterise the slag reactions with the NMD and Mn removal processes. In addition, field data must be incorporated to understand dilution in the local environment with respect to compliance monitoring points.

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