Treatment Of High Mn Concentrations At Waihi Gold Mine, New Zealand By Two Methods: A Limestone Leaching Bed And A Slag Leaching Bed ☾

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Abstract

This work presents results of trial passive treatment systems at sites with up to 114 mg/L average Mn concentrations. Two parallel systems were trialled: one with a slag leaching bed and the other with a limestone leaching bed (LLB). Two types of slag were tested: melter slag and KOBM slag. The KOBM slag contained higher CaO content and outperformed the Melter slag, consistently removing over 97% of Mn and raising the pH to 8.6-12.9. The LLB removed an average of 32% of the Mn, and performance improved with time. Metal removal mechanisms for the two systems are discussed.

Keywords: passive treatment, manganese, steel slag leaching bed, limestone leaching bed

Introduction

The OceanaGold Waihi Gold Operation consists of the Martha open pit and the Favona, Trio, and Correnso underground gold mines located in Waihi New Zealand, North Island. Gold and silver are extracted from the ore and the barren tailings are pumped as a slurry into a tailings storage facility (TSF) containing two tailings storage ponds (TSF-1A and TSF-2). Waste rock from the open pit is utilised in the construction of the embankments for the TSFs. A network of drains collects seepage waters from tailings and waste rock in the TSFs. Some drains meet discharge requirements, but others are treated in an active treatment plant. In planning for eventual mine closure, OceanaGold would like to explore passive treatment options that could be used to treat all TSF drainage. The purpose of this work is to present the preliminary results of small-scale passive treatment systems treating two of the discharges from the TSFs at the Waihi Gold operations.

Methods

The tailings underdrain (TU site) for TSF-1A consists of three drainage lines installed under the tailings which join near the central part of the TSF and then flow underground through a common pipeline to the southwest into Manhole MH-11. Water quality data shows a water chemistry with neutral pH and elevated concentrations of Fe, Mn and, occasionally, Cu. Leachate drainage line L-10 (L-10 site) consist of two drainage lines installed under the northern embankment for TSF-2 which join near the northern edge of the TSF and then flow underground through a common pipeline to the north into collector sump T-13. Water quality data shows a water chemistry with slightly acidic pH and elevated concentrations of Fe, Al, Mn, Ni, Zn, Co and Cu.

Two different treatment systems were installed in parallel at each site: (1) a vertical flow reactor (VFR) for Fe removal followed by a steel slag leaching bed (SLB) for Mn and other trace element removal; and (2) a VFR for Fe removal followed by a limestone leaching bed (LLB) for Mn and other trace element removal.

VFRs are gravel filter beds which remove Fe at neutral and moderately-low pH through oxidation of Fe and precipitation and filtration of particulate and nanoparticulate ferric hydroxide precipitates (Sapsford et al. 2015; Blanco et al. 2018). VFRs are used here as a pre-treatment step prior to the SLB and the LLB systems. Each VFR was constructed

using a 1 m³ intermediate bulk container (IBC) mirroring the systems in Sapsford et al. (2007). Each tank was filled with 2-6 cm size gravel at a thickness of 280 mm (TU site) and 120 mm (L-10 site) which was overlain by 1 cm size stemming gravel at a thickness of 100 mm (both sites). Water flowed vertically down through the gravel bed, into a drainage pipe, and the exit point was outside the IBC through a riser to maintain water level in each tank at 830 mm (TU site) and 800 mm (L-10 site).

Both SLBs were constructed using IBCs filled to a height of 630 mm with waste slag from the electric arc furnace process at New Zealand Steel Limited. The material was Melter slag from iron making (10-20 mm size) and is dominated by TiO_2 (34-36%), AlO (18-19%), CaO (14-17%), and MgO (12.8-13.5%). Water flowed into the top of the SLB, vertically downwards through the bed, and out of the IBC through a riser to maintain water level in the tank at the top of the steel slag. After six months of operation, each SLB was taken off line and a new SLB was constructed at each site using Klöckner Oxygen Blowing Maximillanshuette (KOBM) slag (10-50 mm size). This slag is from steel making and is dominated by CaO (51-58%), FeO (16-23%), and MgO (9-13%).

Although the pH is not raised higher than 8 in an LLB, effective Mn removal has been shown to occur in these beds (Vail and Riley 1995; Tan et al. 2010; Christenson et al. 2016). Both LLBs were constructed using IBCs filled to a height of 900 mm of high-Ca limestone (15-25 mm size). Water flowed into the top of the LLB, flowed vertically downwards through the bed and out of the IBC through a riser to maintain water level in the tank at the top of the limestone.

Monitoring of the influent and effluent for the systems was conducted on an approximately fortnightly basis for 14 months. Samples from the TU systems were laboratory-analysed for pH, alkalinity, bicarbonate, Ca, Fe, Mn and Cu (dissolved), and Fe (total). Samples from the L-10 systems were laboratory-analysed for pH, alkalinity, bicarbonate, Ca, Fe, Mn, Ni, Zn and Co (dissolved), and Fe (total). Only a small percentage of the total flow at each site was treated. Influent and effluent flow measurements were taken during each site visit by timing the length of time to fill a measuring cylinder.

Results

TU Site

The inlet water pH was 6.0-6.5 and contained 17.4-25 mg/L Fe (total), 17.3-23 mg/L Fe (dissolved) and 7.3-10 mg/L Mn (dissolved). Cu concentrations were below detection limits. The flow rate through the VFR and SLB system ranged from 80 ml/min to 550 ml/min (224 ml/min average) and the flow rate through the VFR and LLB system ranged from 26 ml/min to 220 ml/min (129 ml/min average). The VFR preceding the SLB had an HRT of 18-124 h and removed 67-98% of the dissolved Fe and 25-93% of the total Fe. The VFR preceding the LLB had an HRT of 45-370 h and removed 57-98% of the dissolved Fe and 0-94% of the total Fe. Removal in both VFRs was proportional to HRT.

The HRT in the SLB (Melter slag) was 28-62 h (42 h average). Outlet pH was 6.9-7.9. Mn removal was as great as 11.5%, however, most of the data show negligible Mn removal and instead show net export of Mn from the slag (fig. 1). Longer HRTs in the SLB did not improve removal (fig. 2). For the KOBM slag, the HRT was 10-70 h (27 h average). Outlet pH from the SLB was 9.3-12.9 and Mn removal was >99.8% for all sampling events (figs 1 and 2).

The HRT in the LLB was 38-317 h (79 h average). Outlet pH was 6.5-7.8. Mn removal was between 5% and 86% (average of 23%) and showed a general decline in performance during the first three months, stabilising at removal percentages between 10% and 30% over the remaining 11 months (fig. 1). Longer HRTs in the LLB did not improve removal (fig. 2).

L-10 Site

The inlet water pH was 3.7-6.5 and contained 3.3-30 mg/L Fe (total), and 3.0-29 mg/L Fe (dissolved), 92-134 mg/L Mn, 0.94-1.54 mg/L Ni, 0.44-1.68 mg/L Zn and 0.37-0.71 mg/L Co (all dissolved). The flow rate through the VFR and SLB system ranged from 100 ml/min to 485 ml/min (213 ml/min average) and the flow rate through the VFR and LLB system ranged from 92 ml/min to 252 ml/min (150

ml/min average). The VFR preceding the SLB had an HRT of 22-95 h and removed 65-99% of the dissolved Fe and 0-94% of the total Fe. The VFR preceding the LLB had an HRT of 52-127 h and removed 67-99% of the dissolved Fe and 0-94% of the total Fe. Removal in both VFRs was proportional to HRT.

The HRT in the SLB (Melter slag) was 31-62 h (48 h average). Outlet pH was 6.2-7.6. Although net export of Mn occurred on two occasions, removal was documented on all other days (fig. 3). Removal of metals was 0-17% Mn (average of 5.6%), 2.1-64% Ni (average of 28%), 21-96% Zn (average of 46%) and 0-70% Co (average of 24%). Removal of Mn and all other trace elements was proportional to HRT (fig 4). For the KOBM slag the HRT was 11-51 h (25 h average). For all data points except one (an outlier), outlet pH from the SLB was 8.6-12.4 and Mn removal was 96.7% to >99.9%, with an average removal of 99.7% (figs 3 and 4). For all data points except one, the SLB also removed 99.0-99.9% of Ni (99.5% average), 96.2-99.7% of Zn (98.5% average), 99.0-99.9% of Co (99.6% average).

The HRT in the LLB was 31-85 h (57 h average). Outlet pH was 6.7-7.4. Mn removal was between 14% and 51% (average of 32%) and showed a general improvement in performance with time (fig. 3). The LLB also removed 12-58% of the Ni (average of 30%), 12-77% of the Zn (average of 49%) and 26-95%

of the Co (average of 70%). Removal of Mn and all other trace elements was proportional to HRT (fig. 4).

Discussion

VFRs

The VFRs are removing Fe at percentages similar to that observed for other neutral Fe-rich mine drainage water in New Zealand and overseas (Sapsford et al. 2015; Trumm et al. 2015; Blanco et al. 2018). It is likely that Fe is removed through filtration of particulate and nanoparticulate Fe, microbial and heterogeneous oxidation of Fe(II), and heterogeneous precipitation of Fe(III) as ferrihydrite on the gravel substrate. VFRs should be used to remove Fe prior to treatment with either limestone or steel slag in LLBs and SLBs, otherwise, precipitation of iron hydroxides can plug the leaching beds and can armour the treatment media (limestone, slag) reducing treatment effectiveness (Ziemkiewicz et al. 1997; Skousen et al. 2000).

SLBs

The SLBs constructed using Melter slag showed variable removal percentages. At the TU site, increased HRT resulted in increased pH, however, this was unlikely to be high enough for effective removal of Mn as Mn oxides, carbonates or hydroxides. The maximum pH attained at TU was 7.9 and the lowest solubility for Mn is at a pH of 10.6 (INAP 2009).
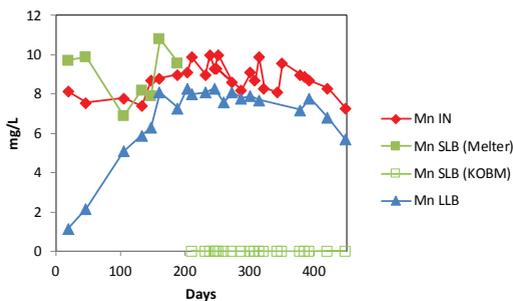

Figure 1 Concentrations of Mn for treatment systems at TU site. IN, into systems; SLB, slag leaching bed (using either Melter or KOBM slag); LLB, limestone leaching bed.
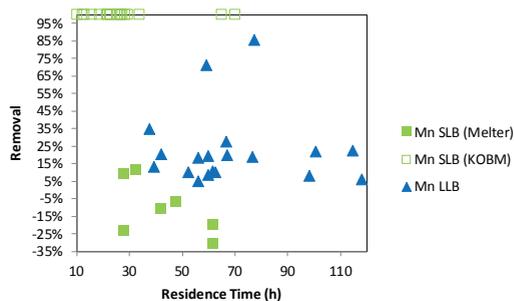

Figure 2 Percent removal of Mn by SLB and LLB for TU site. SLB, slag leaching bed; LLB, limestone leaching bed.
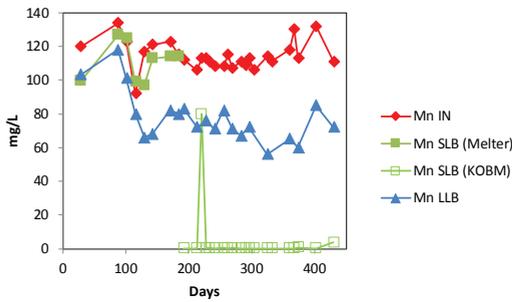
Figure 3 Concentrations of Mn for treatment systems at L-10 site. IN, into systems; SLB, slag leaching bed (using either Melter or KOBM slag); LLB, limestone leaching bed.
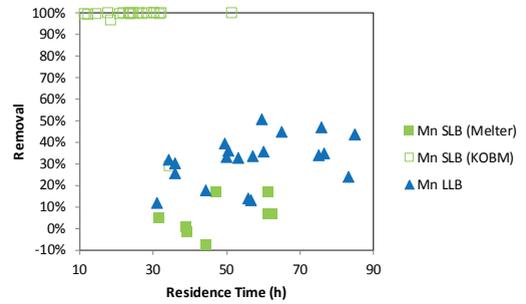

Figure 4 Percent removal of Mn by SLB and LLB for L-10 site. SLB, slag leaching bed; LLB, limestone leaching bed.

Removal of Mn by the SLB at the L-10 site was better than at the TU site. The pH was proportional to HRT and removal of Mn was proportional to pH, however, as with the TU site, the maximum pH attained (7.6) was far less than necessary for theoretical Mn removal. The inlet Mn concentration at L-10 was more than an order of magnitude greater than that at TU. Perhaps this very high concentration enhanced autocatalytic oxidation and precipitation of Mn or perhaps other conditions, such as the community of microbial Mn oxidisers or the oxidation states of Mn in the inlet water, favoured Mn removal at L-10. Regardless, the results at L-10 suggest that Melter slag can remove a proportion of Mn from solution (up to 17%). The percent removal of trace elements by the SLB was in the following order: Zn > Ni > Co. This is in the order of increasing pH of minimum solubilities for these metals (pH 8.5 for Zn, pH 9.3 for Ni, pH 11 for Co; Macdonald et al 1971; INAP 2009) and is also the order of increasing pH at which maximum adsorption of these metals occurs onto hydrous ferric oxide (Dzombak and Morel 1990). If the adsorption pattern onto Mn oxides is similar to that onto ferric oxide for these metals, either or both mechanisms may be removing these metals in the Melter slag SLB (precipitation or adsorption).

The results for the KOBM slag for both sites show exceptional performance in removal of Mn and other trace elements. Removal of these metals is likely to be due to minimum solubilities at the elevated pH achieved by the SLB, which is likely due to the higher CaO content compared to the Melter slag even though the effective surface area of the Melter slag was greater (due to smaller gravel size). Operation of the KOBM SLBs will continue at much shorter HRTs to determine potential operating parameters for a full-scale system.

LLBs

It is unlikely that elevated pH is a major factor in Mn removal in a limestone bed since the pH of minimum solubility for Mn is much greater than can be achieved by limestone alone. It is possible that microbial oxidation of Mn(II) is a primary mechanism and that autocatalytic oxidation and precipitation is enhanced with time as Mn oxides accumulate, as shown in the work by Christenson et al. (2016). Initial increase in pH in an LLB may help to initiate Mn removal. Limestone in both LLBs was coated with black precipitate.

At the TU site, longer HRTs do not result in higher pH, so percent removal of Mn is not affected by HRT (above the minimum 38 h in the trials). Removal percentage by the LLB at the L-10 site, however, has generally increased with time and is positively correlated with both HRT and pH. It is possible that due to the very high Mn concentrations at this site, autocatalytic oxidation and precipitation may be a much more important factor than at the TU site. The percent removal of trace elements by the LLB was in the following order: Co > Zn > Ni. Since cobalt has lowest solubility and maximum adsorption percentage onto

ferric oxide at higher pHs than that of Zn and Ni, this high Co removal percentage is unexplained. However, it is possible that removal of these trace elements is by either or both mechanisms (precipitation and adsorption).

The advantage of an LLB over a SLB for treatment of Mn is that the pH will not increase much more than approximately 8, however, the advantage of an SLB over an LLB is that much lower concentrations of Mn and other trace elements can be achieved.

Conclusions

Two different passive treatment techniques were trialled at two different leachate drainages with elevated concentrations of Fe, Mn and a range of trace elements from the TSFs at the OceanaGold Waihi Operation. The systems consisted of (1) a VFR for Fe removal followed by an SLB (using Melter slag) for trace element removal, later replaced with an SLB using KOBM slag, and (2) a VFR followed by an LLB.

The VFRs in both systems at both sites were effective in removing up to 98% of the dissolved Fe. These systems removed Fe through filtration of particulate and nanoparticulate Fe, microbial and heterogeneous oxidation of Fe(II) and heterogeneous precipitation of Fe(III) as ferrihydrite on a gravel substrate.

Contrary to expectations, the SLBs did not increase the pH to levels high enough for substantial Mn removal. The maximum pH attained was 7.9 (TU site) and 7.6 (L-10 site). The maximum percent removal at the two sites was 12% (TU site) and 17% (L-10 site), and only the L-10 site showed consistent removal. It is possible that the very high concentrations at the L-10 site (112 mg/L Mn) resulted in autocatalytic oxidation and precipitation of Mn or perhaps other conditions, such as the community of microbial Mn oxidisers or the oxidation states of Mn in the inlet water, favoured Mn removal at L-10. In addition to Mn, trace elements were removed by the SLB at the L-10 site in the fol-lowing order of decreasing effectiveness: Zn > Ni > Co. This is the order of increasing pH of minimum solubilities for these metals as well as the order of increasing pH at which maximum adsorption of these metals occurs, suggesting that removal was solubility-controlled and/or due to adsorption onto Mn oxides. Additional SLBs constructed at each site using steel slag with a higher CaO content (KOBM slag) raised the pH of the leachate to between 8.6 and 12.9 and showed consistent removal of >97% of Mn and other trace elements. Experimentation with different HRTs continue for the SLBs containing KOBM slag.

The LLBs were consistently better performers than the SLBs constructed with Melter slag. Percent removal averaged 23% (TU site) and 32% (L-10 site). Removal of Mn is possibly through microbial oxidation of Mn(II) and autocatalytic oxidation and precipitation as Mn oxides. Contrary to the SLB at the L-10 site, the percent removal of trace elements by the LLB was in the following order: Co > Zn > Ni. It is possible that removal of these trace elements is by the same mechanisms that may be occurring in the SLBs (precipitation and adsorption). The experiment will continue at both the TU and L-10 sites order to document performance of the LLBs over time.

Acknowledgements

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