# Passive treatment of Fe and Mn using vertical flow reactors, limestone leaching beds, and slag leaching beds, Waihi Gold

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## Abstract

Mines typically use active water treatment during operations and passive treatment upon closure. To test passive treatment options at the OceanaGold Waihi Operation, small-scale trials were installed at two sites with different chemistries and operated for five months. At the TU site, the water pH is 6.0-6.4, and contains an average of 20 mg/L Fe and 8.5 mg/L Mn (dissolved). At the L-10 site, the water pH is 3.7-6.5, and contains an average of 6.9 mg/L Fe, 112 mg/L Mn, 1.1 mg/L Ni, 0.73 mg/L Zn and 0.47 mg/L Co (dissolved). At each site, two systems were installed in parallel to compare different treatment options. One system consists of a vertical flow reactor (VFR) for Fe removal followed by a steel slag leaching bed (SLB) for trace element removal; the other system consists of a VFR followed by a limestone leaching bed (LLB). The VFRs removed up to 98% of the Fe. At TU, the SLB removed up to 12% of the Mn. The LLB removed up to 86% of the Mn. At L-10, the SLB removed up to 17% of the Mn, Ni 64%, Zn 96%, and Co 70%. The LLB removed up to 44% of the Mn, Ni 40%, Zn 60%, and Co 78%. Removal of Mn in the LLBs is likely through microbial and autocatalytic oxidation on $MnO_2$. Removal of Mn in the SLBs was only successful at L-10, and only at levels of about one fifth that of the LLB. Correlation with pH suggests that removal of Mn in the SLB is likely through precipitation due to low solubility at higher pH. A second SLB was constructed at each site using a slag with greater CaO content. Preliminary results show the pH is raised to >12 and complete removal of Mn and other trace elements occurs.

**Keywords:** acid mine drainage, passive treatment, Waihi Gold, manganese, slag leaching beds

## 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 in a processing plant at the mine. Following removal of the metals, the barren tailings are pumped as a slurry into a tailings storage facility containing two tailings storage ponds. Tailings Storage Facility Two (TSF-2) was constructed in 1987 to contain tailings and waste rock from the Martha open pit. Tailings Storage Facility One-A (TSF-1A) was constructed in 1999 to receive tailings from the Favona, Trio, and Correnso underground mines as well as tailings from the Martha open pit. Waste rock from the Martha mine 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 of these drains meet discharge requirements and discharge water directly to the environment. Some of the drains contain water quality that does not meet discharge requirements and this water is pumped to the water treatment plant for treatment prior to discharge to the environment. When necessary, water produced during mining activities is typically treated using an active treatment system, however, upon closure, most mine sites aim to treat residual mine water using passive treatment systems. In planning for eventual mine closure,

OceanaGold would like to explore passive treatment options that could be used to treat TSF drainage.

The Centre for Minerals Environmental Research (CMER) is currently working on a Ministry for Business, Innovation and Employment (MBIE) research grant focused on understanding and managing environmental impacts of on-shore mining in New Zealand (contract CRLE1403). As part of this research, multidisciplinary science programmes are being completed at proposed, operational and closed mine sites, including the Waihi Gold Mine Operations. An objective of the programme is to determine treatment options for drainage from epithermal gold mines in the North Island of New Zealand. Exploring options at the TSFs at the Waihi Gold operations serves to fulfil this objective.

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.

## Study sites

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 (Fig. 1). Manhole MH-11 receives drainage from multiple drainage lines from the TSF (including TU, UCD, LD6, T15, LM1, and a gravity inlet from MH-12). All these waters are combined and pumped to the water treatment plant. Water quality data for underdrain TU 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 (Fig. 1). Collector sump T-13 receives drainage from multiple drainage lines from the TSF (including L-10, T and SS. All these waters are combined and pumped to the water treatment plant. Water quality data for leachate drain L-10 shows a water chemistry with slightly acidic pH and elevated concentrations of Fe, Al, Mn, Ni, Zn, Co and Cu.

## Treatment system selection

Passive treatment systems employ either a reducing or oxidising strategy in the treatment of mine drainage (Trumm 2010). In the reducing strategy, oxygen is consumed in the reactor, sulphate is reduced to sulphide and metals are removed from solution as metal sulphides. In the oxidising strategy, alkalinity and oxygen are added to the water to raise the pH high enough that metals are removed from solution as metal oxides, hydroxides and carbonates. Some metals, notably Mn, cannot be removed as sulphides and are typically removed in treatment systems through either adsorption onto Fe hydroxides or through the formation of oxides, hydroxides and carbonates. Since Mn is a primary contaminant of concern at both sites, oxidising systems are most appropriate. 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.
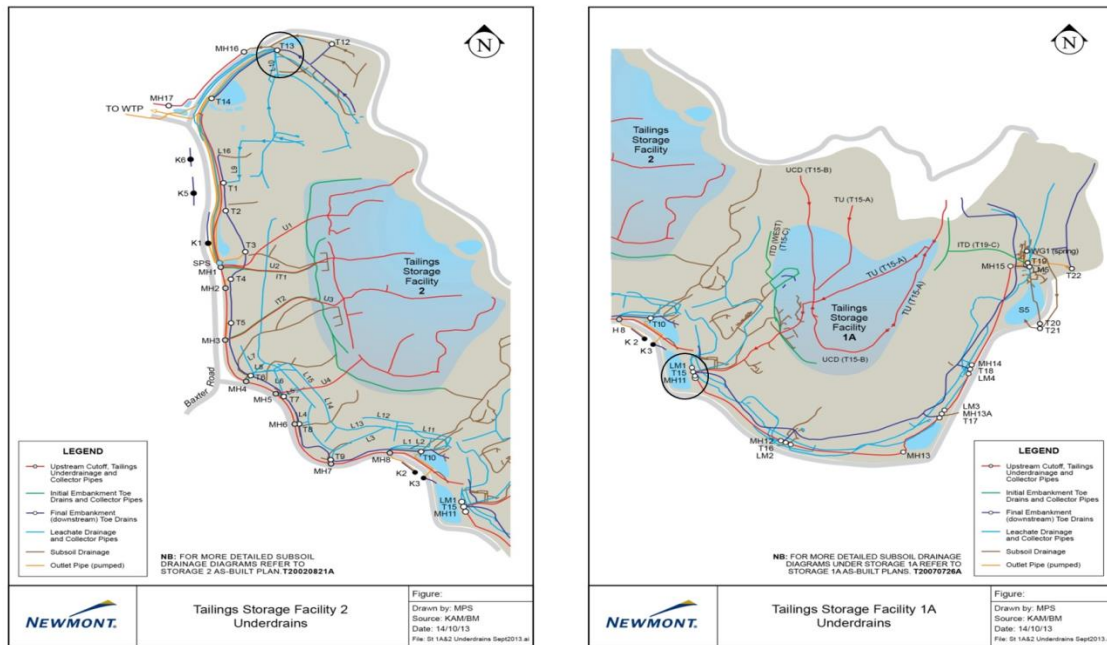
**Figure 1.** Tailings Storage Facility TSF-1A and TSF-2 drainage networks (from annual TSF monitoring reports by the Waihi Gold Operation). MH-11, containing the TU leachate and T-13, containing the L-10 circled.

VFRs for Fe removal are a recent addition in passive treatment technologies (Sapsford et al. 2015; Blanco et al. submitted 2016). These systems are gravel filter beds which remove Fe at neutral and moderately-low pH sites through oxidation of Fe and precipitation and filtration of particulate and nanoparticulate ferric hydroxide precipitates. VFRs have been shown to be very effective in New Zealand (Trumm et al. 2015) and are used here as a pre-treatment step prior to the SLB and the LLB systems.

The metals present in the drainage have their lowest solubilities at the following pH (in order of increasing pH): Fe 3.5, Cu 7.0, Zn 8.5, Ni 9.3, Mn 10.6 and Co 11 (Macdonald et al 1971; INAP 2009). Waste steel slag from the steel making industry is a suitable media when the pH must be raised higher than can be accomplished with limestone (Ziemkiewicz and Skousen 1998; Simmons et al. 2002; Skousen 2002). Peer-reviewed literature on the use of steel slag in the treatment of mine drainage is not abundant, however, field trials completed by Trumm and Pope (2015) at a closed metal mine in the North Island document the effectiveness of steel slag in New Zealand.

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). Work by Christenson et al. (2016) shows that up to 99% of Mn can be removed in a limestone bed (from a starting concentration of 2 mg/L), and that removal is mostly likely through microbial oxidation of Mn(II) and precipitation of Mn oxides.

## Methods

Each of the VFRs was constructed using a 1 m³ intermediate bulk container (IBC) mirroring the systems in Sapsford et al. (2007) and Sapsford and Florence (2013). Each tank was filled with 2-6 cm-sized unreactive gravel at a thickness of 280 mm (TU site) and 120 mm (L-10 site) which was overlain by 1 cm-sized gravel at a thickness of 100 mm (both sites). A

perforated drainage pipe was imbedded in the gravel at the base of the IBC. Water flowed vertically down through the gravel bed, into the 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 steel slag from the electric arc furnace process at New Zealand Steel Limited (NZS). The material was Melter slag from iron making (10-20 mm size) and was reported by NZS to contain 14-17% CaO. Water flowed from one of the VFRs into the top of the SLB, vertically downwards through the bed, into a perforated drainage pipe at the base of the bed and out of the IBC through a riser to maintain water level in the tank at the top of the steel slag.

Both LLBs were constructed using IBCs filled to a height of 900 mm of limestone (15-25 mm size). Water flowed from one of the VFRs into the top of the LLB, flowed vertically downwards through the bed and into a perforated drainage pipe at the base of 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 seven 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). Influent and effluent flow measurements were taken during each site visit by timing the length of time to fill a measuring cylinder.

After seven months of operation, each SLB was taken off line and a new SLB was constructed at each site using KOBM slag (10-50 mm size). This slag is from steel making (rather than the iron making Melter slag) and contained 51-58% CaO.

# Results

## TU site

The inlet water pH was 6.2-6.4, and contained 17.9-25 mg/L Fe (total), 17.6-23 mg/L Fe (dissolved) and 7.56-9 mg/L Mn (dissolved). Cu concentrations were below detection limits. The VFR preceding the SLB had an hydraulic residence time (HRT) of 49-97 h and removed 91-98% of the dissolved Fe and 83-94% of the total Fe. The VFR preceding the LLB had an HRT of 45-97 h and removed 88-98% of the dissolved Fe and 69-94% of the total Fe. Removal in both VFRs was proportional to HRT.

The HRT in the SLB (Melter slag) was 28-62 h. Outlet pH was 6.9-7.9. Mn removal was as great as 11.5%, however, the majority of the data show negligible Mn removal and instead show net export of Mn from the slag (average removal of -10%; Fig. 2). Longer HRTs in the SLB did not improve removal (Fig. 3). The HRT in the LLB was 38-98 h. Outlet pH was 6.5-7.8. Mn removal was between 8% and 86% and showed a general decline in performance during the first three months, stabilising at removal percentages between 10% and 30% over the last three months (overall average removal of 38%; Fig. 2). Removal was generally greater at longer HRTs (Fig. 3). The LLB removed 112 g Mn from 39,600 L water (2.8 mg/L) over 189 days of operation.
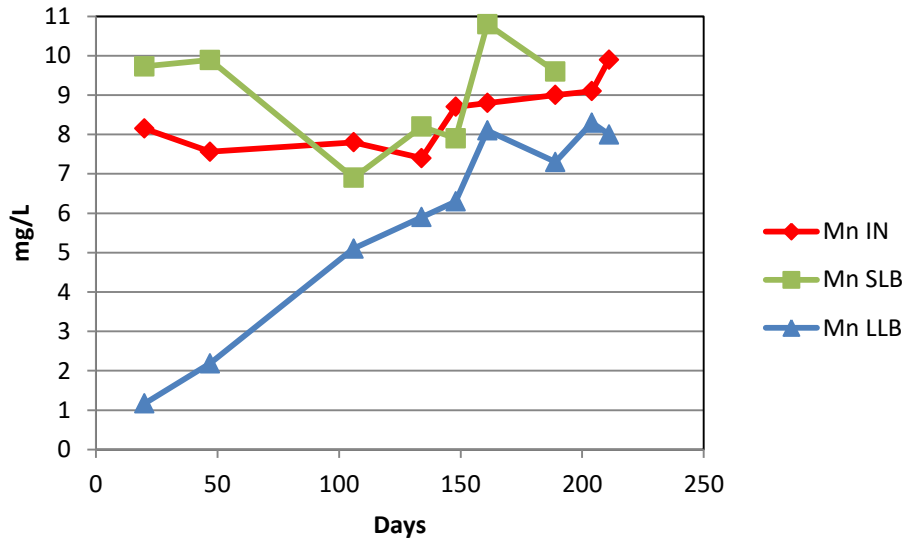
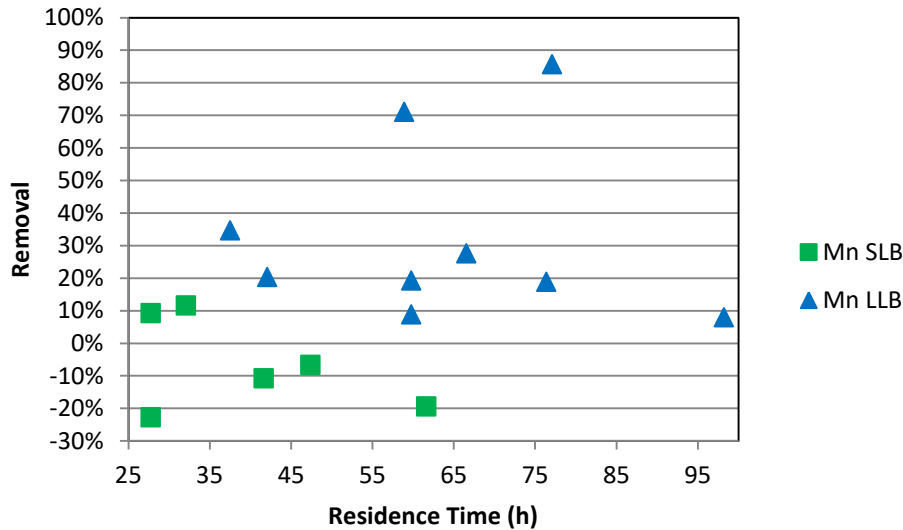**Figure 2.** Concentrations of Mn for inlet to systems and outlet from SLB and LLB for TU site.



**Figure 3.** Percent removal of Mn by SLB and LLB for TU site.

## L-10 site

The inlet water pH was 3.7-6.5, and contained 5.3-30 mg/L Fe (total), and 3.0-29 mg/L Fe, 92-134 mg/L Mn, 0.99-1.54 mg/L Ni, 0.44-1.68 mg/L Zn and 0.4-0.71 mg/L Co (all dissolved). The VFR preceding the SLB had an HRT of 49-95 h and removed 65-99% of the dissolved Fe and 35-94% of the total Fe. The VFR preceding the LLB had an HRT of 51-112 h and removed 67-99% of the dissolved Fe and 0-89% of the total Fe. Removal in both VFRs was proportional to HRT.

The HRT in the SLB (Melter slag) was 31-62 h. Outlet pH was 6.2-7.6. Although net export of Mn occurred on two occasions, removal was documented on all other days (Fig. 4). 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%; Fig. 5). Removal of Mn and all other trace elements was proportional to HRT (Fig 6). The SLB removed 155 g Mn from 36,700 L

water (4.2 mg/L) over 184 days of operation. The SLB also removed 13 g Ni, 14 g Zn and 5.2 g Co.
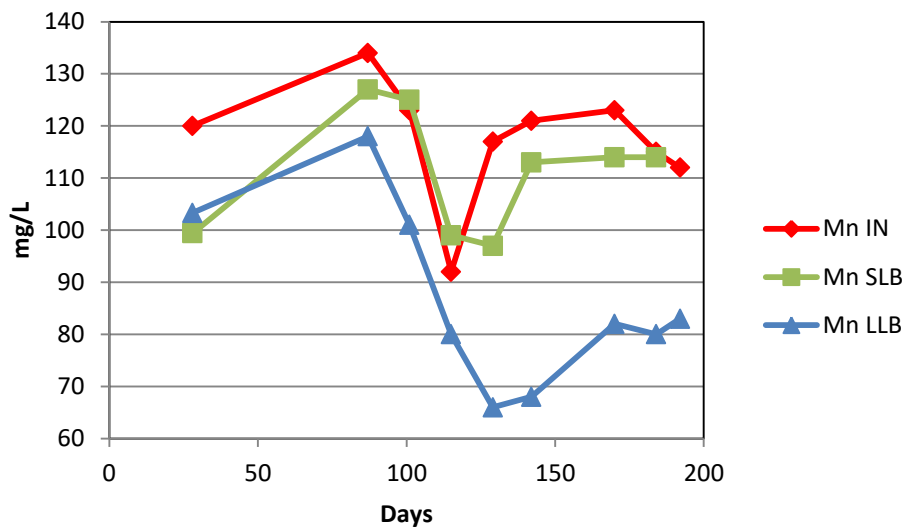


**Figure 4.** Concentrations of Mn for inlet to systems and outlet from SLB and LLB for L-10 site.
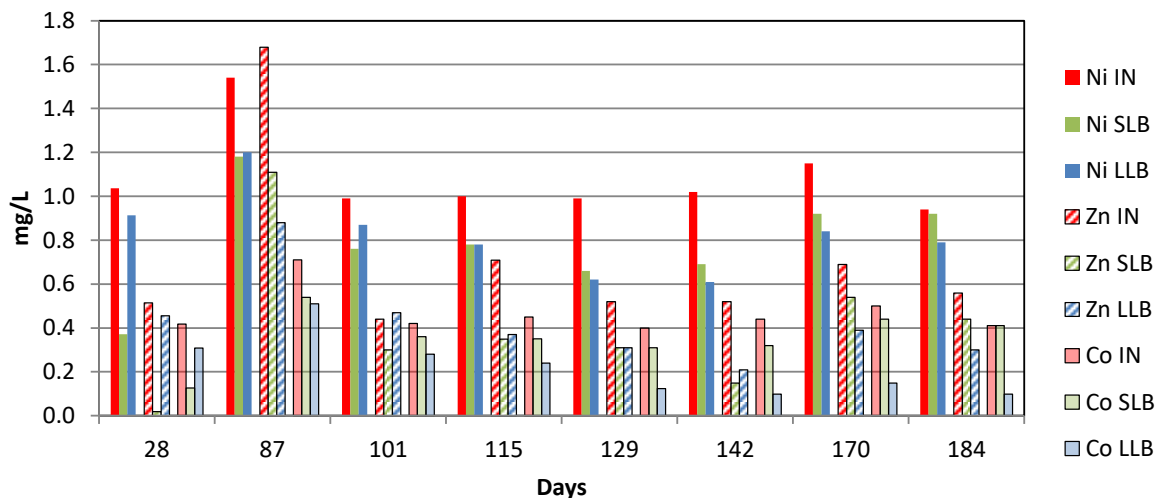


**Figure 5.** Concentrations of trace elements for inlet to systems and outlet from SLB and LLB for L-10 site.

The HRT in the LLB was 31-85 h. Outlet pH was 6.7-7.3. Mn removal was between 12% and 44% (average of 26%) and showed a general improvement in performance with time (Fig. 4). The LLB also removed 12-40% of the Ni (average of 24%), 0-60% of the Zn (average of 37%) and 26-78% of the Co (average of 56%) (Fig. 5). Removal of Mn and all other trace elements was proportional to HRT (Fig. 6). The LLB removed 1,043 g Mn from 42,800 L water (24 mg/L) over 184 days of operation. The LLB also removed 11 g Ni, 18 g Zn and 9.4 g Co.
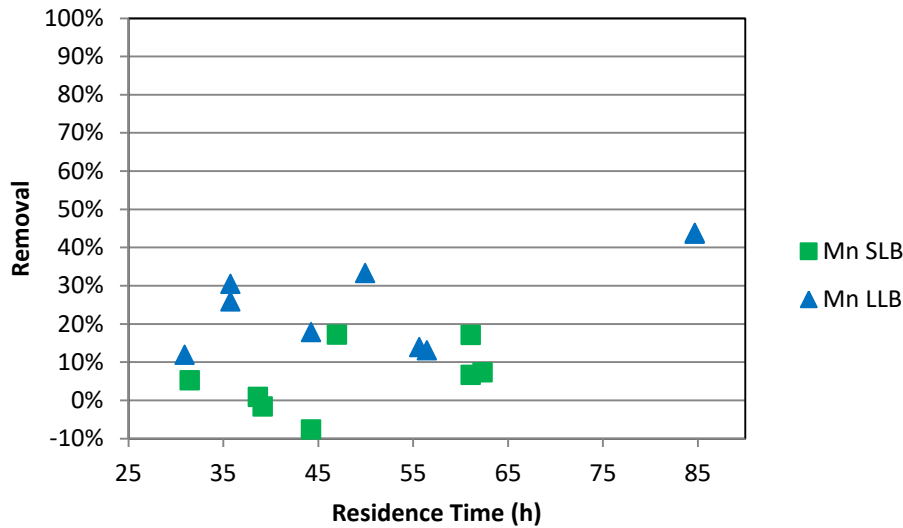
**Figure 6.** Percent removal of Mn by SLB and LLB for L-10 site.

## KOBM SLB preliminary results

One data point is available for the SLBs containing KOBM slag for each site. At the TU site, the HRT was 27 h. Inlet Mn concentration to the SLB was 9.9 mg/L (dissolved). Outlet pH from the SLB was 12.5 and the outlet Mn concentration was 0.0059 mg/L (dissolved), equating to a removal of >99.9%. At the L-10 site, the HRT was 26 h. Inlet Mn concentration to the SLB was 112 mg/L. Outlet pH from the SLB was 12.4 and the outlet Mn concentration was 0.001 mg/L, equating to a removal of >99.9%. The SLB at L-10 also removed 99.9% of Ni, >99.7% of Zn and >99.9% of Co (all dissolved).

# Discussion

The results from the passive treatment trials are promising, and suggest that a full-scale passive treatment system may be effective in treating TSF discharge from the Waihi Gold Mine operations upon eventual closure.

## VFRs

The VFRs are removing Fe at relatively high percentages at both sites, 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. submitted 2016). 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, which has been well documented in the literature (Kepler and McCleary 1994; Ziemkiewicz et al. 1997; Skousen et al. 2000). Further work at both sites will include quantification of Fe(II) and dissolved oxygen concentrations.

## 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). Although Melter slag used in the work by Trumm and Pope (2015) showed a pH increase to as high as 11, with resulting effective removal of Mn from solution, the Melter slag used in this study did not achieve similar increases in pH. It is possible that the CaO content of the Melter slag today is less than it was during the previous work. Further analyses of the Melter slag is planned to confirm the CaO content.

Removal of Mn by the SLB at the L-10 site was much better than at the TU site. The pH was proportional to HRT and removal of Mn was proportional to the increase in 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), but is also the order of increasing pH at which maximum adsorption of these metals occurs onto hydrous ferric oxide (Dzombak and Morel, 1990). Assuming that the adsorption pattern onto Mn oxides is similar to ferric oxide for these metals, either or both mechanisms may be removing these metals in the SLB (precipitation or adsorption).

The preliminary results for the KOBM slag 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 achieved elevated pH by the SLB. Operation of the KOBM SLBs will continue at a range of HRTs to determine potential operating parameters for a full-scale system.

## LLBs

At the TU site, although there was marked decline in Mn removal by the LLB initially, data for the last three months show consistent removal of Mn at between 10% and 30%. There is a weak positive correlation between removal percentage and pH. Surprisingly, however, longer HRTs do not result in higher pH, so percent removal is not affected by HRT. 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 more likely 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).

Removal percentage of Mn by the LLB at the L-10 site has generally increased with time and is positively correlated with both HRT and pH (hence, unlike the TU site, pH increases with HRT). 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. After seven months of operation, over 1 kg of Mn had been captured by the system. The percent

removal of trace elements by the LLB was in the following order: Co > Zn > Ni, which is different to the SLB where the order was Zn > Ni > Co. 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 likely that removal of these trace elements is by either or both mechanisms (precipitation and adsorption). The experiment will continue at both the TU and L-10 sites order to document performance of the LLBs over time.

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 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, 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 following 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 >12 and showed removal of >99.9% 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 38% (TU site) and 26% (L-10 site). Due to the very high Mn concentrations at L-10, over 1 kg of Mn was captured by the LLB. Removal of Mn is likely 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 likely 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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