Manganese removal from New Zealand coal mine drainage using limestone leaching beds

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Abstract

Limestone leaching beds can be utilised as passive treatment systems for oxidative removal of Mn(II) from mine drainage. Oxidation of Mn(II) by O_2 is kinetically inhibited at circumneutral pH, however it can be catalysed by Mn oxidising microorganisms and by mineral surfaces, particularly those of Mn oxides. Although limestone treatment can be effective, the mechanism of Mn removal is not well understood.

A series of six laboratory-scale reactors were built to determine the relative importance of microbial Mn oxidation and autocatalytic Mn oxidation in limestone leaching beds. Duplicate reactors were constructed using limestone, limestone with pyrolusite, and quartz (as a control). Acid mine drainage (AMD) containing 2 mg/L Mn, 0.3 mg/L Zn, and 0.08 mg/L Ni was collected from a stream on the West Coast of New Zealand. The 'biotic' set of reactors had AMD leaching through the rock bed, while AMD treated with biocide was percolated through the 'abiotic' reactors.

The limestone, and limestone with pyrolusite reactors removed Al and Mn from the AMD solution. Removal of Mn by limestone alone is minimal, and is enhanced by the presence of pyrolusite in a reactor. The most effective removal of Mn was achieved in the biotic limestone reactors, and microbial Mn (II) oxidation appears to be important for optimal removal of Mn from solution. Inoculating the limestone beds with pyrolusite boosted removal efficiency of the reactors. Pyrolusite addition to limestone beds could be considered if maximum Mn removal is required immediately, however once microbial communities are established any benefit will be negligible.

Keywords**:** coal mine drainage, limestone bed, manganese oxides

1. Introduction

Manganese (Mn) is a transition metal which occurs in several valence states in the environment. Mn is biochemically important as a trace element, but can become toxic and cause aesthetic effects in aquatic systems at high concentration. Therefore discharge of Mn to waterways is often regulated (ANZECC, 2000; Silva et al., 2010). Mn is a common component of acid mine drainage (AMD), and in AMD impacted streams on the West Coast of New Zealand, Mn concentrations range from 0.007 – 13 mg/L, up to four orders of magnitude above background levels (Pope, 2010).

Treatment of mine water for Mn removal can be performed via active or passive treatment systems. Active treatments typically utilize high pH and/or an oxidant to form solid $Mn(OH)_2$ or Mn(IV) oxides. Passive treatment systems include granite beds (Hedin et al., 2015), limestone beds (Tan et al., 2010), bacterially inoculated limestone beds , benthic and floating microbial and/or algal assemblages, and manganese removal aerated channels. The 'Pyrolusite Process' is a patented system developed by Vail and Riley (1995), where Mn bearing water flows through a Mn-oxidising bacteria inoculated limestone bed. In all of these systems, Mn removal is typically achieved through precipitation of sparingly soluble Mn oxides.

Oxidation of Mn(II) by O_2 is kinetically inhibited at circumneutral pH; however the reaction can be catalyzed by Mn oxidizing microorganisms, and by mineral surfaces (Diem and Stumm, 1984; Stumm and Morgan, 1996; Tebo et al., 2004). Bacteria and fungi species capable of Mn oxidation are widespread, and can accelerate oxidation rates in many environments (Spiro et al., 2009). Biotic Mn(II) oxidation may be caused by several processes: modification of pH and/or redox conditions, release of metabolites that chemically oxidise Mn(II), or production of polysaccharides or proteins that catalyse the reaction (Tebo et al., 2004). The primary products of microbial Mn(II) oxidation are poorly crystalline layered manganese oxides, with high surface area and Mn(IV) as the key Mn species. Mn oxidation can also be an autocatalytic process, and is abiotically catalyzed by Mn oxide surfaces. The surface hydroxyl groups on Mn oxide surfaces bind Mn(II) in inner sphere surface complexes $((>SO)_2Mn)$, which promote rapid oxidation (Diem and Stumm, 1984). As the reaction proceeds, the surface area of the Mn oxide increases, causing an increase in the heterogeneous reaction rate.

In this study an experiment was designed to assess the relative importance of abiotic, autocatalytic and biotic oxidation of Mn(II) in limestone leaching beds using acid mine drainage from the West Coast of New Zealand. Removal efficiencies of Mn and other contaminants are compared in reactors containing limestone, and limestone 'seeded' with pyrolusite to provide a Mn oxide surface for abiotic catalysis.

2. Materials and Methods
2.1. AMD collection and site description

The Island Block Coal Mine sits in the Victoria Range foothills on the West Coast of New Zealand. Coal from the Eocene Brunner Coal Measures sequence was intermittently extracted between 1962 and 2002. The coal is overlain by the Kaiata formation, consisting of marine mudstones and sandstones. Fanny Creek drains the eastern area of the mine, and is impacted by AMD drainage from a number of seeps in the waste rock. The AMD is derived from pyrite oxidation and mineral dissolution, similar to that in other Brunner Coal Measures deposits.

A comprehensive assessment of AMD characteristics was performed in the Fanny Creek catchment in 2008 (Mackenzie thesis). Drainage was typical of coal mines within the Brunner Coal measures, with low pH (2.5-4), elevated iron and aluminium concentrations, and high concentrations of trace elements (Pope et al. NZJGG 2010). For this study, AMD was collected from Fanny Creek on 3 occasions during the experiment, and stored in polyethylene containers. The first two batches of AMD were collected from the same location and had similar chemistry. An obstruction of the access track meant the final collection was from a different location in the creek, and metal concentrations were lower.

1.2 Experimental set-up

Six rectangular reactors were built using polymethyl methacrylate sheets, and polyvinyl chloride tubing (Fig. 1). The two control reactors were filled with 15.6 kg of 12-16 mm quartz pieces, and two limestone (LS) reactors were filled with 15.3 kg of 10 – 30 mm limestone chips. The final two limestone and pyrolusite (LS + PL) reactors were filled with 15.3 kg of 10 – 30 mm limestone chips, with 200 g of 5-13 mm pyrolusite grains mixed throughout. The 'biotic' set of reactors received AMD, and the 'abiotic' set received AMD treated with 1 mL/L biocide (B-AMD). The AMD percolated into one end of the reactors through two perforated pipes, and exited the other end of the reactor by the same method. The experiment began on the 28 August 2016. Flow rates for the first 3 weeks of operation varied between 2.5-4.5 mL/minute. From week 3 the target hydraulic residence time in the reactors was 2 days (1.5 – 2 mL/minute flow rate), and this was decreased to a one day residence time after 14 weeks of operation (2.3 – 4.2 mL/minute flow).
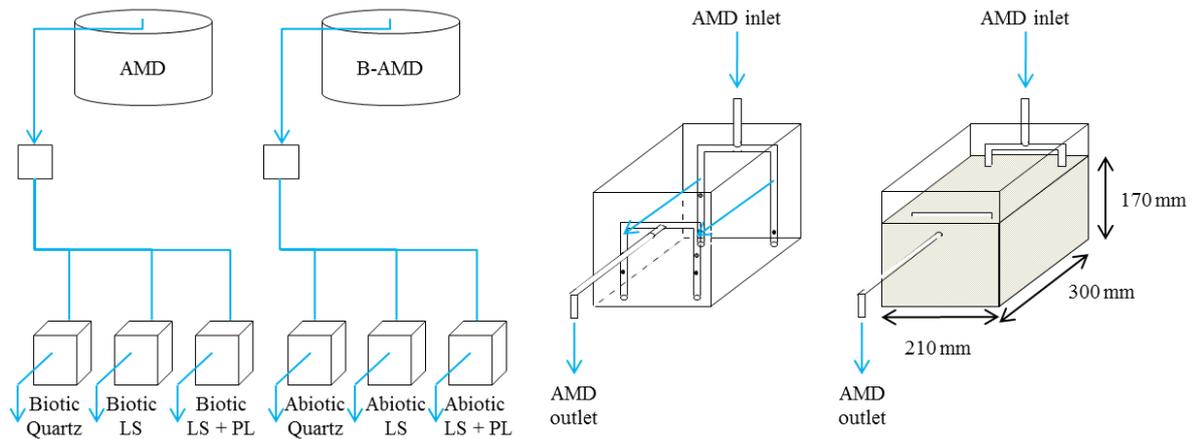
Figure 1 Experimental set up. The reactors contain: A1. Quartz, A2. Limestone, A3. Limestone and pyrolusite, B1. Quartz, B2. Limestone, B3. Limestone and pyrolusite. Reactors 1-3 receive AMD, and reactors 4-6 receive bacteriocide treated AMD (B-AMD).

1.3 Chemical analysis

Each week pH, dissolved oxygen and temperature were measured on the AMD and the reactor effluent, and samples were collected for alkalinity, dissolved metal, ammonia and major ion analysis. Meters used for measurements were calibrated on the day of use. Alkalinity was analysed by titration with 0.1 M HCl, metals were analysed by ICP-MS using the APHA method 3125 B. Major anions were analysed using the APHA ion chromatography method 4110 B.

Solubility modelling was performed using dissolved metal concentration data measured for the AMD and B-AMD solutions, together with the major ion data and pH measured in the reactors. These were entered into Visual MINTEQ 3.1 in order to predict which minerals may become saturated due to the changes in pH and major ion chemistry in the reactors.

3. Results and Discussion

3.1 Mine water chemistry

The four reactors containing limestone altered the pH, major ion and metal chemistry of the mine drainage water, while the quartz reactors had very little influence on the water chemistry. The influent water had pH of 4.3 – 4.9 and sulphate concentrations of 140 – 200 mg/L (Table 1). Metal

concentrations were elevated, with Mn (2 mg/L), Ni (0.08 mg/L) and Zn (0.3 mg/L) concentrations exceeding trigger value guidelines for the protection of freshwater species (ANZECC, 2000). Concentrations of Fe were below 0.2 mg/L, and Al concentrations varied from 1.5 – 2.7 mg/L.

Water treated by the LS and LS + PL reactors had higher pH and alkalinity than the influent water. In the first three weeks of the experiment effluent pH was 6.9 – 7.2, after which the pH of the treated water remained between 7.3 and 7.8. Water pH was largely unchanged by the quartz reactors. The AMD and BAMD were oxygenated, and contained between 5 – 11 mg/L O_2. There was typically little difference between dissolved oxygen concentrations in the influent and effluent water of the reactors.

3.2 Biotic Mn removal

Manganese was removed from solution in both the LS and the LS + PL reactors (Fig. 2). No significant removal of metals occurred in the control quartz reactors. In the initial stages of the experiment, removal efficiencies were approximately 50 % in the biotic LS reactor, and 70 % in the biotic LS + PL reactor. After six weeks, Mn removal increased in both of the biotic reactors, to achieve nearly 100 % Mn removal by the ninth week of operation. The increased removal in the biotic reactors relative to the abiotic reactors is consistent with the presence of Mn oxidising microorganisms in the biotic reactors. The increase in removal efficiency in the biotic reactors after 6 weeks operation is likely due to growth of the population of organisms oxidising Mn(II). Both the biotic LS, and LS + PL reactors showed a slight decrease in removal efficiency when the flow rate was doubled, however this quickly recovered and it is likely this was due to a further increase in the population of Mn(II) oxidising organisms. There was a slight decrease in removal efficiency of the biotic LS + PL reactor in the final two weeks of the experiment, which is due to failure of the flow rate regulator.
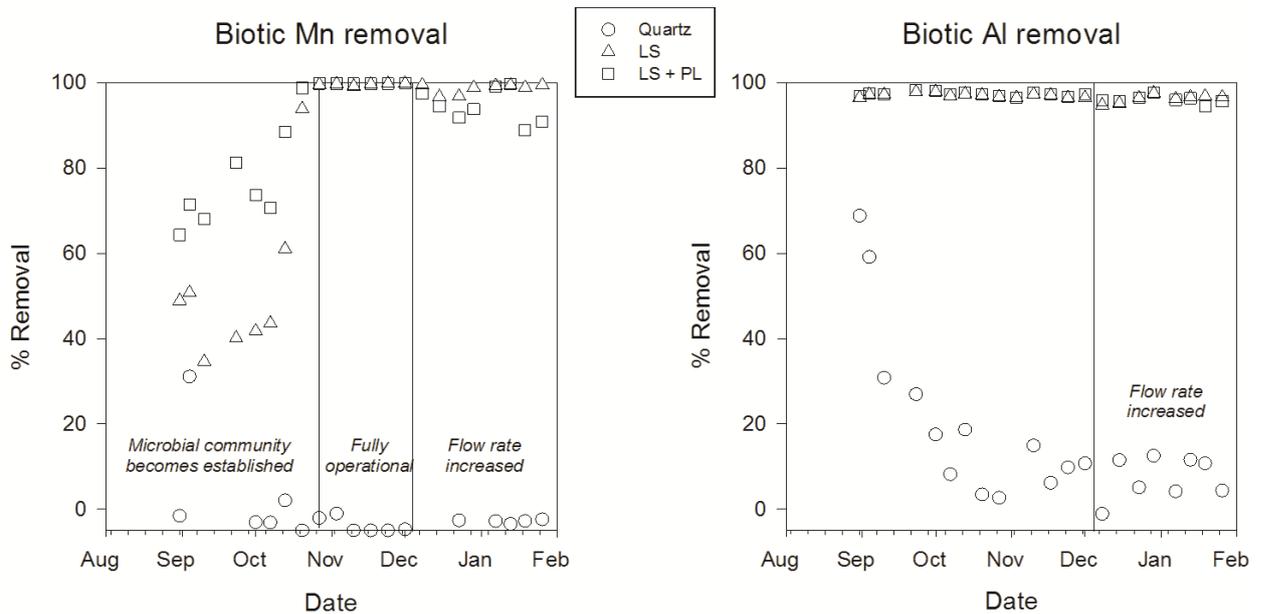

Figure 2 The percent of influent Mn and Al that was removed from solution in the biotic reactors.

The two biotic LS and LS + PL reactors became darker over the time period of the experiment (Fig. 3.). The black precipitates formed were interpreted to be Mn oxides. This precipitate is typically present as a coating on the limestone rocks, with some floc in the interstitial spaces between the limestone rocks. The macroscopic characteristics are consistent with manganese oxide coatings described in limestone leaching beds treating AMD (Tan et al., 2010), and the Mn oxides formed on granite beds (Hedin et al., 2015). However microscopic and mineralogical analysis is required to determine the minerals being formed. The areas of black precipitate were concentrated near the surface of the inlet end of the reactors, after the zone of white precipitate. The concentration of Mn oxide near the surface is likely due to

preferential flow of AMD over the surface of the reactors. This is a function of the reactor design and could be altered so the inflow is at the base of the reactor, rather than several holes in the pipe at different lengths. It is also possible that dissolved oxygen concentrations near the reactor surface promote Mn oxidation, however the oxygen concentration in the outlet water is similar to the inlet concentration, an *in situ* oxygen profile would be required to investigate this.

3.3 Abiotic Mn Removal

Manganese removal was different in each of the four LS and LS + PL reactors, and also showed variations with time (Fig. 3.). The reactors that contained pyrolusite demonstrated increased Mn removal relative to the LS reactors in the initial stages of the experiment, and the biotic reactors showed more Mn removal than the abiotic reactors. The greater removal efficiency of the reactor containing pyrolusite is attributed to an abiotic, autocatalytic oxidation of Mn(II) on the surface of the pyrolusite grains.
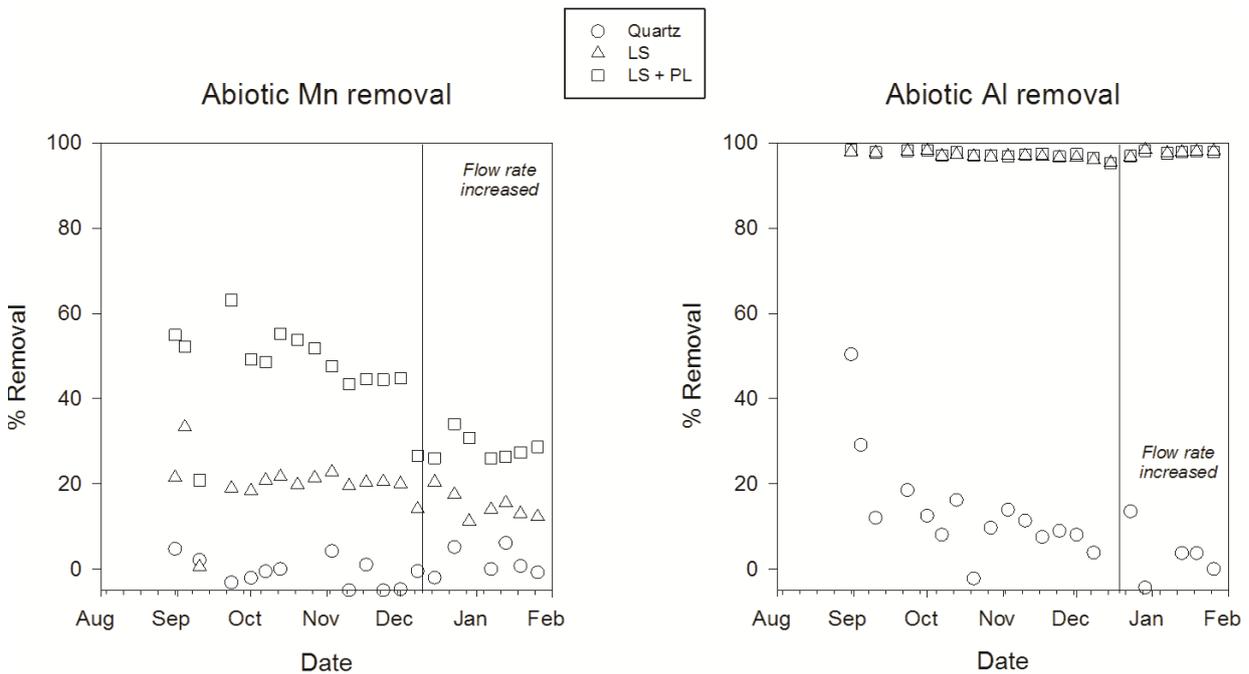

Figure 3 The percent of influent Mn and Al that was removed from solution in the biotic reactors.

The Mn removal efficiency of the abiotic LS reactor was fairly constant over the course of the experiment. Geochemical modelling suggests a slight oversaturation of the B-AMD with respect to rhodochrosite (a manganese carbonate) when treated with limestone. However; pyrolusite remains below saturation in these conditions. In spite of this, the black coatings on some of the limestone chips suggest Mn is being removed as an oxide. The removal that is occurring in the abiotic LS reactor may be a purely pH driven solubility effect. The nearly constant removal efficiency in this reactor despite flow rate changes supports this hypothesis. As the removal rates in these reactors did not increase over time, it is evident that Mn minerals forming *in situ* do not act as catalysts and enhance the rate of Mn removal. The % Mn removal achieved in the LS + PL reactor decreased when the flow rate was doubled. This effect of residence time on Mn removal in the abiotic LS + PL reactor suggests the rate of Mn oxidation by pyrolusite constrains removal efficiency. Therefore longer residence times, and perhaps a greater ratio of pyrolusite to limestone in the reactor may increase Mn removal in this system.

Figure 4 *Reactors after 19 weeks of operation. Flow direction is from left to right.*

3.4 Al Removal

From the first week of the experiment Al removal was close to 100 % in both the biotic and abiotic systems (Fig 2, 3). Solubility modeling demonstrated the solution becomes saturated with respect to several aluminum phases, including gibbsite, alunite, and amorphous $Al(OH)_3$. A white floc was observed near the inlet of the reactors from the initial weeks of the experiment, which spread further into the reactors over the course of the experiment (Fig 3). Precipitation of Al hydroxides, oxides, and hydroxyl sulfates is common in AMD solutions that become neutralized (Lottermoser, 2010; Pope and Trumm, 2014). The removal of Al by the reactors is therefore an example of metal removal due to pH driven solubility changes.

4.0 Conclusions

The reactors containing limestone were effective in raising the pH of the AMD solutions, and removing Al and Mn from solution. It is likely that Mn is being removed as an oxide, which is supported by black precipitates forming in the reactors. The addition of pyrolusite enhanced removal of Mn from solution, however it appears that Mn oxides forming in the abiotic limestone reactor do not further catalyse Mn oxidation. Microbial oxidation is the major process that removes Mn(II) from solution in limestone leaching bed treatment systems, and the population of Mn oxidising organisms can grow to accommodate increased Mn loads. The enhanced removal due to inclusion of pyrolusite in the biotic reactors was minor once microbial populations developed in the limestone reactor. The reactors were not run to failure, however a maximum rate of Mn(II) oxidation by microbes in the system could be measured in this way. Further research will identify the Mn minerals that are forming in the reactors and identify the microbial communities that have developed.

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