

Utilisation of solid waste products for manganese removal from mine waters

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ABSTRACT

Manganese is a common contaminant of mine waters and other waste waters, and is notoriously difficult to remove due to its high solubility over a wide range of pH. Previously, systems designed to remove manganese from mine waters used high pH substrates such as limestone to promote the chemical oxidation of manganese oxyhydroxides, which then act as a catalyst for further manganese oxyhydroxide precipitation. However, these systems tend to require large areas of land due to the requirement to ensure thin films of water to maximise contact time with air. In this work, two mine waters (net-acid and net-alkaline) that had undergone a primary treatment for iron via aerobic wetlands were treated using a novel manganese removal system that utilises concrete and basic oxygen steel slag (BOSS) as high pH substrates to promote manganese oxidation. Oxygenation of the mine waters is accomplished using a passive aeration system that generates air using the mine water flow, and helps prevent the reduction and therefore mobilisation of oxidised manganese. The paper examines the potential use of these waste substrates in removing manganese and other contaminant metals from mine waters.

GENERAL INTRODUCTION

Manganese contamination of water courses

Manganese is a common constituent of many mine waters, and although it is not as ecotoxic as other metals commonly associated with mine drainage, manganese still poses a problem to the water industry. Problems include precipitation within water distribution pipes resulting in blockages, the staining of laundry and also manganese contaminated drinking water has a metallic taste. Therefore, current legislation states that the EQS (in the UK) is 30µg/l Mn II in freshwaters, with the US EPA recommending a maximum level of 50 µg/l.

Due to the high solubility of manganese over a broad pH range (~pH 4.5-pH 8.5), many treatment systems incorporate a pH adjustment to facilitate manganese precipitation via oxidation. Another hindrance to manganese removal from waters is that the metal is highly redox sensitive, and will only oxidise in oxygen rich waters (Sikora and colleagues (2000) state levels of between 0.15 and 0.29mg/l DO for successful Mn oxidation).

Manganese treatment systems

Active systems

Active treatment systems are systems which require regular chemical additions to treat the contaminated water source. Often this can be an alkali that promotes the precipitation of metals, neutralises any acidity and raises the pH. 'Manganese Greensand', a manganese oxide coated glauconite mineral is commonly and successfully employed in water treatment systems to remove up to 99% of iron and manganese from contaminated waters (for a combined concentration of up to 10-15mg/l Mn and Fe; insert reference here?). For higher concentrations of manganese (<10mg/l), chlorination is routinely used to oxidise the soluble Mn II cation, with the insoluble metal oxides removed via filtration. Dosing waters with lime is also successful in removing soluble iron and manganese from mine waters. However all these treatments are costly and require regular maintenance.

Passive systems

Passive treatment systems, as the name implies, do not require any external energy source and/or regular maintenance via the addition of chemicals etc. These systems are designed to exploit natural processes (such as water flow and microbial and plant processes) to ameliorate the contaminated water. Therefore, they are generally cheaper to install and operate compared to active treatment systems.

There are several passive systems that are designed to treat manganese contaminated mine waters. These are often placed at the end of a mine water treatment system so that primary metals such as iron are removed prior to the system, thus helping to prevent the armouring of the manganese treatment system with iron oxyhydroxides. In addition, in mine water that contains a mixture of iron and manganese, it is thermodynamically more favourable for iron to be removed relative to manganese. Therefore, Mn removal rates will be enhanced with lower concentrations of iron. Passive systems often utilise high pH carbonate rich-substrates such as limestone and dolomite to chemically oxidise and precipitate manganese from contaminated waters, whilst simultaneously increasing the pH and decreasing acidity (i.e. Sikora *et al*, 2000; Stark *et al*, 1996, Vail & Riley, 2000). Vail & Riley (2000) have patented a manganese treatment system which utilises an alkalinity-generating limestone bed into which they inoculate a microbial inoculum (as both a liquid inoculum and as a solid inoculum attached to some of the limestone substrate).. These inocula are an assemblage of manganese-oxidising bacteria that promote the removal of soluble manganese from mine water. Their results suggested that optimal manganese removal occurred in inoculated systems rather than systems containing limestone only, with an inoculation decreasing the 'lag-phase' that is commonly associated with microbially-dependant manganese treatment systems.

Similarly to Vail & Riley, work conducted at Bangor University by D. Barrie Johnson and colleagues has focussed upon promoting manganese oxidation in mine water by investigating the potential of inoculating systems with metal-cycling bacteria that are associated with ferro-manganiferous nodules found at abandoned mine sites. The workers used these nodules to inoculate and therefore 'kick-start' manganese oxidation in gravel beds (Hallberg and Johnson, 2005). They attributed an increasing efficiency in manganese removal to the establishment of a viable community of manganese oxidising bacteria.

Philips and Bender (1995) have reported that naturally occurring cyanobacterial mats are highly successful in manganese removal. Manganese is removed in these mats due to a combination of increased pH and oxygen, generated during algal photosynthesis. Approximately 98% manganese removal was noted when a water draining a coal mine in Alabama was treated with floating cyanobacterial mats. Manganese oxide and manganese carbonate precipitates were associated with these mats.

In the following sections, we introduce a passive manganese treatment system that has been developed at the University of Newcastle upon Tyne. Laboratory trials were initially conducted to assess which carbonate substrates were best considered prior to the installation of field scale systems.

EXPERIMENTAL METHODOLOGY AND SYSTEM DESIGN

Laboratory scale manganese treatment systems

In order to assess the best carbonate substrate to remove manganese from contaminated waters, we investigated a range of carbonate minerals to be used in laboratory scale reactors. The substrates calcium carbonate (Derbyshire limestone; TRUCAL 6, Tarmac Ltd), calcium magnesium carbonate (dolomite; Fordaco, Fordamin Ltd) and magnesium carbonate (magnesite; BAYMAG, Canada) were used to treat the mine water, and provided three chemically-contrasting magnesium and calcium bearing carbonates. Quartz was used as a carbonate-free control. Manganite (0.2g), a manganese III oxide mineral was added to the substrate of each reactor to 'kick start' manganese oxidation. Adequate oxygen levels within the substrate were maintained using fish tank aeration pumps. Net alkaline manganiferous mine water was treated (~20mg/l Mn, retention time within the reactors 4 hours), with influent and effluent manganiferous mine water samples analysed for Mn over a 3-month time course. Precipitates that formed on the substrate surface were examined using a combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM) with EDAX.

Pilot scale manganese treatment systems

Manganese treatment system design

Many manganese treatment systems, as discussed in the introduction, tend to require either large areas of land to maximise contact with air and therefore to maintain adequate oxygen levels within the systems or high residence times to ensure complete metal removal from the mine water. In addition, primary materials are often used for the substrates, such as limestone for alkalinity generation and sandstones in gravel beds. In the proposed passive treatment system, we utilise solid wastes (secondary materials such as industrial and construction by-products) as substrates that hold the required alkalinity generating and acid neutralising capacity. Additionally, the proposed system uses a passive aeration system that generates air using the mine water head, which allows a great deal of flexibility in the design and placement of the treatment system, as less surface contact with air is required.

The premise in the design of this treatment system is that manganese will initially be removed abiotically from the mine water via precipitation on the high pH substrate. Following this, a combination of abiotic and biotic manganese removal occurs; deposited manganese oxyhydroxides act as a catalyst for further manganese removal, and a community of manganese-oxidising microorganisms (present within the mine water) will establish and precipitate manganese during respiration. This is preferable to systems that require 'seeding' with

manganese-oxidising bacteria, as often those microorganisms present *in situ* will require less adaptation to the environment, and establish a viable community more rapidly.

A schematic representation of the system design is given in **Figure 1**. The systems were constructed using pre-cast concrete sections to form 3 chambers. Each chamber is 0.7m by 1 m, with a height of 1.5m. Mine water enters the central chamber and is split to feed the passive aeration system and the two reactors (one containing concrete and one basic oxygen steel slag). Influent water is aerated on entrance to the plastic reactor chambers (0.67m by 0.49m by 0.52m) at a flow rate of 300ml/min. This gives an approximate residence time within the substrate of 4 hours. Influent and effluent mine waters are collected daily and analysed by ICP-MS and IC. **Figure 2** shows a photograph of the treatment system at Whittle reed beds, Northumberland, UK (OS map Grid reference 4185, 6045).

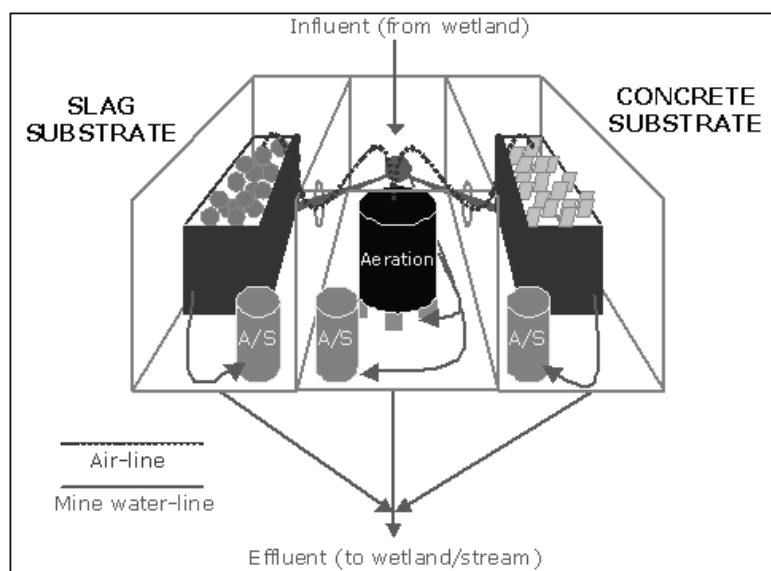


Figure 1: Schematic of the passive manganese treatment systems installed at the Whittle and Shilbottle sites, Northumberland. A/S refers to the autosamplers.



Figure 2: The manganese treatment system in place at Whittle treatment wetlands, Northumberland, UK.

The use of solid waste materials as an alternative high pH substrate to limestone

In order to minimise the use of primary materials such as limestone and dolomites as a substrate in the treatment systems, this work investigated the use of alternative secondary high pH substrates. In this work, we focussed upon two solid waste materials; basic oxygen steel slag (BOSS; a by-product of the steel industry), and

limestone aggregates (such as concrete, often associated with demolition wastes). Both of these wastes have a high alkalinity-generating potential; BOSS contains free lime that is readily leached on contact with water, and concrete contains a high percentage of limestone and calcium hydroxide (lime). In addition, the physical and chemical properties of both BOSS and concrete are amenable to mine water treatment systems, as both wastes have a high porosity and therefore a high surface area to water volume ratio (see **Figure 3** for an example of the BOSS used in the reactors). Although BOSS is produced in a metal rich environment (during the smelting of iron ore), leach tests show that the BOSS does not release any metals or other potentially toxic compounds (BS:EN 1744, Part 3).

Ziemkiewicz (1998) has discussed the use of steel slags in the treatment of AMD, and believes that the alkalinity-generating potential of BOSS is superior to other substrates, as steel slags do not absorb carbon dioxide from the air and convert lime into limestone, which is less soluble, and has a lower alkalinity generating potential. This results in steel slag generating high levels of alkalinity over many years. Preliminary laboratory trials have shown both BOSS and concrete compare favourably with the more commonly used high pH substrates such as limestone and dolomite in manganese removal from synthetic mine waters (Johnson, 2003).

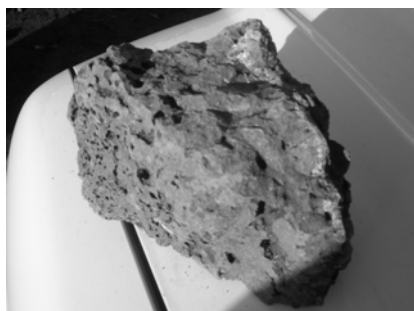


Figure 3: An example of a piece of Basic Oxygen Steel Slag (BOSS) used for the treatment of manganiferrous mine water. Note the vesicles which provide a high porosity/surface area.

Field sites

Whittle

Whittle is located 7 miles south of Alnwick in Northumberland (OS map Grid reference 4185, 6045). A net alkaline ferrous mine water is pumped from the Whittle drift mine (coal) and oxygenated via an aeration cascade prior to entering two parallel settlement lagoons. After initial precipitation of iron oxyhydroxides in the settlement lagoon, the water is further treated via three consecutive reed beds (wetlands 1 and 3 contain *Typha latifolia* and wetland 2 contains *Phragmites australis*). The system successfully removes iron (~26mg/l) from the mine water; however manganese is still a problem (~3mg/l). For further details on the Whittle treatment system see Nuttall (2003). The pilot-scale manganese treatment system has been emplaced between wetlands 1 and 2, to treat the effluent from wetland 1.

Shilbottle

Shilbottle colliery is located 5 miles south of Alnwick, UK (OS map Grid reference 4225 6075) and has one of the poorest quality spoil or mine waters in the UK. Mine water is emanating from a pyritic spoil heap with a pH<3.5; total iron ~ 1,100 mg/l; manganese ~ 300 mg/l; aluminium ~ 700 mg/L and sulphate ~ 15,000 mg/l. At this site, a 170metre long permeable reactive barrier (PRB) containing limestone and manure intercepts this flow, after which the mine water is collected with a settlement lagoon, and further treated via an aerobic wetland containing *Phragmites australis*. For further details on the Shilbottle mine water treatment scheme see Younger *et al*, (2003) and Batty & Younger (2004). Though this system is successfully removing iron, manganese concentrations remain around 60-80 mg/l. The pilot scale treatment system treats the final mine water effluent at this site.

Note:

A third manganese treatment system was installed at Edmondsley, County Durham, to treat net-alkaline manganiferrous mine water. However a major adit collapse has resulted in a natural underground mine water diversion; therefore the system is no longer in operation.

RESULTS AND DISCUSSION

Laboratory scale manganese treatment reactors

In assessing the 'best carbonate substrate' to treat manganiferrous mine water, results show that the magnesium-rich carbonates have the highest manganese removal rates in the laboratory-scale reactors (**Figure 4.**). Manganese removal rates corresponded to the appearance of manganese oxyhydroxides, with up to 80% removal rates accomplished after the accumulation of visible amounts of manganese oxyhydroxides. It should be noted that although the error bars are large, particularly with the quartz substrate, this is indicative of varying amounts of manganese oxyhydroxides present within the reactors.

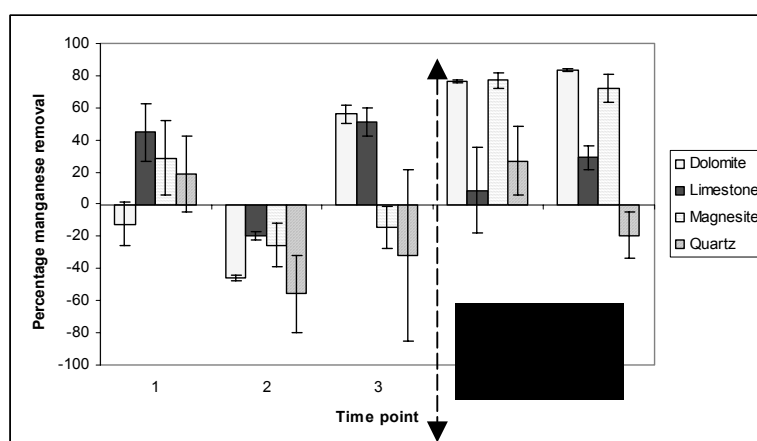


Figure 4: Percentage manganese removal from laboratory scale reactors using the pure minerals dolomite, limestone, magnesite and quartz.

Time point 1 - time zero,

Time point 2 - week 1

Time point 3 - end of month 1

Time point 4 - end of month 2

Time point 5 - end of month 3

Precipitates formed in all the reactors; however manganese oxyhydroxides (initially identified by their black colour) only formed in a selection of the reactors. The main precipitates that formed within the reactors were **manganese oxyhydroxides**, **calcium carbonates** (aragonite), **calcium manganese carbonates** (kutnahorite) and **manganese-rich calcites**. These precipitates formed on all the substrates and also on the reactor plastics prior to contact with the high pH substrates. This indicates that the mine water is the source of the carbonate moiety. In addition, it suggests that the plastics are providing a surface onto which manganese will precipitate. **Figure 5** shows an SEM image of the precipitates that formed on the laboratory reactor plastics

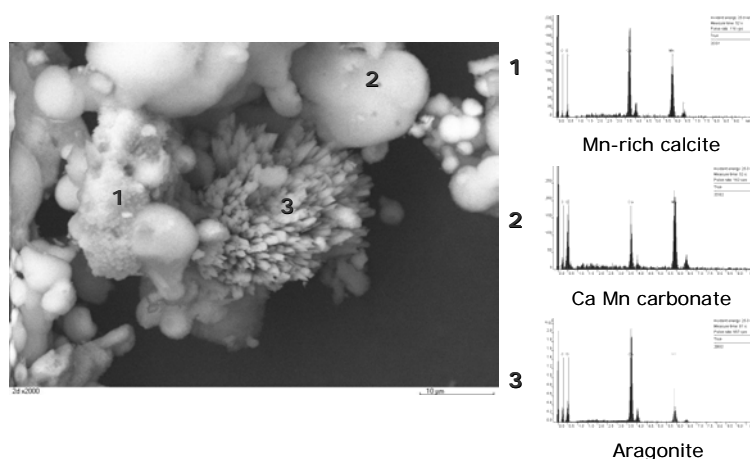


Figure 5: SEM image of Mn-rich precipitate that formed on the composition of each identified mineralogical structure, with each structure containing a mixture of Mn, Ca, C and O.

Manganese-rich carbonates only formed within the quartz reactors and on the reactor plastics. It is hypothesised that the magnesium component of the dolomite and magnesite minerals inhibited manganese carbonate formation; the ionic radii of Mn II and Mg III are similar, therefore the Mg III ion (which is present at a higher concentration than the Mn II ion) may have competed for the carbonate moiety within the reactors.

It is unclear what the 'best substrate' for manganese removal is, as both the Mg-rich and Mg-poor reactors removed manganese with different mechanisms. It was therefore decided to use both concrete (limestone-bearing, low magnesium) and basic oxygen steel slag (BOSS; high magnesium due to use of dolomitic lime during steel production) as substrates in the field-scale reactors.

Pilot scale manganese treatment reactors

In this paper, data will be presented from Whittle only, as samples at Shilbottle were lost by unusual flood events during spring, 2005.

The Whittle manganese treatment system has been running successfully for 4 months (at the time of writing). Basic oxygen steel slag appears to be the best substrate for both manganese and iron removal (see **Table 1**). However, as with the laboratory scale reactors, there is considerable removal of both iron and manganese via the reactor plastics and also via accumulation within and on the sampling buckets. At this date (June 2005), all the reactor plastics that have been in contact with the contaminated mine water are black. Analysis of this material shows that this metal precipitate is a combination of iron and manganese oxyhydroxides.

	Concrete	BOSS
TOTAL IRON	4	22
TOTAL MANGANESE	46	70

Table 1: Percentage removal of iron and manganese from Whittle mine water.

The best substrate for Manganese removal?

From this work, we have identified that manganese-rich carbonates may be an important mechanism for manganese removal in these net-alkaline mine waters and that plastics appear to be an attractive substrate to which manganese-rich precipitates bind. In addition, BOSS shows promise to be used as a substrate in a manganese treatment system.

Manganese carbonates have been identified in several environments that have been contaminated with manganiferrous mine water. In fact, manganese calcites are believed to form in CO₂-rich environments, possibly in preference to manganese oxides (Hem & Lind, 1994). An interesting study by Lind & Hem (1993) observed carbonate-rich manganiferrous 'black-cemented crusts' in the steam bed of Pinal Creek, Arizona. Mine water that had reacted with calcareous rocks prior to emerging at the surface had precipitated on the stream bed, with the Mn-rich carbonate crusts encapsulating particulate Mn oxides that formed in the surface waters. This is creating a natural and very stable sink for manganese in a natural water course (Pinal Creek). A similar process may be occurring in our laboratory scale reactors as SEM and XRD analyses of reactor precipitates confirm the presence of a mixture of carbonates and oxides. The carbonate mineral is stable once formed, thus less susceptible to changes in redox and/or pH relative to Mn-oxides. Therefore it is recommended that the mechanisms to promote this Mn removal process should be investigated further.

Additionally, the observance of significant manganese removal via the reactor plastics may be an important mechanism for future treatment of net-alkaline manganiferrous mine waters. This process is similar to one detailed by Jarvis and Younger (2001), in which the authors coined the phrase 'SCOOFI' (Surface Catalysed Oxidation Of Ferrous Iron) to describe the enhanced oxidation of iron when in contact with a high surface area media (in this case plastic). The metal oxyhydroxides 'armour' the surface of the plastic, thus forming a highly reactive metal hydroxide surface, which acts a nucleation site for the further oxidation of iron. It is highly probable that this mechanism is occurring at Whittle; manganese oxyhydroxides are strong chemical oxidisers thus they will attract and oxidise further Mn II and Fe II from the mine water, forming a metal rich oxyhydroxide layer on the reactor plastics.

In the pilot scale system at Whittle, BOSS removed ~ 25% more manganese relative to the concrete substrate. As discussed earlier, this may be due to the concentration of magnesium within the BOSS, however the high surface area of BOSS relative to the concrete could also be a factor. Further investigation into the role that magnesium plays in manganese removal from mine waters is required.

In this work, it is important to attribute the metal-removal potential of the substrates (BOSS and concrete) relative to the plastics. It appears that the mine water at Whittle is supersaturated with respect to manganese and iron, with the spontaneous precipitation of a manganese-rich mineral on the surface of all reactor plastics. It is therefore important to assess the metal balance of the mine water prior to deciding upon treatment, as in this case, a SCOOFI based substrate appears to work well, without the need for any chemical amendment (as provided by concretes and BOSS).

SUMMARY

- Manganese was removed in all the laboratory-scale reactors.
- Dolomite and magnesite were the 'best' substrates for manganese removal.
- Both Mn oxyhydroxides and Mn carbonates were deposited within the reactors and also on reactor plastics in the laboratory scale reactors, and Mn and Fe oxides formed upon the field scale reactor plastics
- Basic oxygen steel slag (BOSS) reactors show the highest rate of manganese and iron removal from the Whittle mine water.
- The potential of plastic as a high surface area medium will be investigated along side BOSS in future work.

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