CL:AIRE research bulletin

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CL:AIRE research bulletins describe specific, practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This research bulletin describes a novel technique for manganese removal from mine waters.

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Enhanced *In Situ* Bioremediation Technique for Manganese Removal from Mine Waters

1. INTRODUCTION

Mine water is a significant source of freshwater pollution in the UK, second only to sewage in many northern and western districts, such as in the Midland Valley of Scotland (Younger, 2001), and contains elevated levels of manganese. Water quality legislation is currently being reviewed by UK regulators and it is likely that the Environmental Quality Standard (EQS) for manganese will be lowered. This has led to an increased interest in manganese removal treatment systems.

This Research Bulletin describes a novel technique for manganese removal and represents a major advance in passive manganese treatment, since it significantly reduces the amount of land required over previous treatment methods.

The research focussed on mine water discharge from the Frazer's Grove Mine in the North Pennines (see Figures 1 and 2). It was carried out by Newcastle University from 1998 to 2001 and was funded by the Engineering and Physical Sciences Research Council (EPSRC).

2. BACKGROUND TO MINE WATER

Coal and metal mines are often worked at depths below the water table. In order to keep mine workings dry, groundwater is continually pumped to discharge. When mines are abandoned, the pumps which kept the water table below active workings are switched off resulting in groundwater rebound (Younger, 2002). Mining causes profound changes in the underground environment not just in terms of the hydrogeology but also the hydrogeochemistry. Secondary minerals which accumulated during the active life of the mine by the interaction of sulphur-bearing minerals with atmospheric oxygen and moisture dissolve in the rising water.

The term "acid mine drainage" is often used to describe mine waters which emanate from shallow workings or as spoil heap leachates. Many deep mine waters are actually **alkaline** in nature as is the case at Frazer's Grove Mine. The main cause of acid mine drainage is sulphide dissolution from pyrite (iron sulphide) weathering. This process is one of the most acid-generating reactions in nature and a summary of the process of oxidation of pyrite may be written:

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2H^+ \qquad (1)$$

While **acidity** may be determined by the metal minerals present, the overall **pH** will also be dependent on the degree of buffering provided by other minerals in the system. The most common and prolific **buffering reactions** are due to carbonate minerals such as calcite, dolomite, ankerite and siderite. The dissolution equation for calcite is given below:

$$CaCO_3(s) + H^+ \longrightarrow Ca^{2+} + HCO_3^- \qquad (2)$$

If there is insufficient carbonate then the mine water will be **net-acidic** but if there is sufficient then it will be **net-alkaline** as at Frazer's Grove Mine.

Passive treatment technology is increasingly used for the treatment of mine water discharges. It can be defined as: "water treatment utilising only naturally available energy sources such as topographical gradient, microbial metabolic energy, photosynthesis and chemical energy, in a system which requires regular but infrequent maintenance to operate successfully over its design life" (www.piramid.org). Passive technologies such as aerobic and anaerobic wetlands and **oxic** and **anoxic limestone drains** have been successfully treating polluted mine waters for several years in the USA and the UK, and are now beginning to be used more widely.

Figure 1: Photo of the headworkings at the No2 Shaft at Frazer's Grove Mine in the North Pennines

3. WHY IS MANGANESE A PROBLEM?

Manganese is a common contaminant in many mine waters and though not as ecotoxic as other common contaminant metals such as Fe, Al and Zn, it nevertheless has various undesirable properties, including precipitating in water distribution pipe networks (eventually causing blockage), imparting an unpleasant 'metallic' taste to drinking water and staining laundry. Interest in manganese removal technology is increasing due to ever-tightening water quality legislation and the EQS for manganese may be reduced to as low as 0.03 mg/l. This will mean that many discharges which currently comply will fail under the new legislation. Compared with iron, manganese is usually more difficult to remove from water because it generally requires a higher pH and the kinetics of manganese oxidation are much slower (Morgan and Stumm, 1964). Nairn and Hedin (1993) found that no manganese is removed when dissolved ferrous iron is present at concentrations >1 mg/l. This is a huge constraint on the design of current passive treatment systems for the removal of manganese.

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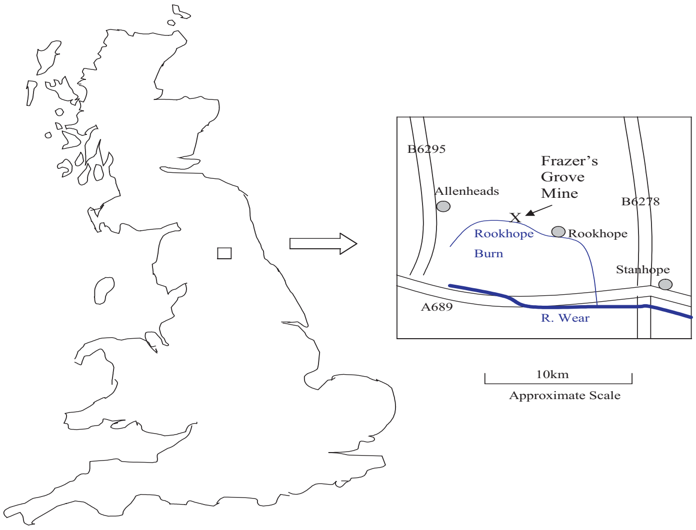

Figure 2: Location map showing Frazer's Grove Mine in the North Pennines

4. PASSIVE TREATMENT TECHNOLOGY FOR MANGANESE REMOVAL

Current passive manganese removal systems in the UK usually consist of oxic rock filters hosting algal and/or bacterial consortia. These organisms remove manganese from the water by creating a suitable microenvironment such as a higher pH which promotes manganese oxidation (Phillips et al., 1995). The algae in particular need light and low influent turbidity to allow **photosynthesis** to take place. These rock filters are usually placed at the end of the treatment process once all of the iron has been removed. Vail and Riley (2000) describe a "Pyrolusite" system for passive removal of manganese, in which a bed of limestone is inoculated with Mn-oxidising bacteria, although it is debatable whether specific inoculation is necessary at all since many authors have found that manganese removal is effective without it (eg Thornton, 1995). Effective manganese removal in all of these systems requires oxidising well-aerated water, prior removal of essentially all dissolved Fe and Al and pH above 6.5. These treatment systems are shallow depth and therefore require large land areas. Removal rates for these systems range from approximately1.5-5 g/m^2/day with **residence times** often in excess of 24 hours.

The recent work at Newcastle University (Johnson and Younger, 2003) presents a major advance in passive manganese treatment, since manganese removal is feasible even where land availability is limited. The removal process is also driven by Mn-oxidising bacteria but is kick-started by **catalysts**: dolomite, bentonite and manganese dioxide. Oxidising conditions are maintained at depth within the system using passive aeration technology. This aeration ensures that the treatment system is rugged enough to operate at low temperatures, in complete darkness and also in the presence of iron. The combined effects of both the catalysts and the aeration provide the conditions required to overcome the usually slow kinetics of manganese oxidation in the presence of dissolved iron. However, although simultaneous iron and manganese deposition is feasible in this system, one problem is that iron oxyhydroxides are much more voluminous than their equivalent manganese oxyhydroxide deposits and therefore porosity and hence permeability are lost more rapidly in a system where iron is deposited.

Manganese removal rates of up to 60 g/m^2/day have been recorded with this new system and residence times have been reduced to less than 8 hours with little reduction in manganese removal efficiency. This is an order of magnitude greater than removal rates quoted by Nairn and Hedin (1993). Furthermore, as operation of this passive treatment process continually generates fresh manganese oxyhydroxide (which is a very powerful sorbent for most pollutant metals) it has major ancillary benefits as a removal process for other mobile metals such as zinc.

5. MANGANESE GEOCHEMISTRY

The favoured oxidation states of manganese are II, III and IV. Oxidation and precipitation of Mn is favoured by high pH (low H$^+$) and high Eh (low e$^-$) as shown below in the two half-reactions for pyrolusite and manganite.

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^- \qquad (3)$$

Log K = -41.89 (Lindsay, 1979)

$$Mn^{2+} + 2H_2O \longrightarrow MnOOH + 3H^+ + e^- \qquad (4)$$

Log K = -25.27 (Lindsay, 1979)

The rate of manganese oxidation can be defined by the rate equation (Morgan and Stumm, 1964):

$$-d[Mn^{2+}]/dt = k_1[Mn^{2+}] + k_2[Mn^{2+}][MnO_x] \qquad (5)$$

This means that the rate is dependent both on the concentration of Mn^{2+} and on the concentration of manganese oxide meaning that the reaction is autocatalytic. Manganese oxides and oxyhydroxides also have a great adsorption capacity for other free metal cations such as zinc and copper (Jenne, 1967).

Manganese oxidation rates are also increased by other catalysts such as clay minerals (eg Ostwald, 1984) and certain microbes. Microbes which oxidise manganese (II) have been known from the beginning of the 20th century and although their role is still not clear it is generally agreed that manganese oxidation which takes place under circum-neutral conditions is bacterially mediated (Ehrlich, 1996).

6. THE RESEARCH

6.1 Site characterisation

The study site chosen for treatment was the recently abandoned (December 1998) Frazer's Grove Mine at Rookhope in the North Pennines (County Durham, UK).

The mine water was net-alkaline with ~20 mg/l Mn, ~5 mg/l Zn and ~5 mg/l Fe, and so provided a suitable source of mine water for use in laboratory experiments for the design of a passive manganese treatment system.

6.2 Experiments

Initially, laboratory work was carried out in order to ascertain which physical substrates and mechanisms promote manganese oxidation. The results suggested that dolomite on a bentonite and MnO$_2$ basal layer was the best substrate combination for promoting manganese oxidation.

Three small-scale continuous flow reactors (A,B,C) were then designed using this combination and operated at room temperature and in natural light conditions for 7 months. Each reactor consisted of a 5 litre rectangular plastic container with an influent pipe near the bottom and an effluent pipe near the top on the opposite side. This arrangement of flow was used to limit the development of preferential flow-paths. The container was filled to a depth of 1 cm with bentonite which was saturated with de-ionised water. A thin layer of manganese dioxide powder was added to the hydrated bentonite surface. Finally the container was filled with clean single-size 20 mm diameter dolomite clasts. Mine water was pumped into and out of the system using two separate **peristaltic** pumps. Aeration of the substrate was provided using a fish-tank aeration pump. However, in the field the aeration is provided by passive means and the development and patenting of a new passive aeration technology has been run alongside this research.

One other reactor was set up as a '**control**', containing only relatively inert silica gravel in place of the dolomite (though still with bentonite as in the other reactors). The 'control' allowed evaluation of the idea (gleaned from the static batch experiments) that the dolomite/MnO$_2$ combination is optimal for manganese removal. The environmental conditions to which the reactors were exposed are shown in Figures 3 and 4.

6.3 Results and discussion

Manganese removal can be categorised into two phases:

- an initial 'start-up' period lasting approximately 2 months where percentage removals were ~60 % manganese removal and 85 % zinc removal;
- the second 'established' part of the experiment when a black precipitate became evident on the dolomite substrate surface. Percentage metal removal with aeration during this phase was 99 % manganese and 95 % zinc.

Analysis of the black deposit using **X-Ray diffraction** and **scanning electron microscopy** showed it to be nsutite, a form of manganite. There was also zinc present with a manganese:zinc relative abundance ratio of 3:1. This was also the approximate molar ratio of manganese:zinc in the influent water for the majority of the time. Small amounts of aluminium and silica were also present suggesting that a clay mineral (possibly bentonite) may be associated with the black deposit.

The overall experiment results showed that dolomite is a much better reactor substrate than the silica gravel. This is shown most clearly in Figure 3 where

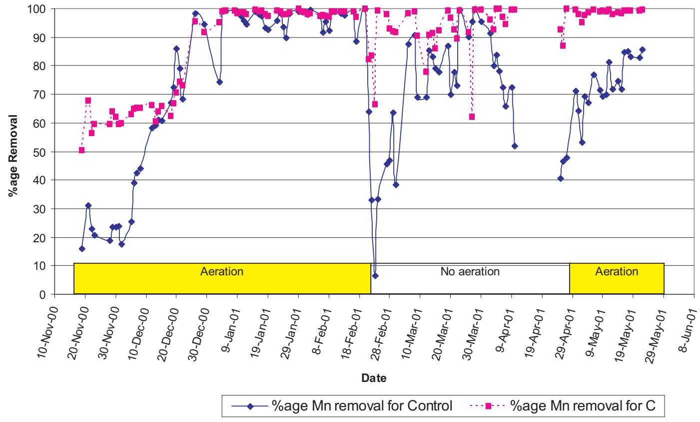

Figure 3: Comparison of percentage Mn removal (both with and without aeration) for Reactors C and Control

percentage manganese removal is compared for both the dolomite reactor ('C' in this case) and the silica gravel ('Control') reactor. The dolomite reactor has a higher and more stable level of percentage manganese removal than the control reactor during the first stage of aeration but it is during the re-aeration process that the real difference in performance becomes clear. Manganese removal in the control reactor never fully recovers from the lack of aeration and in fact much of the manganese oxyhydroxide precipitate is dislodged during the second phase of aeration.

6.4 Is the process of manganese removal biotic or abiotic?

All of the small-scale continuous flow experiments took approximately 8 weeks to become 'established'. This appears to be a common 'start-up' period for bacterial communities engaged in Fe and Mn oxidation (Bourgnine et al., 1994). Percentage metal removal increased during this period and the development of a black manganate precipitate (biofilm) on the substrate surface was noted. However manganese removal rates in the dolomite reactors are much higher and more stable during the start-up phase than in the control reactor.

In later experiments, the disinfectant, Virkon, was added in an attempt to kill all micro-organisms in reactor B. The highly acidic and sulphate-rich solution washed away a large proportion of the black MnOOH biofilm and the effluent remained acidic and effervescent for several weeks afterwards. Percentage manganese removal was ~29 %, with or without aeration, after the disinfectant had been added and percentage zinc removal was 66 %. This figure may give an indication of the amount of manganese removal which is taking place without micro-organisms. However, dead cells may still provide more sorption sites than the inorganic substrate and so this may not be an accurate reflection of manganese oxidation with no micro-organisms (dead or alive) present.

6.5 The importance of aeration

The effects of aeration were examined during the 'start-up' period (from 1st November 2000 to 7th December 2000). In this time interval, reactor A was given twice as much air (two fish tank aeration pumps were used) and reactor B was not aerated at all. Reactor C was left as normal (one fish tank aeration pump used). Percentage manganese and zinc removal did not increase significantly in reactor A, but percentage manganese and zinc removals decreased dramatically in B to ~25%.

In the 'established' phase of the experiments, percentage removal in all three reactors (A, B and C) increased to 99 % manganese removal and 95 % zinc removal as long as aeration was maintained. When aeration was subsequently suspended, manganese removal dropped to ~95 % and zinc removal to ~90 %. With the re-introduction of aeration, percentage manganese removal rates recovered overnight to their previous levels.

The 'control' reactor showed a more pronounced response to the cessation of aeration. Percentage removal in the control reactor during the 'established' phase was ~97 % for manganese and ~91 % for zinc with aeration. With no aeration this dropped to ~72 % manganese removal and ~71 % zinc removal. With the re-introduction of aeration the control experiment took one month to recover to ~80 % manganese removal and ~90 % zinc removal. It was noted that the black manganese oxyhydroxide precipitate which had coated the silica gravel was dislodged by the re-introduction of aeration, whereas the precipitate on the dolomite substrate remained attached during the second phase of aeration. Junta and Hochella (1994) also found that the physical nature of the substrate surface is very important in determining where manganese oxide precipitation takes place.

Dissolved oxygen concentrations measured in both the influent and effluent waters, with or without aeration, were 95 % saturated in all of the experiments (not surprising since both influent and effluent waters were open to the atmosphere). However, when the point of air injection was moved from the substrate to the influent water reservoir in reactor A on 16th March 2001, percentage manganese removal decreased from ~95 % to ~70 % and percentage zinc removal decreased from ~90 % to ~85 %. Percentage metal removal recovered overnight when the air injection position was moved back to its original location within the substrate on 22nd March 2001. Approximately 0.15-0.30 mg/l of dissolved oxygen is required to oxidise 1 mg/l Mn^{2+}, either partially to Mn^{3+} or fully to Mn^{4+} (Sikora et al., 2000) and so there is more than sufficient oxygen present in fully saturated waters (which typically contain ~10 mg/l dissolved oxygen) to oxidise the ~20 mg/L of dissolved Mn^{2+} in the influent water. This suggests that it is not the extra oxygen provided by the aeration which is increasing percentage manganese removal. It is hypothesised that it is the actual aeration process which is increasing the mass transfer of oxygen across the large surface area of the bubbles.

The importance of aeration is also highlighted when the reactors are exposed to stressful environmental conditions such as low temperatures and the addition of iron as can be seen in Figure 4. Without aeration percentage manganese removal falls dramatically under these conditions but with aeration high percentage manganese removal can be maintained.

Interestingly, manganese removal was unaffected by aeration in reactor B, after the addition of disinfectant. As living bacteria were unlikely to have been present, it could be concluded that abiotic manganese oxidation is not increased by the process of aeration. Following this train of thought, it can then be assumed that bacteria were present and taking part in the manganese oxidation process during the 'start-up' period of the small-scale continuous flow experiments. When aeration was removed during the 'start-up' period (in reactor B) manganese removal dropped to ~25 %, which is comparable to the ~29 % manganese removal which was achieved after disinfectant was added which killed all micro-organisms.

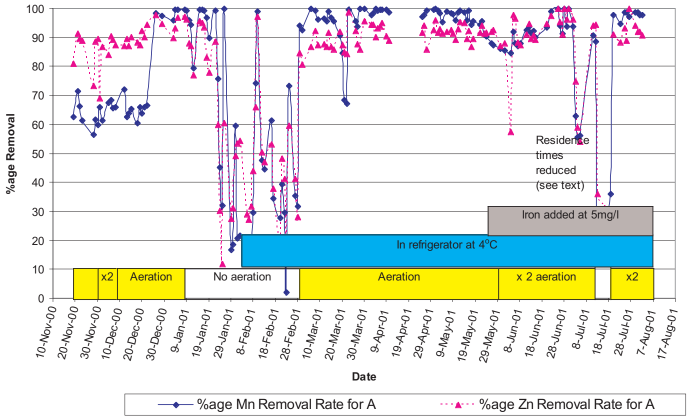

Figure 4: Percentage Mn and Zn removal in Reactor A from November 2000 to August 2001

6.6 Light and temperature effects

Reactors B, C and 'control' were all run at room temperature and exposed to normal daylight. However, reactor A was operated in the cold room (at 4ºC) from 22nd January 2001 onwards. Artificial light in the cold room was continuously supplied until the 7th March 2001 to ensure that any temperature effects could be isolated from those due to loss of light. When the light in the cold room was switched off (on 8th March 2001) reactor A was subjected to continuous darkness, yet there was no significant reduction in percentage manganese and zinc removal while it was aerated.

Figure 4 shows that during the period from 22nd January to 28th February 2001 when reactor A was in the cold room (at 4 ºC) and was not aerated, percentage manganese and zinc removal decreased respectively from values of ~97 % and 91 % (for the same reactor not aerated at room temperature) to ~40 % removal for both metals. In comparison, when aeration was removed from experiments B and C while both were maintained at room temperature percentage Mn and Zn removal decreased from approximately 99 % and 95 % to 95 % and 90 % respectively. It is clear that temperature affects percentage metal removal when there is no aeration present. When aeration (at 4ºC) was introduced to experiment 'A' in the fridge, percentage removal for both manganese and zinc recovered to their previous levels of ~97 % manganese removal and ~91 % zinc removal which is only slightly less than percentage metal removal in experiments 'B' and 'C' at room temperature.

6.7 The addition of iron

To examine the proposition that simultaneous oxidation of Fe^{2+} and Mn^{2+} is not feasible, dissolved ferrous iron was added to reactors A (at 4ºC) and C (at room temperature), from 22nd May 2001 onwards (both of which were aerated during this period). Both experiments removed iron (percentage removal =99 % from initial concentration of ~5 mg/l) at the same time as manganese. There was no significant effect on percentage manganese and zinc removal in reactor C with the addition of iron. However the response to iron addition in reactor A was very clear. There was a decrease in percentage manganese removal from ~95 % to ~85 %. Percentage zinc removal was not significantly affected. When the amount of aeration in reactor A was then doubled (two fish tank aeration pumps were used), manganese removal increased back to ~95 %.

Although the small-scale continuous flow reactors removed both iron and manganese successfully for over two months and showed no signs of deteriorating, once iron precipitation has occurred it is likely that metal removal ability would deteriorate without aeration because iron oxyhydroxides are not such good catalysts for metal oxidation as manganese oxides (Jenne, 1967). The other disadvantage of precipitating iron in the system is that iron oxyhydroxides are much more voluminous and lead to a rapid decrease in permeability.

7. SUMMARY

- A novel subsurface-flow aerated manganese removal reactor has been designed using a dolomite substrate and bentonite and manganese dioxide as catalysts. With an 8 hour residence time, the manganese removal rate was calculated as 60 $g/m^2/d$ which, being an order of magnitude greater than wetland removal rates, demonstrates the ability of the treatment system to overcome the slow oxidation kinetics usually associated with manganese oxidation;
- Manganese removal was not affected by the presence of dissolved iron in the influent water. This is a major advance in manganese removal options since current manganese removal systems fail with iron present;
- Manganese removal was also unaffected by either low light conditions or low temperatures (down to 4ºC). This has important positive implications for manganese treatment as it means that firstly, treatment systems can be based on volume and do not need to cover vast areas in order to maximise light infiltration and secondly the system could be operated in cold climates at high latitudes and/or altitudes;
- The importance of aeration in oxidative manganese passive treatment systems has been proved with high manganese removal rates dependent on aeration in stressful environmental conditions such as low temperature or high influent iron. The system can therefore be regarded as an *in situ* enhanced bioremediation system. Interestingly, abiotic manganese oxidation is not enhanced by aeration and accounts for approximately 25-29 % of manganese removal in the system.

8. APPLICATIONS

The research to date has led to the development of a highly successful and flexible manganese removal passive treatment scheme for the treatment of net-alkaline (pH > 6) manganiferous waters. The next stage of work will involve trialling the system at various sites to prove its viability on a larger scale. The further development of the passive aeration scheme will also take place alongside this research.

The potential market for this technology is huge as numerous discharges including mine waters and landfill leachates contain manganese and with the upcoming changes in water quality legislation, low cost removal methods for manganese are in increasing demand. There is also a potential market for the treatment of drinking water and end-of-pipe treatment systems may be particularly suitable in upland catchments where manganese concentrations can be naturally higher then the maximum admissible concentrations for drinking water, currently at 0.05 mg/l (DETR, 2000).

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