

The importance of aeration in passive treatment schemes for manganese removal

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Abstract

A major breakthrough has been achieved in passive manganese treatment, since manganese can now be removed at the same time as iron, and efficient manganese removal is feasible even where land availability is limited. The active ingredients of this novel sub-surface flow gravel bed are dolomite and manganese dioxide powder. The catalytic action of these substrates combined with aeration provides the conditions required to overcome the usually slow kinetics of manganese oxidation in the presence of dissolved iron. Three small-scale (5 L containers) continuous flow systems were operated for seven months and successfully removed >95% of manganese in this period (raw water Mn concentration ~20 mg/L). The importance of aeration was successfully demonstrated, particularly when the systems were subjected to environmental stresses such as low (or non-existent) light, low temperatures (down to 4°C) and the presence of dissolved iron in the influent water. Spiking with additional iron (to an initial concentration of 5 mg/L) not only failed to significantly lessen manganese removal rates, but complete removal of the added iron itself was also observed. Since current manganese removal systems fail with iron present at such concentrations in the influent water, these results represent a significant advance in manganese removal options.

Key words: aeration, manganese, mine water, passive treatment

INTRODUCTION

Manganese is a common contaminant in many mine waters, and though not as ecotoxic as other common contaminant metals found in such waters (such as Fe, Al and Zn) it nevertheless has various undesirable properties, including a propensity for precipitating in water distribution pipe networks (eventually causing blockage of supply pipes), imparting an unpleasant 'metallic' taste to drinking water and staining laundry. Manganese removal is notoriously difficult when using either active or passive treatment systems. Manganese is generally more difficult to remove from water than iron because rapid oxidation of Mn^{2+} occurs at a much higher pH than the similar process for Fe^{2+} , and even when it does occur, the kinetics of the oxidative process for Mn^{2+} are much slower than that for ferrous iron (Stumm and Morgan 1996). The energetic balance

means that Fe^{2+} ions successfully compete for the attentions of Mn- and Fe-oxidising bacteria in aerobic systems, so that little removal of Mn^{2+} from solution will occur as long as significant concentrations of Fe^{2+} remain available (Hem 1964). Consistent with these fundamental considerations, Nairn and Hedin (1993) found that no manganese was removed from solution in mine water treatment wetlands as long as the dissolved ferrous iron concentration exceeded 1 mg/L. Their observations have since been borne out in practice in hundreds of aerobic wetland treatment systems (Younger *et al.* 2002). This facet of manganese solution chemistry represents a huge constraint on the design of passive treatment systems for the removal of manganese. Since 1994, it has been recommended practice to create vast aerobic wetlands where Mn must be removed from iron-rich waters (Hedin *et al.* 1994). Alternatives to this practice have been slow to emerge. The latest passive treatment unit processes specifically for Mn removal are usually placed at the end of the treatment process stream, so that they receive waters from which all of the iron has already been removed. The manganese removal unit process itself often consists of oxic 'rock filters', hosting algal and/or bacterial

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consortia which create high-pH microniches within which the precipitation of manganese oxyhydroxides and oxides occurs (Thornton 1995; Phillips *et al.* 1995 and Brant *et al.* 1999). For the algae in such systems to photosynthesise effectively, unobstructed daylight and low influent turbidities are necessary. They are therefore subject to marked seasonal (and even diurnal) variations in performance efficiency.

However, antique literature (largely overlooked by other workers in the last two decades) suggests that, given the right conditions, manganese can and does precipitate at the same time as iron. Zapffe (1931) observed simultaneous deposition of salts of both manganese and iron in the water supply pipe network of the city of Brainerd, Minnesota, USA. He also realised that removal of manganese from solution (as present in the water entering the pipe network) was complete. By studying the natural processes responsible for this phenomenon, Zapffe (1931) succeeded in designing and building a treatment plant which mimicked this natural process. The design used the catalyst pyrolusite (manganese dioxide) and maximised aeration using a cascade, thereby highlighting the importance of catalysis and kinetically induced oxidation in manganese removal. The present work seeks to build on these antique results within the modern paradigm of passive treatment.

METHODS

Exploratory static batch experiments (200 mL) were carried out during the summer of 1999 in order to identify suitable substrates and conditions for manganese removal. The results (not discussed in this paper) indi-

cated dolomite rather than other aggregates, as dolomite proved to be the best substrate at promoting manganese oxidation. Four continuous flow experiments were set up and operated at room temperature and in natural light conditions for periods of up to seven months (the total run time for each reactor being determined ultimately by logistic considerations, such as continued availability of serviceable equipment). The set-up of each reactor consisted of a 5 L rectangular plastic container with an influent pipe near the bottom and an effluent pipe near the top on the opposite side (Figure 1). This arrangement of flow was designed 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. The bentonite was used to represent the basal clay liner which could be used in full-scale field applications and also to ensure that the manganese dioxide powder remained *in situ*. 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.

Three of the reactors (labelled A, B and C) were filled with bentonite, MnO₂ and dolomite and the fourth 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/MnO₂ combination is optimal for manganese removal.) The experiments were started on 1 November 2000, but due to a lack of pump availability they

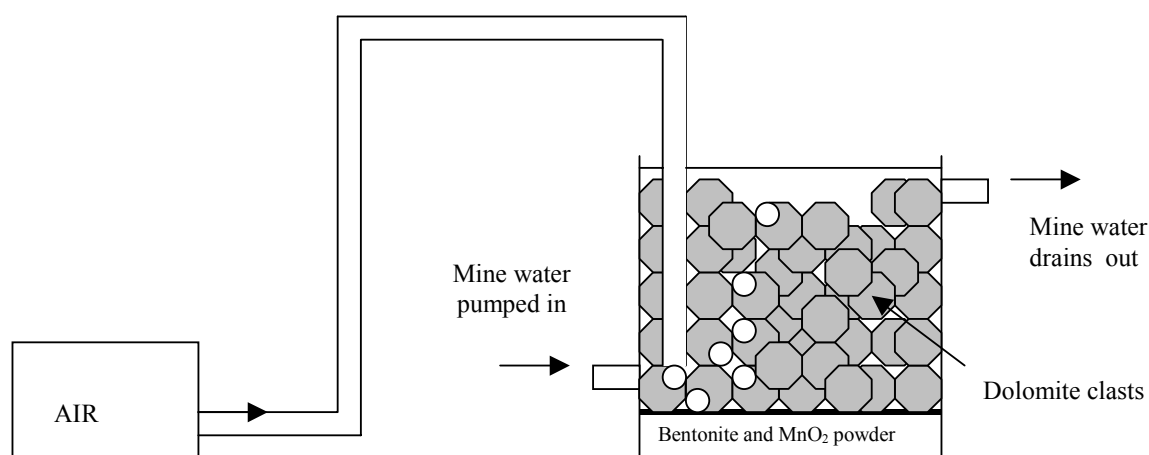


Figure 1. Schematic diagram of the small-scale continuous flow experimental set-up

Table 1. Timetable of events for the small-scale continuous flow experiments

Date	Control	A	B	C
18/11/00 onwards	8 hr residence time	8 hr residence time	8 hr residence time	8 hr residence time
29/11/00 – 7/12/00		2 x aeration	No aeration	
10/1/01		No aeration		
22/1/01		In fridge		
29/1/01				Pump failure
20/2/01	No aeration		No aeration	No aeration
28/2/01		Re-aeration		
8/3/01		In darkness		
9/3/01			Synthetic mine water used	
12/3/01				Blocked pipes
16/3/01	Synthetic mine water used	Aeration moved from substrate to influent water		Synthetic mine water used
22/3/01		Aeration moved back to substrate		
27/3/01			Disinfectant added	
10/4/01	Pipes cleaned		Pipes cleaned	
11/4/01 – 21/4/01	Ran out of water, partially dried out	Ran out of water, partially dried out	Ran out of water, partially dried out	Ran out of water, partially dried out
19/4/01		Synthetic mine water used		
27/4/01 onwards	Re-aeration			Re-aeration
4/5/01			Influent container washed	
9/5/01			Re-aeration	
22/5/01	STOPPED	Iron added		Iron added
1/6/01		2 x aeration		
7/6/01			STOPPED	
10/6/01				
26/6/01 – 28/6/01		2 hr residence time		2 hr residence time
3/7/01 – 6/7/01		0.75 hr residence time		0.75 hr residence time
13/7/01 – 19/7/01		No aeration		No aeration
3/8/01		STOPPED		STOPPED

were initially operated together as three containers in series, and so initial data are not comparable to the rest of the experimental period. The experiments were operated individually from 19 November 2000. Flow rates were measured using a graduated container and stop-watch, and nominal residence times calculated accordingly, taking into account the porosity of the bentonite and dolomite system (determined by lab tests to be about 50%). Flows were generally adjusted to ensure a nominal residence time of around eight hours, because the initial batch experiments had indicated that the majority of manganese and zinc would be removed in this time. The full timetable of events for each of the small-scale continuous flow experiments is given below in Table 1.

Mine water flowing from the recently abandoned, flooded workings of the Frazer's Grove Mine in the North Pennines (United Kingdom) was used in the lab-

oratory experiments. (The geological setting and hydrogeochemistry of this mine during its working life have been described by Younger (2000), and the hydrological and geochemical changes which occurred during and after its flooding are detailed by Johnson and Younger (2002), so will not be discussed further here.) The water used for the experiments was collected on a monthly basis from the Tailrace Level (the main surface outflow point for the flooded workings of Frazer's Grove Mine). During the period of study, the Tailrace Level discharge had a pH around 6.5, an alkalinity of ~120 mg/L as equivalent CaCO₃, and dissolved metals concentrations as follows: ~30–15 mg/L Mn, 10–5 mg/L Fe and 10–5 mg/L zinc. As dissolved iron tended to drop out over the period of one month, the newly collected mine water was not used until all of the iron had precipitated out of solution, in order to ensure consistent influent water quality for the experiments. Iron was

only added to the experiments in their final month of operation when synthetic mine water was used. This was replaced frequently and constant iron concentrations were ensured. Restrictions on field site access in the UK for nine months from February 2001 (due to the national epizootic of foot and mouth disease) meant that it was no longer possible to collect real mine water from Frazer's Grove. Synthetic mine water was therefore prepared by adding 60 mL of stock $MnSO_4$ solution (concentration 20.30 g/L) and 10 mL of stock $ZnCl_2$ solution (concentration 20.85 g/L) to 20 L of tap water. This resulted in an artificial mine water with Mn and Zn concentrations of approximately 20 mg/L and 5 mg/L respectively. When iron was added to the synthetic water, distilled water was used instead of tap water, because the residual chlorine present in the tap water oxidised the dissolved iron within hours. Manganese, iron and zinc concentrations were measured using an Atomic Absorption Spectrophotometer (Unicam 929) in the Environmental Engineering Laboratory at Newcastle University.

RESULTS

Figures 2–5 show the percentage removal rates for manganese and zinc in reactors A, B, C and 'control'. The dashed lines on Figures 2–5 represent the dates when various conditions were changed (as detailed in Table 1). The results can be categorised into two phases:

- an initial 'start-up' period lasting approximately two 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 substrate surface. Percentage metal removal with aeration during this phase was 99% manganese removal and 95% zinc removal for the dolomite substrate.

The role of microbes is not discussed in this paper, but microbes almost certainly take part in the manganese removal process, since two months is a common 'start-up' period for the establishment of microbial communities (Bourgine *et al.* 1994) and details of their role in these experiments can be found in other papers by the author (Johnson and Younger 2002). Despite these very high average removal rates there are some obvious temporary drops in percentage metal removal, particularly in the case of reactor C (Figure 4). Of all the reactors, C suffered from most pipe blockages, and it is likely that particulate matter unavoidably entered the effluent water when blockages were flushed clean, temporarily disturbing the solid–liquid partitioning of Mn.

DISCUSSION AND CONCLUSIONS

The effects of aeration were examined during the 'start-up' period (from 29 November 2000 to 7 December 2000). In this time interval, reactor A was given

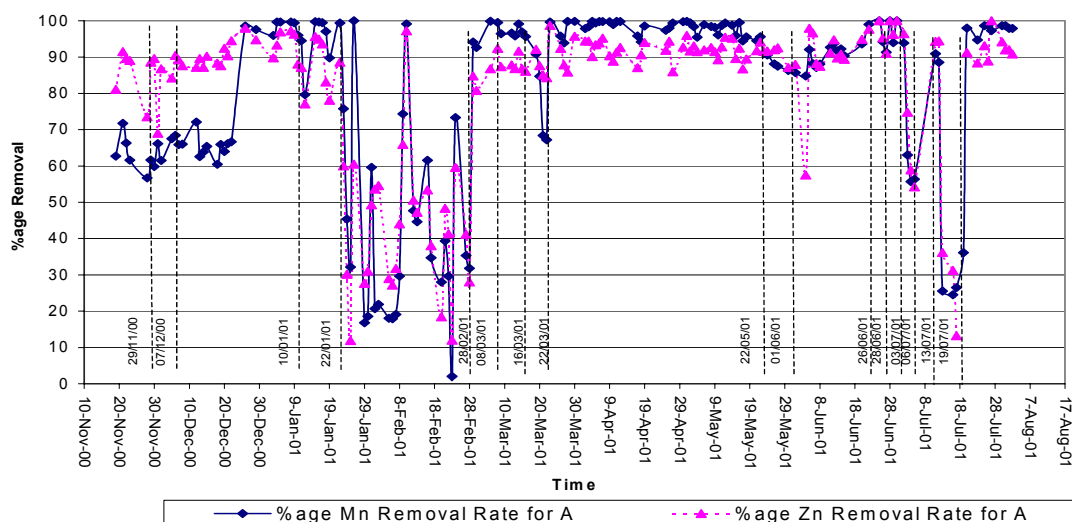


Figure 2. Percentage Mn and Zn removal for small-scale continuous flow reactor A from November 2000 to July 2001

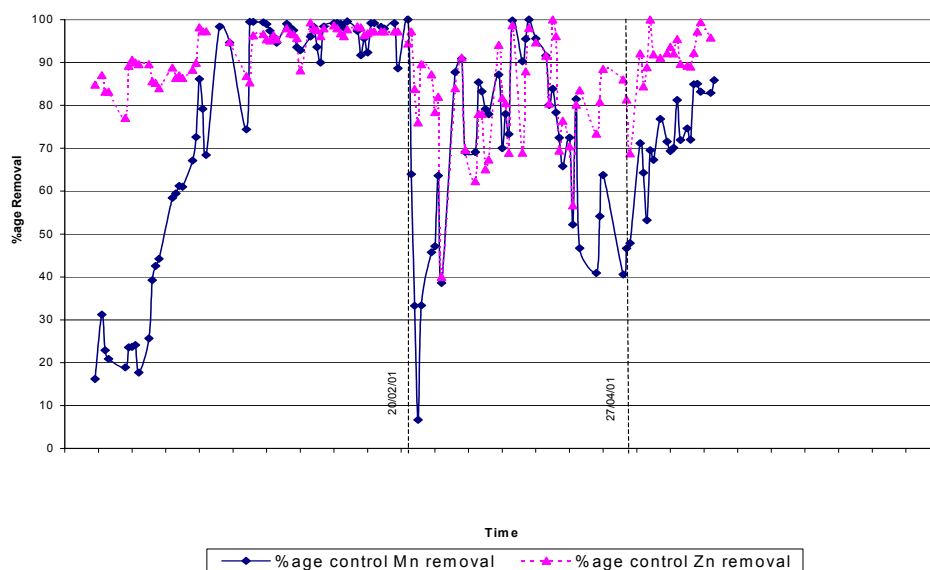


Figure 5. Percentage Mn and Zn removal for small-scale continuous flow reactor 'Control' from November 2000 to May 2001

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 experiment during the 'start-up' phase was less stable than in reactors A, B and C. In fact, percentage removal for both manganese and zinc increased gradually from the beginning of the experiment, and therefore an average figure for metal removal during the 'start-up' phase of the 'control' is not appropriate. 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 aera-

tion the control experiment took one month to recover to ~80% manganese removal and ~90% zinc removal. It was noted that the black 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. This highlights the importance of the nature of the substrate, not just in terms of its catalytic capacity but also in terms of its surface structure for maximum adherence of manganese oxyhydroxides.

Dissolved oxygen concentrations measured in both the influent and effluent waters, with or without aeration, were 95% saturated in all of the experiments. This is no doubt because both influent and effluent waters were open to the atmosphere and therefore able to maintain high concentrations of dissolved oxygen. However, when the point of air injection was moved from the substrate (see Figure 1) to the influent water reservoir in reactor A on 16 March 2001, percentage manganese removal decreased from ~95% to ~70% and percentage zinc removal decreased from ~90% to ~85% (see Figure 2). Percentage metal removal recovered overnight when the air injection position was moved back to its original location within the substrate on 22 March 2001. Approximately 0.15–0.30 mg/L of dissolved oxygen are 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 con-

tain ~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 the percentage manganese removal. The aeration process does promote mixing and will increase the mass transfer of oxygen to the reactive surfaces by the generation of bubbles, but the resulting increased localised oxygen concentrations are not thought to be the main reason for the higher manganese removal rates at colder temperatures. It is hypothesised that the actual aeration process increases manganese removal by creating a high-energy environment and thereby providing the activation energy required to overcome the kinetic restraints (which are greater at lower temperatures) associated with manganese oxidation. This theory is supported by the fact that when the aeration was moved from the substrate to the influent reservoir in reactor A, manganese removal decreased significantly (even though there was more than sufficient oxygen present in the influent water for manganese oxidation to occur), but recovered overnight when aeration was reinstated in the substrate.

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. Figure 2 shows that during the period from 22 January to 28 February 2001 when reactor A was in the cold room (at 4°C) and was not aerated, percentage manganese and zinc removal decreased from ~97% and 91% respectively (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 4°C) 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. Without aeration, percentage manganese removal falls dramatically under these conditions but, with aeration, high percentage manganese removal can be maintained. This also suggests that it is not the extra oxygen provided which is important, but that it is the energy provided by the aeration process which is most important.

To examine the proposition that synchronous oxidation of Fe^{2+} and Mn^{2+} is not feasible, dissolved ferrous iron was added to reactors A (at 4°C) and C (at room temperature), from 22 May 2001 onwards (both of which were aerated during this period). Both experi-

ments 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%.

Therefore, it can be concluded that aeration is required to ensure high Mn removal rates when the system is under environmental stress due to low temperatures or the presence of iron in the influent water. The small-scale continuous flow reactors removed both iron and manganese successfully for over two months and showed no signs of deteriorating. However, once iron precipitation has occurred, it is likely that metal removal ability will be reduced without aeration, because iron oxyhydroxides are not such effective catalysts for metal oxidation as manganese oxides (Jenne 1968). However, these observations have positive implications for Mn treatment using this technique – both in colder climates (in which alternate methods based on photosynthetic algae invariably fail) and on cramped sites.

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