Oxidative passive treatment to remove Mn^{2+} from mine waters: What is the best substrate?

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ABSTRACT

Dissolved manganese is a common contaminant in mine waters and landfill leachates and causes major problems in the water industry as it stains laundry and can cause major pipe blockages. Manganese removal has always been regarded as problematic whether using either passive or active treatment. However, there is very little research into passive manganese removal despite increased interest from regulatory bodies due to upcoming changes in European water quality legislation.

Conventionally, limestones have been used in oxic passive manganese removal treatment systems since limestones have the highest % calcite and thus the greatest long-term alkalinity generating potential. This paper assesses the suitability of alternative substrates, including dolomites and recycled aggregates/industrial by-products, such as concrete and slag. Batch experiments using these substrates were run using real mine water; manganese concentrations were measured every hour. The substrates were each characterised in terms of their mineralogy, geochemistry, and surface geometry, and this information has been correlated with their ability to promote manganese oxidation.

There is no apparent correlation between % manganese removal and % calcite or any other minerals/elements present in the substrates. However, there is a correlation between surface roughness and manganese removal: increased surface roughness is positively correlated with greater manganese removal. The results show that the surface roughness of the substrate is an important characteristic to be taken into consideration when choosing a substrate for Mn removal treatment systems.

BACKGROUND

Mine drainage is a major cause of water pollution worldwide. Passive treatment technology is increasingly used for the treatment of small to medium volume mine water discharges (Younger et al., 2002). Passive treatment is defined by the EU's PIRAMID project (www.piramid.org) 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". In comparison with conventional "active" treatment, which entails the use of chemicals and energy, passive treatment provides an attractive low cost option. Passive technologies such as aerobic and anaerobic wetlands, 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 (Younger et al., 2002).

Manganese is a common contaminant in many mine waters and though not as ecotoxic as other common mine water metals (such as Fe, Al, and Zn), it nevertheless has undesirable properties, such as 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. The UK Environment Agency and the Department for the Environment, Food and Rural Affairs are considering producing an Environmental Quality Standard for manganese, which may be as low as 0.05mg/l dissolved manganese (annual average) if it is to comply with European Directives. Due to such ever-tightening legislation, there has been renewed interest in manganese removal, and successful manganese treatment is in increasing demand.

INTRODUCTION

Manganese removal is notoriously difficult using either active or passive treatment systems. The most kinetically viable method for removing manganese from solution is manganese oxidation. 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.

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (1)$$

Log K = -41.89 (Lindsay, 1979)

$$Mn^{2+} + 2H_2O \rightarrow MnOOH + 3H^+ + e^- \quad (2)$$

Log K = -25.27 (Lindsay, 1979)

According to Sikora et al. (2000), 0.29 and 0.15mg/l of dissolved oxygen are required to oxidise and precipitate 1mg/l of Mn precipitated as MnO_2 or MnOOH respectively. This suggests that manganese oxidation should proceed when concentrations of dissolved oxygen and Mn^{2+} are at levels commonly found in river water and some other natural systems (Hem, 1980). However, since the most common state of manganese in rivers is Mn^{2+}, it is obvious that there are kinetic restrictions at play. However, at circumneutral pH, manganese oxidation will occur under oxic conditions in the presence of a suitable catalyst such as manganite (MnOOH).

The manganese oxidation process is auto-catalytic and is regarded as a two-step process: in the first step Mn^{2+} is sorbed onto the manganese oxide or oxyhydroxide surface with concomitant partial oxidation of Mn^{2+} to Mn^{3+}, and in the second step, the disproportionation of Mn^{3+} to Mn^{4+} occurs (Morgan and Stumm, 1964). The rate of abiotic manganese oxidation has been summarised by Morgan and Stumm (1964) (equation 3), which shows the rate to be

dependent on both the concentration of Mn^{2+} ions and the quantity of manganese oxide present:

$$d[Mn^{II}]/dt = k_0[Mn^{II}]+k_1[Mn^{II}][MnO_2] \quad (3)$$

There are many other catalysts for manganese oxidation, although none so powerful as manganese oxides themselves. Many authors have investigated the catalytic effects of clay minerals on manganese oxidation (e.g., Reddy and Perkins, 1976; Ostwald, 1984; Potter & Rossman, 1979). Reddy and Perkins (1976) found that under alternate wetting and drying conditions, illite was capable of fixing significant quantities of manganese either by physical entrapment or precipitation. Potter and Rossman (1979) also proposed that clay minerals (illite and montmorillonite) are necessary for the formation of certain manganese precipitates such as desert varnish.

Junta and Hochella (1994) characterised the role that mineral surfaces play in the heterogeneous oxidation of Mn(II). They showed that the oxidation of Mn(II) begins through adsorption to 'steps' on mineral surfaces present in solution. It appears that the geometric character, more than the composition, of the immediate surface plays a significant role in controlling the rate of oxidation during the early stages of the reaction. After the initial oxidation of adsorbed Mn(II) at the mineral surface, the newly formed site becomes the most reactive site for continuation of the adsorption-oxidation process.

There are also many strains of bacteria that increase manganese oxidation rates (the rate being dependent on the species of bacteria involved (e.g., Zhang et al., 2002) by as much as five orders of magnitude (Nealson, 1983). Ascertaining the degree of influence that bacteria have on manganese oxidation has proved to be difficult as the majority of metabolic inhibitors used to prevent biotic activity also influence manganese oxidation rates, but it is widely assumed that manganese oxidation occurring at circum-neutral pH is biologically catalysed (Zhang et al., 2002).

Current passive treatment systems for manganese removal

Manganese removal passive treatment systems are usually placed at the end of the treatment process, so that they receive waters from which all of the iron has already been removed, as it is usually difficult to remove much manganese in the presence of ferrous iron (Nairn & Hedin, 1993). The manganese removal process typically consists of oxic 'rock filters', hosting algal and/or bacterial consortia, which create high-pH microniches within which the precipitation of manganese oxyhydroxides and oxides occurs (e.g. Phillips et al., 1995; Hamilton 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.

In the US, the pyrolusite process (Vail and Riley, 2000), a patented bioremediation process, has been successfully used to treat manganiferous waters. In this system, a limestone gravel reactor is inoculated with manganese-oxidising bacteria, which are chosen site-specifically. However recent work (e.g., Johnson, 2003; Rose et al., 2003) suggests that special inoculation may not be necessary.

A new system has been developed at Newcastle University to enhance bioremediation; it operates as a subsurface flow gravel bed. The provision of oxidation by a passive aeration system and the use of catalysts (most notably Mn dioxide) help overcome the slow kinetics usually associated with Mn oxidation. Manganese removal is >95% for initial concentrations of ~20mg/L with residence times as low as 2 hours. % removal is also unaffected by the

presence of ~5mg/L dissolved iron and the system operates equally well at temperatures at least as low as 4°C and in complete darkness. Previous Mn removal technology has failed in the presence of dissolved iron and was also dependent on influent light. Furthermore, operation of this passive treatment process continually generates fresh Mn oxyhydroxide (a very powerful sorbent for pollutant metals, e.g., Jenne, 1967), it has major ancillary benefits as a removal process for other mobile and potentially ecotoxic metals such as zinc. The system is currently operated with dolomite gravel as the substrate.

What is the best substrate for the promotion of manganese oxidation?

It has up till now been tacitly assumed that limestone is the best substrate for promoting manganese oxidation in passive systems, for high pH is widely regarded as the most important factor in manganese oxidation and limestone has the greatest long-term alkalinity generating potential due to its high percentage of calcite. However, because limestone-based systems suffer from substantial kinetic restraints, leading to expensively large systems, we re-examined this tacit assumption. The discovery of natural Mn dendrites on the surface of dolomite (from the Hart quarry in Hartlepool) drew our attention to the possible catalytic capabilities of dolomite with respect to manganese oxidation. The literature also suggests that manganese deposits may have a preference for dolomite over purer forms of limestone but there is little information available as to why this should be the case. McBride (1979) found that Mn^{2+} ions were more strongly adsorbed onto $MgCO_3$ than $CaCO_3$ and he postulated that this was because of similarities between the ionic radii of Mn^{2+} (81pm) and Mg^{2+} (86pm) (by contrast, the Ca^{2+} ionic radius is much larger at 114pm). The structure of $CaMn(CO_3)_2$ is very similar to dolomite, as it is very ordered, although it is much easier to form (Goldsmith and Graf, 1957).

Recycled aggregates such as concrete and slag from the steel industry can provide a high pH environment to help “kick start” manganese oxidation. Manganese oxyhydroxide can then accrete onto the substrate and take over as the main catalyst, thereby inhibiting further dissolution of the substrate so that the general water environment does not suffer from high pH conditions. Using recycled aggregates instead of primary aggregates also reduces primary aggregate extraction and the amount of waste that is landfilled, thereby promoting sustainable development.

The work presented here investigates these alternative substrates and the potential catalytic effect they have on manganese oxidation per se, rather than just their ability to raise pH.

METHODS

The substrates used included a very pure limestone, 6 types of dolomite, steel slag, blast furnace slag, concrete, and silica gravel. Silica gravel was included as a relatively inert substrate for control purposes. The substrates were fully characterised chemically, mineralogically, and geometrically (in terms of surface roughness).

Substrate Characterisation

Thermal Gravimetric Analysis (TGA)

The substrates were ground to less than 0.5mm grain size and 0.3g was subjected to thermal gravimetric analysis (using a Netzsch STA 449C Jupiter machine) under a carbon dioxide atmosphere to a temperature of 1000°C. Subsequent analysis of the results gave the % calcium carbonate and dolomite values for the substrates. However, the process was not

carried out on the silica gravel or the artificial aggregates as it is not a suitable analytical method for these substrates.

Scanning Electron Microscopy (SEM)

Photographs were taken of each substrate surface at x200 magnification using a scanning electron microscope (Hitachi S2400 microscope with an ISIS X-ray detection and analysis system from Oxford Instruments). The samples were air-dried before being placed in the vacuum chamber of the SEM. The photographs were then analysed using an image analysis programme (part of MATLAB), which calculated the mean and standard deviation of the intensity of all the pixels in the tif image (greyscale). The image intensity standard deviation has been used as a proxy for the substrates' surface roughness.

Geochemistry

The natural substrates were ground to less than 0.5mm grain size and then subjected to a partial acid digestion procedure (BS7755, 1995). The filtrates were then analysed for Ca, Mg, K, Na, Mn, Fe, Zn, Al, Ba, Sr, Cr, Cd, Cu, Pb, Ni, and Co. This procedure was not suitable for the slags but XRF data on their composition was available for comparison. 0.5g of the ground substrates was added to 20mL of deionised water, shaken vigorously and left for 12 hours. The pH of the resulting solution was measured using a Camlab MY/6P Ultrameter.

Batch Experiments

The substrates (all 20mm size) were washed with deionised water and subsequently air-dried. 500ml Duran glass bottles were filled to the 100ml mark with substrate and topped up to 200ml with mine water. The bottles were then fitted with a cork that allowed aeration using a fish-tank aeration pump (Peak Aquatics AP-1001) on its highest setting. The systems were aerated for six hours and manganese and zinc concentrations were measured every hour. Figure 1 shows the batch experiment set-up. Three replicates were carried out for each substrate.

Net-alkaline mine water from the recently closed (December 1998) Frazer's Grove Mine in the North Pennines (UK) was used in the laboratory experiments (mine water quality is detailed in Johnson & Younger, 2002). The chemistry of this water is shown in Table 1. The water was not used until all of the iron had precipitated out so that iron would not interfere with the manganese oxidation process.

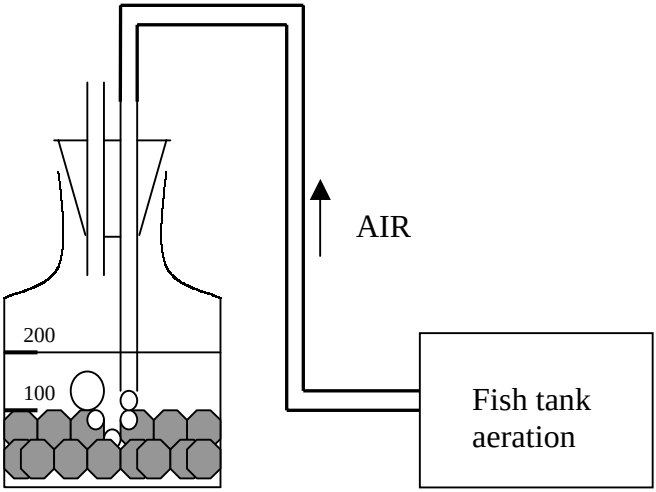

Figure 1. Sketch diagram (not to scale) of aerated batch experiment set-up with substrate

pH	HCO_3^-	Fe	Mn	Zn	Ca	Mg	SO_4
7.00	120	5	20	5	140	30	400

Table 1. Hydrochemistry (pH units and mg/L) of Frazer's Grove mine water which was used in the batch experiments

Manganese and zinc concentrations from the batch experiments were measured using an atomic absorption spectrophotometer in the Environmental Engineering Laboratory at Newcastle University. Detection limits were generally ±0.1mg/L for concentrations measured between 0-20mg/L.

RESULTS

The results of the TG analysis are given below in Table 2:

Name	**% calcite**	**% dolomite**	**% ash**
Coxhoe limestone	97.2	0	2.8
Lower Hart dolomite	60.4	26.9	12.7
Upper Hart dolomite	5.9	92.4	1.7
Lower Witch Hill dolomite	2.7	90.6	6.7
Upper Witch Hill dolomite	20.1	77.0	2.9
Lower Crime Rigg dolomite	11.0	87.6	1.4
Upper Crime Rigg dolomite	13.5	83.3	3.2

Table 2. TGA results for the natural substrates showing % calcite and dolomite

Scanning Electron Microscopy (SEM)

Figures 2 and 3 show the SEM photograph (x200) of the surfaces of both silica gravel (Figure 2) and the Upper Crime Rigg dolomite (Figure 3), which were respectively categorised as the smoothest and roughest surfaces by the image analysis process.

Chemical characterisation of the substrates

The full geochemistry of the substrates is not presented here but the pH of the substrates in deionised water is listed below in Table 4. The pH of the deionised water used was originally 8.45. The natural aggregates all have pHs between 9 and 10 except for the recycled aggregates, which are between 10 and 12.

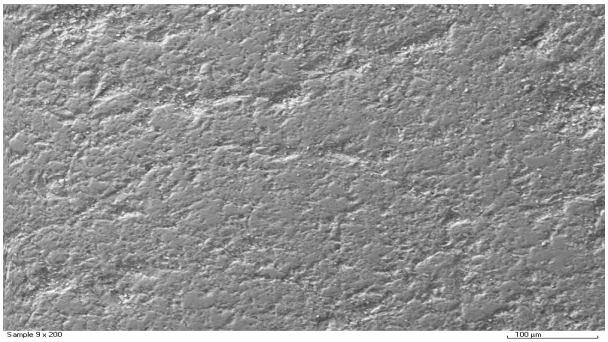

Figure 2. SEM photo (x200) of the surface of silica gravel

Figure 3. SEM photo (x200) of the surface of the Upper Crime Rigg dolomite

Name	Mean image intensity value	Standard deviation for image intensity (related to surface roughness)
Coxhoe limestone	110.6	38.8
Lower Hart dolomite	141.0	53.4
Upper Hart dolomite	124.4	50.0
Lower Witch Hill dolomite	125.4	53.1
Upper Witch Hill dolomite	98.9	46.7
Lower Crime Rigg dolomite	102.4	41.0
Upper Crime Rigg dolomite	118.1	58.3
Blast Furnace Slag	120.9	43.7
Steel Slag	132.0	43.6
Concrete	108.5	41.9
Silica gravel	141.0	28.2

Table 3. Mean and standard deviation of greyscale intensity of SEM photo of substrate surface using image analysis

Name	pH
Coxhoe limestone	9.42
Lower Hart dolomite	9.50
Upper Hart dolomite	9.53
Lower Witch Hill dolomite	9.61
Upper Witch Hill dolomite	9.83
Lower Crime Rigg dolomite	9.30
Upper Crime Rigg dolomite	9.79
Blast Furnace Slag	10.74
Steel Slag	11.69
Concrete	10.11
Silica gravel	8.75

Table 4. pH of solution after 12 hours (0.5g substrate in 20mL deionised water)

Batch Experiments

Manganese and zinc removal at both 2 and 6 hour times is given below (Table 5). Zinc removal is very similar with all substrates except limestone. It is clear that the Lower Hart dolomite is the best substrate for the promotion of manganese removal, with concrete a close second.

Graphs of pH, % calcium carbonate, % dolomite, and substrate surface roughness (using standard deviation of image intensity) were all plotted versus % manganese removal for the various substrates (Figures 4, 5, 6 and 7).

It is clear that there is no correlation between pH (of solution containing 0.5g substrate in 20mL deionised water), % calcite, or % dolomite of substrate with manganese removal at 6 hours in the

Name	% Mn removal at 2 h	% Mn removal at 6 h	% Zn removal at 2 h	% Zn removal at 6 h
Coxhoe limestone	14	22	29	55
Lower Hart dolomite	78	94	98	99
Upper Hart dolomite	53	76	98	99
Lower Witch Hill dolomite	38	62	96	98
Upper Witch Hill dolomite	45	69	98	99
Lower Crime Rigg dolomite	61	79	98	99
Upper Crime Rigg dolomite	56	77	99	99
Blast Furnace Slag	26	29	65	88
Steel Slag	58	79	97	97
Concrete	78	92	97	97
Silica gravel	24	31	32	88

Table 5. % manganese and zinc removal with various substrates at 2 and 6 hours

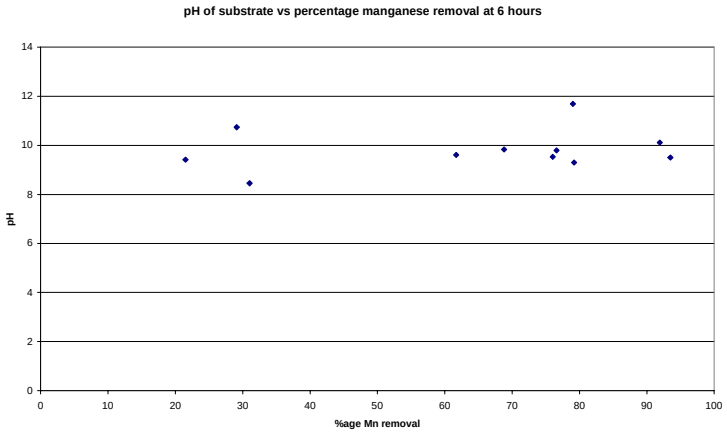

Figure 4. Batch experiment: pH of substrate (0.5g in 20mL of deionised water) vs. % Mn removal at 6 hours

batch experiments. There were also no obvious trends between any trace mineral/metal concentrations in the various substrates (including manganese) and manganese removal although the data is not presented here due to lack of space. However, there was a positive correlation between surface roughness (as characterised by standard deviation of image intensity) and manganese removal, as shown in Figure 6.

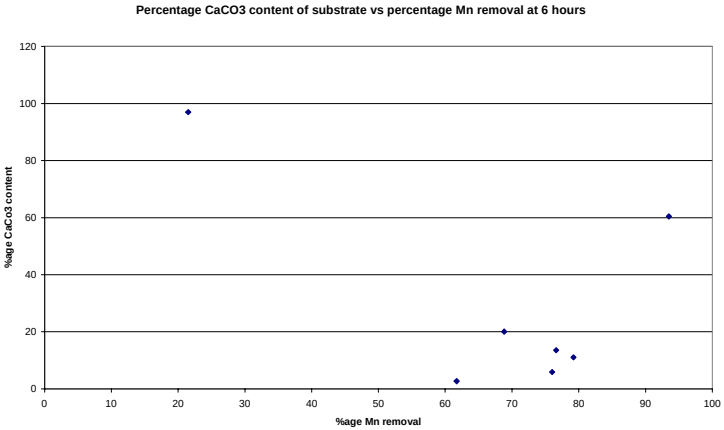

Figure 5. Batch experiment: % $CaCO_3$ of substrate vs. % Mn removal at 6 hours

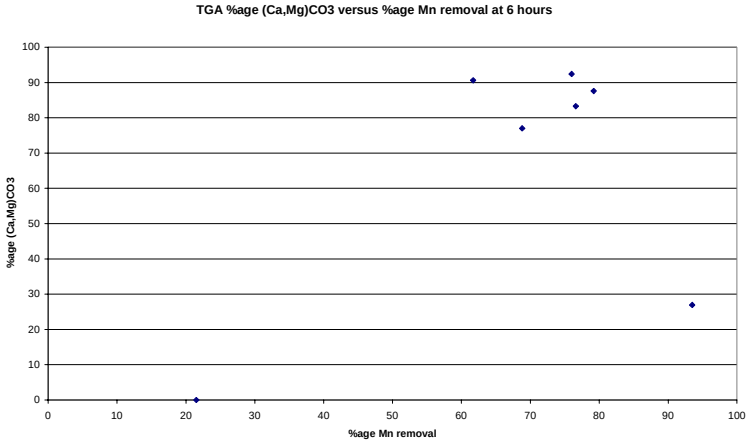

Figure 5. Batch experiment: % dolomite of substrate vs. % Mn removal at 6 hours

CONCLUSIONS AND DISCUSSION

It is clear from comparison between % removal at 2 and 6 hours (Table 5) that Zn removal has practically all occurred within the first two hours of reaction in all cases except the limestone substrate. This suggests that zinc removal is occurring via sorptive processes, which would be expected to occur within the first two hours of reaction (Nicholson, 1997).

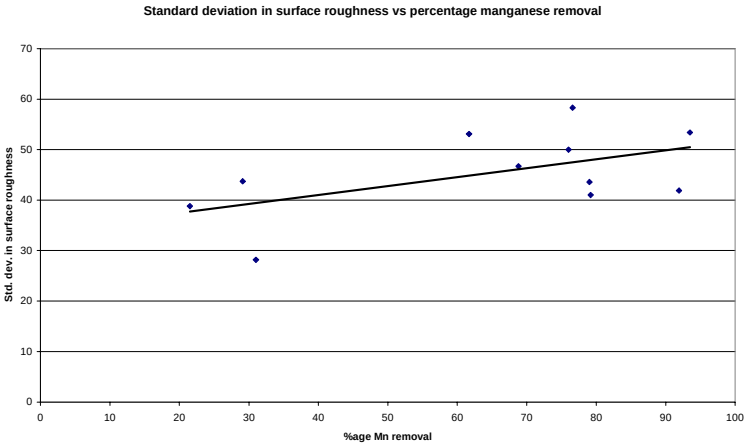

Figure 6. Image intensity standard deviation (in SEM photo of substrate) vs. % Mn removal at 6 hours for batch experiment

Conversely, given the slower removal of manganese, manganese is being removed by a mixture of sorptive and precipitation reactions. Since manganese oxhydroxides are very powerful sorbents, it is most likely that zinc is removed through sorption onto precipitated manganese oxyhydroxides. This, combined with the fact that there is fives times the molar concentration of manganese than zinc present in the mine water means that the reaction kinetics for zinc removal (via sorption), although dependent on manganese removal, will be faster than manganese removal (via sorption and precipitation).

In these experiments, the Lower Hart dolomite was the best substrate for the promotion of manganese removal, closely followed by concrete. Interestingly, the high calcite limestone was (apart from the silica gravel), the worst substrate for the promotion of manganese oxidation. There appears to be no correlation between % manganese removal and the following substrate characteristics:

- pH of a solution containing 0.5g substrate and 20mL deionised water;
- % calcium carbonate content of the substrate;
- % dolomite content of the substrate or;
- % of any other trace metal/mineral concentration.

However, there is a correlation between surface roughness (as represented by the standard deviation of image intensity from SEM photographs) and manganese removal. Junta and Hochella (1994) also discuss the importance of ‘geometric steps’ on the substrate surface in the promotion of manganese oxidation. It is clear that the geometric character of the substrate surface is very important in promoting manganese oxidation in the early stages of the reaction.

However, as manganese oxyhydroxides and oxides themselves are found to be the best catalysts, it is likely that as the manganese oxidation process continues, the nature of the substrate becomes less important as the manganese oxyhydroxides take over as the main catalyst. The substrate surface will be covered with manganese oxyhydroxides so although the geochemical nature of the substrate may be important in the short-term, in the long-term, manganese oxyhydroxide accretion will inhibit further dissolution of the substrate. Therefore, a substrate should not necessarily be picked for its long-term potential for alkalinity generation but for its ability to promote the precipitation of manganese oxyhydroxides in the short-term, whether this be by the generation of a very high pH environment (in the case of concrete and slags) or by having a very rough surface to promote manganese oxyhydroxide accretion.

It can no longer be assumed that limestone is necessarily the best substrate for manganese removal passive treatment schemes. This work has shown that dolomite can be a better substrate than limestone for the promotion of manganese oxidation. Surface roughness is an important characteristic of any potential substrate for manganese removal treatment schemes.

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