THE USE OF BASIC OXYGEN STEEL FURNACE SLAG (BOS) AS A HIGH SURFACE AREA MEDIA FOR THE REMOVAL OF IRON FROM CIRCUM NEUTRAL MINE WATERS[1]

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Abstract. Pilot scale reactors have been installed at a mine water pumping station in County Durham, UK, to investigate the potential of Surface Catalysed Oxidation Of Ferrous Iron (SCOOFI) for rapid removal of iron, using BOS as the treatment medium. The water is circum-neutral, with [Fe] in the range 2–5 mg/L, [Mn] 0.60 – 0.70 mg/L, and [SO_4] approximately 300 mg/L. Saturated flow reactors with residence times of approximately 20 minutes, and a range of BOS particle sizes (20 – 100 mm) have been used to establish the influence of surface area on removal efficiency and system longevity. Iron removal rates are in the order of 80% for all reactors. Differences between reactors, and the potential application of this type of passive treatment, are described in detail in the paper

Additional Key Words: SCOOFI, Basic Oxygen Steel Slag, Iron Removal.
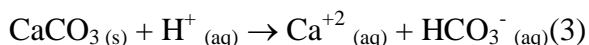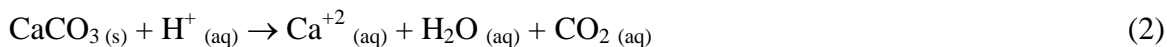
Introduction

Mine Drainage

The problem of mine drainage (acidic or circum-neutral) has been recognized by numerous authors (Blowes et al. 2005 for a recent synthesis). As minerals are extracted, preferential flow paths (shafts and adits) create a pseudo-karstic geology, drawing H_2O and O_2 into contact with rocks and minerals deep underground. In addition to the ingression of oxygenated waters into deep mine voids, waste rock piles are formed at the surface and consequently exposed to H_2O and O_2. The change in environmental conditions results in chemical changes producing a suite of minerals which frequently devolve metalliferous and acid generating leachates. Much of the acidity and metalliferous loading associated with coal mine drainage leachate is from the dissolution of pyrite, the main pollutant mineral found in coal bearing strata. The overall reaction is given in Equation 1.

$$2FeS_{2\,(s)} + 7O_{2\,(aq)} + 2H_2O_{\,(aq)} \rightarrow 2Fe^{+2}_{\,(aq)} + 4SO_4^{-2}_{\,(aq)} + 4H^+_{\,(aq)} \tag{1}$$
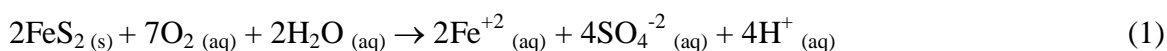
Where there is sufficient buffering capacity provided by the host lithology, for example from the presence of limestones or dolomites, then the acid generated (H^+) in Equation 1 may be consumed under acidic conditions, pH<4.5 (as shown in Equation 2) and at circum-neutral pH (pH4.5-8.3) (as shown in Equation 3) reducing acidity and encouraging the precipitation of metals.

$$CaCO_{3\,(s)} + H^+_{\,(aq)} \rightarrow Ca^{+2}_{\,(aq)} + H_2O_{\,(aq)} + CO_{2\,(aq)} \tag{2}$$

$$CaCO_{3\,(s)} + H^+_{\,(aq)} \rightarrow Ca^{+2}_{\,(aq)} + HCO_3^-_{\,(aq)} \tag{3}$$

In the U.K. much of the surface water pollution from circum-neutral mine waters results from elevated Fe concentrations. The accumulation of voluminous precipitates is not only aesthetically displeasing as the streambed may become stained along its length but may also smother the bed thereby preventing benthic fauna from feeding. The presence of suspended particulates in the H_2O column also reduces the availability of light for photosynthetic organisms and the amorphous precipitates will cover attachment sites available for filter feeders. Since these benthic organisms are at the base of the aquatic food web, the reduction in their populations can seriously affect the ecosystem balance. Scullion and Edwards (1980), observed that Fe^{+3} (oxy)hydroxide choking of stream beds in South Wales decreased macro-invertebrate biomass by 80-90 % from upstream values. Consequently the presence of these precipitates is considered to be the most important cause of reduced invertebrate diversity and abundance below mine waters (Scullion and Edwards 1980, Kelly 1988, Byrne and Gray 1995a, b, Gray 1996, Jarvis and Younger 1997).

Environmental pressures to improve the chemical and biological quality of fresh surface waters have led to an increased need to remediate these sources of pollution. Sustainable treatment options have been the focus of extensive research in both the US and the UK (Spotts and Dollhopf 1992, Hedin et al. 1994, Gazea et al. 1996, Younger et al. 2002, Younger 2003a, b). Treatment of mine waters be they net-acidic or net-alkaline, can take two broad forms: active or passive. For the treatment of net-alkaline waters, the use of passive *in-situ* remediation

is favoured as the pH has already been elevated which is the more costly first step for acidic waters where active dosing is sometimes required before the metals can be removed.

Many forms of passive *in-situ* remediation have been used globally. Amongst the passive *in-situ* remediation techniques that have been trialed for net-alkaline mine waters with low iron loadings using surfaces with high surface area; brush wood filters (Best and Aikman, 1983) and commercially available plastic trickling filter media (Jarvis and Younger, 2000). The Surface Catalysed Oxidation Of Ferrous Iron (SCOOFI) (Jarvis and Younger 2001) occurs due to the adsorption of aqueous Fe(II) species onto an ochre surface; subsequent rapid catalytic oxidation of adsorbed Fe(II) by dissolved O_2 and surface precipitation as a sparingly soluble Fe(III) mineral phase occurs(Burke et al. 2002). This process is irreversible under oxic conditions whereby the Fe(II) is transformed to Fe (oxy)hydroxide (Burke and Banwart 2002). The principal kinetic reactions are discussed by Burke and Banwart (2002), who also give the overall stoichiometry for the oxidation of Fe^{+2} ions by O_2 (as shown in Equation 4).

$$O_2 {}_{(aq)} + 4Fe^{+2} {}_{(aq)} + 6H_2O {}_{(aq)} \rightarrow 4FeOOH {}_{(s)} + 8H^+ {}_{(aq)} \tag{4}$$
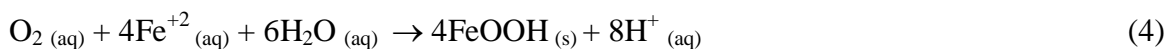
Removal of Fe by SCOOFI relies on the mine water being net-alkaline or circum-neutral, completely oxygenated, and the H_2O must flow over or through a high surface area media to effectively facilitate the process (Best and Aikman 1983, Jarvis and Younger 2001). In addition, Stumm and Lee (1961) identified the HCO_3^- ion, produced from buffering (Equation 3), as an important catalyst to the reaction, encouraging the formation of $FeCO_3$ (Siderite), rather than merely increasing the alkalinity creating the appropriate environment for the reactions to take place. Consequently, higher influent alkalinity increases the initial rate of iron ochre formation, and subsequent removal of iron from the influent water.

Two types of SCOOFI system have been explored:

- Saturated flow SCOOFI reactors (Younger 2000) and;
- Unsaturated flow SCOOFI reactors (Jarvis and Younger 2001).

Saturated flow SCOOFI reactors are more efficient removers of high iron concentrations ($<50mgL^{-1}$) than unsaturated flow reactors ($<5mgL^{-1}$) (Jarvis and Younger 2001). However, saturated flow reactors rely on the influent water being fully aerated, either through pumping or via an aeration cascade. In engineering terms the horizontal alignment of saturated SCOOFI reactors means that they require lower available hydraulic head than unsaturated systems and maintain a much more intimate contact between the water and the media (PIRAMID Consortium 2003). However due to this horizontal alignment they are more land intensive than the vertically constructed unsaturated flow systems.

The choice of passive treatment system to employ is based on a specific number of factors such as flow rate, contaminant, load, hydraulic head, land availability and restrictions imposed by the regulatory authorities. It is suggested that decisions as to which treatment system to select may be based on the relative cost of each system per ton per year of acidity removed, in the case of systems treating low pH waters (Ziemkiewicz et al. 25/03/2003, 2003). Hence the cost of the land, the substrates used and the continued maintenance of the treatment system will have significant implications on the design choice (Jarvis and Younger 2001).

Basic Oxygen Steel Slag (BOS)

BOS is a co-product of steel manufacture. It is comprised of the impurities removed from steel during smelting and from the flux material. The flux used is a blend of limestone, dolomite and silica and as a result the BOS has a very basic mineralogy. The mineralogy of BOS is primarily free lime, ferrite, wustite and di-/tri- calcium silicates, which upon dissolution can produce high pH leachates. BOS has not been extensively used by the environmental sector due to concerns over its high pH generating potential (pH 11-12) and the possibility of toxic metal leaching from some slags (Fallman 2000, Proctor et al. 2002). However, the high pH generating potential, together with its vesicular nature and mineralogical properties (free lime, Fe and calcium silicates) make the material highly attractive for selected environmental engineering applications.

The use of industrial co-products in <u>any</u> application is desirable, helping to reduce primary aggregate extraction and embrace sustainability targets outlined by The E.C. Landfill Directive (1999/31/EC) and The Aggregates Levy in England.

Although worldwide the use of iron and steel industry slags is mostly in building and road construction (Dunster 2001), a small proportion is used in stabilisation of contaminated soils (Sappin-Didier et al. 1997), soil conditioning (Pinto et al. 1995), river bank stabilisation (Motz and Geiseler 2001) and the treatment of contaminated waters (Mann 1997, Ziemkiewicz 1998, Curkovic et al. 2001).

This paper investigates the use of secondary aggregates in the treatment of circum-neutral ferruginous mine waters and system design criteria. The potential for BOS to increase the pH and alkalinity of the system is desirable as it facilitates the formation of $FeCO_3$, an important precursor to the SCOOFI reaction (Equation 4) responsible for the removal of iron onto rough surfaces. In addition, BOS is relatively inexpensive and readily available compared to more expensive commercially produced material (plastic filter media) and is therefore an extremely attractive alternative media for SCOOFI systems.

Field Location

Kimblesworth is located in County Durham approximately 20 km south of Newcastle upon Tyne (Fig. 1). Two pit shafts were sunk on the site in 1873 and the colliery was closed in 1967; after closure, pumping was started to control ground water rebound. The Kimblesworth site is one of several pumping stations in the region maintained to collectively lower the water table over an area of approximately 600 km^2. At the height of pumping they collectively discharged over 100 ML of water per day (of which Kimblesworth contributes 9.1 ML per day) (Younger 1993). The mine water is pumped to the surface from the coal measures 150 m below ground.

Reactor Design

Figure 2 shows the pilot reactor set-up. A bleed was taken from the rising pumped mine water main to supply the distribution tank where the water is allowed to aerate providing the conditions necessary for SCOOFI to occur. The distribution tank allows the flow to be split six ways feeding six individual saturated flow reactors containing different substrates:

    a) 20 mm BOS;

    b) 60 mm BOS;

    c) 80 mm BOS;

d) 100 mm BOS;
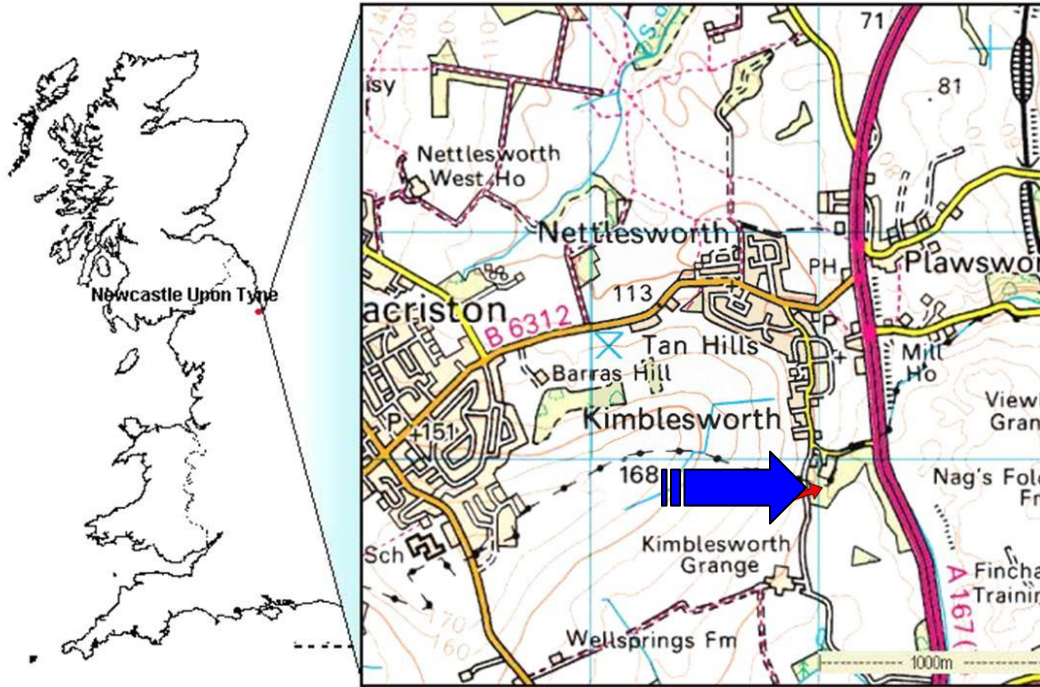e) 20 mm basalt;
f) Control (no media)

Figure 1. Location of Kimblesworth mine water pumping station in the U.K. (Map image taken from www.multimap.com).

Different sizes of BOS were used to assess the relative controls of surface area on removal efficiency versus the loss of hydraulic conductivity and therefore system longevity as the pore spaces become filled. 20 mm basalt was used as a relatively inert, glassy, substrate to assess any chemical rather than physical removal assignable to the BOS, and a control reactor containing no substrate was installed to ensure that the reactors were not merely acting as settling tanks.

The reactors receive influent mine water from an inlet at the top. This fills the reactors and then discharges from the bottom of the rectors via a 'swan-neck', which is arranged at a pre-determined height to control residence time within the reactors. The reactors are 0.8 m^3 in volume and are designed to receive 2 L/min of raw mine water providing a residence time of approximately 20 minutes from measured porosities of the given media (approx. 50 – 65 % dependent on the particle size used).

Figure 2. Photographs of the pilot scale reactors, including the influent feed and distribution system.

Methodology

Field samples have been taken twice weekly where possible from all of the reactors and the influent feed. Field measurements of pH, conductivity, Eh and temperature have been taken using a Camlab Ultrameter 6P which was calibrated on each sampling date. Measurements of alkalinity were taken in the field using a Hach Alkalinity test kit (Model AL-DT). Field measurements of flow were taken for each of the reactors using the bucket and stop watch method on each occasion of sampling. Laboratory analysis of anions was performed using a Dionex (IC-1000) ion chromatogram for determination principally of SO_4^{-2} and Cl^{-1}; a four-point calibration was performed on each occasion. The analysis of major and trace metals was done using a Varian Vista ICP-OES with four calibration standards being run frequently with accuracy checks and blank solutions to ensure consistency. Analysis of filtered and unfiltered water samples was performed.

Results and Discussion

Data for a period of 21 weeks (July to December 2005) are presented in Fig. 3. The Figure shows the removal of Fe from the six reactors (g/m^3/day) versus the Fe loading (g/day); it is clear that with an increased Fe load the removal rate increases. In each case, the reactors out-perform the Control for removal suggesting that the media is playing an important role in the removal of iron from the waters.

The data are dispersed broadly in two ways. The following data (r- and *p*-values) were calculated by transforming the data (Log10) creating a normal distribution of the data allowing the Pearsons Correlation to be used. Outliers in the data set were also removed.

There is a correlation between the Fe removal rate and for the smallest clast sizes BOS 20 mm (r=0.98; *p*<0.001), BOS 60 mm (r=0.99; *p*<0.001) and BOS 100 mm (r=0.93; *p*<0.001) shown in Fig. 3 and this relationship appears to be linear. These reactors also appear to have a higher removal rate than the Control reactor due to the steepness of the regression line.

For the reactors containing the BOS 80 mm (r=0.743; *p*<0.002) and Basalt 20 mm (r=0.757; *p*<0.004) the strength of the correlation between Fe removal rate and loading is less significant than for the BOS 20, 60 and 80 mm, and it would appear that this relationship is not linear. It may be inferred by comparing the data for the BOS (r=0.98; *p*<0.001) and Basalt 20 mm (r=0.757; *p*<0.004) reactors, that the reactivity of the BOS is significant in the removal of Fe in the reactor, opposed to the inert vitreous basalt is more inert than the BOS.
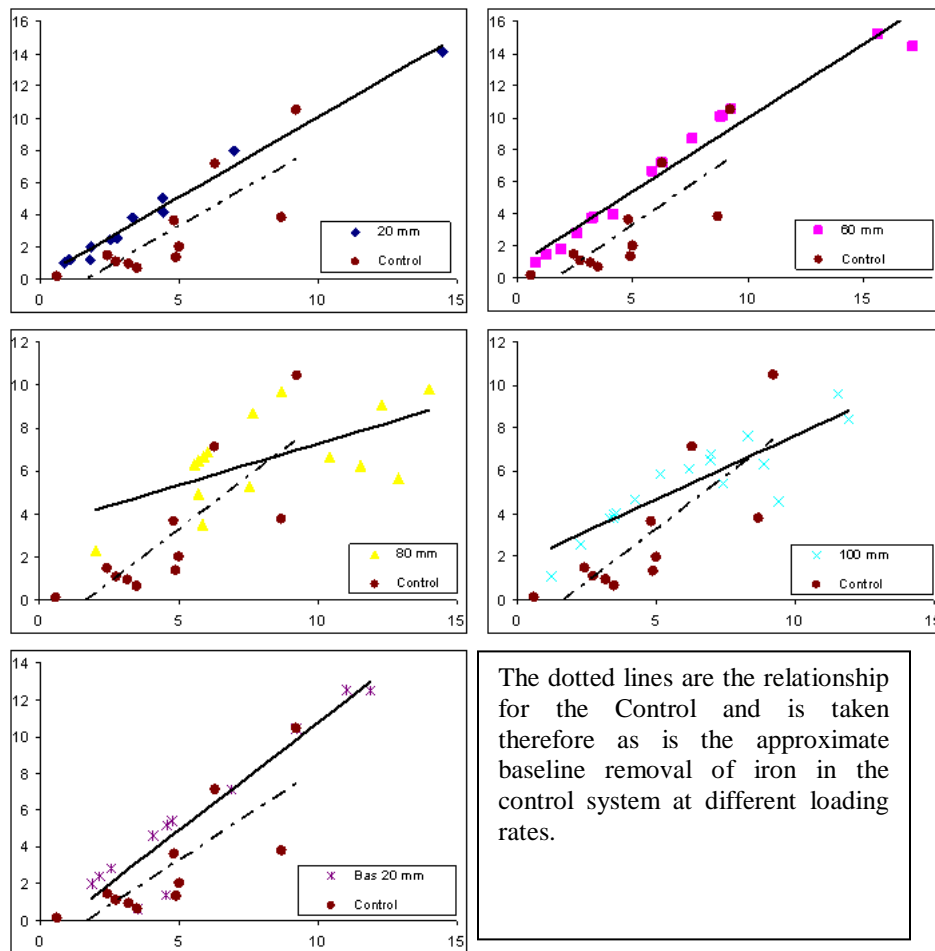

The dotted lines are the relationship for the Control and is taken therefore as is the approximate baseline removal of iron in the control system at different loading rates.

Figure 3. Iron Removal Rate (*y*-axis - g/m^3/day) plotted against Iron Loading (*x*-axis - g/day) for each of the six reactors (the data for the control is plotted on each chart).

Data for the percentage removal of Fe plotted versus Fe loading (Fig. 4) does not show the same relationship that Fig. 3 shows for Fe loading and removal rate. Line B on Fig. 4 shows that broad trend for the percentage removal of Fe in the reactors containing BOS is highest at the lowest Fe loading rates. It is significant that the opposite is observed for the control reactor, containing no media, indicating that the removal of Fe is significantly influenced by the presence of BOS and basalt in the reactors.
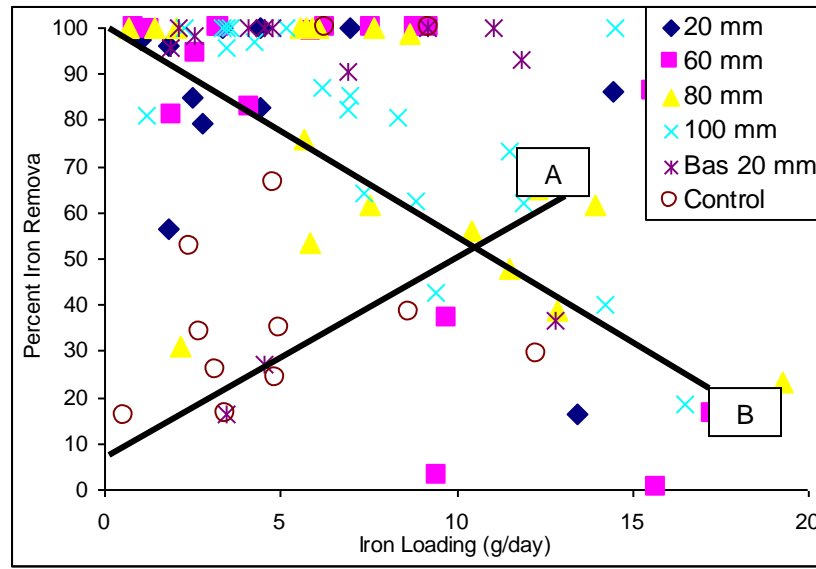

Figure 4. Percent Iron Removal versus Iron Loading (g/day). Line A represents the removal trend in the control (o). Line B is the typical trend of the removal from all of the reactors containing both the BOS and basalt.

On some (approx 35%) of the sampling occasions, the effluent Fe from each of the reactors was measured below detection indicating almost 100 % removal in all of the reactors at specific times. In order to measure meaningful removal rates, the flow was increased in reactors b, c and d (BOS 60 mm, 80 mm and 100 mm) by shutting down reactors a, e and f (BOS 20 mm, BAS 20 mm and the Control) effectively doubling the flow from weeks 15 to 21. It should be noted that more dispersed data for reactors b, c and d may be because these reactors were receiving higher influent loads during this time period. The flow to these reactors was increased to overload the systems to prevent the 100% removal of Fe which had been recorded frequently on previous sampling dates. It was hoped that by overloading the systems the influence of the different sized reactor media would be observed. It is unclear at the present time however which of the reactors is operating most effectively and efficiently.

For the reactors containing the BOS 80 and 100 mm, at iron loadings approximately >8g/day the regression line crosses that of the control suggesting (Fig. 3) that removal efficiency in these reactors is lower than for the Control at this loading rate. The data for these reactors also shows that above an iron loading rate of approximately >8 g/day the relationship to removal appears not to be linear (flattening out); though removal is still occurring (broadly >45%). This finding is

241

consistent with the findings of Jarvis (2000) who noted a similar relationship in reactors containing plastic filter media receiving the same influent mine water where removal rates leveled out above 14 g/day iron loading, albeit these were unsaturated flow compared to the saturated flow conditions presented in this paper.

Figure 5 shows calcium concentrations in effluent water obtained for the reactors during the first two weeks of operation. Figure 5 (A) shows that there is initially both addition and removal of calcium to the system, but this flux reduces over time. The data presented in Fig. 5 (B) show that over the first hour of operation there is an addition of calcium from the reactor containing basalt and a removal of Ca by the BOS reactors.

This observation would at first appear contradictory, it would be anticipated that BOS would contribute Ca to the system as it contains a significant percentage of free lime (CaO, 4-6% by weight). Saturation indices obtained using the modeling program PhreeqC v2.1 (Parkhurst and Appelo 1999) show that the solution is saturated with respect to calcite. With the buffering of the pH of the influent mine water by the BOS, from pH 6.7 to pH 7.1, precipitation of calcite appears to be occurring (confirmed by XRD). The XRD data (and PhreeqC) also indicates the presence of gypsum on the BOS surface, suggesting that the Ca released by the slag is being rapidly sequestered through reaction with sulphate and HCO_3^- in solution. The reaction of the dissolved CaO with the influent mine water solution may explain why the solution pH is not substantially influenced by the BOS which may be expected. Thus the high potential pH generation from the BOS is not a long-term feature of these systems and thus discharges of high pH waters need not be an environmental concern.

It has been postulated that highly reactive fine dust particles deposited on the rough BOS surfaces are liberated and react to form insoluble calcite and gypsum on the BOS surface. As the basalt does not have the same buffering capabilities as the BOS, then the pH is not raised significantly and thus the precipitation of calcite does not occur. It appears that the conditions in the BOS reactors means calcite and gypsum are supersaturated and so Ca is removed. As a result the reactor containing the basalt shows an addition of Ca indicating that the solution is not supersaturated with respect to calcite or basalt and therefore the calcium-containing fine particulates pass through the reactor. The formation of carbonate species is significant in the catalytic sequestration of Fe in the reactors. PHREEQC modelling shows that the waters are supersaturated with respect to siderite ($FeCO_3$) in the BOS reactors. The formation of siderite is known to catalyse the SCOOFI process which is the mechanism for Fe removal in these systems (Stumm and Lee, 1967). XRD data show the presence of siderite ($FeCO_3$), hematite and goethite on the surface of the slag from the reactors and importantly therefore the removal of Fe as crystalline rather than amorphous phases. Samples were taken from the tops of the reactors at different time intervals for analysis and showed amorphous phases present initially followed by the formation of more crystalline iron mineral phases.

Due to the different clast sizes used in each of the reactors the surface area and interstitial porosity vary significantly. The smaller the clast size, the smaller the inter-clastic pore spaces. This is significant as in each of the reactors the interstitial pore volume will be similar as approximately single sized aggregate has been used. However as the pore spaces are smaller they will therefore become blocked more readily. This has been observed as the flow through the reactors containing 20mm BOS and 20mm basalt, the smallest particle size, has decreased over the course of the field trial to date, suggesting a drop in hydraulic conductivity.
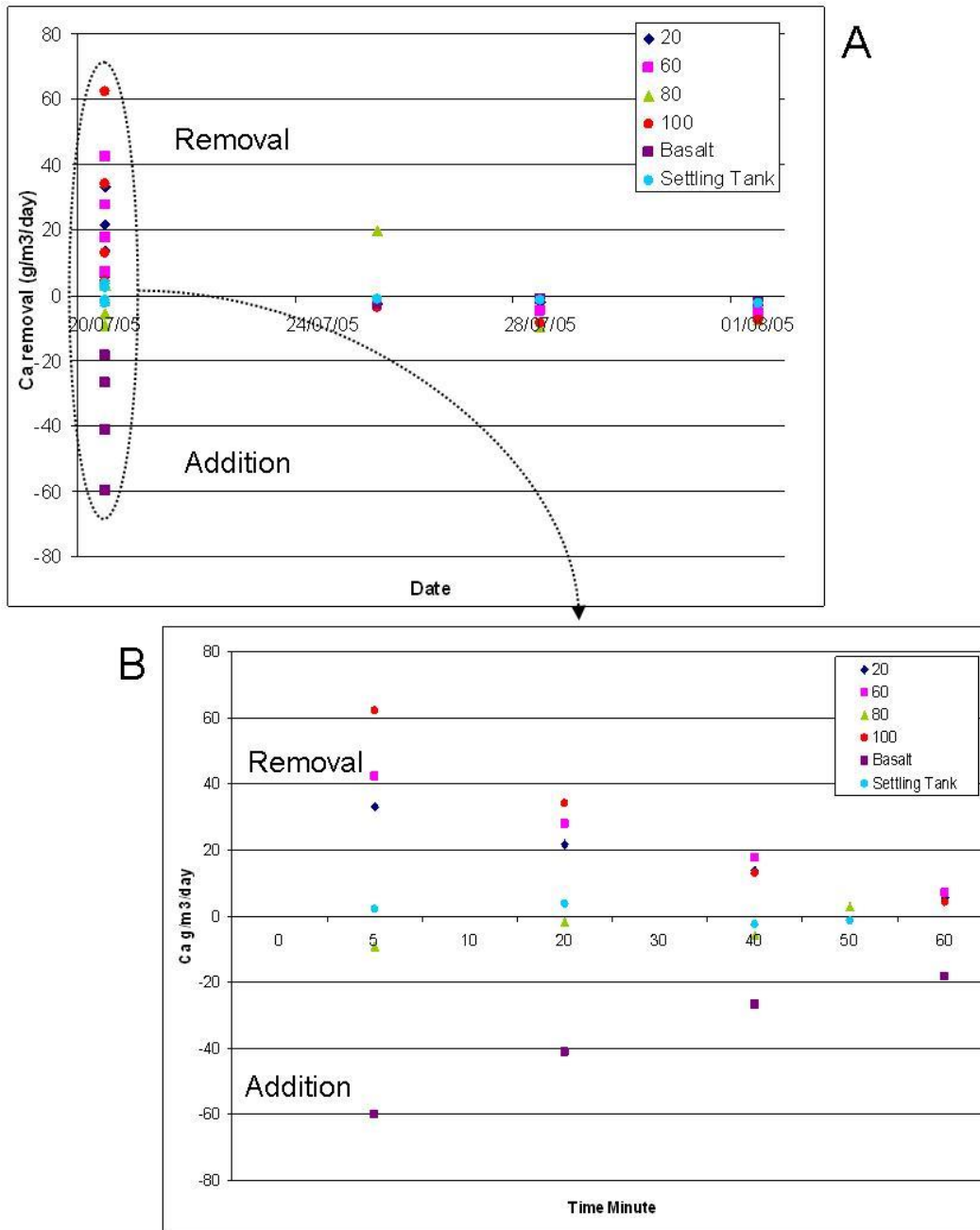
Figure 5. A: Calcium removal from all reactors (g/m^3/day). B: Calcium removal from all reactors (g/m^3/day) for the first 60 minutes of operation (scale is non-linear).

Conclusions

There is efficient (mean 80%) removal of Fe from all of the reactors containing BOS media and basalt, but removal in the control system is consistently <45% on average. It is not currently conclusive with the present data set which of the reactors is performing most effectively.

Although the basalt is removing Fe at a similar rate to the BOS reactors, its use in this type of application would be prohibitively expensive, and thus use of BOS is preferable.

With regard to the lifespan of the systems the partial drop in flow in the reactors containing 20 mm BOS and 20 mm basalt would suggest that there is a decrease in the hydraulic conductivity as the inter-clastic pore spaces begin to be filled with precipitates. If Fe removal rates continue to be similar between systems, this would suggest larger clast sizes would be preferable for full-scale applications, as they would provide greater longevity of operation. The choice however should be coupled with removal efficiency as well as system longevity.

The data for calcium combined with the PHREEQC data and information from XRD indicate the formation of carbonates, both as calcite and siderite occurring in the BOS reactors. This finding is significant as it suggests that the surface chemistry of the BOS may help to accelerate the SCOOFI process.

In these reactors removal rates of ≈ 16 $g/m^3/day$ have been observed which is comparable with rates observed in similar SCOOFI unsaturated flow systems, (12 $g/m^3/day$, (Younger et al. 2002), though the figure is lower than removal rates cited for saturated systems of >100 $g/m^3/day$ (Younger et al. 2002).

In conclusion it appears that BOS provides a suitable surface for SCOOFI to occur, and as a consequence Fe is efficiently removed, this is consistent with findings of other authors. The advantage of the system presented in this paper is that BOS is an extensively tested and relatively inexpensive material compared to the more costly plastic trickling filter media which have been tried to date. In addition the use of an industrial co-product, which may otherwise be deemed a waste, is significant as it is in harmony with the UK governmental policies on reuse and sustainability. In using a secondary aggregate the use of commercially produced materials and primary aggregates may be reduced or avoided.

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