Characterization of Passive Treatment System Substrates and Potential for Zinc Recovery

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ABSTRACT

Treatment of mine drainage, during operation and following abandonment, can represent a substantial cost to mine operators and governing authorities. Recovery of valuable metals from mine drainage as part of the treatment process may offset costs, yet this is rarely seen in practice. Industrial-scale metal recovery from mine waters are the preserve of active treatment systems, where reactor conditions are carefully controlled to ensure consistent quality of product. In many circumstances passive treatment is the preferred approach, but close process control is not feasible in these systems. Analysis of substrate from a pilot-scale compost-based passive treatment system, which operated for two years, has been conducted. The treatment system, which harnessed bacterial sulfate reduction to remove metals as their sulfides, showed that under UK regulations used substrate was within the worst-case 'hazardous' category due to accumulated zinc, and required pre-treatment due to high total organic carbon. Typical costs for disposal are estimated at 1104 US$/tonne, excluding removal and transport. The majority of zinc accumulates in the upper substrate layer. Greatest zinc concentration of 14,050mg/kg (1.4%w/w) was observed in the 0–230mm depth layer; whereas in the corresponding lower layer, 230–460mm, zinc was 808mg/kg (0.08%w/w). This suggests that selective 'harvesting' of upper substrate layers may reduce waste volumes generated, and higher zinc concentrations may be more amenable to metal recovery. Batch-scale leaching tests have also been undertaken, demonstrating recovery in excess of 83 - 96% of zinc from the upper-layer substrate, depending on acid strength used (20; 100; 500mol/m^3 sulfuric acid), within a 100 hour leach test. The results are discussed in the context of the possible economic benefits of metal recovery for passive treatment systems at larger scale.

INTRODUCTION

Pollution of surface waters by drainage from long abandoned metal mines, often sourced from orphan sites, is extensive in the UK (Mayes, Potter and Jarvis, 2010). A national programme of remediation has recently been embarked upon, funded by the UK Government. The programme has the focus of improving water quality in both an effective and cost efficient way. Recovery of metals may offer a way to both reduce costs of waste disposal, and generate revenue for treatment system operators.

Active mine water treatment systems may be amenable to metal recovery, producing potentially valuable metal ores rather than the comparatively voluminous wastes of passive treatment alternatives (Johnson and Hallberg, 2002; Johnson *et al.*, 2006). However, the capital and operational costs of active treatment are high, and they may be visually intrusive. In many cases in the UK, abandoned metal mines are located within centres of significant heritage and ecological importance, and in areas of high recreational amenity, such as the Lake District National Park. In these settings, passive treatment systems, harnessing natural processes and having a minimal impact upon the landscape, tend to be favoured. For the removal of divalent metals such as zinc, the most prevalent contaminant in UK metal mine waters, bacterial sulfate reduction based systems have been shown to be effective (Gandy and Jarvis, 2012; Jarvis *et al.*, 2013). In 2014 the first large-scale metal mine water treatment system of this type (a Vertical Flow Pond; VFP) was built in the UK (see: Jarvis *et al.*, In press). The compost substrate of such VFPs is the main reactive ingredient, providing the reducing conditions and nutrients required to sustain bacterial communities. Sulfate reducing bacteria provide a critical role within the systems, converting dissolved sulfate to sulfide, which reacts with metal ions to form insoluble metal sulfides. This process has been cited as an important mechanism for metal removal within compost-based treatment systems (Machemer and Wildeman, 1992; Jong and Parry, 2004; Pereyra *et al.*, 2008), although some studies suggest that this is not always the case (Matthies, Aplin and Jarvis, 2010).

While there is a significant body of research into the performance of passive treatment systems, there has been little work considering the character of wastes generated, and their amenability to resource recovery. In a review of resource recovery options for passive treatment systems, Gray, Gandy and Jarvis (2012) suggest that further research should be conducted to characterise wastes from treatment systems, and to investigate processes to recover metals from them. In particular, the use of chemical and biological leaching processes should be considered.

METHODOLOGY

Study site

Mine water treatment trials came to an end at Nenthead in Cumbria, UK, in August 2012 after two years of operation. Here, a flow of circum-neutral mine water with zinc concentrations of 2 – 2.5mg/l was treated within a pilot-scale VFP system, as depicted in Figure 1 (photo taken during spring 2012). The system comprised a tank 2.5m x 1.5m x 1.0m (height) configured so that mine water passed vertically down through a 500mm deep substrate of mixed compost (45% v/v); wood chips (45%v/v); activated sewage sludge (10%). Below the substrate, a 200mm deep layer of limestone gravel facilitated underdraining. The compost substrate was completely submerged in water, with water level controlled by the invert height of the raised outlet pipe.

Sample collection

Compost samples were collected at the time the system was decommissioned in August 2012. Figure 2 shows the sample positions within the treatment tank in plan. The system was uncoupled from the mine water feed and allowed to partially drain, such that substrate samples could be collected from just below the water surface. Compost samples were collected from two layers: upper layer (approximately 0 – 230mm depth below compost surface) and lower layer (approximately 230 – 460mm, the base of the compost), which were denoted with postscripts A and B. For example, a compost sample from the upper layer at position A2 (Figure 2) would be denoted A2A. Bulk samples were immediately placed into sealed polyethylene bags before being transported to Newcastle University where they were stored at -20°C until analysis.

Figure 1 Nenthead pilot treatment system

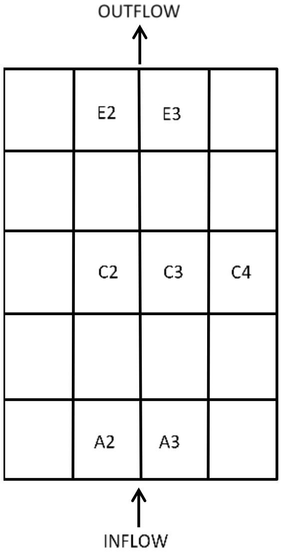

Figure 2 Sample plan of pilot tank

Geochemical analysis of VFP substrate

Relationship between particle size and zinc content

Wet and dry sieving of substrate was conducted on a single sample (C4B), followed by sequential extraction procedures of sieved and bulk samples, in order to determine the relationship between particle size and metal speciation and concentrations. Compost samples were removed from frozen storage and allowed to defrost within their airtight sample bags at room temperature. They were then quartered to obtain suitable subsamples which were oven dried overnight at 105°C, excepting one quartile for wet-sieving. Sieves of 2mm and 212μm were selected, as these provided a relatively even split between particle sizes during preliminary sieving of a test sample. In order to assess the impact of the use of a deionised water flush for wet sieving, compared to dry sieving, the two methods were conducted on quartiles of sample C4B. De-ionised water wash was sampled to determine any solubilised metal. Additional extractions in triplicate were conducted on the remaining two quartiles of the bulk sample in order to test reproducibility of results. Sieved and un-sieved fractions were all ground to less than 212μm and subsampled for sequential extraction. Figure 3 illustrates the quartering and sieving sample preparation procedure.

Spatial distribution of zinc

In addition to determination of the metal distribution in relation to particle size from a single sample location (and the impact of sieving methods on results), investigations were also conducted to assess the spatial variation in metal availability throughout the treatment system. The following twelve samples were investigated from the upper substrate layer: A2A, A3A, C2A, C3A, E2A, E3A; the lower substrate layer: A2B, A3B, C3B, E2B, E3B; plus a blank sample of substrate which had not been exposed to mine water.

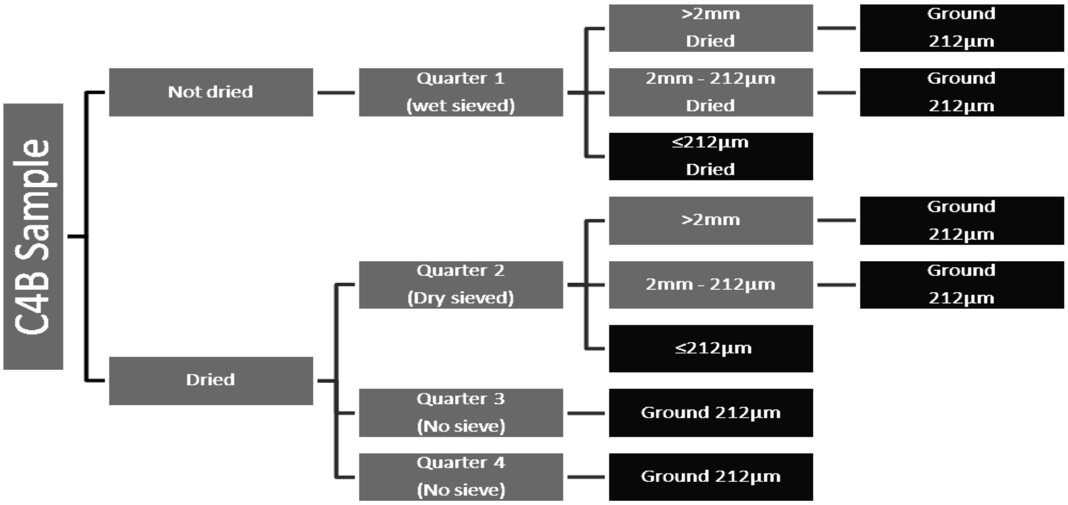

Figure 3 Flow chart showing sieving process

Masses of sieved fractions from sample C4B quartiles were determined and are specified in table 1.

Table 1 Mass of compost fractions following sieving

Sample	Mass (g)
≤0.212mm dry sieved	1.17
2mm - 0.212mm dry sieved	4.58
>2mm dry sieved	7.04
Dry sieved total	**12.79**
≤0.212mm wet sieved	4.56
2mm - 0.212mm wet sieved	3.05
>2mm wet sieved	5.11
Wet sieved total	**12.72**

Sequential extraction procedure

Sequential extractions using procedures developed by Tessier, Campbell and Bisson (1979) were performed on 1.00g of homogenised sample, sieved to ≤212µm. The method (herein referred to as the 'Tessier' method) consists of five operationally defined extraction steps performed in the following order: 1: Exchangeable; 2: Bound to carbonates; 3: Bound to Fe and Mn oxides; 4: Bound to organic matter and 5: Residual. Solutions were recovered following each step by centrifugation for 30 minutes at 10,000rpm and removed using a glass pipette. Between the five steps, samples were washed with 8ml of deionised water, agitated and separated within the centrifuge for 30 minutes. The wash fluid was then discarded. All reagents were made up either from salts or concentrated solutions, diluted with 18.2MΩ/cm deionised water. Samples from step 1 were acidified with one drop of concentrated nitric acid to preserve metals in solution.

Analysis of extraction solutions was undertaken for iron, zinc, lead, manganese, cadmium, copper, cobalt and nickel in accordance with the Tessier method, although only zinc data are presented here.

Acid leaching of VFP substrate

Substrate used for the acid-leach tests was a composite of the upper layer samples from the treatment system (A2A, A3A, C2A, C3A, E2A, E3A) which were sieved to remove fragments greater than 2mm, and homogenised. Batch leaching tests were conducted over 100 hours at room temperature, with lixiviant sampling and measurements of pH, Eh, conductivity and temperature undertaken intermittently throughout the first day, then daily for the following four days. Lixiviant samples of approximately 10mL were collected and passed through 0.45μm syringe filters to remove any suspended material. Batch cells were operated in duplicate and comprised 2L plastic bottles containing 1.2L of lixiviant and 22.5g of substrate, providing a pulp density close to 2%. This ratio was experimentally determined to be effective by Bayat and Sari (2010) during similar leach-tests. Lixiviants were made up from analytical grade sulfuric acid (H_2SO_4) and distilled water. Compressed air was injected into the pulp continuously at a rate of 1 L/min (±0.07L) in order to maintain oxic conditions, and to promote mixing of substrate and lixiviant. Table 2 shows the starting pH of the various lixiviants.

Table 2 Batch leach test variables

Lixiviant	Distilled water		20 mol/m^3 H_2SO_4		100 mol/m^3 H_2SO_4		500 mol/m^3 H_2SO_4	
Sample	DWa	DWb	0.02Ma	0.02Mb	0.1Ma	0.1Mb	0.5Ma	0.5Mb
pH at start	6.63	6.75	1.99	1.96	1.37	1.35	0.93	0.84

Following completion of the leach tests, residues were collected, dried, subsampled and subjected to an aqua regia digest procedure in order to determine residual metal concentrations. The British Standard method ISO11466:1995 was adopted in duplicate, with addition of extra nitric acid to account for elevated Total Organic Carbon, (TOC) above 20% (BSI, 1995).

Lixiviant samples and aqua regia solutions were analysed for iron, zinc, lead, manganese, cadmium, copper and nickel, although only zinc data are presented.

All experimentation was conducted using laboratory grade reagents and acid washed glassware. Metals analysis was conducted using a Varian Vista MPX Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES),

RESULTS AND DISCUSSION

Zinc is the sole focus of the discussion, as it is both the most significant contaminant metal in the mine water discharge treated, and it is due to zinc that the substrate from the Nenthead pilot system has been classified as Hazardous Waste by independent laboratory testing. Hazardous Waste requires special treatment under UK waste regulations.

Relationship between particle size and zinc content

Figure 4 depicts zinc data from wet sieved and dry sieved fractions of substrate sample C4B. Note that in addition to a breakdown of the five extraction steps, the amount of zinc lost from the wash solution (included in ≤212µm wet sieved fraction) is depicted on this bar as 'Loss in wash'.

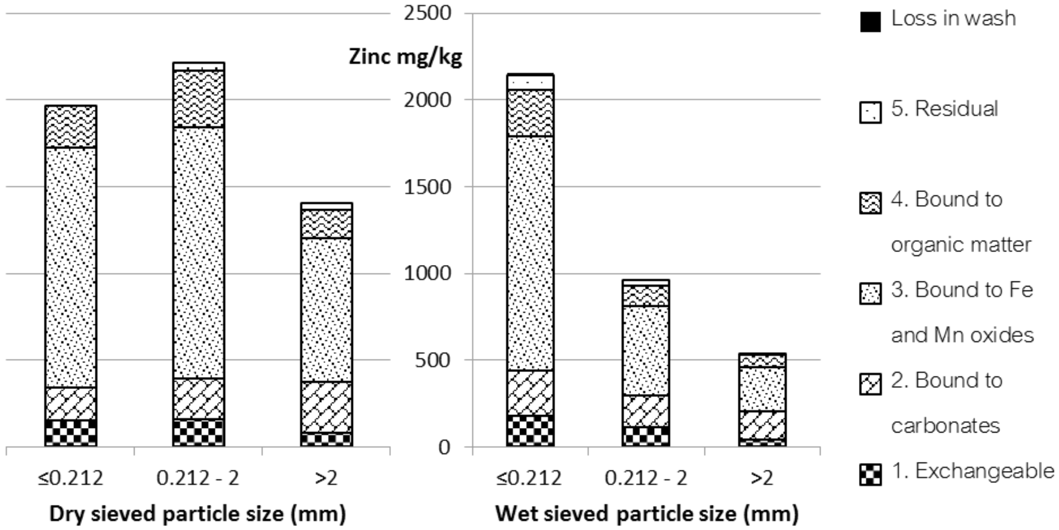

Figure 4 Zinc concentrations in sieved substrate samples

A distinct trend in total metal content was apparent within the wet sieved fraction, with highest zinc concentration in the finest fraction: wet sieved fraction ≤212µm contained 2,158mg/kg of zinc, in contrast to the >2mm fraction that contained just over a quarter of this amount at 541mg/kg. In fact, this trend is apparent for all extraction steps, excepting 2 (bound to carbonates). Dry sieving, however, did not yield such clear results: the ≤212µm fraction contained 2014mg/kg of zinc, in comparison to >2mm which had 1403mg/kg, while the intermediate size fraction contained the greatest amount (2214mg/kg). Such a distinct contrast between sieving methods is thought to be due to the behaviour of materials within the sieves: dry sieved compost, that was pre-dried to remove moisture, was composed of loosely cemented fragments bound to, and together with, fine grained material. Sieving only shows some success in separating these fragments, evidenced in part by the recovery rate of fine grained material (see table 1): just 1.17g passing ≤212µm, compared to 7.04g of material retained on the 2mm sieve. In contrast, 4.56g of material passed the 212µm sieve and 5.11g was retained on the 2mm sieve during the wet sieving operation. From observations during the sieving process, the deionised water wash appeared to aid the separation of compost fragments. It was not unexpected that wet sieving would assist the separation of particles during sieving, but it was recognised that the deionised water wash had the potential to both mobilise weakly-bound metals, and also potentially facilitate geochemical reactions that might alter speciation. Although it was not possible to assess whether metal speciation was influenced by the deionised water, a sample of the deionised water wash solution was analysed by ICP-OES (in parallel with a blank), and revealed that just 13.76mg/kg equivalent of zinc was leached from the compost (see 'Loss in wash' on Figure 4 for relative significance). In order to demonstrate reproducibility of the sequential extraction procedure, triplicate samples were run for the two un-sieved quartiles. Statistically, the standard deviation is less than 7% of the mean for all extraction steps across all sample quartiles, demonstrating good reproducibility.

Spatial distribution of zinc within treatment system

The degree of spatial variation of zinc concentration in the substrate was investigated in a second round of sequential extractions using the methods previously described. Particle size separation was not undertaken as part of these tests, which were conducted to assess the variation (if any) between metal species and their availability throughout different parts of the Nenthead pilot treatment system. Eleven bulk samples in total were analysed, plus a substrate blank. Figure 5 depicts zinc concentrations, and a breakdown of the steps by which they were extracted.

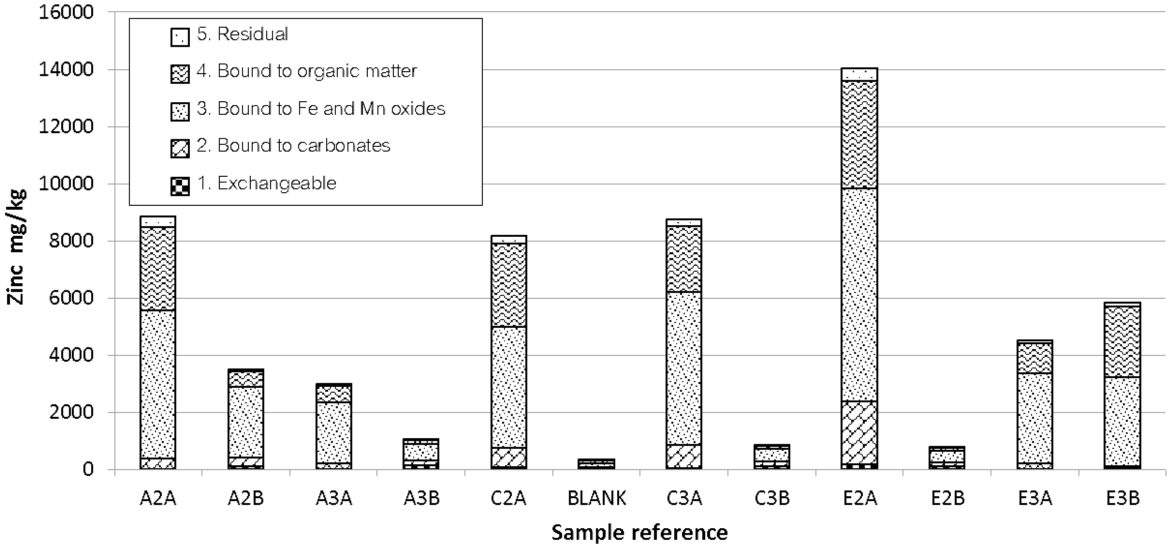

Figure 5 Zinc concentrations from a range of sample locations within the pilot treatment system

In all but one case (samples E3A/B), compost from the upper layer contained substantially more zinc than samples taken from the respective lower layer. Greatest zinc concentration was seen in sample E2A (14,050mg/kg) and the lowest seen in the corresponding lower layer sample (E2B; 808mg/kg). 340mg/kg zinc was measured in the blank substrate. No discernible trend in zinc concentration was evident either laterally or longitudinally.

Exchangeable zinc (step 1) provides perhaps the most pronounced difference between samples, from upper and lower levels, as significant exchangeable zinc is only shown at depth (although it is recognised that this is difficult to see in Figure 5). E3B does not show this clear trend, however this sample was previously identified as a possible outlier. In the upper layer, zinc species are dominated by Fe/Mn oxide and organically bound fractions (steps 3 and 4), with very small concentrations of exchangeable zinc and zinc bound to carbonates (steps 1 and 2 respectively). Residual zinc comprises a small fraction throughout, up to 5% in E2B; whereas most zinc is recovered during step 3: all in excess of 50%, other than C3B where 49% was extracted. Data for the 'blank' sample showed a similar pattern: almost half (46%) zinc was attributed to the Fe/Mn oxide fraction, with significant amounts of zinc extracted during step 2 and 4, and a lesser amount (5%) associated with step 1. Residual zinc in the blank was 8%, which in percentage terms was greater than all residual fractions in the samples from the treatment tank, but was less in absolute terms than all other compost samples. Several samples (A2A, C2A, E2A) had in excess of ten times the absolute amount of residual zinc, compared to the blank. Percentage residual zinc for these samples was 4%; 4% and 3%, respectively for A2A; C2A and E2A.

Neculita, Zagury and Bussière (2008) presented data from extractions using a modified Tessier method on compost from laboratory scale column based bioreactors. Mine water chemistry, treatment configuration and scale all differ from the work conducted here, however some general comments can be made on how both sequential extraction data compare. Samples were taken from both the top and the base of the column – analogous in some ways to the sampling of top and bottom layers of the Nenthead tank. Neculita, Zagury and Bussière (2008) found that, with duplicate columns treating mine water for a 7.3 day residence time, the greatest zinc fraction (37 – 50%) was associated with step 3, comparable with Nenthead data. In contrast, substantial zinc concentrations were associated with steps 4 and 5: specifically 4 in the top layers (36 – 46%) and 5 in the lower (28 – 36%) (Neculita, Zagury and Bussière, 2008). What is of significance is that substantial amounts of zinc appear more tightly bound in the 2008 study compared to Nenthead data, specifically at depth. Furthermore, while data from the Nenthead tank showed typically very low exchangeable zinc (step 1) in the surface layer, Neculita, Zagury and Bussière (2008) found that this was where most exchangeable zinc occurred (8 – 12%). A second duplicate set of columns were investigated, with an increased hydraulic residence time of 10 days. These columns yielded similar results, though there was a slight increase in residual zinc in the bottom layers of the columns: 33 - 41%. The other trend of interest in relation to data from the study of Neculita, Zagury and Bussière (2008) is the higher proportion of exchangeable zinc being identified in the upper part of the column, rather than the bottom in the case of the Nenthead data. It is not clear what this could be attributed to, and the comparison is limited due to modifications of the Tessier method made by Neculita, Zagury and Bussière (2008).

Acid leaching of VFP substrate

Zinc recovery from the substrate is presented in Figure 6, which shows both zinc concentration in the leachate and zinc concentration in substrate residues, determined by aqua-regia digestion. Extraction was shown to be effective with moderately weak strength acids, with extraction efficiencies of over 80% in all acid-leach tests after 100 hours. Zinc recovery of 93.9% and 95.1% was achieved with 100mol/m^3 sulfuric acid, whereas the most concentrated acid (500mol/m^3) achieved extraction efficiencies of 95.1% and 96.0%. There appears to be only a marginal gain in efficiency for a fivefold increase in acid concentration. It is considered that under the conditions of these batch tests, the 100mol/m^3 acid represents the optimum balance between concentration and extraction efficiency.

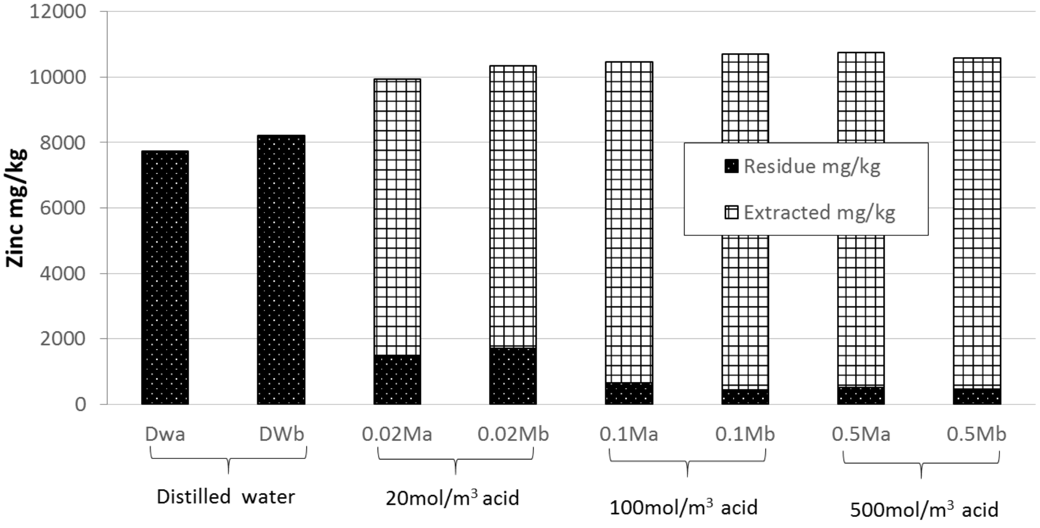

Figure 6 Zinc concentrations from leachate and residue after batch leaching

Batch leach data for zinc show good replication between duplicate columns; less than ±5% variation for all four experimental pairs, and less than ±2.5% variation between the sulphuric acid duplicates. Aqua regia digest duplicates were within 5% for distilled water blank samples and 500mol/m3 acid, but duplicates for 20mol/m3 and 100mol/m3 had 7% and 20% discrepancies, respectively. This is perhaps attributable to heterogeneity of sample residues exposed to aqua regia.

CONCLUSIONS

Geochemical analysis was undertaken on substrate taken from a pilot-scale mine water treatment system following sieving by both wet and dry methods. Samples were also collected and analysed from 11 different positions within the treatment system. In addition, batch-leach tests were conducted on a composite substrate sample, to determine extraction efficiencies for a range of sulphuric acid concentrations.

Wet sieving suggested that substantially more zinc was associated with the fine grained fraction of substrate (≤212μm fraction). This trend was not seen in the dry sieved sample analyses, and these results may have been affected by cementing of substrate fragments during drying. Significantly more zinc was found in the upper layer of the substrate than at depth within the treatment tank. Moreover, zinc in the surface layer was more tightly bound, whereas some zinc at depth was recoverable by ion exchange. Sequential extractions to the Tessier method suggest that in both substrate layers, most zinc is bound with moderate strength and associated with Fe/Mn oxides; however, it should be noted that sample preparation and exposure to oxygen may have influenced speciation (Rapin *et al.*, 1986). Leach tests demonstrated that dilute sulfuric acid was effective at removing zinc from the compost substrate, with 100mol/m^3 providing the optimum balance between concentration and extraction performance. Further experimentation to test the absolute capacity of the acid for metal recovery is planned, in order to assess the feasibility of large-scale metal recovery operations (i.e. how much metal could be solubilised for a given acid volume).

Data presented in this paper indicate that zinc-laden mine water treatment substrates may be decontaminated by: a. separation on the basis of particle size, and b. leaching with dilute acids. Additionally, spatial sampling identified that metals accumulated more rapidly within the surface layers of the treatment system, which may facilitate selective recovery: it may be that periodic removal and replenishment of surface substrate layers may offer a means of effectively extending the life of a given system, as suggested in a review by Gray, Gandy and Jarvis (2012). These processes may offer mechanisms of decreasing whole-life costs by extending system lifetimes, reducing waste and recovering metals. Further research is required to consider the practicalities and costs of substrate decontamination at a large scale, and options for concentrating metals within lower-volume materials to levels at which they might have a commercial value.

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