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Citation for final published version:

Roberts, Mark, Sapsford, Devin, Weightman, Andrew and Webster, Gordon 2017. Changes in metal leachability through stimulation of iron reducing communities within waste sludge. *Solid State Phenomena* 262 , pp. 269-272. 10.4028/www.scientific.net/SSP.262.269 file

Publishers page: <http://dx.doi.org/10.4028/www.scientific.net/SSP.2...>  
<<http://dx.doi.org/10.4028/www.scientific.net/SSP.262.269>>

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# Changes in Metal Leachability through Stimulation of Iron Reducing Communities within Waste Sludge

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**Keywords:** Bioreduction, bioleaching, leachability, metal extraction

**Abstract.** Bioreduction of ferric iron-rich wastes is a rapidly emerging technology for the extraction/recovery of metals from low-grade ores and metallurgical wastes. However, despite studies being successful, they have only been demonstrated at laboratory scale and issues relating to economic, industrial scale application have yet to be studied. Using bioreduction as a pre-treatment to increase recovery yield is a relatively new concept. This study examines the biostimulation of microbial communities to induce bioreduction of metalliferous sludge and the effect that this has on the leachability of metals from the waste using dilute sulphuric acid. Data shows an increase in both zinc and copper leachability after bioreduction, with maximum six fold and eleven fold increase (compared to pre-treatment) in the amount of zinc and copper leached respectively.

## Introduction

As global demand for metals increases and the number of high grade deposits dwindles, processing of lower grade ores has become of vital importance. Biomining has emerged as an important process in processing these low grade ores [1] [2]. Whilst the majority of biomining operations have utilized the biooxidation of reduced sulphidic ores, in recent years there has been an increased focus on oxidised ores and novel anaerobic bioreductive leaching techniques are being developed and used on a range of iron-rich ores and waste materials with recovery of metals such as Ni, Co, Cu, Zn, Pb and Al being targeted. The metabolic mechanism of dissimilative iron reducing microbes (DIRM) has been widely exploited to reductively solubilise the ferric iron within these ores/wastes. This reductive dissolution can result in the release of any metals associated with the ferric (hydroxy)oxides to the aqueous phase, facilitating their extraction [3-10].

In bioreductive extractions DIRM are generally used as the primary extractive technique. However, the majority of these studies, though successful, have only been demonstrated at laboratory-scale and issues relating to scaling up to economically viable processes have yet to be considered. To be widely practicable (especially to metal recovery from wastes), methods will need to be cost effective. Along with its use as a direct extraction method there is interest in the efficacy of bioreduction as a pre-treatment in place of traditional pre-treatments e.g. thermal treatment. Studies have shown that a bioreductive pre-treatment followed by a concentrated acid leach can yield extraction rates, of Co and Ni from chromite overburden, up to 10 times greater when compared to non-treated waste [9].

This study aims to expand on the idea of using bioreduction as a pre-treatment for a subsequent acid leach extraction. However, it differs in that rather than introduce known cultured microbes with their ideal organic carbon source, the indigenous microbial communities within the waste were stimulated to induce iron reduction. Lower concentrations of acid were used during the acid leach extractions to reduce cost, risk and environmental risk with the aim of assessing the potential for the implementation of the method whilst the waste remains in-situ.

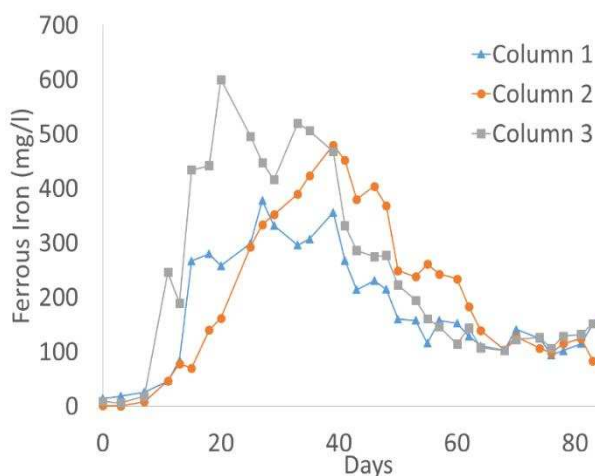
## Experimental Methods

The bioreduction stage of experimentation was carried out within vertical flow columns constructed from one litre high density polyethylene bottles with in/outlet valves attached at either end. The bottles were filled with samples of iron (hydroxy)oxide sludge taken from a settlement pond at Parys Mountain, N. Wales, a former Cu/Zn/Pb mine. The bottles were filled whilst under vibration to ensure even distribution and minimise the potential of trapped air. The columns were fed with a 10 mM glycerol solution (at a rate of  $\approx 0.45 \times 10^{-3}$  kg/day equivalent to 0.05 kg/kg of dry sludge in total) as the organic electron donor to stimulate microbial reduction of iron, and maintained at ambient room temperature for 90 days. The bioreduction stage was carried out in 3 columns with the same homogenised sludge sample to provide 3 replicates. Ferrous iron concentrations within the column effluents were considered as indicative of iron reduction. Dissolved ferrous iron and total iron concentrations within the effluents were measured via colourimetry and induced coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 2100 DV ICP-OES) respectively, these measurements were taken daily. Measurements of the pH, conductivity, redox potential and dissolved oxygen content were also recorded daily.

Following the bioreduction stage the bioreduced sludge was extracted and homogenised within a glovebox under nitrogen, to prevent any mineral changes due to oxidation, and subjected to acid leaching. Leaching was performed on an orbital shaker for 24hrs with sulphuric acid at concentrations of 1 M, 0.5 M and 0.25 M and a 10:1 leaching ratio (cf. Esther et al., [9]). The extracts were filtered through 0.2  $\mu$ m cellulose acetate filter and analysed by ICP-OES. For comparison, leaching tests were also performed on the original, untreated sludge. All acid leach experiments were carried out in duplicate.

## Results

**Bioreduction.** In all 3 replicate columns the addition of glycerol resulted in a sharp increase in the generation of ferrous iron from the columns, suggesting rapid proliferation of iron-reducing microbes, or microbes that indirectly induce iron reduction (Fig.1). Comparison between the ferrous iron release from columns fed with glycerol and the negligible ferrous iron release from columns not fed with glycerol (organic starved) and autoclaved controls confirmed the increase in ferrous iron was the result of microbial action (data not



**Figure 1:** Rate of ferrous iron production in effluent with time from three replicate bioreduction columns.

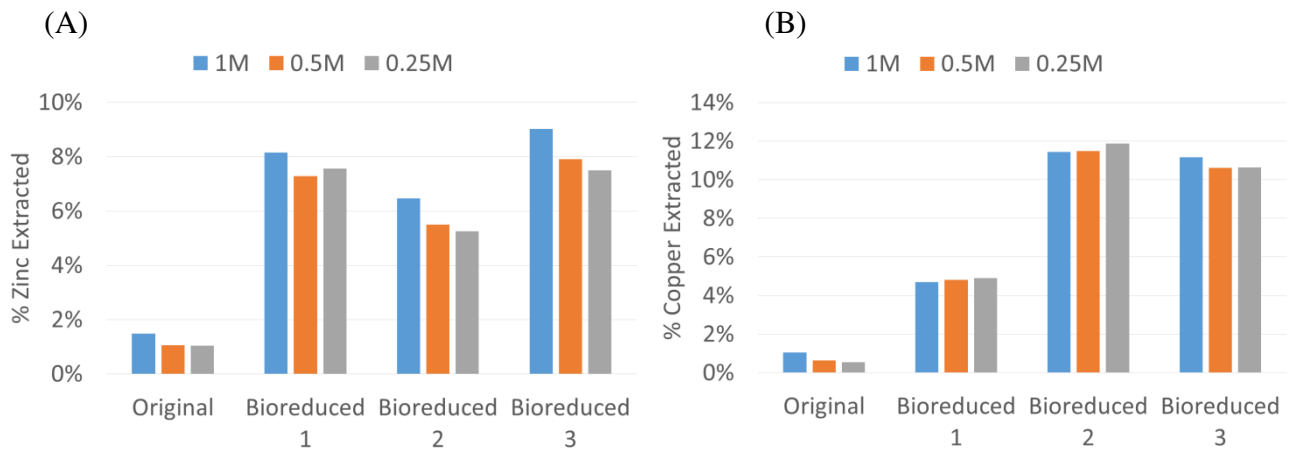
shown). Within the 3 replicate columns the ferrous iron generation followed a broadly similar pattern, though there are some variations in peak iron concentrations. It is likely that the variations in ferrous iron generation are a result of variations in flow paths within the columns and the differing consequent residence times. Redox potential decreased and pH increased concomitantly with the generation of ferrous iron (due to alkalinity produced during bioreduction). Consistently the dissolved oxygen measured within the effluents was negligible, demonstrating that anaerobic conditions prevailed which are needed for iron reduction by the indigenous microbes found in the mine waste (e.g. *Desulfosporosinus* species; data not shown).

**Acid Leaching.** The results of the acid leaching stage of experimentation are displayed in Fig. 2. It is evident that the bioreduction of the waste has increased the leachability of both zinc and copper in comparison to the original, unadulterated sludge. However, it is noted that there is some variability in the effectiveness of the bioreduction for making metals more accessible to acid leaching. Bioreduced column 1 shows a lesser increase in copper recovery compared with either column 2 or 3 but a higher Zn recovery. It is, though, interesting to note the consistent copper extraction rates from each column irrelevant of acid strength. This suggests that the extracted copper is loosely bound within the system. Zinc extractions show a decrease in metal recovery with decreasing acid strength but it is still a relatively minor change, suggesting the redistribution of zinc associated within the ferric (hydroxy)oxide structure to a form amenable to acid extraction. It is likely that the extracted fraction represents metals that were released from ferric (hydroxy)oxides by bioreduction but have then resorbed onto residual ferric (hydroxy)oxides, leaving them more amenable to acid leaching [3]. This sorption of metals released by reductive dissolution of the Fe(III) matrix onto mineral products of bioreduction is likely given the observed pH increase to circum-neutral conditions, lowering the solubility of metals within the system [11].

Though there are variations in extraction rates between replicates, the bioreductive treatment led to a maximum six fold and eleven fold increases in zinc and copper leachability. While metal extractions are not as large as those seen in other bioreduction studies, the relative simplicity of this treatment using only addition of a relatively low-cost organic source, indigenous communities, dilute acid and no control over temperature give added significance to the increased extraction rates. The simplicity of this technique also gives the potential for application *in situ*. The addition of reagents such as chelators and reducing agents during the leaching phase, or electron shuttles to enhance bioreduction, may have the potential to increase leaching efficiency [3, 12]. However, further research is required to assess the efficacy of these additional reagents with this technique.

## Conclusions

Biostimulation of iron reducing microbial communities within ferric (hydroxy)oxide wastes has been demonstrated to cause a significant increase in the leachability of zinc and copper from the waste. Targeted metals have been redistributed within the samples during the treatment and are more easily removed/leached even with dilute acids at room temperature. Whilst metal extractions are not as large as those seen in other bioreduction studies. Here the treatment was with a straightforward addition of a relatively low cost organic substrate without any control over temperature and using indigenous communities and this could be readily applied *in situ*. This treatment led to a maximum six-fold and eleven-fold increase in zinc and copper leachability respectively, representing an easy and potentially significant low-cost technology.



**Figure 2:** Comparison of maximum (A) zinc and (B) copper extracted with varying sulphuric acid concentrations

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