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Selection of thermophiles for base metal sulfide concentrate leaching, Part I: Effect of temperature on copper concentrate leaching and silver recovery

Paul R. Norris *, Ludovic Laigle, Thomas J. Ogden, Oliver J.P. Gould

School of Life Sciences, University of Warwick, Coventry CV4 7AL, UK

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ABSTRACT

The influence of temperature on bioleaching of a copper-silver concentrate of a black shale-ore was observed at 30, 48 and 76 °C. Post-leach residues' weights and copper contents decreased with increase in leaching temperature while the iron contents increased through more iron precipitation. A designed, incremental increase in the concentration of copper in solution resulted in *Sulfobacillus thermosulfidooxidans* replacing a species of Acidithiomicrobium as the dominant iron-and mineral sulfide-oxidizing strain in the mixed culture used at 48 °C. The temperature of bioleaching influenced the hydrometallurgical extraction of silver from post-leach residues. Thiosulfate was most effective with a high temperature bioleach residue while ferric chloride and copper/ammonium/thiosulfate was most effective with a low temperature bioleach residue.

1. Introduction

Extensive research and development of the use of microorganisms to extract base metals from mineral sulfide concentrates has led to only a few industrial scale demonstrations or operations: this partly reflects a lack of economic competitiveness, technical disadvantages of long residence times in bioreactors and, where chalcopyrite is present, incomplete copper extraction. Increased copper yields and concentrate dissolution rates can be achieved with cultures of moderately thermophilic bacteria (Marsh and Norris, 1983) and thermophilic archaea (Marsh et al., 1983). The most rapid and efficient extraction can occur at the highest bioleaching temperatures (up to 85 °C) with particular thermophilic archaea, but these are relatively sensitive to high pulp densities, which has limited concentrate feeds to between 10 and 12.5% w/v in pilot and industrial demonstration plants (d'Hugues et al., 2002; Batty and Rorke, 2006; Neale et al., 2009). Moderately thermophilic bacteria can retain activity at pulp densities that inhibit these archaea (Clark and Norris, 1996) and have been used in refractory gold concentrate processing at about 50 °C with feed concentrations of 15–20% w/v (Miller, 1997).

The most useful moderately thermophilic bacteria for mineral sulfide oxidation appear to be species of Acidithiomicrobium and *Sulfobacillus*. Acidithiomicrobium is the least studied and the name is not yet officially recognized. It is capable of strong autotrophic growth on ferrous iron, pyrite (Davis-Belmar and Norris, 2009) and sulfur (Norris et al., 2011). It was previously referred to as a novel *Acidimicrobium* species when it was found to be the dominant ferrous iron-oxidizing bacterium in continuous, laboratory bioreactors fed with a nickel sulfide concentrate at 49 °C, but it was superseded by *Sulfobacillus thermosulfidooxidans* when the temperature was raised (Cleaver et al., 2007). The presence of these bacteria in bioreactors fed with a copper concentrate from the Lubin Mine in Poland is examined here. This concentrate has previously been the subject of hydrometallurgical and biohydrometallurgical research in the context of reported declining copper and silver content in flotation concentrates and other technological concerns for conventional processing which are associated with its carbon content (Chmielewski, 2015). It was continuously bioleached at 42 °C with a mixed culture of mesophiles and moderate thermophiles which solubilized about 90% of the copper, most rapidly from chalcocite and bornite fractions, while 35% of its chalcopyrite remained in residues (Spolaore et al., 2009). It was efficiently leached at high temperature (78 °C) in an initial batch culture test with thermophilic archaea (Norris et al., 2013), but a high temperature continuous process has not been demonstrated with this concentrate and the relative intolerance of high pulp densities associated with these thermophiles remains a limitation for industrial application. Consequently, with particular

* Corresponding author. Present address: Environment and Sustainability Institute, University of Exeter, Penryn Campus, Penryn, Cornwall TR10 9FE, UK.
E-mail address: P.Norris@exeter.ac.uk (P.R. Norris).

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attention to copper tolerance, this study continues investigation of moderately thermophilic bacteria at a temperature between those used with mesophilic bacteria and high temperature archaea.

Some different extraction reagents were used to assess the influence of bioleaching temperature on availability of silver in post-leach residues to hydrometallurgical extraction. There has been little discussion previously of effects of bioleaching temperature on further downstream processing of post-bioleach residues in an industrial context, except with regard to the presence of sulfur compounds and their influence on cyanidation following biooxidation (van Aswegen et al., 2007).

2. Materials and methods

2.1. Copper concentrate

Hot HCl/HNO_3 digestion and atomic absorption spectrophotometry indicated 13.2% w/w copper, 6.7% w/w iron and 849 ppm silver in the available sample of the Lubin Mine (black shale ore) concentrate. The particle size d_{80} was −80 μm. The typical ratio of various copper sulfides has been estimated by a mineralogical analysis of another sample of the Lubin concentrate as bornite (36%), chalcocite (23%), chalcopyrite (20%), other undetermined copper sulfides (19%) and covellite (1%) (Spolaore et al., 2009).

2.2. Microorganisms

Cultures which had been maintained with pyrite as substrate for many years were grown with 1% (w/v) Lubin concentrate through several serial subcultures before use in leaching tests.

The culture of mesophilic bacteria used at 30 °C comprised various organisms from coal spoil heaps and acid mine waters of several countries (Clark and Norris, 1996). A recent analysis of the 16S rRNA genes found in this culture indicated a prevalence of *Leptospirillum ferriphilum* and *Acidithiobacillus caldus* among the bacteria and the presence of a much smaller population of the archaeon *Ferroplasma acidiphilum* (data not shown).

Two mixed cultures of moderate thermophiles were used. One was used previously in laboratory reactors processing a nickel sulfide concentrate, in which Acidithiomicrobium strain P2 (then referred to as a novel *Acidimicrobium* species), *A. caldus* and *S. thermosulfidooxidans* were the key organisms (Cleaver et al., 2007). The type strain of *A. caldus* (DSM 8584) was added to this culture. The other culture comprised a mixture of *Sulfobacillus* strains which had been individually isolated from samples of various mineral sulfide mines, coal mine spoil heaps and natural geothermal areas. These two mixed cultures were grown separately through several serial cultures with the Lubin copper concentrate and then combined in a single culture to assess the concentrate leaching at 48 °C (Section 3.1) and the culture's adaptation to copper (Section 3.2).

The high temperature culture of archaea (grown at 75–80 °C), which mainly contained an un-named *Sulfolobus*-like strain and a novel species of *Metallosphaera*, has been used in continuous copper concentrate bioprocessing development: the composition of and previous work with this culture has been reviewed (Norris et al., 2013).

2.3. Effect of temperature on bioleaching

Cultures were grown at 30, 48 and 76 °C in air-lift reactors (440 ml cultures, gassed with 400 ml 1% v/v CO_2 in air min^{-1}) after inoculation (10% v/v) and addition of Lubin concentrate (2.5% w/v). The medium contained (g l^{-1}): K_2HPO_4 (0.2), $(NH_4)_2SO_4$ (0.4) and $MgSO_4{\cdot}7H_2O$ (0.5), adjusted initially to pH 1.5 with H_2SO_4. Final leach suspensions were collected, centrifuged (10 min at 14000*g*) and solid residues washed by sequential resuspensions and centrifugations with dilute sulfuric acid (400 ml, pH 1.5) and de-ionized water (400 ml). Dried residues were digested with hot HCl/HNO_3 before analysis by atomic absorption spectrophotometry.

2.4. Adaptation to copper

Two mixed cultures of moderate thermophiles (Section 2.2) were separately adapted to growth with the Lubin concentrate through several serial cultures in air-lift reactors. The adapted cultures were then combined before the concentration of copper (added as copper sulfate) was increased in stages through serial cultures in one of a pair of reactors, with the other maintained as a control (Table 1). These were fed-batch cultures with 10% (v/v) inocula and an initial 1% (w/v) concentrate. Further addition of concentrate was made once per day to each reactor (each addition 0.25% w/v) until the total concentrate added reached 4–5% (w/v) over two to three weeks before inocula were taken to begin the next culture in each series.

Microorganisms were identified from sequences of 16S rRNA genes essentially as described previously (Burton and Norris, 2000; Norris et al., 2013) but with omission of a freeze/thaw step before incubation of culture samples with lysozyme (2 mg ml^{-1} at 37 °C for 1 h) followed by standard Tris/SDS lysis at pH 8, phenol, phenol-chloroform and isopropanol treatments before DNA precipitation, washing with ethanol and final resuspension in water.

2.5. Ferric iron leaching

The concentrate was leached with ferric iron at 70 °C in the absence of microorganisms to produce a residue for comparison to those produced by bioleaching. Concentrate suspensions in stirred reactors (2.5% w/v in 800 ml volumes at 70 °C) were gassed with air or N_2 (500 ml min^{-1}). After reaction with ferric iron (1 M from ferric sulfate or ferric chloride), residues were collected and washed twice by centrifugations (10 min at 14000*g*) and resuspensions in de-ionized water (400 ml) before drying and silver extraction procedures or wet digestion with hot HCl/HNO_3.

2.6. Silver extraction from residues

Samples of post-bioleach residues (0.25 g in 50 ml) were treated in shaken flasks (100 rpm) for 19 h before final residues were washed and analysed as before (Section 2.5). Four extraction protocols were used: (1) alkaline thiosulfate leaching at 48 °C (initial pH 11.3, 0.4 M sodium thiosulfate, 0.84 M sodium hydroxide); (2) cup-

Table 1
The timing of observations in relation to adaptation of moderate thermophiles to copper during leaching of the Lubin concentrate at 48–50 °C.

Serial culture	Reactor 1	Reactor 2	Timing of observations
	Cu added (g l^{-1})		
1	0	0	
2	0	2	
3	0	4	
4	0	6	
5	0	8	
6	0	10	Microscopy (Fig. 2a and b)
7–8	0	10	
9	0	10	DNA analysis (Table 3)
10	0	10	
11	0	10	Microscopy (Fig. 2c and d)
12–19	0	10	
20	0	10	Cu leaching (see text)
21+	0	→ 25	