Hydrometallurgy 94 (2008) 42–47

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Effect of temperature on the bioleaching of chalcopyrite concentrates containing different concentrations of silver

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ARTICLE INFO

Available online 19 June 2008

Keywords:
Acidophiles
Bioleaching
Chalcopyrite
Consortia
Silver

ABSTRACT

The primary copper sulfide mineral chalcopyrite ($CuFeS_2$) is recalcitrant to both chemical and biological leaching, due to the supposed passivation of the mineral surface by sulfur and/or ferric iron compounds. Previous work has shown that addition of soluble silver can enhance solubilisation of copper from chalcopyrite by acidophilic bacteria. Silver may also be present in the concentrate itself. Here we describe the bioleaching of chalcopyrite concentrates with silver contents varying from <1 to 1500 g/t by consortia of thirteen species of mesophilic bacteria and eleven species of moderately thermophilic acidophiles in shake flask cultures incubated at between 30 °C and 45 °C. The compositions of the microbial consortia that established in each culture were determined using a combined cultivation-based and biomolecular approach. The most effective solubilisation of copper from the 1500 and 800 g/t Ag-concentrates occurred at 30 °C, while concentrates that contained <1 and 26 g/t of silver displayed the opposite (and predicted) pattern of mineral dissolution increasing with incubation temperature. The type strain of *Acidithiobacillus ferrooxidans* was the sole dominant iron-oxidising autotroph in the 800 and 1500 g/t silver concentrates, and was present in similar numbers to *Leptospirillum ferrooxidans* in the <1 and 26 g/t silver concentrates, leached at 30 °C. Obligate and facultatively heterotrophic acidophiles (e.g. *Acidiphilium* and Gram-positive acidophiles) were also usually present, but in much smaller numbers. In contrast, at 45 °C the dominant (or sole) bacterium present at day 30 was the iron/sulfur-oxidising mixotroph *Sulfobacillus thermosulfidooxidans*. *Sulfobacillus* spp. also tended to dominate cultures incubated at 37 °C, although other bacteria, including *At. ferrooxidans*, were present in some mineral leachates. Highly efficient dissolution of copper (76 to >98% over 30 days) from the 1500 g/t chalcopyrite concentrate at 30 °C was achieved using pure and mixed cultures of *At. ferrooxidans*. The results indicated that chalcopyrite concentrates that contain significant concentrations of silver are highly amenable to bioleaching at relatively low temperatures, using well-known acidophilic micro-organisms.

1. Introduction

Bioprocessing of ores and concentrates to recover gold, copper and other metals, is now an established as well as an evolving area of biotechnology (Rawlings and Johnson, 2007a).

Chalcopyrite ($CuFeS_2$), the most abundant copper sulfide in the lithosphere, is however notoriously difficult to bioleach effectively. Typically, microbially-enhanced leaching of copper from chalcopyrite effectively comes to a halt after only 20–30% of copper has been extracted. Various hypotheses have been proposed to account for this phenomenon, mostly involving passivation of the mineral by ferric precipitates and/or sulfur, though there is no consensus on the exact mechanistic reason for the recalcitrance of chalcopyrite to leaching (Watling, 2006). Various methods have been proposed (and in some cases demonstrated) to enhance the bioleaching efficiency of chalcopyrite (reviewed in Watling, 2006). These include: bioleaching at elevated temperatures (70–80 °C) using thermo-acidophilic archaea, silver catalyzed catalysed bio-oxidation using mesophilic and moderately thermophilic bacteria, leaching at low redox potentials, and the addition of chloride.

The diversity of acidophilic micro-organisms that have direct and indirect roles in the oxidation of sulfidic ores and concentrates is considerable (Schippers, 2007). Although the "primary" micro-organisms involved are generally considered to be autotrophs that catalyse the dissimilatory oxidation of ferrous iron to ferric, other autotrophs that oxidise sulfur to sulfuric acid, and a third group that utilise the dissolved organic carbon released by active and dead primary producers in these systems (facultative and obligate heterotrophs, some of which also catalyse iron and/or sulfur oxidation) also play important roles. Microbiological analyses of both stirred tank and

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doi:10.1016/j.hydromet.2008.06.005

heap leaching operations has shown that, in all cases so far reported, the bioleaching populations include both iron- and sulfur-oxidisers, and both autotrophs and (facultative) heterotrophs (reviewed in Rawlings and Johnson, 2007b).

Chalcopyrite concentrates produced from different ores may contain varying concentrations of "contaminant" metals. Generally, the presence of significant concentrations of metals such as silver is considered to be undesirable from a bioleaching perspective. However, given previous reports of enhanced chalcopyrite bioleaching resulting from addition of soluble silver, the question of whether silver present in the concentrate itself could also impact extraction of copper was tested. This involved bioleaching four chalcopyrite concentrates containing different amounts of silver (ranging from <1 to 1500 g/t) under controlled laboratory conditions by defined microbial consortia of mesophilic and moderately thermophilic acidophiles.

2. Materials and methods

2.1. Mineral concentrates

Four finely ground (<20 μm) chalcopyrite concentrates, with silver contents varying between <1 and 1500 g/t, were used in bioleaching experiments. The elemental and mineralogical compositions of the concentrates are listed in Table 1. The silver in three of the concentrates was thought to be present as metallic Ag, silver sulfide, silver sulfate and silver jarosite (Mariekie Gericke, Mintek, South Africa; personal communication).

2.2. Microbial consortia

Two microbial consortia, each including a diverse range of iron- and sulfur-oxidising prokaryotes, and autotrophic and heterotrophic acidophiles, were assembled from the *Acidophile Culture Collection*, which is maintained at the University of Wales, Bangor. One group consisted of mesophilic acidophiles, and the second of moderately thermophilic and/or thermo-tolerant bacteria and one archaeon (Table 2). The acidophiles were grown as pure cultures in appropriate liquid media (ferrous sulfate/basal salts for autotrophic iron-oxidisers, elemental sulfur/basal salts for autotrophic sulfur-oxidisers, ferrous sulfate/yeast extract for heterotrophic and mixotrophic iron-oxidisers, and glucose (or fructose)/yeast extract for other heterotrophic acidophiles). Different culture volumes were added to the chalcopyrite cultures in order to inoculate the flasks with similar numbers (approximately 10^8) of cells in each case.

Table 1
Composition of the chalcopyrite concentrates used in bioleaching experiments

	Concentrate 1 (zero Ag)	Concentrate 2 (low Ag)	Concentrate 3 (medium Ag)	Concentrate 4 (high Ag)
Metal contents				
Cu	17	24	22.5	22
Fe	35	28.5	28	21
Zn	<0.1	<0.1	2	6.5
Si	6	7.7	2.8	1.9
S^{2-}	35	31	24	26
Ag (g/t)	<1	26	800	1500
As	0.005			1
Pb	<0.01		2.8	2.9
Major minerals				
Chalcopyrite	50	70	Major (~60)	45–50
Pentlandite				
Pyrrhotite			6	4
Pyrite	35	11	2	2
Sphalerite			4	6
Covellite			4	3
Bornite				11
Molybdenite				3

All data are shown as percentages (by weight) except where indicated, and the mineralogical data are shown as approximate relative amounts present.

Table 2
Compositions of the mesophilic and moderately thermophilic acidophilic consortia used in the present study (Rawlings and Johnson, 2007b)

	Strain	Physiological Traits
(i) Mesophilic consortium		
Acidithiobacillus (*At.*) *ferrooxidans*	Type (ATCC 23270)	Autotrophic Fe^{2+}/S-oxidiser
Acidithiobacillus-like isolate	NO37	Autotrophic Fe^{2+}/S-oxidiser
Leptospirillum (*L.*) *ferrooxidans*	CF12	Autotrophic Fe^{2+}-oxidiser
β-proteobacterium isolate	PSTR	(Autotrophic Fe^{2+}-oxidiser)
Ferrimicrobium acidiphilum	Type (strain T23)	Heterotrophic Fe^{2+}-oxidiser
Firmicute isolate	SLC66	Heterotrophic Fe^{2+}-oxidiser
Frateuria-like isolate	WJ2	Heterotrophic Fe^{2+}-oxidiser
Sulfobacillus (*Sb.*) isolate	L15	Mixotrophic Fe^{2+}/S-oxidiser
Thiomonas sp.	WJ68	Mixotrophic Fe^{2+}/S-oxidiser
At. thiooxidans	Type (ATCC 19377)	Autotrophic S-oxidiser
Acidiphilium sp.	SJH	Heterotrophic Fe^{3+}-reducer
Acidocella sp.	PFBC	Heterotrophic Fe^{3+}-reducer
Acidobacterium sp.	WJ53	Heterotrophic Fe^{3+}-reducer
(ii) Moderately thermophilic consortium		
L. ferriphilum	BRGM1	Autotrophic Fe^{2+}-oxidiser
Acidimicrobium ferrooxidans	TH3	Heterotrophic Fe^{2+}-oxidiser
Ferroplasma sp.	MT17	Heterotrophic Fe^{2+}-oxidiser
Ferrithrix thermotolerans	Y005	(Heterotrophic Fe^{2+}-oxidiser)
Sb. thermosulfidooxidans	Type (DSM 9293)	Mixotrophic Fe^{2+}/S-oxidiser
Sb. acidophilus	YTF1	Mixotrophic Fe^{2+}/S-oxidiser
Sb. benefaciens	Type (DSM 19468)	(Mixotrophic) Fe^{2+}/S-oxidiser
Firmicute isolate	G1	(Mixotropic) Fe^{2+}-oxidiser
At. caldus	Type (KU)	(Mixotrophic) S-oxidiser
Acidicaldus organivorans	Type (Y008)	Heterotrophic S-oxidiser
Alicyclobacillus isolate	Y004	Heterotrophic Fe^{3+}-reducer

2.3. Bioleaching cultures

Replicate shake flasks (250 ml), each containing 100 ml of basal salts/trace elements medium and 2 g of chalcopyrite concentrate, adjusted to pH 2.0 with sulfuric acid and sterilized at 120 °C for 20 min, were inoculated with either: (i) the mesophilic consortium; (ii) the moderately thermophilic consortium; or (iii) a mixture of both consortia. Cultures were incubated at 30 °C, 45 °C, or 37 °C, respectively, shaken (100 rpm) for 30 days. Samples were removed at weekly intervals and concentrations of soluble metals measured. Microbial populations were determined using both a culture-dependent method (at 15 and 30 days) and a culture-independent method (at day 30), as described below. Culture pH and redox potentials were measured at the start and end of incubation.

2.4. Microbiological analysis

Viable bacteria and archaea present in mineral leaching cultures were isolated and identified on days 15 and 30 by streak-inoculating solid media that have been devised to promote the growth of acidophilic micro-organisms. A variety of "overlay" media were used that, together, facilitated the growth of all of the bacteria and archaea included in the mesophilic and moderately thermophilic consortia. These were: ferrous iron/tryptone soya broth (TSB) overlays (Fe*o*), ferrous iron/tetrathionate/TSB overlays (FeS*o*), ferrous iron/thiosulfate/TSB overlays (FeT*o*), "inorganic" ferrous iron overlays (iFe*o*), and yeast extract overlays (YE3*o*). Detailed descriptions of the compositions and methods for preparing these media are given in Johnson (1995) and in Johnson and Hallberg (2007). Inoculated plates were incubated at the same temperature as the corresponding liquid cultures for 7–14 days. Colonies were examined using a binocular microscope, and isolates recognized, where possible, from colony morphologies (Johnson et al., 2005) and phase contrast microscopic observation of cells. Identities of isolates were confirmed by