Hydrometallurgy 127-128 (2012) 70–76

Contents lists available at SciVerse ScienceDirect

Hydrometallurgy

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

# Ore column leaching with thermophiles: II, polymetallic sulfide ore

Paul R. Norris *, Carly F. Brown [1], Paul E. Caldwell [2]

*School of Life Sciences, University of Warwick, Coventry CV4 7AL, United Kingdom*

ARTICLE INFO

*Article history:*
Received 4 July 2011
Received in revised form 4 June 2012
Accepted 10 July 2012
Available online 20 July 2012

*Keywords:*
Ore bioleaching
Polymetallic sulfide ore
Pyrrhotite
Thermophiles

ABSTRACT

A polymetallic sulfide ore from which several metals are commercially extracted has a high pyrrhotite content that results in elevated temperatures in the ore leaching heaps. Laboratory ore columns were inoculated with moderately thermophilic bacteria and thermophilic archaea to assess the influence of microbial activity on leaching of metals from the ore at 47 °C and 68 °C. The populations of moderately thermophilic bacteria that became established on the ore were dominated by acidophilic Actinobacteria. Excessive precipitation of oxidized iron compounds in the presence of microbial activity hindered extensive leaching from small-scale ore columns (0.7 kg ore). Copper extraction was generally delayed in comparison to that of the other target metals (principally nickel and zinc) when ore column effluent solutions remained above about pH 2.5.



## 1. Introduction

The industrial heap leaching of polymetallic black schist ore at the Sotkamo mine in Finland began in 2008, with reserves for over 40 years production of nickel, zinc, copper and cobalt. Bioleaching studies with the ore began over 25 years ago and have been reviewed (Puhakka et al., 2007). Metal leaching from the ore generally increases with greater acidity but pH 2 was recommended for heap leaching in order to produce acceptable metal solubilization while limiting unwanted dissolution of gangue minerals (Halinen et al., 2009a). Over a range of 7 °C–50 °C, highest metal recoveries were obtained at 21 °C, but generally lower cell counts at the higher temperatures and limited ferrous iron oxidation at 50 °C (Halinen et al., 2009b) indicated optimum microbial activity was not obtained at the higher temperatures. However, oxidation of the pyrrhotite-rich ore is exothermic and effluent solution from a pilot heap that preceded commencement of production was at 40–50 °C, with up to 90 °C measured inside the heap (Riekkola-Vanhanen, 2007).

Leaching of the polymetallic sulfide ore from Talvivaara with thermophilic bacteria and archaea is described here with small laboratory scale ore columns. These columns were used previously with copper ore when the activity of thermophiles promoted copper release without ferric iron being added to feed solutions, while extensive leaching of copper from un-inoculated ore required addition of ferric iron (Norris et al., 2012). The possible limitation of copper release by extensive iron oxyhydroxysulfate precipitation at high temperature was noted. Here, the aims were to assess the capacity of thermophiles to become established in columns of a polymetallic sulfide ore with a high iron content and to assess the potential interference of solution flow and metal release by precipitation at high temperature of a fraction of the iron solubilized from the ore or supplied with the percolating solution.

## 2. Materials and methods

### 2.1. Ore

A sample of the polymetallic ore was obtained from the Talvivaara mine, Sotkamo, Finland. It contained (w/w) 0.31% nickel, 0.58% zinc, 0.22% copper, 0.03% cobalt. 0.97% manganese, 13.2% iron and 13% sulfur. The nickel was mostly present as an altered pentlandite and associated with pyrrhotite, with a lower amount in pentlandite. Pyrrhotite and pyrite were the main iron sulfides. Copper, zinc and manganese were present primarily in chalcopyrite, sphalerite and alabandite respectively (analyses by the Geological Survey of Finland).

### 2.2. Ore leaching columns

The columns used for ore leaching were described previously (Norris et al., 2012) and contained 0.7 kg ore. The ore fragments used were free of fine particles, retained by an 8 $mm^2$ sieve-mesh and had a mean weight of 1.07 g. As previously, a salt solution at pH 1.5 was fed to columns at a flow rate of 150 ml $day^{-1}$, corresponding to a surface application rate of approximately 4 l $m^{-2}$ $h^{-1}$. There was no recycling of column effluents through the ore. Ferric sulfate was added to irrigation solutions where indicated to give 10 mM (0.55 g $l^{-1}$) or 20 mM iron (1.1 g $l^{-1}$). The feed solution, reservoirs and tubing leading to columns, but not the ore or columns, were sterilized and sodium benzoate

* Corresponding author. Tel.: +44 2476 523733; fax: +44 2476 523701.
*E-mail address:* P.R.Norris@warwick.ac.uk (P.R. Norris).
[1] Present address: Department of Plant Sciences, University of Oxford, South Parks Road, Oxford OX1 3RB, UK.
[2] Present address: Biotechnology Services, Covance Laboratories Ltd., Otley Road, Harrogate, HG3 1PY, UK.

0304-386X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.hydromet.2012.07.005

(50 mg $l^{-1}$) was added to the irrigation of un-inoculated columns to inhibit acidophilic iron- or sulfur-oxidizing bacteria.

In some experiments at high temperature (68 °C), two columns were arranged in series with effluent from an upper column drained into a lower column. This was intended to allow ore in upper columns to reduce the ferric iron provided with the irrigation to ferrous iron so that changes at an ore depth beyond that influenced by the added ferric iron could also be observed. Metals released into solution from the ore in upper columns of each linked pair were measured in samples taken at the connection point between the columns. The extractions from (or depositions in) the lower ore columns were estimated by subtracting the metals added (in feed solution from the upper columns) from the metals in effluents from the lower columns. Metal ions were measured by atomic absorption spectrophotometry and ferrous iron by titration with ceric sulfate and 1,10-phenanthroline ferrous complex (Fisher Scientific) as indicator.

### 2.3. Microbial cultures and ore column inoculation

Ore columns were inoculated with cultures grown on finely ground pyrite (1% w/v) in shaken flasks. At 47 °C, a culture containing a variety of moderately thermophilic, mineral sulfide-oxidizing bacteria and archaea was used. The same culture was used in the associated description of copper ore leaching (Norris et al., 2012) and previously in bioreactor processing of copper (Dew et al., 1999) and nickel concentrates (Cleaver et al., 2007; Dew et al., 1999). At 68 °C, separate cultures of *Sulfolobus metallicus* strain BC, *S. metallicus* strain LM, *Acidianus brierleyi* and *Metallosphaera sedula* were grown at 68 °C and mixed to provide inocula. Only the upper column was inoculated when two columns were operated in series. The organisms associated with ore fragments after leaching were identified from 16S rRNA genes amplified from DNA that was associated with ore fragments, as described previously (Norris et al., 2011).

## 3. Results and discussion

### 3.1. Ore leaching with thermophiles at 47 °C and 68 °C

Nickel release from the un-inoculated ore column ore was slow before the feed solution was supplemented with ferric iron (Fig. 1A), consistent with previous observations of the positive effect of ferric iron on leaching of the Talvivaara ore (Halinen et al., 2009a). Nickel release from the inoculated ore column at 47 °C was initially greater than from the un-inoculated column and was further stimulated when the solution feed was supplemented with ferric iron, but by then the rate of microbially-catalyzed leaching was declining (Fig. 1A). The decline continued after the supplementation with ferric iron to the feed such that at the end of the experiment after one year the nickel extraction was about 42% (mean of cumulative nickel measured in ore column effluent and nickel in final leached residue) compared to 56% from an un-inoculated column (Table 1).

At 47 °C, a similar pattern of metal ion release and response to additional ferric iron was shared by nickel, zinc and cobalt (see Section 3.2), but with smaller yields of zinc and cobalt when the irrigation was stopped after one year (Table 1). The sum of the cumulative yields of individual metals measured in column effluents and the values remaining in final leached residues as assessed by wet acid digestion were in the range of 84 to 102%, with the exception of poor recovery of copper in samples from the inoculated ore at 68 °C.

In previous work with copper ore in the same columns, the relative concentration of ferrous and ferric iron in effluents was an indication of microbial activity (Norris et al., 2012). In this first attempt at high temperature leaching with the Talvivaara ore at 68 °C (Fig. 1), essentially all iron in solution was ferrous iron for almost a year (data not shown), which indicated the reaction of ferric iron with the mineral sulfides was more rapid than any re-oxidation of the ferrous iron by the archaea

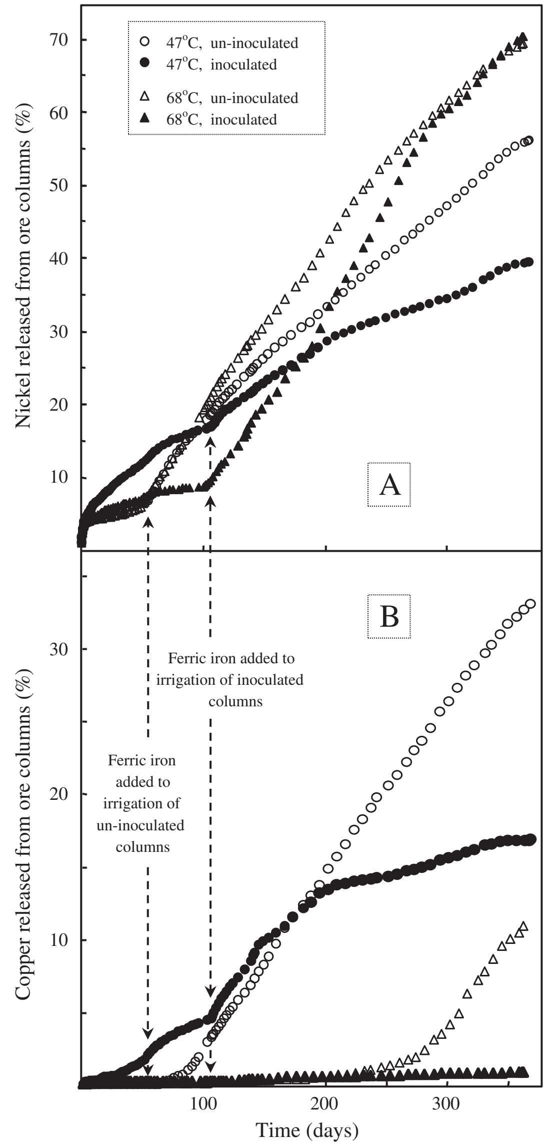


**Fig. 1.** Release of (A) nickel and (B) copper from ore columns. Where indicated, the irrigation contained ferric sulfate (1.1 g Fe $l^{-1}$).

or a failure of the organisms to establish a significantly active population in the column. At 47 °C after 200 days, essentially 100% of the iron in the effluent from un-inoculated ore remained as ferrous iron while 20% of the iron was ferrous iron in the effluent from inoculated ore. In the apparent absence of significant microbial activity at the higher temperature, there was still greater leaching of nickel, zinc and cobalt than at 47 °C (Table 1).

Copper leaching was limited with responses to temperature and ferric iron unlike that of the other metals (Fig. 1B, Table 1). At 47 °C, copper leaching began from inoculated ore while there was very limited leaching in the absence of bacteria. The first appearance of copper in effluent from un-inoculated ore at 47 °C was after 58 days and followed addition of ferric iron the feed solution. There was an increase in acidity of the effluent to pH 2.2 from 2.5 at 50 days and to pH 2 when there was a steady rate of copper release after 90 days. The appearance of some copper in the effluent from un-inoculated Talvivaara ore at 68 °C occurred after 130 days when the pH of the effluent was 2.3 and the rate of release was more rapid after 300 days at pH 2 (Fig. 1B). Apart from the commencement of copper release from inoculated ore at 47 °C after 9 days when the effluent pH was 2.8, these observations at