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Effect of water quality on the leaching of a low-grade copper sulfide ore

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ABSTRACT

Copper extractions from a low-grade, ground copper sulfide ore (0.7% Cu) leached in three media were freshwater $<$ seawater $>$ double-strength seawater and pH 1.5 $\geqslant$ pH 2; 84% extraction was achieved in pH 1.5 seawater in 28 days at 23 °C. Cu-oxide and carbonate dissolved completely and chalcocite was altered to secondary covellite, some of which persisted in all media for the duration of the 28-day experiment. Chalcopyrite and bornite were both oxidised more readily in saline water. Iron, sodium, potassium and sulfur (sulphate) concentrations in leach solutions diminished and the amounts of insoluble iron(III) reaction products increased with increased salinity and increased solution pH. While, overall, silicate dissolution was small, the amounts of poorly crystalline phases (both iron(III) and silica-rich phases) increased with increased salinity and were greater in pH 1.5 media. In the context of heap leaching, the increased amounts of secondary precipitates formed if saline water was used could result in lower extraction efficiency and the increased total dissolved solids, density and viscosity could result in increased energy costs for solution management at operations.

The software package Geochemist's Workbench was evaluated by modelling the synthetic seawater – pH 2 test. It was possible to predict the evolution of the solution composition, the main species and phase boundaries at the start and end of leaching, and the formation of three reaction products in accord with experimental data by applying the React sliding function.

The tests were conducted using a pulverised ore sample to increase dissolution reaction kinetics, particularly for chalcopyrite. Future tests should be conducted using ore particle sizes appropriate to heap leaching. The copper distribution within particles indicated that the test ore may not be suited to heap leaching because the surface exposure of copper sulfide grains is limited. Therefore reactor designs better suited to smaller sized particles with/without pre-treatment should be considered.

1. Introduction

In the Copper Technology Roadmap of 2004 (AMIRA International, 2004), more efficient use of water in the unit processes associated with extraction, comminution and separation was given "top priority". In addition, the use of saline water and recycled water in processing were among the proposed strategies for improvements in water efficiencies. The use of seawater, brackish water, hypersaline water and recycled process water have been variously trialled and/or implemented at mining operations around the world over many years, mainly in respect of substituting seawater for freshwater in flotation circuits (e.g., Drelich and Miller, 2012; Smith and Heyes, 2012) but less often for leaching circuits (e.g., Weston et al., 1995; Aroca, 1999; Dreisinger, 2009). In addition to those applications, a survey of 25 solvent extraction plants showed that 18 were operated with a PLS containing high sulphate, chloride and cation concentrations, four of them with chloride concentrations >35 g L^{-1} (Hein and Joly, 2011).

There are few data in the public domain concerning the use of sea water for metal extraction at atmospheric pressure and near-ambient temperature. In comparison, there are numerous publications on the dissolution of copper oxide and sulfide minerals (hand-picked specimens, concentrates or ground massive minerals) in acidic media containing sodium chloride at concentrations from dilute to concentrated (e.g., Lu et al., 2000; Miki et al., 2011) extending, in some developments, to the application of high temperature leaching with brine (e.g., Hyvärinen and Hämäläinen, 2005; Harris and White, 2008). The published data most relevant to the present study were those obtained using solutions in the range 0.5–1.5 M chloride. They included studies on the mechanisms by which copper sulfides dissolved and the rates of copper extraction for chalcocite (Senanayake, 2007), djurleite, digenite and covellite (Herreros et al., 2006; Miki et al., 2011), bornite (Pesic and Olson, 1983), enargite (Herreros et al., 2002) and chalcopyrite (Lu et al., 2000; Carneiro and Leão, 2007; Nicol et al., 2010). In general, findings from the

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above studies can be summarised as: (i) the extent of extraction and leaching rate was dependent on mineral particle size; (ii) extraction rates increased with increased temperature; (iii) sulfur was the main product of sulfide dissolution in saline systems and diverse sulfur morphologies were obtained under different leaching conditions; and (iv) amenability to leaching tended to be chalcocite > djurleite/digenite ≫ covellite > bornite ≫ chalcopyrite > enargite. In a number of those studies, solution speciation in the relevant leach medium was discussed in respect of proposed leaching mechanisms and kinetics.

Both Australia and Chile are endowed with mineral resources but many of those resources are located in arid regions. In addition, the two countries have applied heap leaching technology to the extraction of metals from low-grade oxide and sulfide ores over many years. In Australia, heap operations tended to be implemented at small, short-lived deposits (e.g., Readett et al., 2003) but in Chile, some of the developments have been on a much larger scale and of long duration (Domic, 2007). Water use in heap leaching partly drives the search for alternative water sources to replace the use of scarce potable water in Chile (Philippe et al., 2010).

Some characteristics of heap leaching operations impact on process water quality and heap efficiency, regardless of the water source. Acidified heap process water is recycled, meaning that concentrations of elements, other than those that are purified and separated (target elements) or removed in a side stream, build up in the process water, sometimes to saturation concentrations. Increased element concentrations result in increased density and viscosity of the process water and the formation of secondary insoluble reaction products that may migrate through the bed and block solution channels (Miller, 1998) or coat mineral surfaces (Watling et al., 2009). Heap beds range from a few to tens of metres high. Depending upon ore mineralogy and bed height, process water composition, acidity and oxidation reduction potential (ORP) change markedly during the passage of solution through the bed as reactions with both the target and gangue minerals occur.

In this study, some of the deficiencies of results obtained using 'pure' minerals and simple media enriched with sodium chloride were addressed by comparing metal extraction from a low-grade, ground copper sulfide ore during its leaching in acidified fresh water, synthetic seawater and double-concentration synthetic seawater. The double-concentration synthetic seawater simulated the effect of using hypersaline water, such as may be available from underground reservoirs, or the increased salt concentrations resulting from the use of seawater as 'make-up water' to counter evaporation in an open system. Base metal and gangue-element concentrations were monitored during extraction and the residues obtained at the end of the experiments were characterised. The results, highlighting some differences between the chemistry of leaching in fresh and seawater, are discussed in relation to the substitution of seawater for freshwater in the heap leaching of low-grade ores. The ability of the solution speciation software package Geochemists Workbench to simulate some aspects of the laboratory study was evaluated.

2. Materials and methods

A low-grade copper ore containing 0.7% Cu predominantly as chalcocite and covellite and 7% Fe mainly as pyrite was pulverised, characterised and representatively split for these experiments. The pulverised ore had a surface area of $6.42\ m^2\ g^{-1}$ and a P_{80} of 16.31 μm.

Media were prepared in bulk (4 L) using analytical grade reagents (unless otherwise stated) and autoclaved at 121 °C and 120 kPa for 20 min. The freshwater medium (FW) was prepared using deionised water acidified with 18 M H_2SO_4. Synthetic seawater (SW) was prepared by dissolving 96 g NaCl, 44 g $MgCl_2 \cdot 6H_2O$, 16 g Na_2SO_4, 8 g $CaCl_2 \cdot 6H_2O$ and 2·8 g KCl in 3500 mL of deionised water. The solution was adjusted to pH 7 using dropwise addition of 18 M H_2SO_4 and the volume made up to 4 L. Double-strength seawater (2SW) was prepared in the same way by adding twice the amounts of salts.

Aliquots (100 mL) of media were transferred to 500 mL Schott bottles and the pH adjusted appropriately (pH 1.5 or pH 2) using 18 M H_2SO_4. Subsamples from each bottle were removed and 0.498 g $FeSO_4 \cdot 7H_2O$ dissolved in them. The ORP was adjusted to 650 mV (versus Ag/AgCl reference electrode) with dropwise addition of 30% H_2O_2 to oxidise all the iron(II) to iron(III) and the solution pH adjusted appropriately. Each subsample was then filter-sterilised through a 0.2 μm pore size membrane into the relevant Schott bottle. The final solution was again adjusted to the required pH and then ore (10 g) was added to the solution and the bottle sealed. The bottles were agitated in an orbital shaker (Innova) operated at 150 rpm and 23 °C.

Leach solutions were sampled periodically during the four-week experiments using a syringe filter fitted with a 0.2 μm pore-size membrane (Pall acrodisc filter). ORP was measured using a redox electrode (Ionode model IP1306, internal $Ag/AgCl_{(Sat\ KCl)}$ reference electrode). A pH meter (TPS – Smartchem model) and glass membrane electrode (Ionode GL20), calibrated using pH 1.00 and 4.00 buffers, were used to measure solution pH. A 4 mL aliquot of each sample was acidified with 1 mL HNO_3 and refrigerated prior to analysis. Element concentrations were determined using inductively-coupled plasma–atomic emission spectrometry (ICP–AES).

After 28 days, leached residues and precipitates were separated from their solutions by filtration through 0·2 μm pore-size membranes. Residues and precipitates were not washed to avoid the dissolution of readily-soluble precipitated material. The residues and precipitates were dried at 30 °C for 48 h. Portions were digested using a borax flux and the element composition determined using inductively coupled plasma–atomic emission spectroscopy.

The major mineral phases in the ore and residues were identified using powder X-ray diffraction (XRD) using a Philips X'pert Automated Powder Diffractometer fitted with a Cobalt Long Line Focus X-ray tube using Kα radiation operating at 40 kV and 30 mA. Patterns were collected between 3° and 120° 2θ with a 0·02° 2θ step size and a scan rate of 0·6° 2θ per minute. Data were interpreted using a combination of X-plot for Windows (Version 1.34) and PCPDFWIN database (Version 2.02). Mineral compositions of the ores and residues were obtained using Topas® Version 3.0 from Bruker Advanced X-ray Solutions, employing the fundamental parameters approach to Rietveld analysis, using ~10% w/w calcium fluorite as internal standard (quant-XRD). The mass balance was checked using residue element compositions.

Samples were analysed by quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN, E430 running Idiscover 5.2). The mounts were prepared by mixing graphite with the sample and mounting in resin. The samples were analysed using a CSIRO-developed species identification protocol (SIP) for 1 h, running a particle scan.

Geochemical modelling was undertaken using Geochemists Workbench v 9.07 (Bethke, 2011, Bethke and Yeakel, 2011). The program Spec8 was used to calculate species activities for each of the system components and was used as the data input to Act2 and React, which were used to create Eh-pH diagrams, and to simulate the dissolution of the ore over 28 days, respectively.

3. Results and discussion

The chemical and mineralogical characteristics of the low-grade copper sulfide ore are summarised in Table 1. Data obtained from the leaching tests as a function of time are illustrated in Fig. 1-3 as