



# Ionic liquids as additives for acid leaching of copper from sulfidic ores



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## ABSTRACT

Two acid imidazolium-based Ionic liquids (ILs) were evaluated for use in the leaching of a real non-concentrated chalcocopyrite ore in an aerated system at different temperatures, monitoring copper recoveries in aqueous solution and in the presence of sulfuric acid. When ILs were used contemporaneously with the acid, synergic effects were found; these effects were mainly related to the IL action of decreasing the solid-solution hydrophobic resistance to electron transfer, thus enabling continuous acid leaching of the solid surface.

Temperatures higher than 60 °C trigger high increases in copper recoveries (up to 70% copper recovery); this could occur due to the promotion of the parallel chemical decomposition of metal sulfide intermediates and the decrease of mass transfer limitations.

In light of the obtained results, it is proposed that ionic liquids could be considered as catalyst or leaching additives rather than leaching agents itself.

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## 1. Introduction

Ionic liquids (ILs) are salts comprising highly asymmetric ions consisting of an organic cation with an organic or inorganic anion that remain in the liquid state at temperatures of less than 100 °C; even, in many cases, at room temperature (Rogers and Seddon, 2003; Seddon, 1997; Seddon et al., 2000). ILs represent new liquid media that possess particular properties; as new tools for process engineers, these media enables the use of disruptive thinking to propose new processes or substantial improvements to existing processes.

These properties include low vapor pressure (expanding the liquid state operating temperature range), tunable water miscibility, high solubility of both inorganic or organic solutes and high chemical, thermal and electrochemical stability (Marsh et al., 2004; Welton, 1999).

Among the myriad of IL applications that have been suggested and tested, some are relevant for the field of extractive metallurgy; indeed, in some cases, these chemicals have been used even before their identification as ionic liquids (for example, the use of Aliquat® 336 as hydrophobic media in the liquid–liquid extraction of gold (Mikkola et al., 2006)). Several solvent extraction applications of IL have been identified (Guo-cai et al., 2010; Luczak et al., 2008), as well as for metal electrodeposition (Zhang and Hua, 2009) and, less frequently, for leaching processes. In the latter field, ILs exhibits a great capacity to dissolve metals and metal oxides (Chen et al., 2015; Kilicarslan et al., 2014);

thus, it is possible to further selectively extract various dissolved metals. This has opened up great possibilities for the processing and enrichment of metals, having even proposed the term of ionometallurgical processing (Welles et al., 2014).

In the case of the oxidative leaching of sulfides ores, which is one of the main issues currently facing the metallurgical industry having the challenge of continuous adaptation to lesser oxidized, more refractory, and lower grade sulfides ores, the studies of ILs remain scarce. The most relevant works were published by an Australian group (Whitehead et al., 2007) and by a Chinese group (Dong and Zhang, 2009).

The first report describes an increase in copper recovery from chalcocopyrite (CuFeS<sub>2</sub>) concentrate at 70 °C from 55% to 87% when the IL 1-butyl-3-methyl-imidazolium hydrogen sulfate (BmimHSO<sub>4</sub>) concentration was increased from 10% to 100% in aqueous solution. The authors also observed that the addition of a ferric oxidant increases the rate of oxidation only during the early stage of the treatment. The second group also studied a chalcocopyrite concentrate and obtained analogous results for copper recovery and similar trends regarding the effects of temperature and apparent dissolution kinetics. Both groups proposed that the improved oxygen solubility capacity of ILs in aqueous sulfuric acid solution contributed to the improvement and assigned an important role to Brønsted acidity, which provides the proton present in the HSO<sub>4</sub><sup>-</sup> counter ion.

The aim of the present work was to evaluate a similar leaching method using ILs to that used by the previous mentioned groups apply to a real non-concentrated chalcocopyrite ore and to evaluate the use of this

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new solvent as a leaching agent or as an additive for the leaching of this refractory mineral.

## 2. Experimental procedures

### 2.1. Mineral samples

The mineral was received from Codelco (the Chilean state mining company) at Division Andina (located more than 3000 m above sea level in the central zone of Chile). The samples were prepared from 30 kg of copper ore that had been crushed to a particle size of 1 in. The ore was dried in an oven at 105 °C and was then crushed further and dry sieved, yielding a particle size of +45/–106 µm for use in the leaching tests.

The recovered samples were digested in acid for total copper and soluble copper analysis by atomic absorption spectrometry. The total copper content was 0.552%, and the soluble copper content was 0.015%; thus, less than 3% of the copper content was soluble.

The mineral particles comprised 4.25% of sulfides, of which pyrite and chalcopyrite were the main constituents. The remainder included 94% gangue and 2% non-copper metal oxides. Table 1 lists the sulfides present in the ore; pyrite and chalcopyrite were present at similar levels.

### 2.2. Ionic liquids

In this study, the studied ILs included that considered in the main reference works (BminHSO<sub>4</sub>) and HminHSO<sub>4</sub> (1-H-3-methyl-imidazolium hydrogen sulfate).

The latter compound (designated IL1) was synthesized by mixing methyl-imidazolium (mim) (SIGMA-ALDRICH, CAS# 616-47-7, purity ≥99%) with a molar excess of 1% (stoichiometric ratio) of concentrated sulfuric acid (98% v/v). The mixture was created by slowly dropping the acid over the organic solvent, which was contained in a glass beaker. The beaker was immersed in an ice bath because the reaction is highly exothermic, and the solution was continuously stirred to promote heat and mass transfer. The resulting ionic liquid (HmimHSO<sub>4</sub>) is crystalline and slightly yellow in color; any orange or red color appearing in the mixture indicates imidazolium decomposition resulting from poor temperature control during the mixing. After complete reaction, the IL product was evaporated under vacuum at 110 °C in a rotary evaporator to eliminate water and any residuary odor.

BmimHSO<sub>4</sub> (IL2) was synthesized in two steps. In the first step, methyl-imidazolium (mim) (SIGMA-ALDRICH, CAS# 616-47-7, purity ≥99%) was mixed with chlorobutane (bCl) (SIGMA-ALDRICH, CAS# 109-69-3, purity 99%) (using a 5% molar excess of the latter) to form the ionic liquid 1-butyl-3-methylimidazolium chloride (bminCl). This IL was evaporated at 80 °C in a rotary evaporator to eliminate the excess of bCl until constant weight was achieved. In the second step, the bminCl product was mixed with concentrated sulfuric acid (at a stoichiometric ratio) in a Pyrex glass container, and the mixture was stirred under ultrasonic irradiation (53 kHz) at a controlled temperature of 60 °C for 12 h. The obtained IL was then mixed with a similar volume of pure ethyl acetate, forming a two-phase system. The phases were then separated, and the operation was repeated three times, each time using fresh acetate. In this way, the hydrochloric acid formed in the

previous reaction is removed. After liquid extraction was complete, the IL product was evaporated under vacuum at 110 °C in a rotary evaporator to eliminate any remaining acetate and water.

### 2.3. Analytical methods

Mineralogy was assessed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscope (EDX) (JSM 6380LV–JEOL microscope) and automated using QEMSCAN. The ultrasound equipment used for agitation included a HILAB Model SK03GT and a KUDOS Model SK221OHP. A Thermo Electron Corporation Atomic Absorption Spectrometer (AAS) Model M5 AA System was used to analyze copper content. pH was measured using a pH-meter IONALYZER® Digital, Model 601 A, Orion Research Incorporated. Oxidation–Reduction Potential (ORP) was measured using a Hanna, HI 991003N extended range potentiostat. Viscosity was measured using a Fungilab VISCO BASIC + L viscometer.

### 2.4. Leaching tests

All leaching tests were run in 20-mL uncapped glass tubes containing 10 mL of leaching solution and 1 g of mineral. Each tube was placed in an ultrasound thermo-regulated bath at 20, 40, or 60 °C, the leaching solutions were agitated using ultrasonic irradiation at 53 kHz and the solution was O<sub>2</sub> saturated through constant air bubbling.

In order to no modify the volume of the leaching medium by the continuous sampling, thirty six tubes with same original content were considered for each experimental condition corresponding to the twelve data points in triplicate. The tubes were withdrawn periodically from the ultrasound bath and then were immediately filtered and analyzed the Copper content by using atomic absorption spectroscopy. Copper recovery was calculated regarding the total copper content in the sample.

Leaching solutions were assayed by comparing to a 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution that was used as a blank; HmimHSO<sub>4</sub> (IL1) and bmimHSO<sub>4</sub> (IL2) were mixed with distilled water at concentrations of 10, 20 or 50% v/v, and IL 1 (10, 20 or 50% v/v) was mixed with 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution.

## 3. Results and discussion

### 3.1. Leaching with aqueous solutions of ionic liquids

A series of leaching tests was carried out using the described leaching media. The results are summarized in Fig. 1, and the final copper recoveries at 20, 40 and 60 °C (after 20 h of processing) are presented.

The results show in general copper recoveries below 20% and lower than H<sub>2</sub>SO<sub>4</sub> blanks at each temperature. Only at concentrations of 50% v/v and 60 °C IL1 and IL2 aqueous solutions exceeds 20% copper recovery, and clearly surpass 1 M H<sub>2</sub>SO<sub>4</sub> solution blank recovery.

According to Fig. 1, no clear relationship existed among increases in IL concentration and improvements in copper recovery for both ILs at each tested temperature. In addition, neither IL presented a clear advantage over the other. In particular, the performance of IL2 surpassed that of IL1 only at the highest tested temperature (60 °C).

Higher temperatures clearly improved copper recovery, and the increase in recovery was most effective at 50% v/v concentration, yielding a 100 and 350% increases in recovery at 60 °C compared to those at 20 °C for IL1 and IL2, respectively. This effect of temperature might be related to physicochemical properties, that affect mass transport phenomena, and also to the intrinsic chemical reaction rates, which generally do not present a linear behavior with temperature variations.

This high dependence on temperature has also been reported for concentrated copper ores by Whitehead et al. (2007) and Dong and

**Table 1**  
Mineralogical analysis of the mineral sample.

Mineral	% (w/w)
Chalcopyrite	46.97
Pyrite	49.26
Molybdenite	1.27
Other Cu sulfides	1.70
Other non-Cu sulfides	0.46

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