



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



Carlos Carlesi ^{a,*}, Enrique Cortes ^b, Gianfranco Dibernardi ^a, Jaime Morales ^a, Edmundo Muñoz ^c

^a Escuela de Ingeniería Química, Pontificia Universidad Católica de Valparaíso, Avenida Brasil 2147, Valparaíso, Chile

^b Departamento de Ingeniería Ambiental, Universidad de Playa Ancha, Av. Leopoldo Carvallo N°270, Valparaíso, Chile

^c Center for Sustainability Research, Universidad Andres Bello, República 440, Santiago, Chile

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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 (CuFeS₂) concentrate at 70 °C from 55% to 87% when the IL 1-butyl-3-methyl-imidazolium hydrogen sulfate (BmimHSO₄) 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 HSO₄⁻ 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

* Corresponding author.

E-mail address: carlos.carlesi@ucv.cl (C. Carlesi).

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 (BminHSO₄) and HminHSO₄ (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 (HmimHSO₄) 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.

BmimHSO₄ (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 O₂ 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 H₂SO₄ aqueous solution that was used as a blank; HmimHSO₄ (IL1) and bmimHSO₄ (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 H₂SO₄ 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 H₂SO₄ 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 H₂SO₄ 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 |

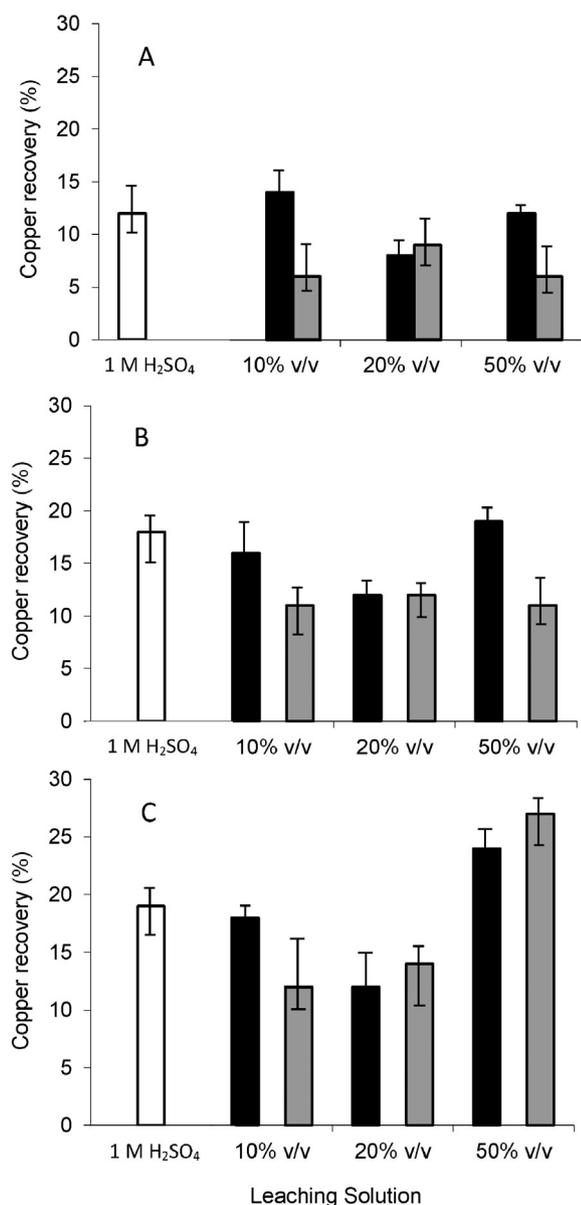


Fig. 1. Copper recovery at 20 h and A) 20 °C, B) 40 °C, C) 60 °C for H₂SO₄ 1 M (white bar), IL1 (black bar) and IL2 (gray bar) in aqueous solution at 10, 20 and 50% v/v.

Zhang (2009); however, the dissolution mechanism proposed by these researchers was based on hydrogen sulfate anion dissociation from IL and further leaching analogous to that of leaching only with sulfuric acid. Such a mechanism is not clearly supported by the acidity measurement of the solutions.

The measured solution acidities are presented in Table 2. All IL solutions were less acidic than the sulfuric acid solution, indicating

Table 2
Initial pH, viscosity and HSO₄⁻ anion concentration in the studied leaching solutions at room temperature.

| Leaching solution | pH | Viscosity (cP) | [HSO ₄ ⁻] (M) |
|------------------------------------|------|----------------|--------------------------------------|
| H ₂ SO ₄ 1 M | 0.31 | 6.40 | 1.00 |
| IL1 10% v/v | 0.98 | 6.44 | 0.64 |
| IL1 20% v/v | 0.85 | 9.74 | 1.29 |
| IL1 50% v/v | 0.39 | 10.53 | 3.22 |
| IL2 10% v/v | 1.11 | 3.30 | 0.49 |
| IL2 20% v/v | 1.05 | 4.04 | 0.98 |
| IL2 50% v/v | 0.95 | 6.29 | 2.45 |

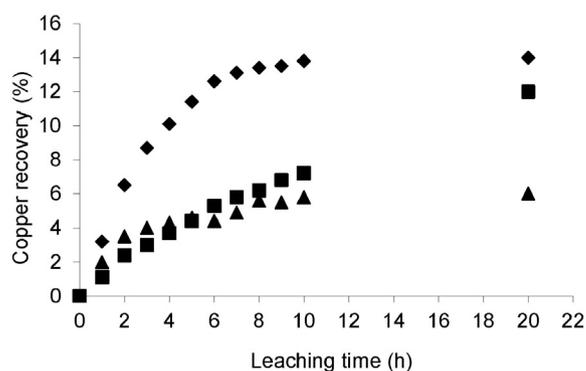


Fig. 2. Representative behavior of the leaching solutions H₂SO₄ 1 M (■), IL1 10% v/v (◆), and IL2 10% v/v (▲) at 20 °C.

that acidity was not the cause of the increased copper recoveries of the IL solutions. The dynamic viscosity values are also presented in Table 2; although this property increases with increasing IL content, it does not appear to importantly hinder the leaching process, especially at higher temperatures. The concentration of HSO₄⁻ anion is also presented in Table 2 to facilitate in comparing the availability of the anion in each solution. At 20% concentration, the ILs presented comparable amounts of acid-sulfate anion to that of the 1 M sulfuric acid solution but exhibited lower leaching capacities.

In the analysis of the overall leaching kinetics, the process exhibited certain differences when IL1, IL2 and sulfuric acid solutions were used, especially at low temperatures; representative behavior is presented in Fig. 2. The overall kinetics for IL2 was more linear and was more similar to those observed in sulfuric acid solution; in contrast, IL1 exhibited an initial pronounced passivating behavior. These differences were less pronounced at higher temperatures, thus indicating a lower temperature-dependent resistance to leaching when using the IL1 solution. As was the case for temperature, the kinetics behaviors were analogous to those previously reported for leaching with ionic liquids (Whitehead et al., 2007; Dong and Zhang, 2009).

3.2. Leaching using ionic liquid as an additive

While testing the ability of IL aqueous solutions to leach non-concentrated copper ores, further leaching runs were performed to assess the possibility of promoting a synergic effect between the ILs and sulfuric acid in the leaching process. The methodology was the same as that described earlier for the IL aqueous solutions. However, in this case, IL1, which presented better results in aqueous solution and was easier to synthesize, was dissolved in a 1 M sulfuric acid solution. Table 3 presents the chemical parameters of the resulting leaching solution.

The results obtained at temperatures below 60 °C did not differ from the results obtained using the IL aqueous solutions without sulfuric acid; conversely, at 60 °C, the results show an improvement in copper recovery of up to 70% at an IL1 concentration of 50% v/v (Fig. 3). This value compares with a value of 20% obtained using IL1 in a 1 M solution at lower concentrations and a value of 15% obtained using a H₂SO₄ blank.

Table 3
pH, and HSO₄⁻ concentration in leaching solutions prepared using H₂SO₄ and IL1.

| Leaching solution | pH | [HSO ₄ ⁻] (M) |
|---|------|--------------------------------------|
| H ₂ SO ₄ 1 M | 0.31 | 1.00 |
| IL1 10% v/v in H ₂ SO ₄ 1 M | 0.28 | 1.54 |
| IL1 20% v/v in H ₂ SO ₄ 1 M | 0.64 | 2.08 |
| IL1 50% v/v in H ₂ SO ₄ 1 M | 0.56 | 3.70 |

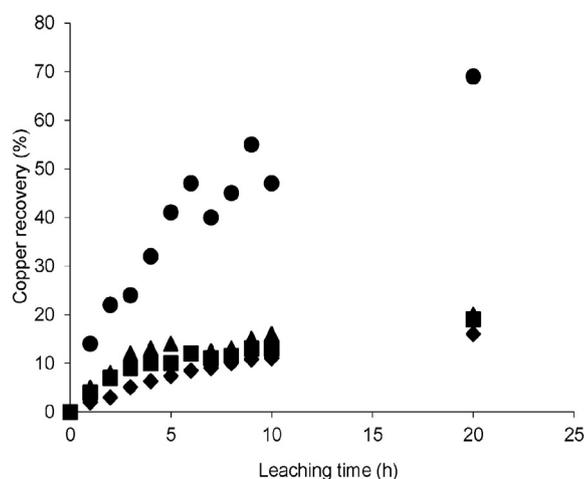


Fig. 3. Copper recovery at 60 °C using leaching solutions of (♦) H₂SO₄ 1 M, and H₂SO₄, all mixed with IL1 as an additive at (■)10% v/v, (▲)20% v/v, and (●) 50% v/v.

Fig. 3 presents high copper recovery (70%) at 60 °C for a mixture of 50% v/v IL1 with 1 M H₂SO₄. Solutions of 10 and 20% v/v in sulfuric acid did not present a significant increase in recovery over that obtained in 1 M sulfuric acid. This strongly increased recovery at 50% v/v at 60 °C compared with IL in aqueous solution under the same conditions (24%) indicates a synergistic effect between IL1 and H₂SO₄ in solution.

The appreciable differences exhibited by the more concentrated IL1 acid solution can be ascribed to the oxidizing potential of the solution. To support this assumption, the oxide-reduction potential (ORP) of the solutions were measured, and the results are presented in Table 4.

The value of ORP increased with the amount of IL1 in the solution; but the obtained potentials were all lower than that obtained in the 1 M sulfuric acid solution at each temperature. Thus, the IL solutions are not strong oxidants in themselves and, as noted by the Whitehead group, the leaching action of these solutions is not related to the presence of other oxidants or to a higher oxygen solubility, in fact, has been reported that the oxygen solubility in IL is lower than in water (Dyson and Geldbach, 2010).

In addition, the ORP differences between IL1 contents of 20% and 50% were negligible; consequently, the increase in copper extraction at 50% IL is not explained by ORP measurements.

The obtained experimental evidence noted various important aspects, such as the strong effect of temperature on performance apparently not related with the reduction in viscosity, rather, seems to influence more in chemical related processes, such as the decomposition of a sulfidic intermediate promoted by the presence of the IL. On the other hand, the importance of the oxidizing potential of the solution and the initial acidity was minor. A decrease in the solution potential might have a positive effect on preventing the formation of metal polysulfur compounds or iron oxyhydroxides, such as jarosite, which can hinder dissolution (Debernardi and Carlesi, 2013).

These findings are consistent with those of Crundwell (2013), who critically analyzed the literature regarding the pathways by which acid leaching occurs in sulfidic ores and concluded that the initial acidic attack and issues related to diffusion do not control the overall dissolution kinetics; however, electrochemical mechanisms (electron transfer

phenomena) are consistent with the experimental observations. Considering this proposal and the semiconductor nature of the mineral (Debernardi and Carlesi, 2013) the positive results obtained for the ionic liquid leaching of sulfidic ores might be due to improved solution-solid surface electron transfer processes or to a decrease in the resistance at the solid-liquid interface due to the affinity of ILs with sulfur and sulfidic-hydrophobic surfaces (Boros et al., 2009). In fact, decreased hydrophobic resistance is reportedly crucial to bacterial bioleaching through the secretion of surfactants that promote contact between the bacteria and oxidants containing sulfur and sulfidic matter (Steudel and Holdt, 1988). The same effect might be attributed to the experimental observations made by Solis-Marcial and Lapidus (2013), who found that adding organic solvents had a positive effect on the leaching of chalcopyrite concentrate. This decreased interfacial hydrophobic resistance might be more relevant than the lesser acidity and oxidizing power of the liquid media; more rapid electron transfer through the interface might allow a continuation of the sulfuric acid leaching action over the solid surfaces.

4. Conclusions

- Acid ionic liquid, when used solely as leaching agent in aqueous solution, do not present clear advantages over sulfuric acid leaching.
- High temperature (60 °C) triggers a strong increase in copper recovery, mainly due to the promotion of the chemical decomposition of metal sulfidic intermediates and a decrease in mass transfer limitations.
- When ionic liquids are used in combination with sulfuric acid, a synergistic effect is observed. The main action of the ionic liquid could be a decrease in the solid-solution hydrophobic resistance to electron transfer, thereby enabling a continuous acid leaching on the solid surface. Therefore, the ionic liquid could be considered a catalyst or a leaching additive rather than a leaching agent per se.

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Table 4
ORP (mV Ag/AgCl) for leaching solutions at various temperatures.

| Leaching solution | 20 °C | 40 °C | 60 °C |
|---|-------|-------|-------|
| IL1 10% v/v in H ₂ SO ₄ 1 M | 274 | 310 | 386 |
| IL1 20% v/v in H ₂ SO ₄ 1 M | 414 | 468 | 500 |
| IL1 50% v/v in H ₂ SO ₄ 1 M | 444 | 467 | 498 |
| H ₂ SO ₄ 1 M | 471 | 501 | 527 |

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