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Disentangling chemical effects in ionic-liquid-based Cu leaching from chalcopyrite

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ABSTRACT

Hydrometallurgical copper extraction from chalcopyrite is a slow and often incomplete process that relies on corrosive and environmentally unfriendly H_2SO_4-based leaching systems. Some ionic liquids (ILs), including imidazolium- and ammonium-based ILs, have previously been suggested as better performing alternatives, but at present it is not clear whether the leaching mechanism is different than in H_2SO_4-based lixiviants. Here, we study a range of different, structurally simple ILs using a robotic screening platform and other methods, to address this question. Indeed, we do find differences between ILs, in that IL-based lixiviants with more polar cations (NH_4^+, K^+, $[C_1Him]^+$) appear to show better extraction than those with less polar cations ($[C_2C_1im]^+$, $[C_4C_1im]^+$). However, none performed better than aqueous H_2SO_4, when corrected for differences in pH. Notably, results are qualitatively very similar: three leaching stages were seen in all cases, presumably involving leaching of a Fe rich/Cu poor layer first, followed by leaching of bulk chalcopyrite and eventually passivation. During the second stage, the apparent activation energies in aqueous NH_4HSO_4, and H_2SO_4 are similar in that both rates are first order with respect to the proton concentration in both cases. The leaching rate increases with stirring, suggesting some degree of mass transport-control on the leaching process. The poorer leaching performance for $[C_2C_1im]HSO_4$ and $[C_4C_1im]HSO_4$ is consistent with physical blocking of the mineral surface, presumably by the IL cation, in accordance with contact angle data.

1. Introduction

Owing to its industrial importance, copper is a heavily used metal, with chalcopyrite, $CuFeS_2$ being the most important copper bearing mineral at present [1,2,3,4]. Copper is most commonly extracted using pyrometallurgical methods. However, as high-grade ores have been used heavily over time, many copper deposits, and previously discarded tailings, now have relatively low copper content. Hence, large quantities of ore need to be treated for a relatively small amount of Cu [5]. This makes pyrometallurgical methods rather energy intensive and increasingly expensive, with significant environmental impact [5]. Leaching, i.e. the chemical dissolution of a material of interest from the ore, has been identified as a potentially more economical alternative [5]. A schematic of the commonly accepted mechanism of chalcopyrite leaching in acidic media is shown in Fig. 1a. It is generally understood to involve oxidation of the chalcopyrite surface by the lixiviant, destabilizing the structure, and subsequent break down into $Cu^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$ and S_n [6,7,8]. The rate determining step either lies in the initial oxidation or the diffusion of oxidant to the chalcopyrite surface. Oxidation can be through dissolved O_2, to give water as by-product, or via $Fe^{3+}_{(aq)}$ (in the absence of other oxidants). The resulting Fe^{2+} is subsequently regenerated to Fe^{3+} by reaction with dissolved O_2. Hence, in many commonly used, H_2SO_4-based leaching systems oxidants, such as ferric ions are added to speed up the extraction process. Nevertheless, extraction is generally slow and inefficient, i.e. not all of the available Cu is leached from the mineral [4,5]. Conventional lixiviants are also not very specific, in that other trace metals such as Mo may be leached at the same time, potentially complicating subsequent processing steps [9,10].

Recently, ionic liquids (IL) have been proposed as a potential alternative. While typically more expensive than H_2SO_4, the chemical flexibility in designing their structure and hence properties as a solvent may hold prospects of faster and perhaps more specific extraction of trace metals from ore [11]. Indeed, some quite promising initial results have appeared in the scientific as well as the patent literature recently [4,12,13,14,15,16,17]. ILs are salts with a melting point below 100 °C and generally consist of a large organic cation, such as an N,N-dialkylimidazolium or alkylammonium derivative, and a smaller organic or inorganic anion [18,19]. In particular, $[C_4C_1im]HSO_4$ has been explored by several groups for leaching. Three groups [12,13,15] found

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that at high concentrations (above 50% w/w) $[C_4C_1im]HSO_4$ performs better than 1 M H_2SO_4. Whitehead et al. [12] for example, found that neat $[C_4C_1im]HSO_4$ extracts 86.6% of Cu, while 1 M H_2SO_4 only extracts 23% under the same conditions. For 10% (w/w) and 20% (w/w) $[C_4C_1im]HSO_4$ in H_2O they observed superior performance, too, while Carlesi et al. [13] found that these lixiviants performed worse than 1 M H_2SO_4. They also explored $[C_1Him]HSO_4$ and found faster and more efficient copper extraction compared to $[C_4C_1im]HSO_4$. Godfrey et al. [4] tested aqueous solutions of $[C_4C_1im]HSO_4$, NH_4HSO_4 and $[C_4Him]HSO_4$ and the latter two indeed showed better Cu extraction than $[C_4C_1im]HSO_4$. In the case of NH_4HSO_4, a maximum in the extraction performance for an aqueous mixture of 0.45 M (10% w/w) NH_4HSO_4 was observed at room temperature, albeit with significant sample-to-sample variation. This is different to previous results by Dong et al. who observed a monotonous increase with $[[C_4C_1im]HSO_4]$ at low concentrations, and little change for $[[C_4C_1im]HSO_4]$ larger than about 50% (v/v) at 363 K after 24 h [20]. Equally, Kuzmina et al. studied the concentration dependence of chalcopyrite leaching in aqueous mixtures of $[C_4Him][HSO_4]$ at 298 K and found no effect between 10 and 80% (w/w) after 7 days [21].

So, on the one hand, IL-based systems have in some cases outperformed H_2SO_4-based lixiviants, and differences between different ILs may point towards IL-specific factors affecting Cu extraction from $CuFeS_2$. On the other hand, it is not obvious which factors these might be and how they would affect the process. Intuitively, they could include improved surface interactions between liquid and ore (e.g. more efficient wetting) [12,16], an effect on the passivating or blocking layer that eventually forms during leaching, or enhanced solubility of Cu^{2+} or oxygen in solution [12]. However, as this study finds, Cu^{2+} solubility is actually lower in HSO_4^--based, aqueous ILs. Furthermore, oxygen solubility appears to be similar to that in water [12]. Pure and even some diluted ILs also tend to be more viscous than aqueous solutions, rendering mass transport less efficient. Again, this would decrease, not increase the leaching performance, if mass transport were a limiting factor.

This leaves factors that are specific to the 'chemistry' of the IL ions. To this end, some pure ILs have been shown to form N-heterocyclic carbenes [22], which can in turn react with elemental sulphur. The latter is a likely component of the passivating layer, in addition to jarosites, so the IL ions attacking the sulphur layer could represent an avenue towards enhancing the leaching performance. However, such carbenes are normally unstable in the presence of water, especially at low pH. Thus, even residual water content in the IL would make it rather difficult to maintain a significant concentration of carbenes close to the surface. Equally at low pH, the concentration of free base, e.g. imidazole or ammonia, is negligible and therefore the coordinating effect of the nitrogen (to Cu) is unlikely to be important. On the other hand, if the cations are merely 'innocent bystanders', why should they have any effect on the leaching performance at all?

Thus, a need for further study is evident, in order to shed light upon these aspects. We do this here with a focus on diluted aqueous IL-based lixiviants, which have shown promising performance previously and are less viscous and less expensive than pure ILs. We do not aim to replicate lixiviants that are currently in use in the industry, which can have rather complex composition. Instead, the study aims to employ simplified leaching solutions with a small number of components, in an effort to isolate individual parameters affecting the overall extraction performance. Specifically, we use a previously developed robotic screening platform [4] that allows for multiplexed, 'combinatorial' monitoring of the leaching performance in a sample array, as illustrated in Fig. 1. We monitor the concentration of dissolved Cu^{2+} using electrochemical, potentiostatic deposition of Cu^0, followed by anodic stripping using differential pulse voltammetry (EDAS) [23,24]. Compared to conventional ('ex-situ') detection methods, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), the electrochemical method is advantageous, as it is more easily automated and allows for (quasi) continuous monitoring of the Cu^{2+} concentration without user intervention. In previous work, we also explored Cu^{2+}-selective electrodes, but found those to be too insensitive in the presence of ILs to monitor the early stages of leaching in particular [4].

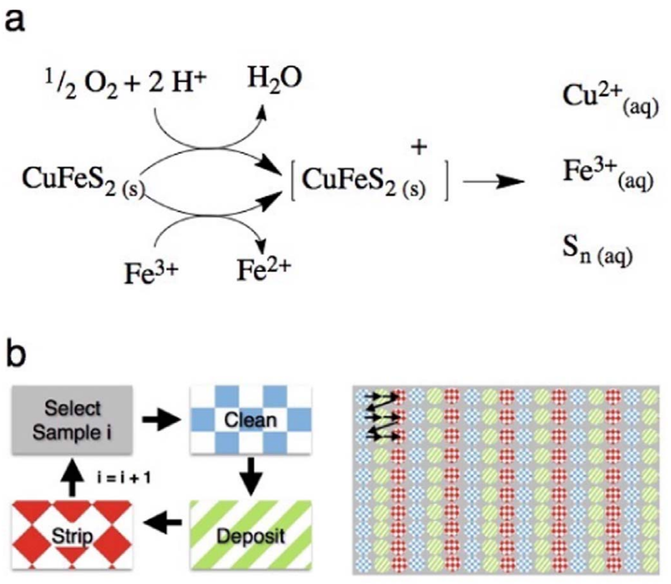

Fig. 1. a) Mechanism of chalcopyrite leaching, showing the two commonly accepted reaction pathways, with O_2 or Fe^{3+} as oxidants. b) Schematic representation of measurement sequence on the robotic screening station, which allows for monitoring Cu extraction in a large number of reaction vials in parallel. Once a sample is selected, the Pt WE is first cleaned ('Clean'), see Section 2. The copper concentration in solution is then determined by electrodeposition of Cu^0 ('Deposit') and subsequent anodic stripping ('Strip'). The whole cycle, which takes approximately 5 min, depending on the experimental conditions, is then repeated with sample 'i + 1'. The stripping charge is converted into a solution concentration after calibration. The Cu concentration in solution was typically in the high μM or low mM range, covering predominantly the early stages of leaching.

Using the robotic platform with small sample volumes minimizes reagent consumption, in terms of both lixiviant and solid, and facilitates the relatively quick assessment of a number of different lixiviants at the same time. In the case of ILs, this is particularly useful, due to the large number of available ILs, the prospect of exploring mixtures with other ILs as well as conventional solvents, and the mechanistic complexity of the leaching process. However, the platform is less suitable for detailed mechanistic studies, typically involving stirring and real-time monitoring of various process parameters such as solution redox potential, temperature, and pH. We therefore complement those experiments with studies on selected lixiviants in upscaled reactors, approximately 25 mL in volume, see below.

2. Materials and methods

All chemicals, including all ILs, were purchased from Sigma-Aldrich and used as received, unless otherwise noted. The pH values of the aqueous IL solutions were measured using Mettler Toledo 'SevenEasy' pH meter, calibrated against standard solutions at pH 1 and 4. Electrochemical measurements were performed with commercial potentiostats, either integrated with the robotic platform ('Compactstat', Ivium Technologies B.V., Eindhoven/The Netherlands) or coupled to an individual 'batch' reactor ('Reference 600', Gamry Instruments, Warminster/USA). The solubility of Cu^{2+} in different lixiviants was tested by creating saturated solutions of $CuSO_4$ (Sigma-Aldrich, 99.99%). The solution above the precipitate was filtered (0.2 μm porous, Acrodisc Supor), diluted (1:2000 v/v) and the concentration of dissolved Cu measured using ICP-AES. The design of the robotic platform was reported previously [4] with minor adaptations for the

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