International Journal of Minerals, Metallurgy and Materials
Volume 21, Number 2, February 2014, Page 138
DOI: 10.1007/s12613-014-0876-y

Use of ionic liquid in leaching process of brass wastes for copper and zinc recovery

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(Received: 5 August 2013; revised: 2 October 2013; accepted: 8 November 2013)

Abstract: Brass ash from the industrial brass manufacturer in Turkey was leached using the solutions of ionic liquid (IL) 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO_4) at ambient pressure in the presence of hydrogen peroxide (H_2O_2) and potassium peroxymonosulfate (oxone) as the oxidants. Parameters affecting leaching efficiency, such as dissolution time, IL concentration, and oxidizing agent addition, were investigated. The results show that [bmim]HSO_4 is an efficient IL for the brass ash leaching, providing the dissolution efficiencies of 99% for Zn and 24.82% for Cu at a concentration of 50vol% [bmim]HSO_4 in the aqueous solution without any oxidant. However, more than 99% of zinc and 82% of copper are leached by the addition of 50vol% H_2O_2 to the [bmim]HSO_4 solution. Nevertheless, the oxone does not show the promising oxidant behavior in leaching using [bmim]HSO_4.

Keywords: leaching; recovery; copper; zinc; ionic liquids; oxidants

1. Introduction

Utilization and recovery of copper and zinc from industrial wastes are particularly important from economic and environmental viewpoints [1-4]. Typically, the brass production generates large quantities of various wastes, containing significant amounts of copper and zinc. Slag generated during brass alloy melting is the main source of copper-based wastes. The metallic and nonmetallic parts of slag are separated by a series of processes, i.e., crushing, washing, natural drying, wet grinding, and sieving, in that order. Then, the separated metallic parts are recycled in a melting furnace, and the residual nonmetallic part, called “brass ash”, is stored for the recovery of copper and zinc [5-6].

Studies on the recovery of metals from brass ash are generally focused on the hydrometallurgical treatments. Metal recovery by the conventional acid or alkali leaching techniques may not be environmentally friendly because of the large amounts of acid/alkali consumed and the generation of high amounts of waste water. Therefore, to mitigate these adverse effects, the alternative extractants are required to be developed. In recent years, ionic liquids (ILs) have been found to be the most promising candidates for leaching agents with the aim of achieving a new yet green hydrometallurgical process. Room-temperature ILs (RTILs) are considered as the next-generation molten salts, which are generally composed of organic cations and organic or inorganic anions. These molten salts may be synthesized with different anion and cation combinations to obtain the desired physicochemical properties. This is a great opportunity to obtain the task-specific ILs. Important properties of these ILs, such as low vapor pressure, nonflammability, low toxicity, negligible volatility, and thermal stability, make them useful for various applications, including separation techniques, biochemistry, catalytic reactions, and electrochemical applications [7-11]. Furthermore, it is possible to recover certain types of ILs after using them for the further reuse without any appreciable loss of their purity and activity [12-20].

The acidic nature and water solubility of ILs allow their application to the dissolution of metals [21-22]. Leaching of sulfidic copper, gold, and silver ores in the IL 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO_4) has been studied by Whitehead *et al.*, who have reported the

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promising results for the extraction of these metals [23-24]. Other researchers have also used this IL for leaching of chalcopyrite, and it has been found that pure IL and its aqueous solutions are more effective than the conventional acid solutions used for leaching [25].

In this study, the recovery of copper and zinc from the industrial brass ash was attempted using [bmim]HSO_4 in the leaching process. Furthermore, the parameters affecting leaching efficiency, such as dissolution time, IL concentration, and oxidizing agent addition, were evaluated.

2. Experimental

2.1. Brass ash

The brass ash used in the experiments was supplied by a brass manufacturing plant in Turkey. The chemical composition of brass ash was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), and the results are presented in Table 1. The phases of brass ash were analyzed by X-ray diffraction analysis (XRD), as shown in Fig. 1. The brass ash exists mostly in the form of metal oxides. A significant amount of copper is also found to be present as the metallic phase in brass ash. Chemical and spectrometry analyses show that ZnO, CuO, and Cu are the major components of brass ash.

Table 1. Chemical composition of brass ash **wt%**

Zn	Cu	Ca	Al	Mg	Na	K	S	Cl	Si
53.92	22.00	5.81	3.40	0.31	0.30	0.35	0.32	0.35	12.17

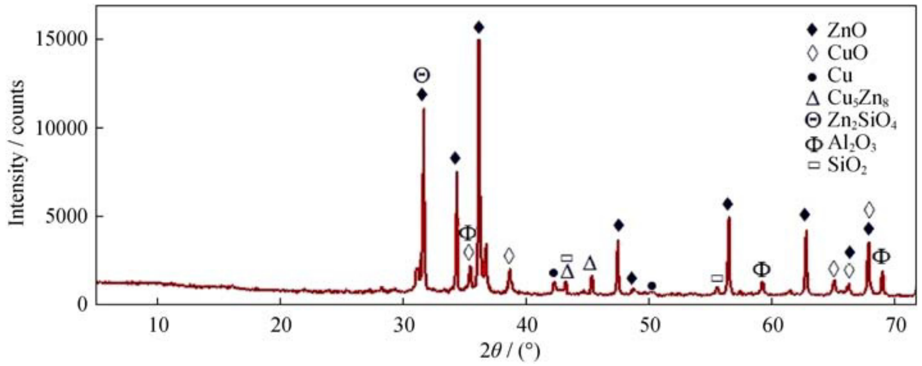

Fig. 1. XRD spectra of the brass ash sample.

2.2. Reagents

The IL ([bmim]HSO_4) and two analytical-grade oxidants (potassium peroxymonosulfate (oxone) and hydrogen peroxide (H_2O_2) solution (30wt%)) were used in the experiments. All aqueous IL leach solutions were prepared using deionized water.

2.3. Leaching tests

The vessel used in leaching tests was a closed glass beaker, which was placed in a temperature-controlled water bath. The leaching tests were carried out at pulp densities of 100 g/L using a constant volume of 100 mL of leach solution at a temperature of 70°C. The solutions were stirred magnetically at 400 r/min during leaching. The IL concentrations in aqueous solution were 10%, 30%, and 50% by volume. To investigate the effect of oxidizing agent addition on the leaching process, varying amounts of H_2O_2 were added to aqueous leach solutions with a constant IL concentration (50vol%). As an alternative oxidant, the oxone was also added at the concentrations of 0.3 mol/L and 0.5 mol/L to the aqueous IL leach solution containing 50vol% [bmim]HSO_4. The samples for analysis were obtained through a pipette dipped into the top part of solution. Subsequently, the samples were filtered using filter paper, and the metal concentrations in the liquors were analyzed by ICP-OES. The leaching efficiency for copper and zinc was determined according to the following equation.

$$\text{Dissolution efficiency} = (\text{Metal amount in the liquor/Metal amount in the brass ash}) \times 100\% \tag{1}$$

The leach residues were characterized by scanning electron microscopy (SEM). Prior to the leaching tests, the pH value and reduction oxidation potential (Eh) values of [bmim]HSO_4 solutions containing various concentrations of H_2O_2 and oxone were measured using a pH meter and a potentiometer, respectively.

3. Results and discussion

3.1. Evaluation of Eh-pH values of solutions and chemical dissolution

According to the Pourbaix diagram of a Cu-H_2O system, copper dissolution is possible at pH values lower than 6 and oxidizing redox potentials higher than +0.2. Fig. 2 shows the

Eh-pH diagram obtained from the measurement of [bmim]HSO$_4$ solutions containing various concentrations of H_2O_2 and oxone. It is obvious from Fig. 2(a) that, when increasing the H_2O_2 concentration from 0vol% to 50vol% in the aqueous IL solution, the pH values decrease from 1.1 to 0.31, whereas the Eh values increase from 0.67 to 0.683. Fig. 2(b) shows that the pH values range between 1.1 and 0.89 and the Eh values range between 0.95 and 0.67 for various oxone concentrations in the aqueous IL solution. Therefore, it can be claimed that the Eh-pH values of solutions are in good agreement with those from the Pourbaix diagram for a Cu-H_2O system. Furthermore, since zinc is easily soluble in aqueous solution, the evaluation of its Eh-pH diagram was omitted in this study.

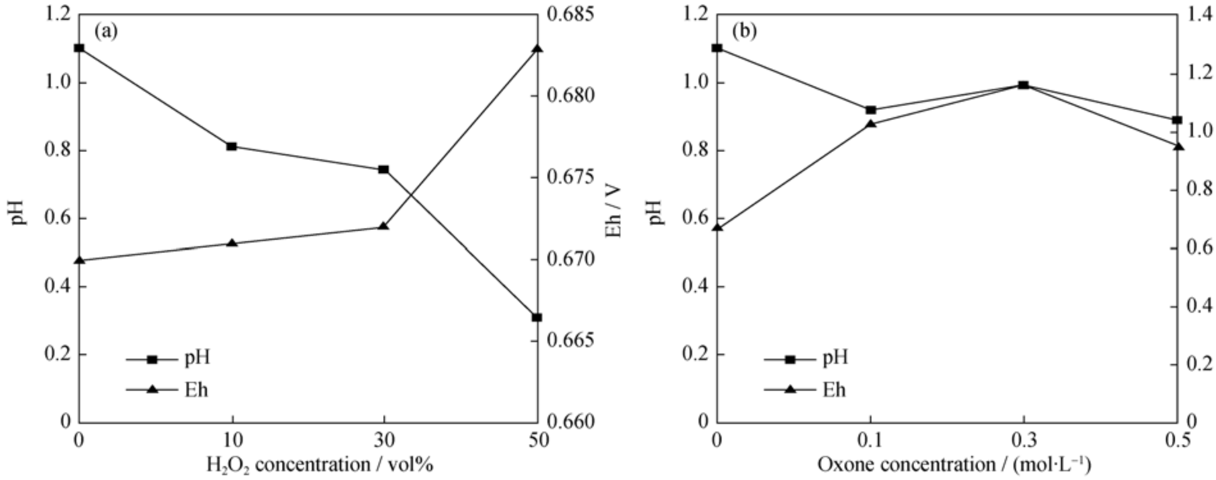

Fig. 2. Variation of acidity and redox potentials of [bmim]HSO$_4$ solutions containing H_2O_2 (a) and oxone (b) at 25°C.

The IL solutions containing different concentrations of oxidizing agents were able to dissolve both copper and zinc according to their Eh-pH values. The possible dissolution reactions of metallic copper and/or copper and zinc compounds in [bmim]HSO$_4$ solution containing oxidizing agents, such as H_2O_2 and oxone, are proposed as the following equations.

H_2O_2 may decompose into water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + 2[O]. \quad (2)$$

Oxone ions may decompose into sulfate and oxygen:

$$2HSO_5^- \rightarrow H_2O + 2SO_4^- + [O]. \quad (3)$$

Anodic and cathodic reactions occur among copper, dissolved oxygen, and the IL:

$$Cu \rightarrow Cu^{2+} + 2e^-, \quad (4)$$

$$2H^+ + [O] + 2e^- \rightarrow H_2O. \quad (5)$$

Alternatively, the IL and H_2O_2 molecules may react with the metallic copper directly as

$$2Cu + H_2O_2 + 4H^+ + [O] \rightarrow 2Cu^{2+} + 3H_2O. \quad (6)$$

Zinc oxide may dissolve in IL solution according to the following reaction.

$$2ZnO + 4H^+ \rightarrow 2Zn^{2+} + 2H_2O \quad (7)$$

3.2. Effect of IL concentration

The IL [bmim]HSO$_4$ was selected as a leaching agent because of its advantages, such as solubility in water, low cost, environmental friendliness, and easy availability. It is also known that [bmim]HSO$_4$ acts as an acid in the aqueous solutions [23-24]. Fig. 3 shows the effect of the selected IL concentrations on the percentage of dissolved copper as a function of leaching time. It can be seen that no remarkable copper dissolution is achieved at the [bmim]HSO$_4$ concentrations of 10vol% and 30vol% in a leaching time of 5 h. However, when the [bmim]HSO$_4$ concentration is increased to 50vol%, copper starts to dissolve gradually, and its dissolution ratio becomes to 25% after 5 h. However, this dissolution ratio is still insufficient in view of the expected dissolution ratio of 90% for copper. The main reason for this limited solubility of copper in the aqueous IL solution may be the fact that the metallic copper is present in greater quantity than the oxidic copper in the brass ash.

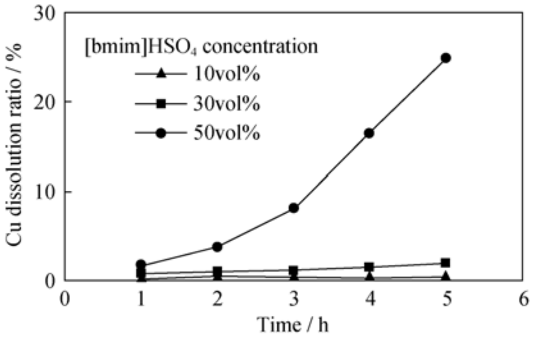

Fig. 3. Effect of [bmim]HSO$_4$ concentration on copper dissolution.

Fig. 4 shows the dissolution ratio of zinc in aqueous IL solutions of different concentrations. As can be seen from this figure, the percentage of dissolved zinc increases significantly as the IL concentration is increased from 10vol% to 30vol%. The leaching time has no significant effect on the dissolution ratio of zinc for both these IL concentrations. Further, the increment in the dissolution ratio is not negligible when the IL concentration is increased from 30vol% to 50vol%. A dissolution ratio of 99% for zinc is achieved at the IL concentration of 50vol% at the end of 4 h of leaching.

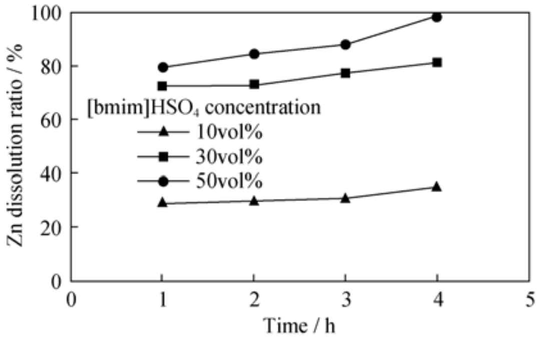

Fig. 4. Effect of [bmim]HSO$_4$ concentration on zinc dissolution.

3.3. Effect of H_2O_2 addition

Although almost the entire amount of zinc in brass ash was dissolved at the IL concentration of 50vol%, the dissolution ratio for copper was unsatisfactory because of the metallic form. Oxidizing agents were then added to the leach liquor to increase the dissolution ratio of copper. As is known from the literature, oxygen solubility in [bmim]HSO$_4$ is similar to that in water [23]. Because the oxygen-dissolving ability of ILs is comparable with that of water, these ILs can easily be used when oxidant action is needed. Then, two different oxidizing agents, H_2O_2 and oxone, were used to obtain a higher copper dissolution ratio. H_2O_2 is known to be one of the most powerful oxidizing agents in acidic solutions. To investigate the effect of H_2O_2 addition on the leaching efficiency, different concentrations by volume of H_2O_2 was added to an aqueous IL solution of constant concentration (50vol%).

The effect of H_2O_2 addition on the copper dissolution ratio in neat and aqueous IL leach solutions is shown in Fig. 5. It is clearly seen that the dissolution ratio of copper increases from 24.82% to 34.58% when the concentration of added H_2O_2 is increased from 0vol% to 10vol% after 5 h. Adding a higher concentration of H_2O_2 (30vol%) to the leach solution increases the dissolution ratio further to 44.48%. More than 82% of copper is leached at the H_2O_2 concentration of 50vol%. H_2O_2 makes the IL solution more oxidative, and the copper metal dissolves more easily with a higher leaching ratio than in experiments without H_2O_2.

The effect of H_2O_2 addition on zinc dissolution ratio is shown in Fig. 6. Since zinc is present in oxide form in brass ash, higher dissolution ratios are already achieved without the presence of any oxidant in the IL solutions. However, H_2O_2 addition results in the higher dissolution ratios in shorter leaching times. Almost the entire amount of zinc dissolves at the end of 30 min when 30vol% H_2O_2 is added.

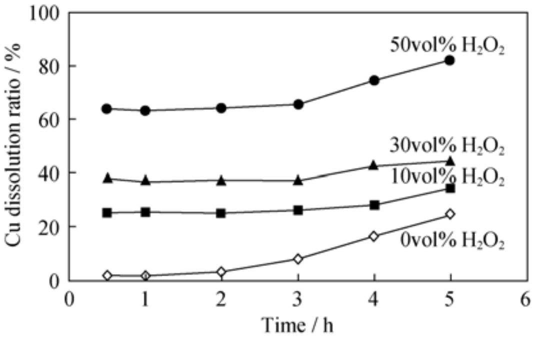

Fig. 5. Effect of H_2O_2 addition on the dissolution ratio of copper in [bmim]HSO$_4$ solution.

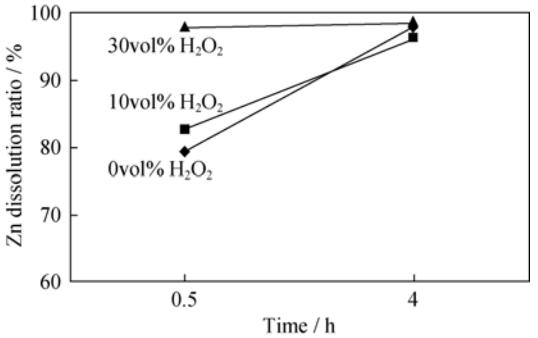

Fig. 6. Effect of H_2O_2 addition on the dissolution ratio of zinc in [bmim]HSO$_4$ solution.

3.4. Effect of oxone addition

As mentioned earlier, the potassium peroxymonosulfate (oxone) was also examined as an alternative oxidant. Its addition to acidic solution causes it to decompose into oxygen and sulfate. Its nontoxic nature, low cost, and simple handling properties are other reasons for its preferred use as an oxidant.

Oxone with the concentrations of 0.3 mol/L and 0.5 mol/L was added to the aqueous solution having a constant IL concentration of 50vol%. Figs. 7 and 8 show the effects of oxone addition on the dissolution ratio of copper and zinc, respectively. The dissolution ratios for both copper and zinc decrease with the addition of 0.3 mol/L and 0.5 mol/L oxone. This decrease may be attributed to several factors, such as chemical changes in the structure of [bmim]HSO_4 in the presence of oxone. Therefore, a further investigation is required to better understand this negative impact of oxone on leaching efficiency.

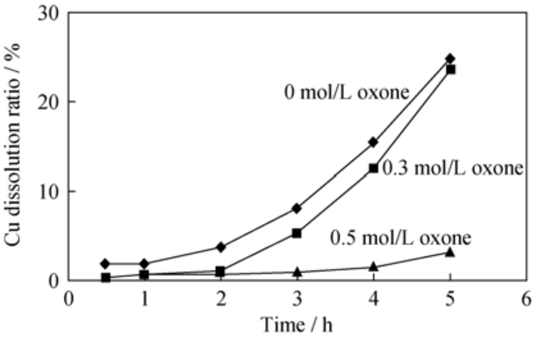

Fig. 7. Effect of oxone addition on the dissolution ratio of copper in aqueous [bmim]HSO_4 solution.

3.5. Characterization of residues of leaching process

Fig. 9 shows the SEM images of brass ash and residues after leaching using [bmim]HSO_4 in the absence of any oxidant and in the presence of H_2O_2. From Figs. 9(c) and (d), the positive effect of H_2O_2 on copper dissolution is clear. It appears as if some ash particles disintegrate into subparticles in the presence of H_2O_2. In particular, in the presence of 30vol% H_2O_2, the particle size of the leach residue is smaller than that of the brass ash when H_2O_2 is not used.

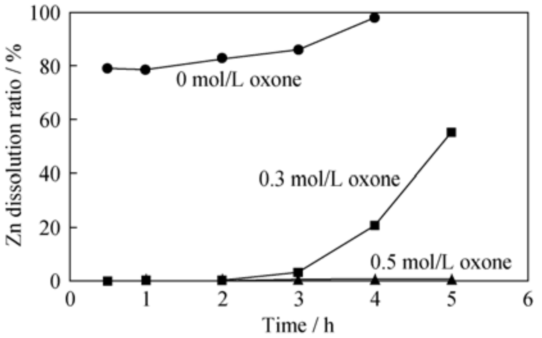

Fig. 8. Effect of oxone addition on the dissolution ratio of zinc in aqueous [bmim]HSO_4 solution.

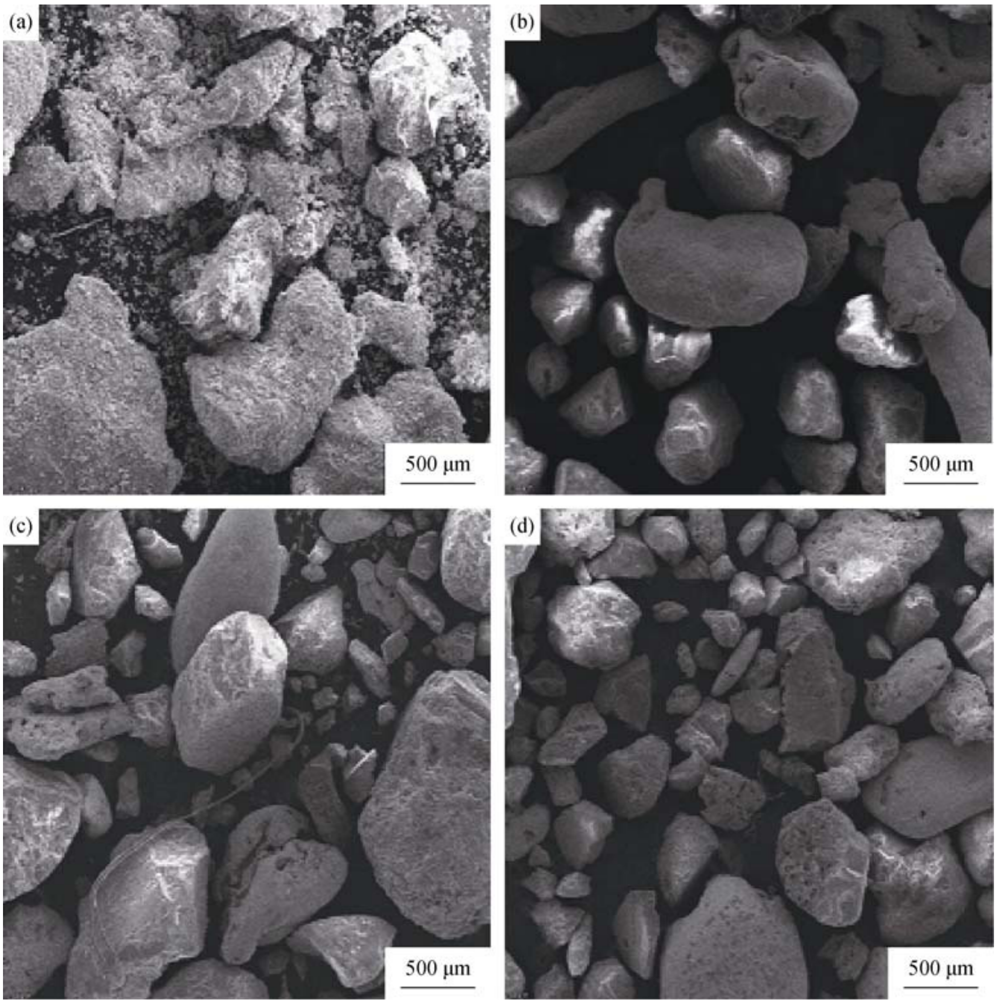

Fig. 9. SEM images of brass ash and leach residues obtained after filtering: (a) brass ash; (b) residue without oxidant; (c) residue after leaching with 10vol% H_2O_2; (d) residue after leaching with 30vol% H_2O_2.

4. Conclusions

(1) The IL [bmim]HSO_4 can act as an efficient acidic leaching agent for leaching of brass ash. Almost the entire amount of zinc (99%) dissolves successfully in 50vol% aqueous [bmim]HSO_4 solution without adding any oxidant.

(2) Though it is known that oxygen-containing [bmim]HSO_4 plays the role of an oxidant in the leach solution, the dissolution ratio of metallic copper from brass ash in the absence of additional oxidant is unsatisfactory.

(3) A copper dissolution ratio greater than 82% is achieved in the presence of H_2O_2 with a concentration of 50vol% in [bmim]HSO_4 solution. H_2O_2 addition to [bmim]HSO_4 also leads to a higher dissolution ratio of zinc in a shorter time than that in the case of IL solution without H_2O_2.

(4) Oxone addition to the leach solution decreases the dissolution ratios for both copper and zinc. However, a further investigation is required to better understand this negative impact of oxone addition on the dissolution of copper and zinc.

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