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Research Paper

Kinetics Investigation of Chalcopyrite Dissolution in the Presence of Acidic Ionic Liquid

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Abstract: Today, the adoption of green technologies and sustainable development has dragged more attention in the metallurgical industry. Accordingly, in this study, the leaching kinetics of chalcopyrite ($CuFeS_2$) concentrate using 1-Butyl-3-methylimidazolium hydrogen sulfate ($BmimHSO_4$) as an acidic ionic liquid was investigated. Effects of operational parameters including temperature, $BmimHSO_4$ concentration, H_2O_2 concentration, solid-to-liquid ratio and particle size on the rate of copper dissolution from $CuFeS_2$ were systematically examined. The results showed that the concentration of hydrogen peroxide and temperature had the greatest and the least effect on the dissolution of chalcopyrite, respectively. Also, the highest Cu extraction (ca. 97%) in this work was achieved using 40% $BmimHSO_4$, 30% H_2O_2, and 10 g/L solid to liquid ratio for particle sizes less than 37 µm and 45 °C for leaching time of 180 min. Kinetics study using Shrinking Core Model (SCM) revealed that $CuFeS_2$ leaching process using $BmimHSO_4$ follows the chemical reaction-controlled process. In addition, the orders of reaction with respect to $BmimHSO_4$ and H_2O_2 concentration, solid to liquid ratio, particle size were estimated to be 0.5386, 0.933, -0.676 and -1.1078, respectively. Under these circumstances, the activation energy and Arrhenius constant were 46.63 kJ/mol and 0.2596×106, respectively.

Keywords: Ionic liquids, Leaching kinetics, Chalcopyrite concentrate, Hydrogen peroxide, Shrinking Core Model.

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INTRODUCTION

Chalcopyrite, with the chemical formula of $CuFeS_2$, is highly resistant to dissolution, mainly due to its chemical structure, variations on the surface of mineral, and formation of passive layer with substantial porosity on its surface [1]. Therefore, there are numerous studies on leaching of copper from $CuFeS_2$. Due to low dissolution rate of this mineral, several processes including chloride leaching [2], ammonia leaching [3], bio-leaching [4] and pressure sulfate leaching [5] have been developed for Cu extraction from $CuFeS_2$. However, due to the issues regarding solvent extraction from the product, incomplete extraction, safety, toxicity, environmental pollution, and high expenses for solvent management, there are some controversies about the applicability of solvent-based leaching of Cu from $CuFeS_2$ [6]. Therefore, novel hydrometallurgical processes are necessary for the green and sustainable development of metallurgy industry for efficient Cu production with low energy consumption, minimal acid requirement, and less pollution under ambient conditions. As a result, ionic liquids have been considered as a viable alternative in metallurgic processes, due to their higher solubility in organic/inorganic compounds, non-volatile nature, and thermal stability [7]. In recent years, several studies on leaching of Cu from $CuFeS_2$ with ionic liquids as solvent have been conducted successfully [6-10]. All of the works done in this field reveal the significant effect of ionic liquids during chalcopyrite leaching. In addition, achievement of considerable efficiency using ionic liquid requires utilization of oxidative agent. The main oxidative agents are KNO_3, $NaClO_3$, $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, H_2O_2, and Fe^{3+} which have been used in $CuFeS_2$ dissolution [8]. Among them, hydrogen peroxide constitutes a potentially green and environmentally-friendly oxidant because it releases only water as by-product. Therefore, In the current study, the dissolution of chalcopyrite using $BmimHSO_4$ in the presence of H_2O_2 as an oxidizing agent, was investigated. In addition, the effects of operational parameters such as temperature, $BmimHSO_4$ concentration, H_2O_2 concentration, solid-to-liquid ratio, and particle size on the leaching of chalcopyrite have been investigated. Also, the kinetics of chalcopyrite leaching and the effects of operational parameters on the kinetics using the shrinking core model method were investigated.

METHODS

X-ray diffraction (XRD) analysis (D8-Advance, Bruker axs, USA) was carried out in order to identify the minerals. Accordingly, the main mineral in the sample was CuFeS2 along with trace amounts of Pyrite. Microscopic mineralogy revealed less than 5% Cu with trace amounts of Cu oxide minerals, chalcocite, and bornite which were not detectable by XRD analysis. $BmimHSO_4$ (≥94.5% purity), H_2O_2 (30 wt%) and de-ionized water were used throughout the experiments. The leaching solution was prepared in a 50 ml Erlenmeyer flask using digital magnetic stirrer-hot plate. Aliquot samples of the solution were drawn and filtered at certain times from start of each experiment. The amount of leached Cu was analyzed using Atomic Absorption Spectrophotometer (Varian, AA240, USA).

FINDINGS AND ARGUMENT

Effect of $BmimHSO_4$ concentration

The influence of $BmimHSO_4$ concentration on the degree of copper leaching was investigated in solutions containing different initial $BmimHSO_4$ concentrations (10%, 20%, 30% and 40%) at 30% H_2O_2, 40 °C, 10 $g.L^{-1}$ solid to liquid ratio, particle size of less than 37 μm and leaching time of 180 min. Results showed that, by increasing the $BmimHSO_4$ concentration from 10 to 40%, Cu extraction increases from 57.6 to 89.1% after 3 h of leaching.

Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the dissolution of chalcopyrite was investigated for 7.5, 15, 22.5 and 30% at 40% $BmimHSO_4$, 40 °C, 10 $g.L^{-1}$ solid to liquid ratio, particle size of less than 37 μm, and leaching time of 180 min. Studies on the H_2O_2 concentration indicated that the copper recovery increases by enhancing the H_2O_2 concentration. Also, was observed that the improvement of CuFeS2 dissolution by increasing H_2O_2 concentration in the range of 7.5 to 15% was more significant than in the range of 15 to 30%.

Effect of solid to liquid ratio

The influence of solid to liquid ratio on the dissolution of chalcopyrite was investigated at different levels of 10, 20, 30 and 40 g.L^{-1} at 40% $BmimHSO_4$, 30% H_2O_2, particle size of less than 37 µm, 40 °C, and leaching time of 180 min. It was found that, by increasing the solid to liquid ratio, copper recovery decreased; after 180 min, increasing the ratio from 10 to 40 g L^{-1} led to the decrease in copper recovery 89.1 to 50%.

Effect of particle size

The influence of particle size on the copper leaching rate was examined for four different size fractions (-37, 37-53, 53-74, and 74-88 µm) at 40% $BmimHSO_4$, 30% H_2O_2, 10 g.L^{-1} solid to liquid ratio and leaching time of 180 min. The results indicated that after 180 min, the Cu extraction efficiency increased from 45.8 to 89.1% by decreasing the particle size from 74-88 µm to less than 37 µm.

Effect of temperature

The influence of temperature on the dissolution of chalcopyrite was investigated at temperature of 30, 35, 40, and 45 °C at 40% $BmimHSO_4$, 30% H_2O_2, 10 g.L^{-1} solid to liquid ratio, particle size of less than 37 µm, and leaching time of 180 min. Results showed that the copper recovery increases as the temperature increases. Also, was observed that the improvement of $CuFeS_2$ dissolution by increasing temperature in the range of 30 to 40 °C was more significant than in the range of 40 to 45 °C.

Kinetic model of dissolution in ionic liquid

*I*nvestigation of kinetic models showed that dissolution of $CuFeS_2$ using $BmimHSO_4$ in it, is well described by Shrinking Core Model (SCM). Also, results of leaching kinetics study using SCM demonstrated that the leaching process using $BmimHSO_4$ does not follow the diffusion-controlled reaction and the results fit better with the chemical reaction-controlled mechanism. Under these circumstances, the calculated activation energy was 46.63 kJ/mol. Moreover, the orders of reaction with respect to BmimHSO4 and H_2O_2 concentration, solid to liquid ratio, particle size were estimated to be 0.539, 0.933, -0.676 and -1.108, respectively, and the obtained Arrhenius constant was 0.26×10^6. Finally, the kinetic model for $CuFeS_2$ leaching using $BmimHSO_4$ in the presence of H_2O_2 oxidative agent is obtained as Equation 1.

$$1-(1-x)^{\frac{1}{3}}=0.26\times10^{6}[BmimHSO_4]^{0.54}[H_2O_2]^{0.93}\left[\frac{s}{l}\right]^{-0.68}[size]^{-1.11}\exp\left(\frac{-46625.74}{RT}\right)t \qquad (1)$$

CONCLUSIONS

In the current study, the effects of leaching operational parameters, i.e. $BmimHSO_4$ concentration, H_2O_2 concentration, solid to liquid ratio, temperature, and particle size on leaching of $CuFeS_2$ were investigated. The results are summarized as follows:

• The highest Cu extraction was achieved using 40% $BmimHSO_4$, 30% H_2O_2, and10 g.L^{-1} solid to liquid ratio for particle sizes less than 37 µm and 45 °C for leaching time of 180 min.

• It was found that the increase in $BmimHSO_4$ and H_2O_2 concentration, and temperature content, as well as the decrease in solid to liquid ratio and particle size, contribute to the dissolution of chalcopyrite.

• Results of $CuFeS_2$ leaching kinetics study using SCM demonstrated that the leaching process using $BmimHSO_4$ does not follow the diffusion-controlled reaction and the results fit better with the chemical reaction-controlled mechanism. The calculated activation energy was 46.63 kJ/mol.

• The orders of reaction with respect to $BmimHSO_4$ and H_2O_2 concentration, solid to liquid ratio, particle size were estimated to be 0.539, 0.933, -0.676 and -1.108, respectively. Under these circumstances, the calculated Arrhenius constant was 0.2596×10^6.

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