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Dissolution kinetics of smithsonite ore in ammonium chloride solution

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Abstract

The results of a dissolution kinetics study of smithsonite ore in ammonium chloride are presented. Effect of stirring speed, ore particle size, reaction temperature, and the concentration of ammonium chloride on zinc dissolution rate are determined. The results obtained show that leaching of about 91.2% of zinc is achieved using 84–110 μm ore particle size at a reaction temperature of 90 °C for 240 min reaction time with 5 mol/L ammonium chloride. The solid/liquid ratio was maintained constant at 1:10 g/mL. Leaching kinetics indicates that chemical reaction at the new particle surface and the diffusion through the inert particle pores together are the rate control steps. A corresponding mixed control model is found suitable to explain the relationship between the reaction time and the fraction of zinc leached. The apparent activation energy of this process is determined to be 21.3 kJ/mol.

Keywords: Chloride hydrometallurgy; Kinetics; Ammonium chloride; Smithsonite; Leaching

1. Introduction

It is well known that sulfuric acid is often used as the leaching reactant in most of the hydrometallurgical processes. However, other reactants, such as ammonia with or without sulfate or carbonate, nitric acid, caustic soda and chlorides, can be considered [1]. Nowadays, hydrometallurgy in ammonium chloride solution has been considered as a prospective medium for extracting nonferrous metals [2]. The reason probably lies in its advantages of both ammonia metallurgy and chloride metallurgy. Firstly, many minerals such as ZnO, PbO, CuO and Ag, can easily dissolve into the solution, because of the high complexation characteristics of both ammonia and chloride ions. In addition, due to the relatively high pH (6–7) of the medium, impurities such as Fe_2O_3, SiO_2, CaO and MgO are not soluble in the resulting solution. Thirdly, the purification of the leaching solution becomes very simple, since either metallic powder reduction or solvent extraction can be used [8,9]. Finally, treating the ore with high alkaline gangues in ammonium chloride

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solution will not cause excessive consumption of leaching reagent and so much trouble with filtration, as is the case in sulfuric acid media [3–5].

A typical example of using ammonium chloride as a leaching medium is the CENIM-LNETI process [2,6–8] in which a heated and concentrated ammonium chloride solution is used to extract valuable metal elements from complex zinc sulfide ores. The results show that, at 105 °C, 150 kPa oxygen partial pressure, and two countercurrent stages, the extractions of all important metal values, such as Zn, Pb, Cu and Ag, are above 95%. The advantages of the process also lie in the fact that the resulting solution is totally free of iron, as a consequence of the high pH value at which leaching takes place; other impurities such as As, Sb, Bi and Sn are found only at trace levels. The pregnant solution is cooled to crystallize $PbCl_2$; after separating Cu and Zn with solvent extraction, these metals are selectively stripped into sulfate solution for electrolysis.

The CENM-LNETI process is, however, not a fully chloride metallurgy process, because the solution medium is finally changed to sulfate system. As would be reasonably expected, the change of solution medium can bring about a number of complications. To break through this limitation, we have developed a process [9] in which smithsonite is leached with ammonium chloride, and then after purification with zinc powder, the result solution containing about 40 g/L zinc is directly electrolyzed in ammonium chloride media with the addition of ammonia. High purity cathode zinc (>99.998%) can be obtained with a relatively low consumption of electrical energy (about 3100 kW h/t zinc). What is more, the gas evolved at the anode is N_2 rather than Cl_2. This means that this process is more environment friendly.

In this paper, the results of leaching of smithsonite ore with ammonium chloride are presented. The kinetics characteristics of the leaching process are analyzed. A corresponding mixed control model is found suitable to explain the relationship between the reaction time and the fraction of zinc leached; and the apparent activation energy of the process is determined.

2. Experimental

2.1. Materials and apparatus

Smithsonite ore from Guangxi province of China was used. After being ground and dry sieved, the ore was analyzed in the Analysis and Detecting Center of the Central South University, China. Table 1 shows the chemical analysis of the ore, while Table 2 shows the mineralogical composition. The tables show that smithsonite ($ZnCO_3$) was the major mineral. In fact, ammonium chloride could only attack smithsonite ($ZnCO_3$) and part of ZnS and $ZnSiO_3$.

Industry grade ammonium chloride with a content of 99.2% was used in this study. The reaction between zinc ore and ammonium chloride solution was performed in a 2000-mL round-bottom flask with 3 holes, placed in a thermostatically controlled water bath. Because, at high temperature, there would be a very high water vapor pressure above the liquid phase with the possibility of water loss, a condenser was placed in one of the holes and the other holes were sealed to prevent water loss.

2.2. Procedure

150 g of the smithsonite ore of required size was added at one time to the agitated 1500-mL ammonium chloride solution of the required concentration at the required temperature. At an interval of every 30 min, 5 mL solution sample was taken out using a volumetric pipet. Each sample was then filtered and washed. The solids corresponding to that volume were discarded. Finally, the sample of filtrate was chemically analyzed to determine zinc content at a certain time. Consequently, the solid/liquid ratio was maintained constant at 1:10 g/mL.

Table 1
Chemical analysis of the ore

Element	Zn	Cu	Pb	Cd	Co	S	Al_2O_3	SiO_2	Fe_2O_3	CaO
Content (wt.%)	30.28	0.011	0.51	0.081	0.0029	0.40	20.72	15.32	10.15	2.13