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Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore

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ABSTRACT

Affecting factors, such as ore size, leaching temperature, holding time, alkaline concentration and liquid: solid ratio (volume/weight) (L/S), were studied to leach refractory hemimorphite [$Zn_4(Si_2O_7)(OH)\cdot H_2O$] zinc oxide ores with NaOH solution in this paper. The impact of leaching recovery of Zn and its concomitant metals was checked through experiments. Results showed that when the ores of 65–76 μm size were leached for 2 h at 358 K in the presence of 5 mol/L sodium hydroxide and liquid:solid ratio of 10:1, the leaching rate of Zn, Al, Pb and Cd were about 73%, 45%, 11% and 5%, respectively, but that of Fe was less than 1‰. Moreover, the leaching experiments were repetitive and reliable. And the kinetic study indicates that the calculated activation energy is 45.7 kJ/mol, which illuminates that alkaline leaching the refractory hemimorphite [Zn_4 $(Si_2O_7)(OH)*H_2O$] zinc oxide ores is controlled by the chemical process of the reaction of leach liquor and ores in the whole leach process.

1. Introduction

Nowadays, new technologies to produce zinc metal from oxidized zinc ores are being developed as it is becoming more difficult to find new sphalerite mines. Oxidized ores contain zinc in various carbonate and silicates minerals, such as smithsonite ($ZnCO_3$), hydrozincite ($2ZnCO_3\cdot 3Zn\ (OH)_2$), zincite (ZnO), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2\cdot H_2O$) and so on.(Shirin et al., 2006; Navidi Kashani and Rashchi, 2008).

Now, extensive study has been carried out on the treatment of zinc silicate ores by hydrometallurgical and pyrometallurgical methods(Qin et al., 2007). Though the pyrometallurgical process can treat low-grade ores, it is difficultly accepted because of heavy pollution, high consumption of energy and high capital investment (Choi et al., 1993).

Abdel-Aal and Shukry (1997) and Feng and Yang (2007) found Zn and many other metals, such as Fe, Ca, Mg, and SiO_2, etc, were dissolved from zinc oxide ores with sulfuric acid. Various flocculating agents have been tried to coagulate the silicic acid from the slurry (Dufresne, 1976; Abdel-Aal, 2000; Ikenobu, 2000). De Wet and Singleton (2008) and Gnoinski (2007) used Skorpion sulphuric acid process to extract zinc from non-sulphide (commonly called zinc oxide) ores. Iron cannot be easily stripped from the organic phase in the process of solvent extraction although silica can be precipitated by adding $CaCO_3$. Moreover, it was a longer process route. Frenay (1985) found that sulfuric acid leaching is not advisable for the processing of ores because silica gel is formed and causes great problems in solid–liquid separation and these ores consume too much acid. And he convinced that caustic soda leaching could be more convenient than sulfuric acid to process some kinds of ores including oxidized zinc ores.

To this day, more has been published as related to an alkaline treatment of low grade zinc oxide ores or dust partly because Fe can't be leached and silica gel can't be formed during the process. Zhao and Stanforth (2000) and Feng and Yang (2007) studied the production of zinc powder by alkaline treatment of smithsonite ores. Over 85% of both Zn and Pb, and less than 10% of Al can be leached from the ore, respectively, when the leaching operation is conducted at over 95 °C using 5 mol/L NaOH solution as leaching agent. Zhao and Stanforth (2004) reported that electric arc furnace dust containing zinc was also directly contacted with 5 mol/L NaOH solution.

Mineralogical studies showed that smithsonite($ZnCO_3$) can be completely leached but hemimorphite($Zn_4Si_2O_7(OH)_2\cdot H_2O$) is relatively refractory to leaching (Frenay,1985). Moreover, there are less reports on leaching zinc oxide ores containing hemimorphite without smithsonite ($ZnCO_3$) with alkaline solution. Thus, the objective of this research was to study the extraction of zinc and its concomitant metals using alkaline solution and the kinetics of leaching process. After removing silicon by adding lime, zinc oxide can be crystallized by decompositing the pregnant solution through dilution, and NaOH leaching solution can be regenerated by condensing the mother liquor, but it would be discussed later.

2. Experimental

2.1. Materials

The zinc oxide ores used in the present study were from Lanping town in Yunnan Province of China. The particle size distribution and chemical analysis of the concentrate were shown in Table 1. The major

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Table 1
Chemical analysis of different sieve fractions of zinc oxide ore.

Serial no.	Size/μm	Fraction/ wt.%	Chemical analysis/%				
			Zn	Pb	Cd	Fe	Al
1	630–1000	0.71	23.3	0.32	0.02	28.9	1.22
2	450–630	3.60	22	0.43	0.02	29.6	1.28
3	105–150	6.90	23.3	0.4	0.02	29	0.93
4	76–105	14.35	24.9	0.39	0.02	28.6	0.98
5	65 –76	20.19	26.2	0.38	0.02	26.1	1.23

amount (20.19%) of the concentrate was very fine size (between 65 μm and 76 μm) whereas the three size fractions viz. 630 μm–1000 μm, 450 μm–630 μm and 105–150 μm were almost in equal amounts. The fraction 76 μm–105 μm was in minor amount (14.35%). Zn, Pb, Cd and Al contents in all the size fractions were similar. The oxidized zinc ores were characterized by X-ray powder diffraction analysis using CuK_a radiation in a Philips Model 1010. The different diffraction peaks were analyzed for various phases and compared with the ASTM standard, as shown in Fig. 1. X-ray diffraction (XRD) analysis showed the zinc-bearing minerals such as hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) and quartz ($SiO_2$) as the major components in raw ores. But Pb, Cd and Al were present in trace amounts from chemical composition analysis.

2.2. Experimental procedure

Leaching experiments were carried out in a closed polyethylene vessel in a water bath, which was placed on a thermostatically controlled magnetic stirrer. The leaching of the ground ore (− 0.076 + 0.065 mm) was carried out in a 50 g batch using 20 g NaOH, whose molar concentration was l–6 mol/L. L/S was kept from 6 to 12. The desired amount of ores was added to 0.1 L leaching solution containing a known amount of alkaline maintained at the required temperature. Temperature was monitored and controlled by passing water through the bath. L/S was maintained by adding additional water. The stirring recovery was held at 400 rpm. Variables, such as alkaline concentration, temperature, time of leaching and L/S, were studied. After completion of the leaching, the hot slurry was filtered with Whatman 41 filter paper in a Btickner funnel. The residue was washed with 0.1 mol/L diluent NaOH solution. Zn content in the solution was determined. Zn in the filtrate was analyzed titrimetrically using standard methods. The concomitant metals were analyzed with an atom absorption spectrophotometer AAS 1 N (Zeiss Jena, Germany). The samples were chemically analyzed for Zn and its concomitant metals content. Their leaching recovery (η_{Me}) was calculated according to the following equation:

$$\eta_{Me} = \frac{C_{Me} \times V}{m \times C^0_{Me}} \times 100\%$$

Where, η_{Me} (%) is the leaching recovery of metals, C_{Me} (g/L) the metals concentration of leaching solution, V (L) the leaching volume, C^0_{Me} (%) the metals content of the zinc oxide ore, m (g) the mass of the zinc oxide ore.

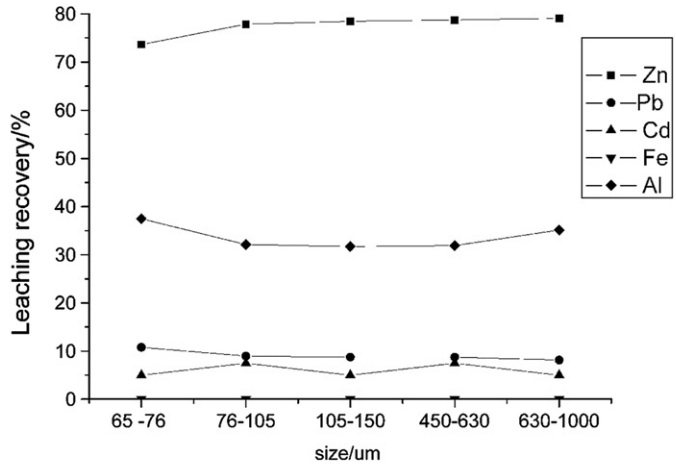

Fig. 2. Effect of particle size on leaching recovery.

In the kinetic tests, 20 g of ore was added to the 1500 mL of 5 mol/L sodium hydroxide solution at a fixed temperature. The temperatures studied ranged from 298 K to 358 K and the ore size from −240 to + 200 mesh (65–76 μm). L/S was kept at 75:1. The fraction (R) of zinc reacted at any time, t, can be calculated from the following equation:

$$R = \frac{C_{Zn} \times 1000}{10 \times 0.262 \times 1000}$$

3. Results and discussion

The effects of particle size, alkaline concentration, leaching temperature, holding time and L/S on the leaching recovery of Zn and its concomitant metals, such as Al, Pb and Cd, from zinc oxide ore were carried out.

3.1. Effects of ore particle size

The effect of particle size on the leaching of metal from the zinc concentrate was studied. In these experiments, the initial alkaline concentration 5 mol/L, leaching temperature (358 K), L/S 10:1 and leaching for 2 h were maintained as shown in Fig. 2. The results of Fig. 2 showed that Zn leaching recovery kept at the level between 79% and 77% when ores size was more than 76 μm. With the decrease of ores particle size, Zn leaching recovery decreased a little. When ores size was between 65 μm and 76 μm, Zn leaching recovery arrived the lowest at 73.65%. While for Al, its leaching recovery kept at the level between 35% and 32% when ores size was more than 76 μm, and it increased to 34.47% when ores size was between 65 μm and 76 μm.

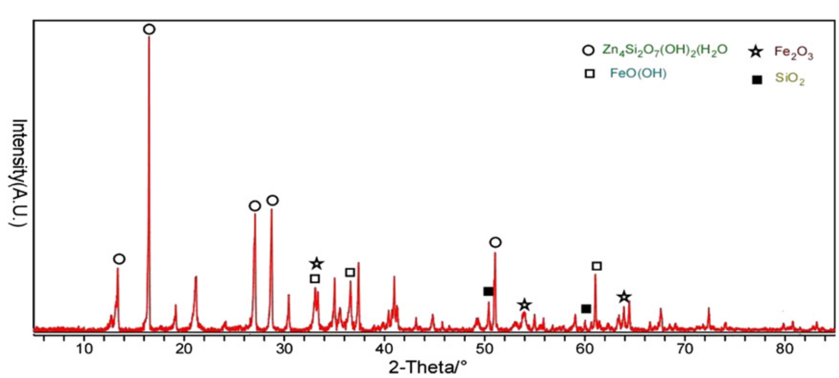

Fig. 1. XRD patterns of zinc oxide ore.