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Reductive leaching of zinc and indium from industrial zinc ferrite particulates in sulphuric acid media

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Abstract: Zinc ferrite is the principal constituent in zinc neutral-leach residue (NLR) which is commonly treated by hot-acid leaching in electrolytic zinc plants. Reductive leaching of zinc ferrite with sphalerite concentrate as a reducing agent was performed. It was found that leaching of zinc ferrite in the presence of sphalerit concentrate was a viable process that effectively extracted zinc and indium and converted Fe^{3+} into Fe^{2+} at the same time. Reflux leaching tests by two stages were performed to achieve extractions of 98.1% for zinc and 97.5% for indium, and a Fe^{2+}/Fe^{3+} molar ratio of 9.6 in leach solution was also obtained. The leaching behaviors of other elements, such as iron, copper and tin were also studied. The results showed that iron and copper were completely leached, whereas tin presented lower extraction values.

Key words: reductive leaching; zinc ferrite; zinc; indium; sphalerite concentrate

1 Introduction

Indium is an important metal used in electrical industries extensively [1,2]. It is mostly associated with zinc ores, and has therefore been recovered as a by-product of zinc metal processing operations. The modern extractive metallurgy of zinc is dominated by the roast−leach−electrowin (RLE) process. Sphalerite present in sulfide ores is the main mineral source for the zinc and indium production [3]. In sphalerite concentrates, iron is present as: 1) in iron sulphide minerals (pyrite FeS_2, pyrrhotite FeS, chalcopyrite $CuFeS_2$, etc.), and 2) a substitute of zinc in sphalerite (Zn, Fe)S. During oxidative roasting, nearly all the iron in the sphalerite concentrate are converted to zinc ferrite which is a stable composition [4,5]. Under the mild conditions of temperature and acidity employed in the neutral-leach stage, zinc ferrite remains almost inert. The neutral leaching residues (NLR), usually contain 25% of zinc, 30% of iron (mass fraction) as well as a few hundred parts per million of indium, which is an important resource for recovery of indium and zinc [6].

The Waelz kiln process is the traditional way to recover zinc, indium and lead from the NLR, and nearly 95% of zinc and 80% of indium can be recovered. It has obvious disadvantages: high consume of energy, causing air pollution, the resulting slag causing eco compatibility problems [7−9]. The hot acid leaching is another conventional method to recover valuable metals from the NLR [10]. By dissolution of the NLR, ferric ion is released. However, the high concentration of ferric ion decelerates the dissolution rate of zinc ferrite [11,12]. Also, it is difficult to separate and recover zinc and indium from acidic ferric sulfate solution.

Besides the two methods mentioned above, the reductive leaching is another effective method to extract zinc and indium from the NLR. Many researchers have noted that the reducing conditions in the leaching process could improve dissolution rates of zinc from zinc ferrite [13−15]. Various electrochemical studies also have confirmed it [16,17]. Furthermore, indium can be selectively extracted by direct solvent extraction after iron reduction [18,19]. The remove of iron from sulfuric solution by the reduction of ferric to ferrous, and then oxidation and precipitation of ferrous iron as hematite

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would solve the problems in jarosite process [20,21].

The leaching of sphalerite concentrate with ferric iron has been studied in acidic solution [22−25]. In the leaching process of sphalerite concentrate with ferric iron, zinc and iron are dissolved, and the ferric iron is simultaneously reduced to ferrous iron. The spalerite concentrate can be used as a reducing agent to reduce the ferric iron and then be leached at the same time. In this work, the reductive leaching behavior of zinc and indium from the NLR using sphalerite concentrate as a reducing agent has been investigated. The aim is to provide an effective method to recover zinc and indium from the NLR by reductive leaching.

2 Experimental

2.1 Materials

The NLR and sphalerite concentrate were received from Yunnan Province of China. The particle size analysis of the used NLR and sphalerite concentrate is given in Table 1. The chemical compositions of the two materials are listed in Table 2.

Table 1 Particle size distribution of NLR and sphalerite concentrate

NLR		Sphalerite concentrate	
Size/μm	Cumulative percentage passed/%	Size/μm	Cumulative percentage passed/%
150	100.0	75	100.0
105	90.9	63	80.8
75	69.3	53	54.5
63	35.1	45	23.6

X-ray diffraction of the NLR indentified zinc ferrite ($ZnFe_2O_4$) and zinc silicate ($ZnSiO_3$) as the main mineral components in the residue (Fig. 1(a)), and sphalerite (ZnS), christophite ((Zn,Fe)S) and pyrrhotite (FeS) as the main mineral components in the sphalerite concentrate (Fig. 1(b)).

2.2 Methods

A five-necked, round-bottomed flask (2 L) was fitted with a mechanical stirrer, a sample collection, a pH/Eh meter and two condenser tubes were used as the leaching reactor. The flask was then immersed in a water bath and kept at the selected temperature with accuraay of ±1.0 °C. 1.14 L of leaching reactant was placed in the flask and heated to the desired temperature while being magnetically stirred (400 r/min). 100 g of the NLR and the required amount of sphalerite concentrate was then added to the reactor. In the preliminary investigations, 5 mL of the solution was withdrawn from the flask to determine the dissolved contents of zinc, indium, iron and the residual H_2SO_4 concentration. In other experiments, the dissolved contents were calculated from the solid chemical analysis.

Zinc was analyzed by complex titration with EDTA. The concentrations of ferrous ion were analyzed by complex titration with potassium bichromate. The concentration of ferric ion was determined by finding the difference between overall iron and ferrous ion concentrations. Indium, copper and tin concentrations were determined by ICP with mass spectrometric detection (Agilent 7900, USA). X-ray powder diffraction was carried out using Rigaku D/MAX 2500v diffractometer (Japan). The redox potential of solution

Table 2 Chemical compositions of NLR and sphalerite concentrate

Material	Zn	Fe	In	S	Cu	Pb	Sn	Ag)
NLR	30.61	31.4	0.067619	1.501	1.14	0.032	0.113	0.007314
Sphalerite concentrate	43.43	16.12	0.041345	33.59	0.66	0.021	0.069	0.004368

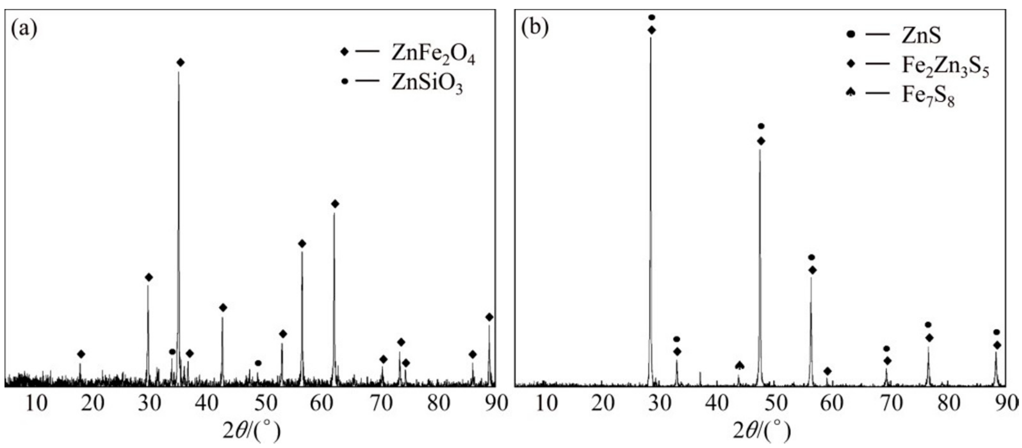

Fig. 1 XRD patterns of NLR (a) and sphalerite concentrate (b)