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Technical note

Leaching of low grade zinc oxide ores in nitrilotriacetic acid solutions

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ABSTRACT

A new method for the selective extraction of zinc from low grade zinc oxide ore in nitrilotriacetic acid solutions was proposed. A thermodynamic study indicated that the leaching process could be made efficient and selective by controlling the pH of the leaching solution. When low grade zinc oxide ore samples were leached in a 0.25 M nitrilotriacetic acid solution at 40 °C for 2 h with a liquid–solid ratio of 10 mL/g, the leaching ratios of zinc and iron were 91.0% and 4.1%, respectively. Additionally, the nitrilotriacetic acid was regenerated by adjusting the pH of the leaching solution after the leaching process.

1. Introduction

Currently, the main source of zinc metal is zinc sulphide ore. However, as zinc consumption increases and zinc sulphide ore grades decrease, the supply gap has been a major problem for the zinc industry (Abkhoshk et al., 2014; Ejtemaei et al., 2014). Therefore, the development of new technologies to produce zinc from zinc oxide ore has become an important research field in recent years.

Zinc is mainly extracted from zinc oxide deposits using hydrometallurgical methods. Basically, this process contains three steps, leaching, purification and electrolysis (Safari et al., 2009). During the leaching process, the most common leaching agent is sulfuric acid. However, for low grade zinc oxide ore, especially those with high contents of iron, calcium and silicon, excessive acid consumption and complex purification process have caused significant concerns (Xu et al., 2010, 2012).

The alkaline leaching process has attracted a great deal of attention due to its higher selectivity. Recently, extensive studies have been conducted on the treatment of zinc oxide ore by alkaline agents such as sodium hydroxide (Chen et al., 2009; Santos et al., 2010) and ammoniacal solutions (Ding et al., 2010; Liu et al., 2012a, 2012b; Yin et al., 2010). During the leaching process, OH^- and NH_3 serve as ligands by coordinating with Zn^{2+} to form soluble $Zn(OH)_i^{2-i}$ ($i = 1-4$) and $Zn(NH_3)_i^{2+}$ ($i = 1-4$) complexes, respectively. However, a relatively high leaching ratio can only be achieved under certain specific conditions, such as a large liquid–solid ratio or a high leaching agent concentration. This can be attributed to the low stability of zinc complexes that cannot completely dissolve insoluble zinc minerals (Yang et al., 2010). Therefore, it is imperative to identify new ligands (or leaching agents) for the treatment of low grade zinc oxide ore.

In this paper, a new ligand, nitrilotriacetic acid (H_3NTA), is proposed as a leaching agent for treating low grade zinc oxide ore. Nitrilotriacetic acid is well known as a metal chelate agent that has been successfully employed in the electrogalvanizing industry. With nitrilotriacetic acid as a leaching agent, NTA^{3-} can coordinate with Zn^{2+} to form soluble $Zn(NTA)_i^{2-3i}$ ($i = 1-2$) complexes. The formation constant of these zinc complexes is relatively high due to the effect of the chelate ring configuration. Therefore, the purpose of this study is to develop a novel hydrometallurgical process for the extraction of Zn from low grade zinc oxide ore that uses nitrilotriacetic acid as the leaching agent.

2. Experimental

2.1. Materials and analysis

The low grade zinc oxide ore investigated in the present study was from Lanping town in the Yunnan province of China. Prior to the leaching experiments, all of the samples were washed, dried, ground and sieved until their particle sizes were below 74 μm. The phases of the low grade zinc oxide ore samples were detected using X-ray diffraction analysis (Rigaku TTR-III) on a 2θ scale with Cu Kα radiation (λ = 1.5406 Å, 50 kV and 100 mA) at a scanning rate of 10°/min from 10° to 80°. The XRD pattern is shown in Fig. 1; it indicates that hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) and cerussite ($PbCO_3$) comprised the main mineral phase, and quartz (SiO_2) and calcite ($CaCO_3$) were identified as the main gangue components. The elemental composition of the samples was characterized using X-ray fluorescence (XRF, Rigaku ZSX Primus II), and the results are listed in Table 1. They show that the

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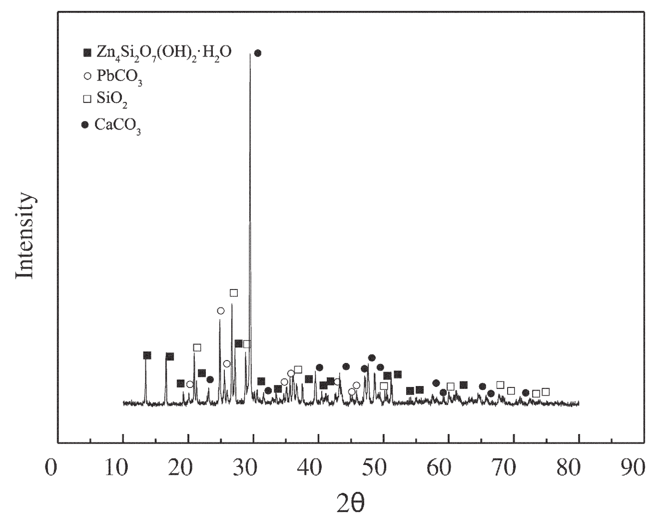

Fig. 1. The XRD pattern of the low grade zinc oxide ore samples.

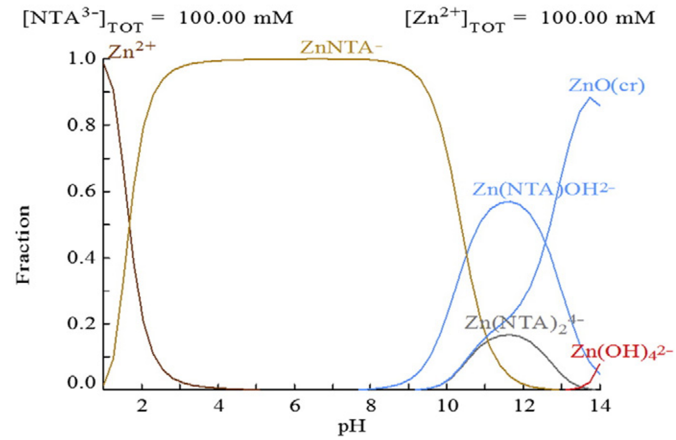

Fig. 2. The distribution of zinc species in the Zn^{2+}–NTA^{3-}–H_2O system as the pH varies.

main components of the low grade zinc oxide ore samples were Zn—10.82%, Fe—7.38%, Pb—7.80%, Ca—21.31% and Si—13.53%.

The zinc and iron contents of the leaching residues were determined using potassium dichromate titration and EDTA titration, respectively (Vogel, 2000). Their leaching ratios were calculated using the following equation:

$$\eta_{Me} = \frac{m_1 \times wt_1 - m_2 \times wt_2}{m_1 \times wt_1} \times 100\%, \tag{1}$$

where η_{Me} is the leaching ratio of a metal, m_1 and m_2 are the mass of the low grade zinc oxide ore and the leaching residue, respectively, and wt_1 and wt_2 are the metal contents of the low grade zinc oxide ore and the leaching residue, respectively.

2.2. Leaching experiments

The leaching experiments were conducted in a 250 mL three-neck flask immersed in a thermostatically controlled water bath and equipped with a mechanical stirrer, a thermometer and a reflux condenser. A total of 100 mL of the leaching solution was prepared using reagent-grade nitrilotriacetic acid and deionized water. The desired amount of ore was added to the leaching solution when the temperature reached the pre-set value. After the completion of the leaching experiment, the hot slurry was filtered, and the solid residue was dried at 363 K until a constant weight was obtained. The phases and elemental composition of the leaching residue were detected by XRD and XRF, respectively. The pH of the leaching solution was measured using a Mettler MT320-S pH metre with a LE438 electrode.

3. Results and discussion

3.1. Thermodynamic study of the Zn^{2+}–NTA^{3-}–H_2O and Fe^{3+}–NTA^{3-}–H_2O systems

To elucidate the predominant species in the leaching system, species distribution diagrams were constructed using Medusa (Puente-Siller et al., 2013). This software is based on an algorithm developed by Eriksson (Eriksson, G., 1979) that minimizes the Gibbs free energy of the equilibrium reactions that occur in an aqueous leaching system and determines the predominant species in the solution under specific conditions.

Fig. 2 shows diagrams of the distribution of zinc species in the Zn^{2+}–NTA^{3-}–H_2O system. It demonstrates that free Zn^{2+} accounts for most of the total zinc concentration when the pH is less than 1.0, and the $Zn(NTA)^-$ complex becomes the predominant species when the pH is between 3.0 and 8.0. It is worth noting that zinc oxide is present when the pH is greater than 9.0. This indicates that zinc ions in solution can be stabilized by NTA^{3-} but can also precipitate as oxides. During the leaching process, the formation of the soluble $ZnNTA^-$ complex improves zinc extraction. Therefore, the pH of the leaching solution should be kept below 9.0.

Fig. 3 illustrates the distribution of the iron species in the Fe^{3+}–NTA^{3-}–H_2O system. Obviously, the FeNTA complex is predominant when the pH is less than 2.0, and iron oxide predominates when the pH is greater than 6.0. Because the dissolution of iron during this leaching process is undesirable, the pH of the leaching solution should be kept above 6.0.

Based on this analysis, a leaching solution with a pH between 6.0 and 9.0 should be selected to ensure a selective and efficient leaching process.

3.2. Effects of the nitrilotriacetic acid concentration and the reaction temperature

The effect of the nitrilotriacetic acid concentration on zinc and iron extraction was studied. In these experiments, the leaching temperature

Table 1
The elemental composition of the low grade zinc oxide ore samples.

Component	O	Ca	Si	Zn	Pb	Fe	Al	S	Cu
Wt.%	34.24	21.31	13.53	10.82	7.80	7.38	1.66	0.39	0.03

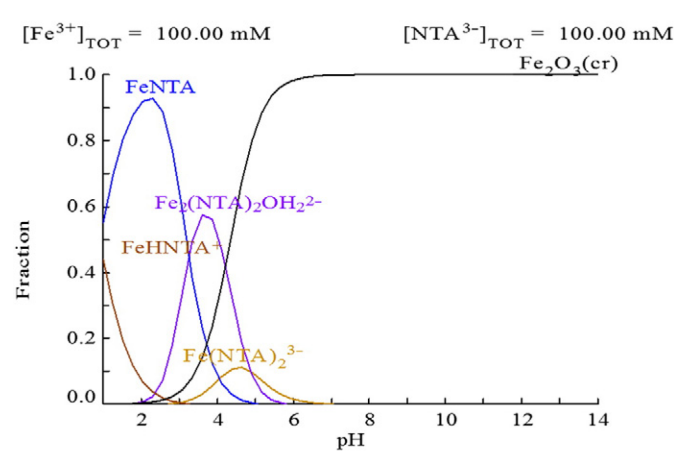

Fig. 3. The distribution of iron species in the Fe^{3+}–NTA^{3-}–H_2O system as the pH varies.