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Extraction of zinc from zinc ferrites by alkaline leaching: enhancing recovery by mechanochemical reduction with metallic iron

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Synopsis

This study evaluates the efficiency of using mechanochemical reduction to assist the extraction of zinc from zinc ferrites by alkaline leaching. The transition of zinc ferrite into a metastable state after mechanochemical reduction with metallic iron contributes to the ready dissolution of zinc from the activated zinc ferrites in alkaline solution. Zinc ferrites were mechanochemically reduced under conditions of Fe:$ZnFe_2O_4$ mole ratio of 2:1, using 5 mm diameter stainless steel balls as the activation medium at a mass ratio of balls to raw materials of 25:1. Subsequent leaching in 6 mol/L NaOH solution at 90°C resulted in more than 70% Zn extraction. These results may be used to further develop a hydrometallurgical process for recovering zinc from zinc ferrites in alkaline solution.

Keywords

zinc ferrite, mechanochemical reduction, metallic iron, alkaline leaching.

Introduction

Zinc is an important nonferrous metal required for various applications in batteries, solder, dielectric materials, and piezoelectric materials. High-grade, easily concentrated ores are becoming scarcer: to meet world demands for zinc, it is necessary to develop economical and environmentally safe metallurgical technologies that use secondary materials such as leach residues of roasted zinc concentrates and electric arc furnace dusts. The zinc in the majority of these wastes occurs in the form of zinc ferrite (franklinite, $ZnFe_2O_4$), which is very stable and insoluble in most acidic and alkaline solutions (Langová and Matýsek, 2009; Youcai and Stanforth, 2000).

Several pyrometallurgical and hydrometallurgical processes (Jankovi *et al.*, 2014; Langová and Matýsek, 2010; Morcali *et al.*, 2012; Shawabkeh, 2010) have been proposed for the treatment of zinc ferrites. Pyrometallurgical methods are costly owing to high energy consumption and their emissions of toxic gases are considered an environmental problem; hydrometallurgical methods are preferred for process economy and environmental reasons (Copur *et al.*, 2004).

Because of the need to eliminate elements such as Fe, Cd, Ni, and Co from the leachate and the high acid consumption incurred for the digestion of iron oxides, industrial-scale utilization of acidic leaching processes has been impeded. Only Zn and Pb dissolve effectively in caustic alkaline solution, so alkaline processes are often chosen to leach Zn and Pb selectively from Zn-bearing dusts and secondary resources (Youcai and Stanforth, 2001). However, it is difficult to extract zinc from zinc ferrite by NaOH solution under atmospheric pressure: the maximum reported extraction of zinc from decomposed zinc ferrite was only about 9%, after leaching in 10 M NaOH solution for 3 hours at 93°C (Xia and Pickles, 1999).

Youcai and Stanforth (2000) showed that the zinc ferrite structure could be broken by fusing it with sodium hydroxide: the dust was hydrolyzed in water and then fused with caustic soda at 350°C, following which 95% of the zinc was leached. However, in addition to leachable Zn, elements such as Fe and Ca may also react with sodium hydroxide during fusion of the zinc ferrite, resulting in high consumptions of this reagent.

Mechanical activation of minerals nowadays represents an important contribution to different fields of solids processing technology. Mechanical activation comprises high-energy ball milling, during which the particles undergo repeated fracturing and cold welding during collisions either between balls or between a ball and the inner wall of the mill (Gilman and Benjamin, 2009). In extractive metallurgy, activation by high-energy milling is reported to decrease the reaction temperature in pyrometallurgical processes and

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increase the leaching kinetics of several sulphide and oxide minerals in (Baláž and Ebert, 1991; Ping *et al.*, 2011; Tiechui *et al.*, 2010; Zhao *et al.*, 2009).

The aim of this study was to investigate the effect of using mechanochemical reduction with metallic iron on the extraction of zinc from zinc ferrites in alkaline solution.

Experimental

Materials

The zinc ferrites were provided by Nubiola Pigments Co., Ltd (Shanghai, China). X-ray diffraction (XRD) analysis confirmed their high purity (

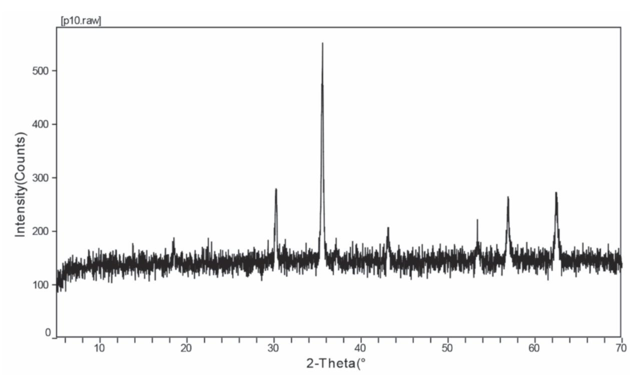

Figure 1—X-ray diffraction pattern of the zinc ferrite raw material

Mechanical activation and mechanochemical reduction of zinc ferrites

Mechanical activation or mechanochemical reduction of zinc ferrite was carried out using a planetary ball mill (QM-QX04, Nanjing NanDa Instrument Plant, China). Stainless steel balls with diameters between 1 mm and 5 mm were used as the grinding medium. The mass ratio of balls to ferrite was 25:1.

Alkaline leaching

Leaching of mechanically activated or mechanochemically reduced zinc ferrite was carried out in a flask placed on a thermostatically controlled magnetic stirrer. Zinc ferrite was added to 250 mL of NaOH solution and then leached at constant temperature. The volume was kept constant by adding water. The leach residue was thoroughly washed with NaOH solution and water and then dried. The zinc in solution was analysed by inductively coupled plasma atomic emission spectroscopy (ICP–AES). The percentage of zinc leached was calculated according to Equation [1]:

$$\text{Zinc extraction (\%)} = [(C_1 \times V_1)/(W_1 \times C_2)] \times 100\% \qquad [1]$$

where W_1 (g) is the mass of zinc ferrites; V_1 (L) is the volume of the leach solution; C_1 (g/L) is the zinc concentration in the leach solution; and C_2 (%) is the zinc content in the zinc ferrites.

Results and discussion

Direct alkaline leaching of $ZnFe_2O_4$

Zinc ferrite was leached in 6 M NaOH at 90°C. Less than 2% of the total zinc was released from the zinc ferrite (Figure 2), indicating that direct alkaline leaching is not an effective means of extracting zinc from this source.

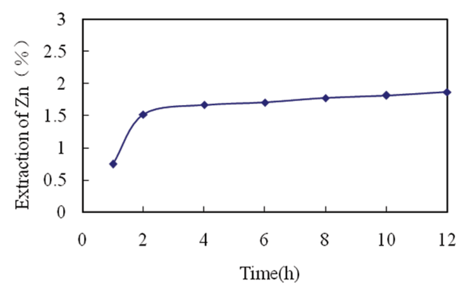

Figure 2—Direct alkaline leaching of $ZnFe_2O_4$ (temperature 90 °C; NaOH concentration 6 M; solids density (v/w) 25)

Alkaline leaching after mechanical activation

The results for the leaching of zinc ferrite that was mechanically activated in a planetary ball mill are shown in Figure 3. Compared with the non-activated sample, the zinc extraction increased slightly: about 13% of the contained zinc was released after 4 hours of mechanical activation.

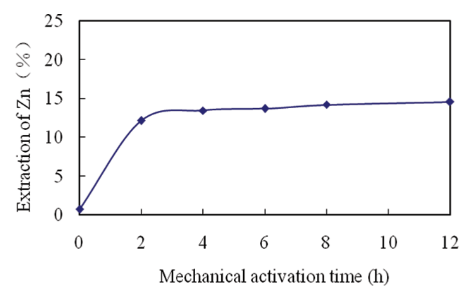

Figure 3—Effect of mechanical activation time on zinc extraction from $ZnFe_2O_4$

Alkaline leaching after mechanochemical reduction with metallic iron

Because the zinc was not extracted from zinc ferrites by alkaline leaching after mechanical activation, mechanochemical reduction with metallic iron was tested.

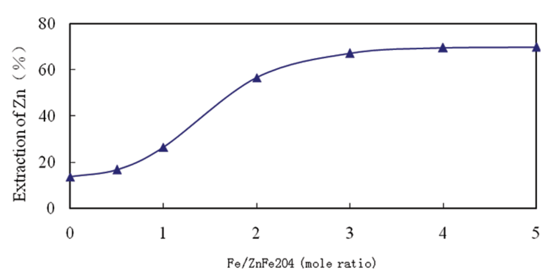

Figure 4—Effect of Fe:$ZnFe_2O_4$ ratio during mechanochemical reduction on zinc extraction during subsequent alkaline leaching

Effect of Fe:$ZnFe_2O_4$ ratio

The zinc ferrites were leached in 6 M NaOH at 90°C after 4 hours of mechanochemical reduction at different Fe:$ZnFe_2O_4$ ratios. The leaching efficiency increased considerably as the proportion of metallic iron increased (Figure 4). Maximum leaching efficiency was obtained when the Fe:$ZnFe_2O_4$ mole ratio exceeded 2:1.

XRD patterns of the $ZnFe_2O_4$ after grinding with Fe at different molar ratios for 6 hours are shown in Figure 5. The intensities of the main diffraction peaks of $ZnFe_2O_4$ tended to decrease as the Fe:$ZnFe_2O_4$ mole ratio increased. It is reported that mechanically induced structural changes in zinc ferrite cause its gradual transition into a metastable state (Boldyrev, 2006; Tkacova *et al.*, 1996) as a result of mechanically induced inversion and deformation of its octahedral geometry, which can be enhanced by the addition of metallic iron.

The chemical bonding environments of Fe2p, Zn2p in zinc ferrite after mechanochemical reduction were analysed by XPS, and the results are shown in Figure 6. As shown in Figure 6A, it was found that the binding energy for Fe 2p3/2 in zinc ferrite is 710.15 eV, which matches well with the Fe^{3+} components in $ZnFe_2O_4$ (Pan *et al.*, 2011; Bear *et al.*, 2001). After grinding with Fe, the peaks shift to lower positions by about 0.18–0.19 eV, which indicates that the content of Fe^{2+} is increased according to the reduction of Fe^{3+} to Fe^{2+} (Hou, 2014) .

The zinc spectra of mechanochemically reduced zinc ferrite in Figure 6B with the binding energies of $Zn2p_{3/2}$ and $Zn2p_{1/2}$ are measured as 1021.47 eV and 1044.58 eV, which is consistent with the XPS results for the standard $ZnFe_2O_4$ materials (Tahir and Upul Wijayantha, 2010.). The peak positions of $Zn2p_{3/2}$ and $Zn2p_{1/2}$ shift to the lower binding energy side after mechanochemical reduction with Fe, which is evidence for the decomposition of zinc ferrite and formation of $Zn_xFe_{3-x}O_4$ solid solution (Hou , 2014; Kaneko, 2004).

Effect of mechanochemical reduction time

The effect of mechanochemical reduction time on zinc extraction is shown in Figure 7. As expected, the rate of zinc leaching increased with an increase in reduction time. Maximum extraction was achieved after about 6 hours.

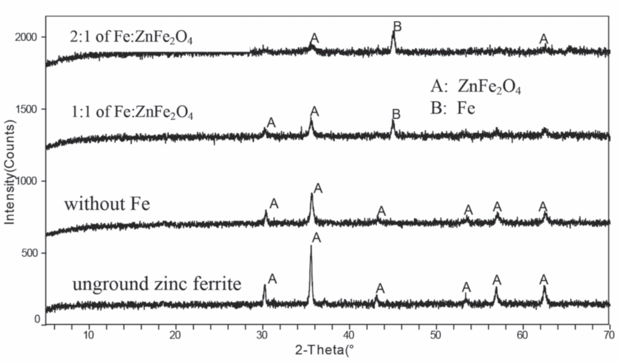

Figure 5—X-ray diffraction patterns of zinc ferrite after grinding with Fe at different molar ratios for 6 hours

Effect of milling rotational speed

In planetary ball milling, energy is supplied by the rotation of the mill. Different rotational speeds therefore supply different energies. This can significantly affect the reaction rate of the mechanochemical reduction.

The effect of rotational speed of the mill on zinc extraction is shown in Figure 8. Zinc extraction increased with increasing rotational speed: 70.38% extraction was achieved at speeds greater than 500 r/min.

Conclusions

Zinc in zinc ferrites can be leached in NaOH solution after mechanochemical reduction with metallic iron. A mechanically induced inversion and deformation in the octahedral geometry leads to the transition of zinc ferrite into a metastable state. Over 70% of the contained zinc was extracted from mechanochemically reduced zinc ferrites, compared with less than 2% extraction for alkaline leaching

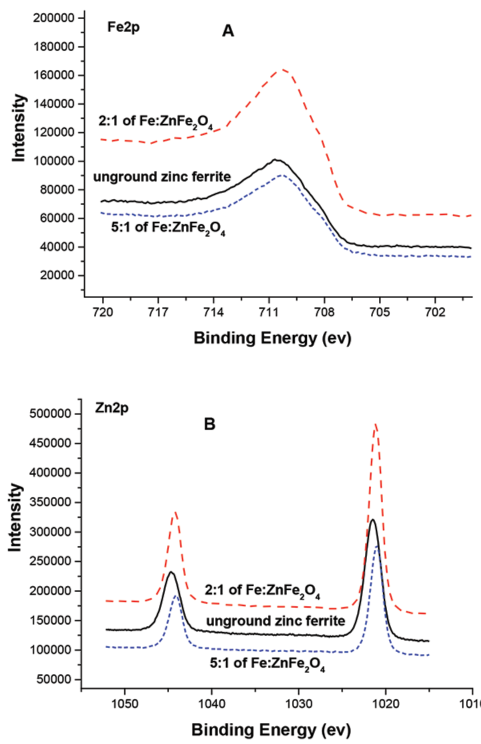

Figure 6—Fe2p, Zn2p spectra of raw and mechanochemically reduced samples

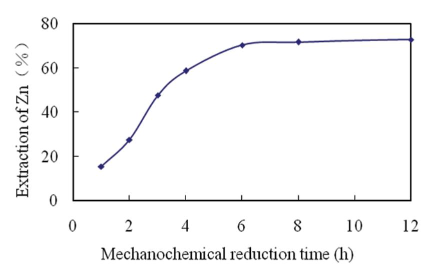

Figure 7—Effect of mechanochemical reduction time on zinc extraction from $ZnFe_2O_4$

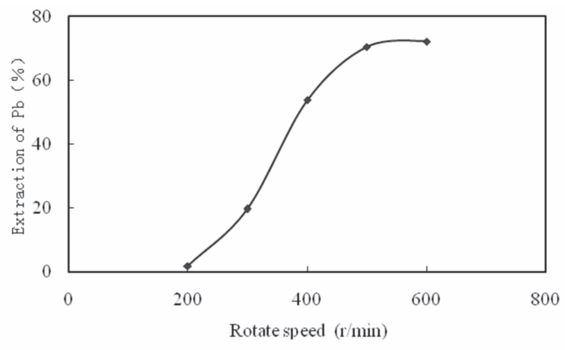

Figure 8—Effect of rotation speed on zinc extraction

of non-activated samples and 13% extraction for alkaline leaching of activated samples following 2 hours of planetary ball milling. The proposed alkaline leaching processes to recover Zn from zinc ferrite-bearing dusts and secondary resources can therefore be enhanced by mechanochemical reduction with metallic iron.

Acknowledgements

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