Flotation of a Low-Grade Zinc Oxide Ore After Surface Modification at High Temperature

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1.—State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China. 2.—Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China. 3.—e-mail: yongxingzheng2017@126.com. 4.—e-mail: jflv2017@126.com

There are abundant low-grade zinc oxide ores in Yunnan Province, China, but it is extremely difficult to recover Zn and Pb from them using traditional technology. They are often stockpiled during the exploitation of sulfide ores and high-grade zinc oxide ores and become a kind of solid waste. In this study, a novel methodology using surface modification by sulfidation and reduction at high temperature followed by flotation is proposed. Several factors, such as the sulfur dosage, roasting temperature, coal powder dosage and holding time, that affect the flotation performance of the Zn concentrate were examined in detail, and the optimum process parameters were determined. A flotation concentrate containing 32.1% Zn and 8.0% Pb was obtained with zinc and lead recoveries of 91.3% and 92.3%, respectively. To further interpret the surface modification mechanism of smithsonite, the surface morphology and constituents of the sample before and after reaction were investigated by electron probe microanalysis and thermodynamic calculations. The results showed that zinc sulfide was generated at the outer layer of the zinc oxide mineral after thermal modification, resulting in an improvement of the flotation performance. The purpose of the present study is to apply the surface modification technology previously applied to pure smithsonite to low-grade zinc oxide ore or solid waste to convert them into valuable resources.

INTRODUCTION

Zinc and lead are mainly extracted by pyrometallurgy or pyrometallurgy combined with pyrometallurgy.[1,2] With continuous exploitation of sulfide ores and high-grade zinc oxide ores, the remaining low-grade oxide ores, containing 1–10% Zn and 1–5% Pb, may be an important alternative.[3] However, recovery of valuable metals, especially Zn, from oxide ores is difficult because of their complex composition and high content of slime (particles < 10 μm in size).

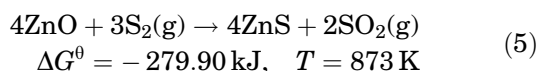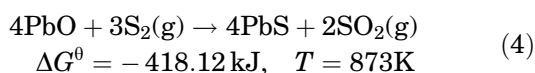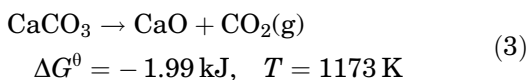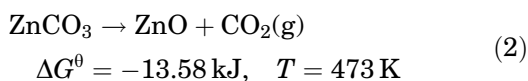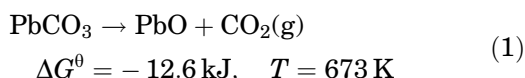Smithsonite ($ZnCO_3$) and cerussite ($PbCO_3$) are the main valuable minerals found in oxide ore. Flotation is the method most often applied commercially for concentrating Pb–Zn oxide minerals.[4,5] In the available literature, it was found that flotation with xanthate as the collector and Na_2S as the modifier is widely used for treating non-ferrous

oxide ores.[6–8] After being treated with Na_2S at a moderate dosage (400–3000 g/t), the hydrophilicity of the mineral surface decreases because of the presence of chemisorbed sulfide ions. In practice, sulfidation of zinc oxide minerals is difficult to achieve in contrast to sulfidation of copper and lead oxide minerals, often resulting in ineffective mineral processing. To improve zinc recovery, the sulfidation-amine flotation method can be used. However, the effectiveness of this method is unsatisfactory, especially in the presence of abundant slimes.[9,10]

By contrast, the sulfidation-xanthate flotation method is less sensitive to the slime. If an effective method to sulfurize zinc oxide mineral could be developed, the traditional flotation method using xanthate as the collector could be well applied to treat these pre-treated oxides. Wu et al.[11] found that the solubility of the smithsonite significantly

decreased in the presence of ammonium and sulfur ions, resulting in an increase in its flotation recovery of 25%. However, the flotation performance of zinc oxide ore with a complex composition was not described. Wang et al.[12] adopted a mechanical-chemical method to transform zinc oxides into zinc sulfides. Although a desirable level of sulfidation was obtained, the flotation response was not presented. Liang et al.[13] and Ming et al.[14] proposed hydrothermal sulfidation to convert zinc oxide material to sulfides, but its further application seemed to be difficult because of the slow transformation process and fine crystalline nature. Generally, high temperatures were advantageous for improving the reaction rate and crystallinity. Therefore, a roasting process was proposed to sulfurize zinc oxide minerals. In our previous studies,[5,15,16] a surface modification mechanism of the zinc oxide minerals was described, and it was confirmed that after surface modification at a high temperature, pure smithsonite exhibited an excellent flotation performance.

However, there are few reports on the flotation of low-grade zinc oxide ore after surface modification by sulfidation and reduction at high temperature. There are significant amounts of zinc oxide ore in Yunnan Province, China. In the past few years, sulfide ores and high-grade oxide ores have been continuously exploited while large quantities of low-grade mining ores have been produced. These ores have been stockpiled in the open air, becoming a type of industrial solid waste. The present study focused on applying the surface modification technology described in our previous studies to treat the low-grade zinc oxide ore. Smithsonite and cerussite were sulfurized by elemental sulfur, and calcite may be decomposed during the roasting, which can be described as follows:

$$PbCO_3 \rightarrow PbO + CO_2(g)$$
$$\Delta G^\theta = -12.6 \, kJ, \quad T = 673 \, K \tag{1}$$

$$ZnCO_3 \rightarrow ZnO + CO_2(g)$$
$$\Delta G^\theta = -13.58 \, kJ, \quad T = 473 \, K \tag{2}$$

$$CaCO_3 \rightarrow CaO + CO_2(g)$$
$$\Delta G^\theta = -1.99 \, kJ, \quad T = 1173 \, K \tag{3}$$

$$4PbO + 3S_2(g) \rightarrow 4PbS + 2SO_2(g)$$
$$\Delta G^\theta = -418.12 \, kJ, \quad T = 873K \tag{4}$$

$$4ZnO + 3S_2(g) \rightarrow 4ZnS + 2SO_2(g)$$
$$\Delta G^\theta = -279.90 \, kJ, \quad T = 873 \, K \tag{5}$$

In this article, surface modification of zinc oxide ore in the presence of sulfur and carbon was carried out, resulting in a hydrophobicity improvement of zinc and lead oxide minerals. After flotation with a conventional collector (xanthate), a Zn-Pb bulk concentrate was obtained. The surface changes of the zinc oxide minerals were investigated by EPMA and thermodynamic calculations to further interpret their modification mechanism.

EXPERIMENTAL

Materials

A representative sample was provided from a mine in Yunnan Province, China. The chemical composition of this sample, as shown in Table I, indicates a low-grade zinc oxide ore. The phase compositions of zinc and lead in the ore are shown in Table II, indicating a high oxidization ratio. Figure 1 shows the XRD pattern of the sample. It is observed that the main zinc oxide mineral was smithsonite and the major gangue was calcite and quartz.

Sulfur and coal powder (52% C) were applied as the sulfidation and reduction reagents, respectively. Sodium silicate as the modifier and copper sulfates as the activator were of chemical grades and purchased from the Komeo Chemical Reagent Co., Ltd., in Tianjin City. Butyl xanthate as collector and aerofloat as frother in the flotation tests were of industrial grades and purchased from the Xishan Beneficiation Reagent Plant in Yunnan Province.

Experimental Methods

The low-grade zinc oxide ore was ground to $-74 \, \mu m$ and then mixed with sulfur and coal powder at a desired weight ratio. The mixed sample was loaded into an alundum crucible equipped with a cover. The crucible was placed in a muffle furnace and heated. After a holding time of 30–90 min, the sample was cooled and used for flotation tests. The effects of parameters including the sulfur dosage, temperature, reduction reagent dosage and modification time on the Zn/Pb recovery were investigated in detail by flotation (roughing). The flotation behavior of the lead oxide after thermal modification in the presence of sulfur and carbon was similar to that of the treated zinc oxide.[3,17,18] Therefore, only the flotation performance of zinc oxide minerals was examined during the roughing. When the optimal modification conditions were determined, closed-circuit flotation tests were performed, as shown in Fig. 2. The concentrate and tailing were dried, weighed and analyzed. The surface changes of the zinc oxide mineral in the ore before and after thermal modification were investigated by EPMA line scanning and thermodynamic calculations.

Analytical Techniques

Chemical analyses were carried out to determine the elemental content. The sample was selectively dissolved and then examined using an ICP-AES (ICP, IRIS Intrepid II XSP). The phase changes of the sample before and after surface modification by

Table I. Chemical composition of the zinc oxide ore (%)

Element	Zn	Pb	Fe	SiO$_2$	CaO	Al$_2$O$_3$	MgO	S	P
Content	7.8	2.0	4.0	31.7	18.1	2.9	1.0	3.1	0.5

Table II. Phase composition of zinc and lead in the ore (%)

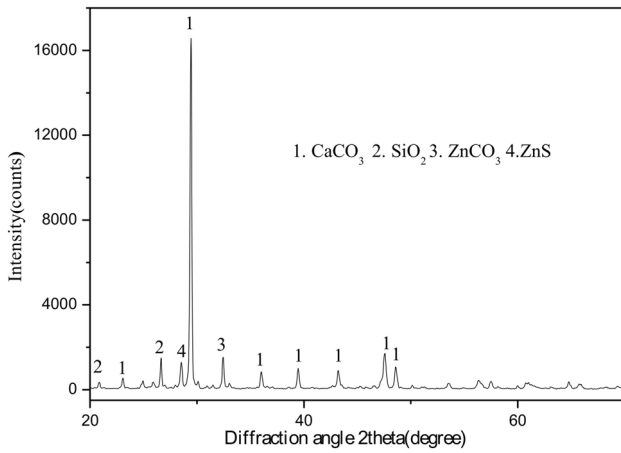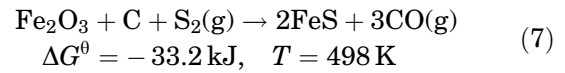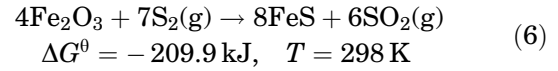| Constituent	Zinc	Lead
Carbonate/oxides	53.98	81.36
Sulfide	44.87	11.52
Others	1.15	7.12

Fig. 1. XRD pattern of low-grade zinc oxide ore.

sulfidation and reduction were examined on a Germany Bruker-AXS D8 Advance x-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). EPMA (JXA-8230) was used to determine the surface morphology and composition of the obtained sample before and after thermal modification. The acceleration voltage of the EPMA was set to 20 kV and the probe current to 20 nm using a focused electron beam.

RESULTS AND DISCUSSION

Flotation Tests of the Treated Zinc Oxide Ore

The dosage of the sulfidation reagent generally played an important part in the modification process of the Pb–Zn oxide mineral. Therefore, the dosage of the sulfidation reagent was initially investigated under the following conditions: particle size of − 74 μm (85%),coal powder dosage of 3%, modification temperature of 650°C and modification time of 60 min. The results are shown in Fig. 3a. It was observed that the Zn recovery increased from 79.6% to 87.7% and the Zn grade decreased from 30.9% to 28.8% when the sulfur dosage increased from 0% to 1%. The Zn grade and recovery only slightly changed when the sulfur dosage increased to 2%. With the further increase of the sulfur dosage, the Zn recovery increased somewhat more, but the Zn grade sharply decreased. These results may be explained by the fact that the surface of iron oxides can also be sulfurized by sulfur (Eqs. 6 and 7) and that the obtained iron oxide reports in the flotation concentrate along with zinc sulfides. Therefore, the optimal sulfur dosage was determined to be 1%.

$$4Fe_2O_3 + 7S_2(g) \rightarrow 8FeS + 6SO_2(g)$$
$$\Delta G^\theta = -209.9 \, \text{kJ}, \quad T = 298 \, \text{K} \quad (6)$$

$$Fe_2O_3 + C + S_2(g) \rightarrow 2FeS + 3CO(g)$$
$$\Delta G^\theta = -33.2 \, \text{kJ}, \quad T = 498 \, \text{K} \quad (7)$$

The effect of the modification temperature on the flotation performance of Zn concentrate is presented in Fig. 3b. It is observed that the Zn grade slightly fluctuated, but the Zn recovery continuously increased when the modification temperature increased from 350°C to 650°C. With the further increase of the temperature, the Zn recovery slightly fluctuated, but the Zn grade sharply decreased. These results could be explained by nonselective aggregation of the gangue at a high temperature, resulting in a poor flotation separation performance. Accordingly, the optimal modification temperature was determined to be 650°C.

Figure 3c shows the relationship between the flotation performance of Zn concentrate and coal powder dosage. It was observed that the Zn grade was nearly constant, but the Zn recovery increased from 84.3% to 86.8% when the coal powder dosage increased from 0% to 1%. Coal powder plays an important role in thermal modification, and the related reactions can be described as Eqs. 8 and 9.[1,19,20] The Zn grade kept constant and the Zn recovery slightly increased when the coal powder dosage increased to 3%. With the further increase of the coal powder dosage, the grade and recovery of zinc decreased. This result may be accounted for by the nonselective adsorption of flotation reagent on the surface of the reduction agent. Therefore, the optimal coal powder dosage was determined to be 1%.
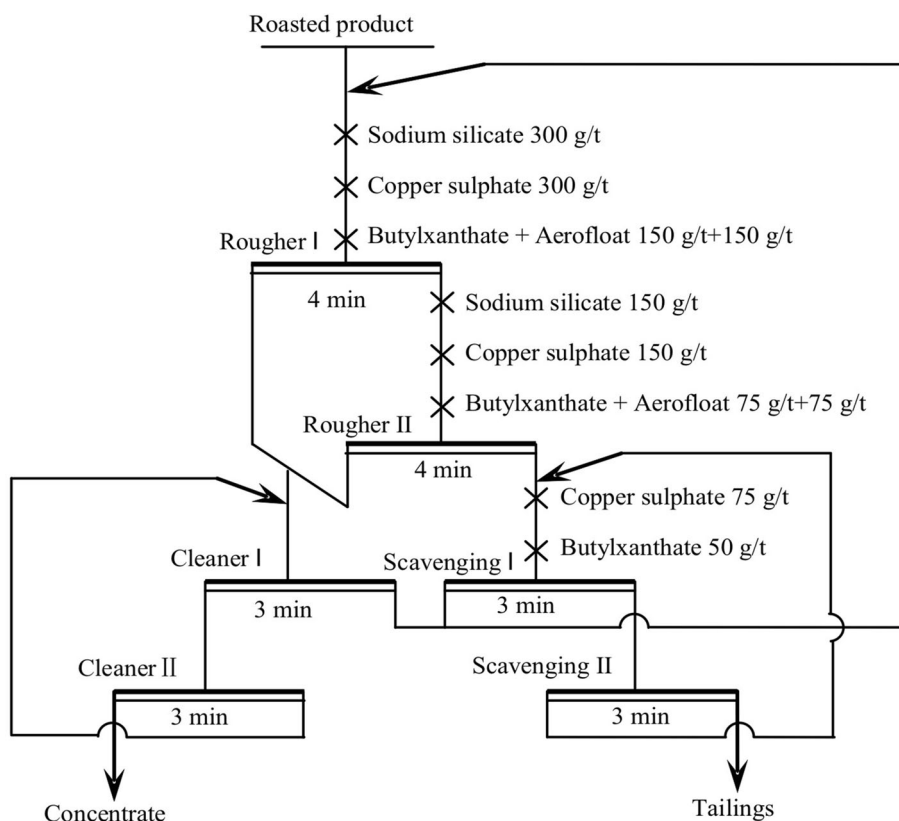
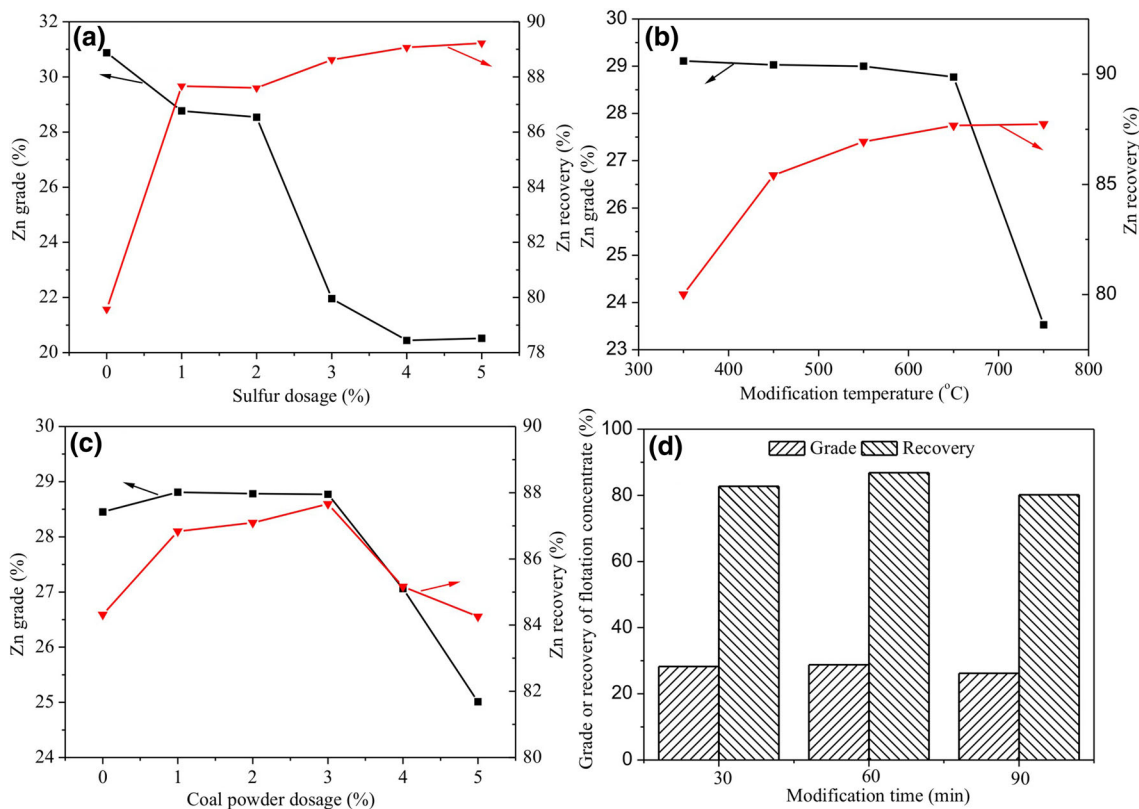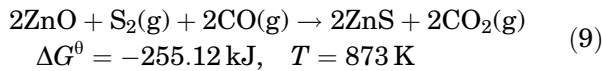Fig. 2. Closed-circuit flotation flow sheet of low-grade zinc oxide ore after surface modification.
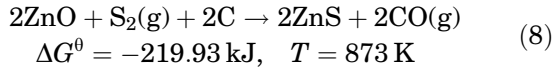

Fig. 3. Factors influencing the flotation performances: (a) effect of the sulfur dosage; (b) effect of the modification temperature; (c) effect of the coal powder dosage; (d) effect of the modification time.

Table III. Results of closed-circuit flotation experiments

Products	Yield	Grade		Recovery	
		Zn	Pb	Zn	Pb
Concentrate	21.7	32.1	8.0	91.3	92.3
Tailing	78.3	0.9	0.19	8.7	7.7
Feeding	100.0	7.6	1.9	100.0	100.0

$$2ZnO + S_2(g) + 2C \rightarrow 2ZnS + 2CO(g)$$
$$\Delta G^{\theta} = -219.93\,kJ, \quad T = 873\,K \tag{8}$$

$$2ZnO + S_2(g) + 2CO(g) \rightarrow 2ZnS + 2CO_2(g)$$
$$\Delta G^{\theta} = -255.12\,kJ, \quad T = 873\,K \tag{9}$$

The flotation performance of the Zn concentrate with respect to the modification time is presented in Fig. 3d. It was observed that the Zn grade slightly varied from 28.3% to 28.8% and that the Zn recovery increased from 82.8% to 86.8% when the modification time increased from 30 min to 60 min. With the further increase of the modification time to 90 min, the Zn grade had little change, but the Zn recovery decreased to 80.2%, which may be explained by the fact that the zinc sulfide films began to be oxidized with the consumption of carbon or carbon oxide. Therefore, the optimal modification time was determined to be 60 min.

Closed-Circuit Flotation Tests

After the optimal surface modification parameters at high temperature were determined, the flotation tests involving types and dosages of the floatation reagent and flotation time were examined. Finally, the closed-circuit flotation tests for the roasted material were carried out (Fig. 1), and the flotation results are shown in Table III. It was observed that a flotation concentrate containing 32.1% Zn and 8.0% Pb was obtained and that the zinc and lead recoveries were 91.3% and 92.3%, respectively. The XRD patterns of the flotation concentrate and tailing are shown in Fig. 4. It was observed that the flotation concentrate was mainly composed of sphalerite, galena and calcite, but the flotation tailing consisted of calcite. The peak of smithsonite disappeared, while the peak of sphalerite appeared in the flotation concentrate in contrast to the raw sample (Fig. 1). This result indicated that the smithsonite was decomposed to zinc oxide and then sulfurized by sulfur vapor (Eqs. 4, 5, 8, and 9). These results confirmed that the flotation performance of zinc concentrate was satisfactory and that the developed process was successful.
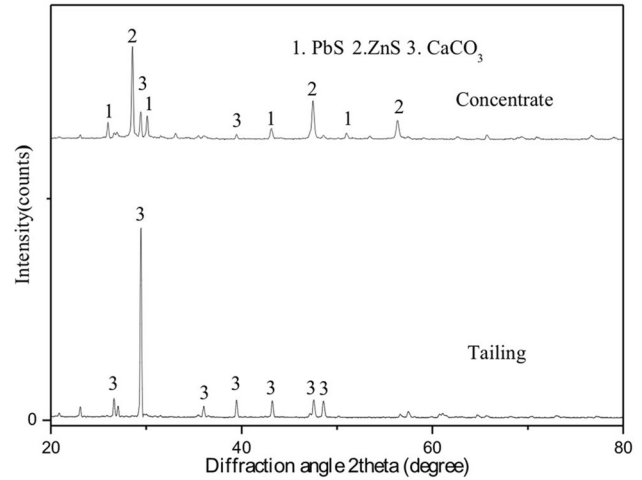

Fig. 4. XRD patterns of the flotation concentrate and tailing.

Surface Modification Mechanism of Zinc Oxide Ore

EPMA was carried out to investigate the surface modification mechanism of the zinc oxide ore, and the results are shown in Fig. 5. Figure 5a1 shows that the smithsonite occurred as a lump with smooth dissociation surfaces. The concentration of C, Zn and O at the surface of smithsonite slightly fluctuated (Fig. 5b1). In addition, zinc sulfide mineral was also found (Fig. 5a2), and the concentrations of S and Zn (Fig. 5b2) at the surface were close to that of sphalerite,[15] especially for a distance > 0.020 mm. When the raw ore was roasted at 650°C without any additive, the smithsonite after thermal treatment presented rough surfaces (Fig. 5c). Figure 5d shows that the carbon signal disappeared while the S concentration increased, on average, to 15% at the surface. Sulfur originated from iron sulfide in the raw sample, which was decomposed into sulfur vapor during the roasting, resulting in the occurrence of sulfidation reactions.[4,5] This result further confirmed that a Zn recovery of 79.6% was obtained when no sulfur was added (Fig. 3a). Figure 5e–f shows the results of the EPMA analyses for zinc oxide ore after roasting under optimal conditions. Comparing Fig. 5c–d, it is observed that the S concentration increased by > 15%, and the maximum concentration reached 25%, which was close to the S concentration of the zinc sulfide mineral (Fig. 5b2). Additionally, it was also observed that these formed surfaces were rough, which could be attributed to the uneven adsorption of sulfur vapor at the surface.

To further gain insight into the surface modification mechanism of the smithsonite, the equilibrium amounts of products were calculated using the Equilibrium Composition module of Out-okumpu HSC6.0,[21] as shown in Fig. 6. The calculations were performed in 1 kmol zinc carbonate, 0.5 kmol carbon
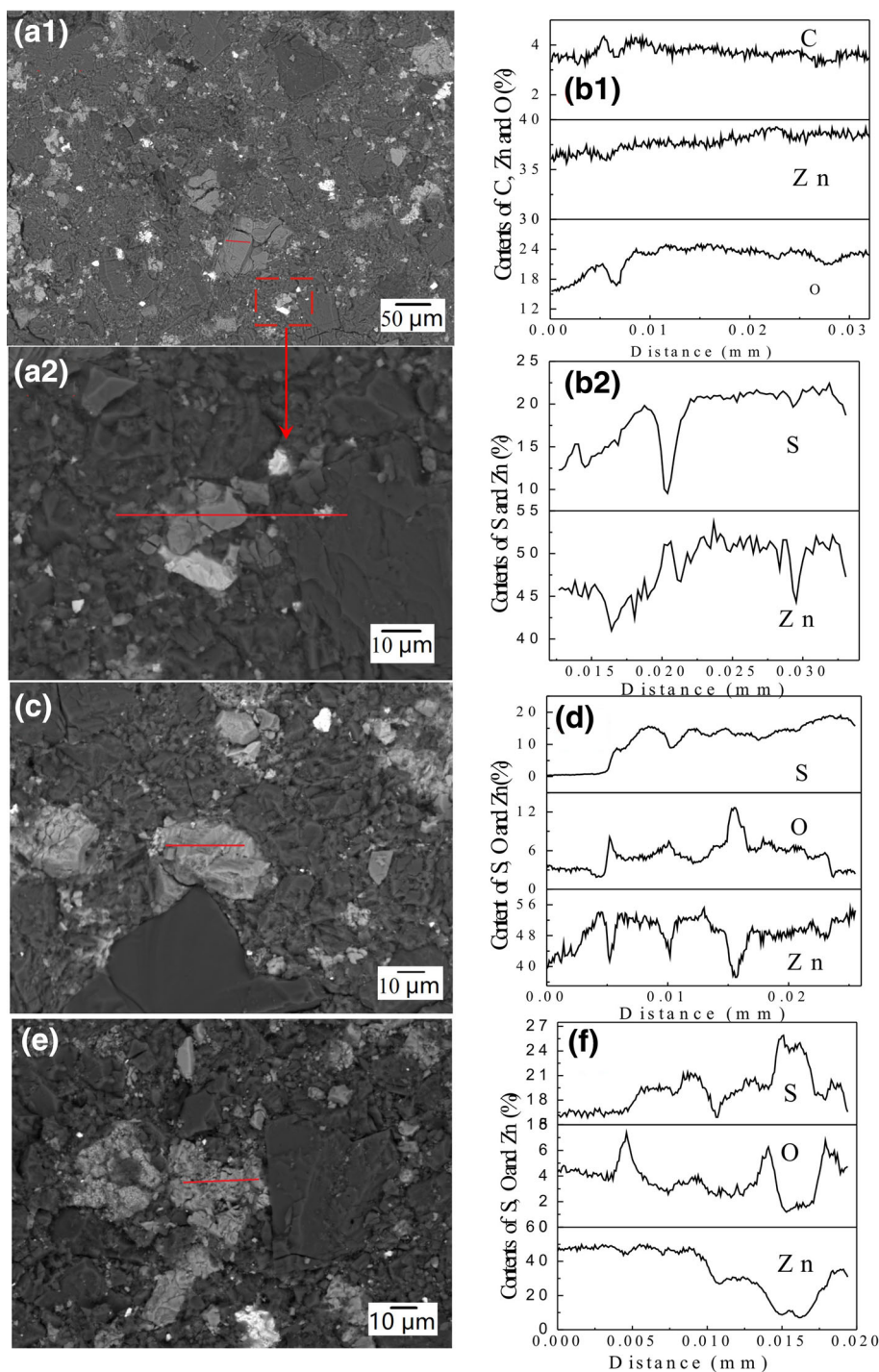
Fig. 5. EPMA line scan spectra of smithsonite before and after surface modification (a and b: raw sample; c and d: roasting without additive; e and f: roasting with 1% sulfur and 1% coal powder).

and atmosphere pressure of 1 bar at 650°C. It can be seen that the zinc oxide reacts completely with any amount of sulfur added: the amount of ZnS increased from 0.1 kmol to 1.0 kmol and the amount of the ZnO decreased from 0.9 kmol to 0 kmol when the sulfur dosage increased from 0.1 kmol to 1.0 kmol. These analyses further confirmed the results

obtained by XRD detection. In our experiments, the added amount of sulfur was 1%, and the mole ratio of sulfur to zinc carbonate is always much lower than 1. This finding further illustrated that the outer layer of the zinc oxide mineral, not the whole particle of the zinc oxide mineral, was transformed into zinc sulfide.
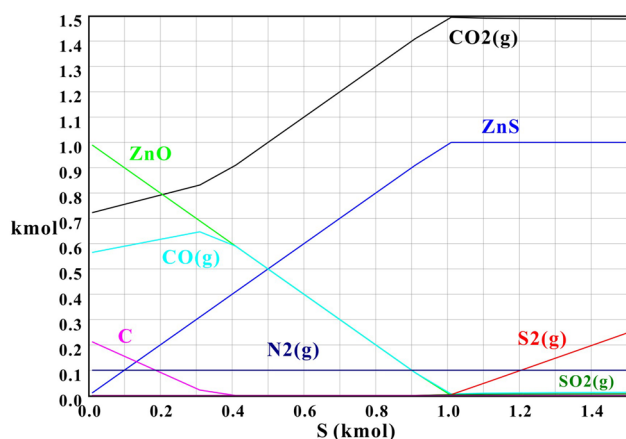
Fig. 6. Equilibrium amounts of the modification products as functions of sulfur dosage (1 kmol zinc carbonate, 0.5 kmol carbon, atmosphere pressure of 1 bar and 650°C).

CONCLUSION

Abundant low-grade zinc oxide ores have to be stockpiled because of the lack of effective technology to treat them, and they become a kind of solid waste. Flotation of the low-grade zinc oxide ore was achieved after surface modification by sulfidation and reduction at high temperature. A flotation concentrate containing 32.1% Zn and 8.0% Pb was obtained, and the Zn and Pb recoveries were 91.3% and 92.3%, respectively.

The optimum thermal modification parameters were determined to be a sulfur dosage of 1%, temperature of 650°C, coal powder dosage of 1% and modification time of 60 min. These factors had an obvious effect on the flotation performance of Zn concentrate. In particular, increasing the sulfur dosages was beneficial for Zn recovery, but decreased the Zn grade of the concentrate.

Zinc sulfide was generated at the outer layer of the zinc oxide mineral after thermal treatment. The film of sulfides was distributed on the surface of the zinc oxide mineral. The concentration of sulfur at the surface increased after thermal modification, and correspondingly, the flotation performance of Zn concentrate improved. These results agreed with our previous micro-mechanism study of pure smithsonite. Further tests at pilot scale will be carried out in the future to confirm the results in practice.

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