Chlorination Behaviors of Zinc Phases by Calcium Chloride in High Temperature Oxidizing-chloridizing Roasting

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The high temperature oxidizing-chloridizing roasting is one of useful methods to separate nonferrous metals from pyrite cinder and metallurgy slag. However, as one kind of main nonferrous metals in pyrite cinder and metallurgy slag, the occurrence of zinc is complicated and its chlorination behavior is not demonstrated. In the present study, chlorination behaviors of ZnO, ZnS and ZnFe2O4 at the temperature range of 1 025–1 175°C in air by simulating the chloridizing roasting process of pyrite cinder and metallurgy slag have been investigated. It is shown that ZnS and ZnO is much easier to remove, ZnFe2O4 is refractory to remove because of the presence of gangues. If enough chloride additives were added, the differences of Zn removal rate among ZnS, ZnO and ZnFe2O4 would disappear. In addition, the presence of Al2O3, SiO2, CaO and MgO decreases the Zn removal rate from ZnFe2O4, and the presence of Al2O3 and MgO decreases the Zn removal rate from ZnO while the presence of SiO2 and CaO improves the Zn removal rate from ZnO. Fe3O4 influences the Zn removal rate from ZnO and ZnFe2O4 positively.

KEY WORDS: chlorination behavior; zinc oxide; zinc sulfide; zinc ferrite; calcium chloride.

1. Introduction

As two kinds of significant secondary resources, pyrite cinder and metallurgy slag contain not only abundant iron but also considerable copper, lead, zinc etc. Millions of tons of pyrite cinder and metallurgy slag were discharged from nonferrous metal and chemical industries annually in China. The pyrite cinder and metallurgy slag are formed by roasting of minerals at a high temperature, so the properties of them are distinctly different from the natural iron ores, and the iron in them is closely associated with copper, lead, zinc and other nonferrous metals. High-quality pyrite cinder and metallurgy slag containing high iron and low impurities can hardly be obtained, leading to their low utilization degree. Chlorination is characterized by the high reactivity of chloridion, the high volatility and low melting point of metal chlorides, and the big differences in the formation of metal chloride. Therefore, chlorination is widely applied in extraction metallurgy.

The authors have already developed the high temperature oxidizing-chloridizing reduction roasting technology in grate-kiln to efficiently recover the valuable metals of iron, lead, zinc and copper. However, the occurrences of nonferrous metals are complicated because of abundant iron oxides, silica and alumina in pyrite cinder and metallurgy slag, mainly existing in the form of oxides, sulfides, ferrites and silicates. As one kind of main nonferrous metals in pyrite cinder and metallurgy slag, zinc mainly exists in the form of ZnS, ZnO and ZnFe2O4.

In the 1970s, Titi-Manyaka and Iwasaki formulated the chlorination and chloridization behaviors of zinc oxides by thermogravimetric analyses in Cl2 and HCl atmosphere below 1 000°C, which clarified chlorination reaction steps and possible mechanisms. Matsuura et al. measured chlorination behaviors of zinc oxide and zinc ferrite between 750°C and 1 000°C in Ar–Cl2–O2 atmospheres, and it has been demonstrated that chlorination process is effectively operated to remove Zn and the chlorination rate increases with increasing the partial pressure of Cl2.

Few researches have been done on the chloridization behaviors of zinc phases with CaCl2 additive while with the existing Al2O3, SiO2, CaO, MgO and Fe3O4 by simulating system of chlorination of pyrite cinder and metallurgy slag in the temperature range of 1 025–1 175°C in air. Thus, this work focuses on studying the chlorination behaviors of ZnO, ZnS and ZnFe2O4 with the aim to understand their differences and the effects of Al2O3, SiO2, CaO, MgO and Fe3O4 on the chlorination and to improve the high temperature oxidizing-chloridizing roasting technology.

2. Experimental

The chloridizing roasting tests were performed in a tube furnace (an open system in air) to simulate the chloridizing roasting in grate. Mixture of reagent grade powders were used to prepare briquettes (Φ10 mm×12 mm) and the compositions of briquettes (0.2 mass% Zn) which used to investigate the effects of chlorination temperature, time and molar ratio of Zn to Cl (nz0/nCl ratio) on Zn removal rate are shown in Table 1. These compositions were determined to simulate the contents of pellet feed, which was composed of metallurgy slag and pyrite cinder. Table 2 lists the com-
positions of briquettes which were used to investigate the effects of Al₂O₃, SiO₂, CaO and MgO on the chlorination of ZnO and ZnO·Fe₂O₃. Tables 3, 4 and 5 present the compositions of briquettes which were used to investigate the effects of Al₂O₃, SiO₂, CaO, MgO and Fe₂O₃ dosages on the chlorination. When the experimental temperature of the tube furnace centre reached to the target value, ten dry briquettes loaded in a corundum crucible were pushed into the corundum tube (Φ50 mm x 600 mm). In order to simulate the rotary grate technology, five minutes were required for moving the corundum crucible into the centre of tube furnace. After staying in the centre for the setting time, the corundum crucible loaded with briquettes was drawn out immediately and cooled by nitrogen gas. The removal rate of nonferrous metals was worked out by Eq. (1) based on the chemistry of fired briquettes and dry briquettes.

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R_m = \frac{(M_0 \times m_0 - M_t \times m_t)}{(M_0 \times m_0)} \times 100 ....... (1)
\]

Where \(R_m\) is removal rate (%), \(M_0\) is the content of nonferrous metals in dry green briquettes (%), \(m_0\) is mass of dry
green briquettes (g), \( M_i \) is the content of nonferrous metals in fired briquettes (%) and \( m_i \) is mass of fired briquettes (g).

3. Results and Discussion

3.1. Chlorination Behavior of Zn Phases

Figure 2 illustrates the effect of chlorination temperature on Zn removal rates from zinc phases including ZnS, ZnO and ZnO·Fe\(_2\)O\(_3\). It is observed that the removal rate increases with an increase in the chlorination temperature. The Zn removal rate from ZnS is similar to that from ZnO in oxidizing atmosphere, while the Zn removal rate from ZnO·Fe\(_2\)O\(_3\) is much lower than that from ZnO. But the thermodynamic calculation (Fig. 3) shows that ZnS is much more difficult to remove than ZnO, and ZnO·Fe\(_2\)O\(_3\) is easier to remove than ZnO when the chlorination temperature is over 732°C. Oxidation of ZnS in the literature\(^{11}\) shows that more than 80% ZnS has been oxidized to ZnO within 5 min in air at 850°C and more ZnS will be oxidized at higher temperature. Therefore, it can be concluded that the Zn removal rate from ZnS is similar to that from ZnO. Matsuura, Hamano and Tsukihashi\(^{10}\) investigated the chlorination behavior of

| Effect of CaO | Effect of MgO |
|--------------|--------------|
| 98.85 0 0.41 0 0.74 | 98.85 0 0.41 0 0.74 |
| 96.35 2.5 0.41 0 0.74 | 97.60 1.25 0.41 0 0.74 |
| 93.85 5.0 0.41 0 0.74 | 96.35 2.50 0.41 0 0.74 |
| 91.35 7.5 0.41 0 0.74 | 95.10 3.75 0.41 0 0.74 |

Table 5. Chemical compositions of various briquettes (mass%).

| \( \text{Fe}_2\text{O}_3 \) | \( \text{Fe}_3\text{O}_4 \) | \( \text{CaCl}_2 \) | \( \text{ZnO} \) | \( \text{ZnO}·\text{Fe}_2\text{O}_3 \) |
|-----------------|-----------------|-----------------|-------------|-----------------|
| 99.34 0 0.41 0.25 0 | 66.23 33.11 0.41 0.25 0 | 33.11 66.23 0.41 0.25 0 | 0 99.34 0.41 0.25 0 | 98.85 0 0.41 0 0.74 |
| 65.90 32.95 0.41 0 0.74 | 32.95 65.90 0.41 0 0.74 | 0 98.85 0.41 0 0.74 |

Fig. 2. Effect of temperature on Zn removal rates from zinc phases (chlorinating for 10 min, \( n_{\text{Cl}}/n_{\text{Zn}} = 2.4:1 \)).

Fig. 3. Relationships between Gibbs free energy of zinc phases chlorination and temperature.

Fig. 4. Effect of Al\(_2\)O\(_3\), SiO\(_2\), MgO and CaO on Zn removal (chloridizing at 1 125°C for 10 min, \( n_{\text{Cl}}/n_{\text{Zn}} = 2.4:1 \)).
ZnO and ZnO·Fe₂O₃ in an Ar–Cl₂–O₂ gas stream and found that ZnO·Fe₂O₃ is easier to remove than ZnO. However, briquettes contain many gangues (Al₂O₃, SiO₂, MgO and CaO) in this test, which dramatically influence the Zn removal from ZnO and ZnO·Fe₂O₃. The presence of Al₂O₃, MgO and CaO decreases the Zn removal rate from ZnO·Fe₂O₃ while the presence of SiO₂ and CaO dramatically increases the Zn removal rate from ZnO (Fig. 4). That is why Zn removal rate from ZnO·Fe₂O₃ is lower than that from ZnO in Fig. 2.

As the chlorination time extends, the Zn removal rates from ZnO, ZnS and ZnO·Fe₂O₃ slightly increase (Fig. 5).

The chlorination speed is so high that most of chlorination reaction is finished within 5 min. Furthermore, the volatilizations of CaCl₂ and HCl are extremely fast at high temperature.⁷ So, there is a little Cl remained after 5 min. Although the optimization of the chlorination temperature and time, it is more difficultly to remove Zn from ZnO·Fe₂O₃ than from ZnO and ZnS in the briquettes with an nZn/nCl ratio of 2.4.

As the nCl/nZn ratio increases from 1.2 to 6.0, the Zn removal rates from ZnO, ZnO·Fe₂O₃ and ZnS dramatically increase (in Fig. 6). The differences of Zn removal rate dis-

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**Fig. 5.** Effect of time on Zn removal rate from various zinc phases (chlorinating at 1125°C, nCl/nZn = 2.4:1).

**Fig. 6.** Effect of Cl dosage on Zn removal rate from various zinc phases (chlorinating at 1125°C for 10 min).

**Fig. 7.** Effect of Al₂O₃, SiO₂, CaO and MgO dosage on Zn removal (chloridizing at 1125°C for 10 min, nCl/nZn = 2.4:1, a- effect of Al₂O₃ on Zn removal, b- effect of SiO₂ on Zn removal, c- effect of CaO on Zn removal, d- effect of MgO on Zn removal).
appear when the nCl/nZn ratio is 6. It is probably the reason that the higher the nCl/nZn ratio, the higher HCl concentration for chlorination, which promotes the Zn removal from zinc phases. Therefore, the dosage of Cl is important for the chlorination of zinc phases, especially zinc ferrite.

3.2. Effect of Al₂O₃, SiO₂, CaO, MgO and Fe₃O₄ on Chlorination of Zn Phases

As shown in Fig. 7, the Zn removal rate from ZnO·Fe₂O₃ is much higher than that from ZnO, and Al₂O₃, SiO₂, CaO and MgO decrease the Zn removal from ZnO·Fe₂O₃ considerably. The presence of Al₂O₃ and SiO₂ contributes to the formation of more stable aluminite ZnO·Al₂O₃ and silicate ZnO·SiO₂ by reacting with the ferrite ZnO·Fe₂O₃. CaO promotes ZnO·Fe₂O₃ changing into ZnO, which possesses lower Zn removal rate than that of ZnO·Fe₂O₃, so CaO dramatically reduces Zn removal rate from ZnO·Fe₂O₃. In contrast, CaO, which captures the released Cl and reduces the HCl volatilization into air, results in the increase of Zn removal rate from ZnO. The presence of SiO₂ increases Zn removal from ZnO as SiO₂ promotes the formation of HCl (Fig. 8). Al₂O₃ also leads to the formation of the aluminite ZnO·Al₂O₃, which results in the decrease of Zn removal rate from ZnO. Similar to CaO, MgO promotes ZnO·Fe₂O₃ changing into ZnO, which causes the decrease of Zn removal rate from ZnO·Fe₂O₃. In addition, the reaction of MgO with Fe₂O₃ can reduce the reaction of CaCl₂ with Fe₂O₃ and H₂O from which HCl is produced, so the production of HCl decreases and the volatilization of CaCl₂ into air increases. That is why Zn removal rate from ZnO and ZnO·Fe₂O₃ decreases.

As shown in Fig. 9, the presence of Fe₃O₄ increases the Zn removal rate from ZnO and ZnO·Fe₂O₃. Fe₃O₄ oxidized from Fe₂O₄ is easier to promote the formation of HCl (Fig. 8), so Fe₂O₄ activates Zn removal from ZnO and ZnO·Fe₂O₃. Furthermore, oxidation of Fe₂O₄ decreases the oxygen concentration in the briquettes and provides more energy for chlorination reactions. Son and Tsukihashi [12] investigated the effect of oxygen partial pressure on the vapor pressure of ZnCl₂ and found that the vapor pressure of ZnCl₂ increases with decreasing the oxygen partial pressure.

4. Conclusions

(1) The thermodynamic equilibrium calculations and experiment results show that ZnS is the easiest to remove, ZnO·Fe₂O₃ is the most difficult to remove and ZnO is in the middle in the high temperature oxidation-chlorination technology. Most of ZnS are oxidized to oxides and then chloridized. In addition, the differences of Zn removal rates among ZnS, ZnO and ZnO·Fe₂O₃ would disappear, if there was enough dosage of Cl additive.

(2) The experiment results indicate that the gangues (Al₂O₃, SiO₂, CaO and MgO) and Fe₃O₄ clearly influence Zn removal. The presence of Al₂O₃ and MgO dramatically decreases Zn removal from ZnO and ZnO·Fe₂O₃. SiO₂ influences the Zn removal positively from ZnO and negatively from ZnO·Fe₂O₃. In addition, CaO decreases Zn removal from ZnO·Fe₂O₃ while it increases Zn removal from ZnO. The existence of Fe₃O₄ increases the Zn removal from ZnO and ZnO·Fe₂O₃.

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