Kinetics of Zn Removal from ZnO–Fe$_2$O$_3$–CaCl$_2$ System

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The chlorination and evaporation behaviors of Zn in the ZnO–Fe$_2$O$_3$–CaCl$_2$ system was studied by gravimetry from 1 173 to 1 323 K and the effects of carrier gas flow rate, temperature and the initial Zn content of specimen on the chlorination rate were investigated. Moreover, thermodynamic calculation was carried out. Fe and Zn were separated because Zn was selectively chlorinated by CaCl$_2$ from ZnO–Fe$_2$O$_3$ system and volatilized as ZnCl$_2$ while Fe remained as oxide in chlorinated residue. From the chemical analyses, it was clarified that the volatilization of ZnCl$_2$ mainly cause the weight loss of specimen. Based on these results, the chlorination mechanism and kinetic model were discussed. The weight change of specimen was expressed as a function of reaction time reasonably well by assuming the first order reaction with respect to presumed ZnCl$_2$. Apparent activation energy of chlorination reaction, calculated from obtained reaction rate constants for various initial Zn contents, was in the range between 107 and 172 kJ/mol. It is considered the rate determining step of chlorination is chemical reaction, such as the reaction between ZnO and CaCl$_2$, or the interfacial evaporation of ZnCl$_2$ from the specimen.

KEY WORDS: steelmaking dust; recycling; chlorination; kinetics; ZnO–Fe$_2$O$_3$–CaCl$_2$ system.

1. Introduction

Amounts of the electric arc furnace (EAF) dust in steelmaking companies have increased with the development of steelmaking industry. These dusts contain abundant metallic elements such as Fe, Zn, Pb and so on. Direct disposal or landfill of such dusts without appropriate treatment can result in serious pollution of the environment due to the leaching of toxic element. However, these metals contained in dust could become valuable metal resources if the efficient separation processes would be developed.

The recent researches on EAF dust treatment method can be classified as hydrometallurgical or pyrometallurgical process. The typical pyrometallurgical refining process such as Waelz kiln process mixes the dust with carbonaceous materials as reductants and roasts the mixture at a high temperature more than 1 473 K. Zn and Pb were recovered as metal by volatilization. Therefore, CaCl$_2$ was employed as the additive to remove Zn as chloride by volatilization in the present study. From the chemical analyses, it was clarified that the volatilization of ZnCl$_2$ mainly cause the weight loss of specimen. Based on these results, the chlorination mechanism and kinetic model were discussed. The weight change of specimen was expressed as a function of reaction time reasonably well by assuming the first order reaction with respect to presumed ZnCl$_2$. Apparent activation energy of chlorination reaction, calculated from obtained reaction rate constants for various initial Zn contents, was in the range between 107 and 172 kJ/mol. It is considered the rate determining step of chlorination is chemical reaction, such as the reaction between ZnO and CaCl$_2$, or the interfacial evaporation of ZnCl$_2$ from the specimen.

KEY WORDS: steelmaking dust; recycling; chlorination; kinetics; ZnO–Fe$_2$O$_3$–CaCl$_2$ system.

2. Thermodynamic Analysis of ZnO–Fe$_2$O$_3$–CaCl$_2$ System

The chlorination process of ZnO–Fe$_2$O$_3$ with CaCl$_2$ would be expressed as following reactions,

\[
\text{ZnO (s)+CaCl}_2(l)\rightarrow\text{ZnCl}_2(g)+\text{CaO (s)}
\]

\[
\Delta G^0=226\text{ kJ/mol}^{(1)}
\]
Although the calculated standard Gibbs energy changes of above reactions show reactions cannot proceed at 1273 K, the reactions will occur if the partial pressure of gaseous products were decreased to enough low pressure. Because standard Gibbs energy changes of reactions (1) and (2) were smaller than the other reactions, these two reactions will occur more easily when the partial pressure of gaseous products are decreased simultaneously.

Figure 1 shows the chemical potential diagram for the Zn–Fe–Ca–O–Cl system at 1273 K calculated by FactSage 6.1, where mole ratios of both Zn and Fe to Fe–Zn–Ca are 0.25, and the activity of CaCl$_2$ (l) is unity. Zinc could be selectively chlorinated while iron oxide is stable in a hatched region in the figure. It is considered that the predominant compound of Zn is ZnCl$_2$, and the weight of specimen will decrease by the chlorination and evaporation of Zn.

3. Experimental

In the present study, the chlorination rate of ZnO–Fe$_2$O$_3$–CaCl$_2$ was measured by gravimetry in the temperature range between 1173 and 1323 K in N$_2$ gas atmosphere. Figure 2 shows the schematic diagram of experimental apparatus. Reagent grade of ZnO and Fe$_2$O$_3$ powders were mixed (Zn content: 5 to 27 mass%) and sintered at 1173 K for 12 h. Reagent CaCl$_2$ powder was dehydrated at 423 K for 120 min. One gram of sintered ZnO–Fe$_2$O$_3$ was mixed with CaCl$_2$ with Zn/Ca molar ratio of unity and the mixture was put into an Al$_2$O$_3$ crucible (OD 22 mm x ID 19 mm x H 28 mm). The crucible was inserted into a hot zone of an electric furnace with a mullite reaction tube (OD 50 mm x ID 38 mm x L 600 mm). Purified N$_2$ gas was used as carrier gas and flow rate was controlled by mass flow controller. Experimental temperature was measured and controlled by Ni–10%Cr/Ni–3%Si thermocouple. The experimental time started when the crucible with sample was inserted into the hot zone. After 10 to 600 min, the crucible was taken out from the furnace, quenched under an N$_2$ gas stream, and weighed to measure the weight loss of the sample. The composition of residue in the crucible was analyzed by chemical analyses. Zn, Fe, Ca contents were determined by ICP-OES (Seiko SPS7800, Japan), chlorine content was determined by Mohr method with silver nitrate and ferrite content was determined by titration method with potassium dichromate. In addition, some residues were powdered to identify phases by XRD analysis. Al content in the sample was not measured in the present study, and the effect of dissolution of Al$_2$O$_3$ on the chlorination reaction in the specimen is unknown. However, the erosion of Al$_2$O$_3$ crucible was not clearly seen from the observation of the cross section of Al$_2$O$_3$ crucible after some experiments. Therefore, it is believed that the effect of Al$_2$O$_3$ dissolution is limited under the present experimental conditions.

4. Results and Discussion

4.1. Effect of Carrier Gas Flow Rate

The effect of carrier gas flow rate on the chlorination rate of 23mass%ZnO–46%Fe$_2$O$_3$–31%CaCl$_2$ was investigated. Figure 3 shows the relationship between weight loss of...
sample and the carrier gas flow rate for 60 min. The weight loss of sample was independent on the carrier gas flow rate from 600 to 1200 cm³/min, which means that the gas phase mass transfer is not the rate determining step. Therefore, the gas flow rate of 600 cm³/min was determined as a constant carrier gas flow rate for the following experiments.

4.2. Effect of Reaction Temperature

The effect of reaction temperature on the chlorination of ZnO–Fe₂O₃ mixture was investigated from 1173 to 1323 K. Experimental conditions are shown in Table 1. Figure 4 shows the weight change of specimen with time at various temperatures for the various initial Zn contents. It was shown that the weight loss increased with chlorination time and the rate of weight loss increased with increasing temperature.

The chlorination residue was identified by powder XRD pattern. Figure 5 shows the diffraction patterns of residues which initial Zn content is 27 mass% in the ZnO–Fe₂O₃ system. After the chlorination with CaCl₂, ZnO–Fe₂O₃ was almost converted to CaFe₂O₄ or Ca₃Fe₂O₆.

4.3. Effect of Initial Zn Content in ZnO–Fe₂O₃

The effect of initial Zn content in ZnO–Fe₂O₃ mixture on the chlorination reaction was investigated from 1173 to 1323 K with Zn content range between 5 and 27 mass%. The results are shown in Fig. 4. Weight losses of ZnO–Fe₂O₃–CaCl₂ system with different initial Zn content at 1223 K were summarized in Fig. 6. It was shown that the initial rate of chlorination reaction was almost constant with various initial Zn contents under the same experimental condition. The dot lines in Fig. 6 represent the maximum weight losses which can be theoretically calculated by assuming that all of Zn is chlorinated to ZnCl₂ and the weight loss of system is only caused by the evaporation of

| Exp. No. | Initial Zn content mass% | Δωmax g | Temp. K | Initial weight g | k min⁻¹ |
|---------|--------------------------|---------|---------|------------------|---------|
| 1       | 5                        | 0.10    | 1173    | 1.062            | 0.0167  |
| 2       | 10                       | 0.21    | 1173    | 1.151            | 0.0093  |
| 3       | 15                       | 0.31    | 1223    | 1.252            | 0.0026  |
| 4       | 20                       | 0.41    | 1273    | 1.313            | 0.0016  |

Fig. 4. The weight change of sample with time from 1173 to 1323 K. Initial Zn content is (a) 5 mass%, (b) 10 mass%, (c) 15 mass%, (d) 20 mass%, and (e) 27 mass%.
ZnCl₂. The rate of weight change decreased with time and weight loss became almost constant after certain reaction times. The observed maximal weight losses were lower than that calculated theoretically. Though the reason for this phenomenon is not clear, it is expected that the reaction rate between CaCl₂ and ZnO became too low to observe the weight loss, and some portion of CaCl₂ evaporated in gaseous phase before reacting with ZnO, especially at the latter stage of reaction due to lower reaction rate.

The chemical compositions of the chlorination residues (initial Zn content in ZnO–Fe₂O₃: 27 mass%) at 1 223 K are shown in Table 2. The chlorination experiments were done at the same conditions above mentioned except difference in a crucible size (OD 38 mm × ID 34 mm × H 45 mm). The table shows that the content of Zn decreased sharply after chlorination, content of Ca slightly decreased, and Fe content was almost stable. Therefore, it was considered that the volatilization of ZnCl₂ and CaCl₂ causes the weight loss of specimen. These results calculated from the mass balance indicate that weight loss of specimen was mainly due to the volatilization of ZnCl₂ and few amount of unreacted CaCl₂ was volatilized with ZnCl₂.

4.4. Reaction Mechanisms of the ZnO–Fe₂O₃–CaCl₂ System

According to the thermodynamic calculation and experimental results, reactions (1) and (2) are considered as the main reactions in the chlorination and evaporation processes. The overall reaction rate of chlorination reactions (1) and (2) can be expressed by the differential of weight loss of specimen with time. However, reaction rates in the middle period of chlorination in the present study would be affected by many reactions, such as dissolution of solid reactants, diffusion of reactants in liquid phase, chemical reaction with liquid CaCl₂, diffusion and volatilization of the gaseous products and so on. Though the phase diagram for Zn–Fe–Ca–O–Cl system has not been reported so far, it seemed that solid and liquid coexisted in specimens from the exterior. Therefore, analysis of the chlorination reaction rate was conducted for the overall chlorination reaction in the following. As the weight loss of reaction system is only caused by the volatilization of the gaseous products, the reaction (4) is the overall chlorination reaction.

\[
\text{ZnCl}_2 \text{(in ZnO–Fe}_2\text{O}_3–\text{CaCl}_2 \text{mixture}) \rightarrow \text{ZnCl}_2 \text{(g)} \ldots (4)
\]

Assuming the reaction (4) is the first order reaction with respect to ZnCl₂ content, the reaction rate is expressed as Eq. (5),

\[
\frac{dC_{\text{ZnCl}_2}}{dt} = k C_{\text{ZnCl}_2}
\]

where \( C_{\text{ZnCl}_2} \) is the mass concentration of ZnCl₂ in system, and \( k \) (min⁻¹) is the reaction rate constant.

The change of ZnCl₂ content is expressed as a function of weight loss from the mass balance as follows,

\[
C_{\text{ZnCl}_2} = \frac{\Delta w_{\text{max}} - \Delta w}{\Delta w_{\text{max}} - C_{\text{ZnCl}_2,0} \Delta w} C_{\text{ZnCl}_2,0} \ldots (6)
\]

where \( C_{\text{ZnCl}_2,0} \) is the initial mass concentration of ZnCl₂. As mentioned above, it seemed that solid and liquid coexisted in specimens from the exterior. Therefore, actual ZnCl₂ content in the liquid phase is unknown in the present work and presumed ZnCl₂ content was calculated by assuming

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**Table 2.** Compositions of (a) initial specimen (initial Zn content: 27 mass%) and (b) the chlorination residue at 1 223 K.

| Sample | Initial reactants weights (g) | Initial weight of constituents (g) | Zn | Fe | Ca | Fe⁺⁺⁺ | Cl⁻ | Total |
|--------|-----------------------------|----------------------------------|----|----|----|-------|-----|-------|
| A      | ZnO–Fe₂O₃ | CaCl₂   | 1.0045 | 0.4638 | 1.4683 | 0.2712 | 0.4668 | 0.1671 | - | 0.2963 |
| B      | ZnO–Fe₂O₃ | CaCl₂   | 1.0120 | 0.4608 | 1.4728 | 0.2732 | 0.4703 | 0.1661 | - | 0.2947 |

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*Reference weight loss is calculated from the weight decrease of Zn and Ca by assuming the evaporation as ZnCl₂ and CaCl₂, respectively.*
that the whole specimen is homogeneous.

From Eqs. (5) and (6), the weight loss of the specimen is expressed as a function of time as Eq. (7),

$$\Delta w = \frac{e^{-kt} - 1}{C_{ZnCl_2} \cdot \beta e^{-kt} - 1} \Delta w_{max} \quad \text{...........(7)}$$

By Eq. (7) and theoretical maximal weight loss $\Delta w_{max}$, all experimental data were fitted. Equation (7) was adopted to data in the range that the weight of samples decreased with reaction time. The fitted curves were shown in Fig. 4. It is found that the fitted curves represent the experimental results reasonably well at the early stage of chlorination reaction. On the contrary, the weight of the samples did not decrease as expected from the mass balance as mentioned in the previous section, and the following reasons are brought: (1) since the ZnO–Fe$_2$O$_3$–CaCl$_2$ system is not homogeneous as presumed but solid–liquid coexisting in fact at the present experimental conditions, the chlorination rate of ZnO by CaCl$_2$ drastically decreased and the effect of mass transfer in the specimen became relatively large, (2) the remarkable decrease of chlorination rate caused the increased amount of evaporation of unreacted CaCl$_2$. Therefore, it is considered that the proposed reaction model above explains the reaction mechanism at the early stage. For each experimental condition, the reaction rate constants obtained by the fitting of measured results are summarized in Table 1.

Figure 7 shows the reaction rate constants as a function of the reciprocal of temperature. From slopes of lines, the apparent activation energy was calculated to be in the range between 110 and 175 kJ/mol, and the activation energy was independent of initial Zn content as shown in Fig. 8. Therefore, it is considered that Eq. (7) expresses the weight loss by the chlorination reaction of ZnO–Fe$_2$O$_3$ by CaCl$_2$, reasonably well and the rate determining step of chlorination reaction is chemical reaction such as the chlorination of ZnO with CaCl$_2$, or the interfacial evaporation of ZnCl$_2$ from the specimen as reaction (4).

5. Conclusions

The chlorination behavior of Zn in the ZnO–Fe$_2$O$_3$–CaCl$_2$ system was investigated by gravimetry from 1 173 to 1 323 K with N$_2$ gas of 600 cm$^3$/min. It was demonstrated that ZnO in ZnO–Fe$_2$O$_3$ system could be selectively chlorinated and removed by CaCl$_2$ while Fe was stable in the chlorination residue as oxides. The expression gives a well fit to the measured weight loss with experimental time. Obtained results are summarized as follows:

(1) The weight loss of specimen was mainly due to the volatilization of ZnCl$_2$.
(2) The weight loss of specimen increased with increasing temperature.
(3) The chlorination rate increased with increasing initial Zn content of sample.
(4) Apparent activation energy of chlorination of ZnO–Fe$_2$O$_3$–CaCl$_2$ system was in the range between 110 and 175 kJ/mol.

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