Experimental validation of the reaction mechanism models of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process

Abstract: The reaction mechanism models of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process are studied. The dust collected from a steelwork contains 63.8% zinc and 3.18% chlorine (mass percent), of which, almost all zinc elements exist in ZnO and ZnCl₂ forms, and all the chlorine elements are stored in ZnCl₂. When the dust is roasted at above 732°C in an air atmosphere, the ZnCl₂ in the steelmaking zinc-rich dust is volatilized into steam and then oxidized into ZnO. Finding the position where the chemical reaction occurs is the key to determining the reaction mechanisms of dechlorination and [Zn] reclaiming. In this study, two groups of thermal experiments are designed and executed for roasting in different atmosphere environments and at different roasting temperatures. Based on the experiment results, the mechanism model is discussed and built, and the reaction of dechlorination and [Zn] reclaiming is shown to be a multi-step process. Because O₂ from the air cannot transmit into the dust particle interior or dust bed effectively, the chemical reaction of [Zn] reclaiming occurs in the external gas environment outside of the dust, where the [Zn] recalculating reaction should be limited by the dynamics of new nucleation of ZnO solids.

Keywords: mechanism model; dechlorination; thermal experiment

1 Introduction

The shortage of raw materials is becoming an increasingly prominent issue for the zinc smelting industry in China [1]. Secondary resources, such as steelmaking dust, galvanizing dross, and blast furnace dust, are important raw material supplies [2]. Because of circulation and accumulation effects, EAF steelmaking by galvanized steel and scrap parts produces a large amount of zinc-rich dust. If the steelmaking dust can be fully utilized, it will effectively alleviate the domestic shortage of raw materials.

Steelmaking zinc-rich dust cannot be directly used for zinc smelting. The contained [Cl] element enters the electrolyte in ion form (Cl⁻) and corrodes the system’s equipment, such as the positive plate. Eventually, the zinc hydrometallurgy process and the working environment are affected and they deteriorate [3]. Dechlorination from the steelmaking zinc-rich dust is necessary. Some scholars have done a lot of work on dechlorination of steel-making dust [4], including sulfation roasting, water washing process [5], microwave roasting [6], etc. The roasting method is commonly used for defluorination and dechlorination, which gives obvious advantages of being a simple process and having good effects.

In the process of roasting steelmaking zinc-rich dust, the synchronous loss of zinc is large. It is necessary to extensively study the internal reaction mechanism to reduce the actual [Zn] loss and achieve complete dechlorination. The reactions of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process occur through a typical multi-step process, which results in morphology changes and the mass transport of reactants and products.

In this paper, the physical and chemical properties of steelmaking zinc-rich dust are confirmed firstly. Then, thermal experiments are designed to validate the key reaction characteristics. Finally, the reaction mechanism model of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process is discussed and built.
2 Discussion about the reaction mechanism

2.1 The physical and chemical properties of the steelmaking zinc-rich dust

In steelmaking using scraps in an electric arc furnace or induction furnace, zinc and other elements are evaporated into the furnace gas at a high temperature, and then they condense with the oxygen in the furnace gas gradually. Finally, the combination product aggregates into fine particles, which is steelmaking dust. The steelmaking dust is commonly processed into auxiliary materials and reused in steelmaking production to recover \([\text{Fe}]\). \([\text{Zn}]\) gradually circulates and accumulates, and the heavy use of galvanized scrap steel and scrap parts aggravates the enrichment. Finally, steelmaking zinc-rich dust forms.

In this study, steelmaking zinc-rich dust was collected from a steelwork. A chemical composition analysis was carried out firstly, and the dust was shown to contain 63.8% zinc and 3.18% chlorine, as shown in Figure 1a. Then, the crystal structure of the dust was determined by XRD, and the results (Figure 1b) show that almost all zinc exists in the form of ZnO or ZnCl\(_2\); The content of ZnO is extremely high in the dust, and all chlorine is stored in ZnCl\(_2\). Finally, the particle size was measured by a laser particle size distribution analyzer, and the steelmaking zinc-rich dust particles were all found to be very small, mainly in the range of 1–10 µm and mostly 2–5 µm. The statistics of the particles size are shown in Figure 1c.

The chemical composition of experimental raw materials is mainly determined by chemical detection. Among them, zinc is determined by coordination titration method (GB/T 6890-2000), Cl by titration method (GB/T 11896_1989), F by ion-selective electrode method (GB/T 6730.28-2006).

The flue dust used in this paper has very low Fe content. Zinc mainly exists in the form of ZnO, and other impurity elements are low. After chlorine is removed, it can be directly used in hydrometallurgy.

2.2 Thermodynamics analysis of dechlorination and \([\text{Zn}]\) reclaiming

ZnCl\(_2\) is volatile matter, whose melting point, boiling point and saturated vapor pressure at different high temperatures are shown in Table 1. The saturated vapor pressure of ZnCl\(_2\) changes by order of magnitude from temperatures of 550 to 650°C, which means a greater gasification rate, and ZnCl\(_2\) boils at a temperature of 732°C. In the roasting process, the ZnCl\(_2\) in the dust volatilizes by following the reaction equation shown below:

\[
\text{ZnCl}_2 (s/l) = \text{ZnCl}_2 (g)
\]

When the steelmaking zinc-rich dust is roasted under atmospheric pressure or negative pressure at temperatures above 650°C, ZnCl\(_2\) will evaporate into the gas phase and be dechlorinated directly. As reported in reference [7], the method of roasting at the temperature of 700°C for 3 hours is commonly used for dechlorinating some \([\text{Zn}]\) or \([\text{Pb}]\) rich raw materials.
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In the process of ZnCl\textsubscript{2} transformation into the gas phase, synchronous loss of zinc is unavoidable. ZnCl\textsubscript{2} may react with O\textsubscript{2} following the equation below in an oxygen-containing atmosphere such as air. In view of the phase change of ZnCl\textsubscript{2}, the relationship between the Gibbs free energy of the chemical reaction and the temperature \cite{8} is shown in Figure 2.

\[
2\text{ZnCl}_2 + \text{O}_2 \rightarrow 2\text{ZnO} + 2\text{Cl}_2
\]

According to the reaction thermodynamics data, when ZnCl\textsubscript{2} is in the solid or liquid phase at temperatures below 732°C, the Gibbs free energy is always above 0 kJ/mol, and no reaction occurs. At temperatures above the boiling point, the Gibbs free energy falls to below 0 kJ/mol.

There is opportunity for ZnCl\textsubscript{2} in the steelmaking zinc-rich dust to be volatilized into steam and then be oxidized into ZnO when the dust is roasted at above 732°C in air atmosphere. If the two-step reaction occurs in an ideal position, efficient dechlorination and no loss of zinc elements will be achieved at the same time.

2.3 Discussion on the reaction mechanism and hypotheses

The dust particles can be approximated as spheres. The unidirectional mass transfer process of ZnCl\textsubscript{2} from the inner of the dust particle to the outside conforms to the shrinking unreacted core model with a constant particle size. ZnCl\textsubscript{2} diffuses into the gas phase on the surface of the unreacted core, and nonvolatile matter forms the layer of residual porous media, which is almost all ZnO. ZnCl\textsubscript{2} steam transmits through the layer of residual porous media first, and then diffuses into the gas phase. As the reaction progresses, the diameter of the unreacted core decreases, the thickness of the residual porous media increases, and the overall size of the dust particles remains the same, as shown in Figure 3a. For the overall dechlorinating process of the accumulation layer with a large number of dust particles, the reaction time for dechlorination of a single dust particle can be ignored, and the dechlorinating process of the accumulation layer conforms to the shrinking unreacted core model too, as shown in Figure 3b.

Roasting steelmaking zinc-rich dust in the air atmosphere at a temperature above 732°C causes mass transportation of ZnCl\textsubscript{2} steam from the inner and oxygen from the gas environment in opposite directions. Affected by the two mass transportations and the chemical reaction, the reaction process of dechlorination and [Zn] reclaiming may be complicatedly changed and constrained by four influential factors, which are shown below:

1. The diffusion rate of O\textsubscript{2} transmission through the boundary layer and the layer of residual porous media;
2. The diffusion rate of ZnCl\textsubscript{2} steam transmission through the layer of residual porous media and the boundary layer;
3. The chemical reaction rate of ZnCl\textsubscript{2} and O\textsubscript{2} reacting with each other;
4. The diffusion rate of generated Cl\textsubscript{2} transmission into the gas atmosphere.

Sufficient reactants are required for the chemical reaction. In the roasting process, if the internal diffusion rate of O\textsubscript{2} is higher and the external diffusion rate of ZnCl\textsubscript{2} steam is lower, adequate reactant concentrations will be available in the internal slot of the residual porous media. On the contrary, if the internal diffusion rate of O\textsubscript{2} is lower and the external diffusion rate of ZnCl\textsubscript{2} steam is higher, the necessary reactant concentration may only be provided in the gas environment outside of the particles. In a general situation, the speed of the chemical reaction between gaseous reactants is especially fast, but the nucleation of the ZnO generated from the gas phase may be a restricted link, which is in the solid-phase at the reaction temperature. If the chemical reaction occurs in the internal slot of the residual porous media, because the ZnO existing in the dust particles is already the best nucleation agent, the chemical reaction will complete quickly, and ZnO will be reclaimed in the dust particles internally. If the chemical reaction occurs in the gas environment, the chemical reaction process may last for a long time, and the generated ZnO will leave away the original dust particles, which makes it difficult to reclaim zinc.
Figure 3: Shrinking unreacted core model of the dust dechlorination process with a constant particle size

Figure 4: Hypotheses about the dechlorination and [Zn] reclaiming reactive processes

In essence, the position at which the chemical reaction occurs is the key characteristic for the reaction mechanism of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process. There are two possibilities in our assumptions: In Hypothesis A, O$_2$ from atmospheric enters the residual porous media and reacts with ZnCl$_2$, and the generated ZnO is attached to the gaps in the layer of the residual porous media (as shown in Figure 4a); in Hypothesis B, the ZnCl$_2$ steam crosses the layer of residual porous media and diffuses into the gas phase, where it reacts with O$_2$ to generate ZnO in the solid phase. Then, the solid ZnO settles onto the surface of the dust or dissipates into the environment (as shown in Figure 4b). All the generated Cl$_2$ gas discharges into the exhaust gas. To verify which hypothesis is consistent with reality, some thermal experiments are necessary.

3 Experimental schemes

According to the characteristics of the mechanism models, the atmospheric environment and the roasting temperature have different impacts on the reactive results. In this paper, two groups of thermal experiments were designed to discuss and identify the reaction mechanisms of dechlorination and [Zn] reclaiming in the roasting steelmaking zinc-rich dust process.

3.1 Experiments (a) involving roasting in different atmosphere environments

In experiment (a), dust in crucibles was heated and roasted under different gas atmospheres, and the results
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To prepare the experiment objects, every 100 g of dust was weighed and charged into each crucible, and the dust was flatly paved on the bottom of the crucible. The crucibles were made of alumina material and were cylindrical in shape with a diameter of 60 mm and a height of 75 mm. Under different atmospheres, argon or air was sprayed by a quartz tube or no air was sprayed for 60 minutes. The quartz tube was vertically inserted 2 cm below the upper edge of the crucible along the central axis of the crucible. During blowing, a forced gas flow formed in the free space of the crucible. The forced gas flow should not disturb the tiled dust, and the flow rate was confirmed as 100 mL/min.

In terms of the experiment equipment, a fast heating muffle furnace of 1600°C was prepared, and its semi-sealing and big free space guaranteed the long-term stability of the atmosphere. The experimental gas was supplied by high pressure vessels, and the flow rate was controlled by a pressure-reducing valve and gas flowmeter. The gas was carried through gas pipes, and a heat exchange pipe was equipped in the furnace hearth to ensure that the temperature of the blowing gas was consistent with the furnace. The equipment system for experiment (a) is shown in Figure 5.

The experiment operation was determined as described below: The muffle furnace was first heated up while empty, and the blowing gas started up too. When the temperature reached the set point, and the gas blowing flow was stabilized, the prepared dust with the crucible was put into the furnace, and after adjusting the position of the blowing pipe and closing the furnace door, the roasting experiment was timed. When the experiment was finished, the dust with the crucible was removed and covered, and the argon gas was blown for dust cooling during sealing. After the experiment, the mass of the dust was weighed, and the compositions of [Zn] and [Cl] in the remaining powder were measured too. To reduce the error, each experiment scheme was carried out three times on average. The specific experimental schemes are shown in Table 2.

### Table 2: Schemes for experiment (a) involving roasting in different atmosphere environments

|                | a-1 | a-2 | a-3 |
|----------------|-----|-----|-----|
| Temperature /°C| 900 | 900 | 900 |
| dust Weight /g | 100 | 100 | 100 |
| roasting time /min | 60 | 60 | 60 |
| atmosphere     | flowing | stationary | flowing |
|                 | Argon | air | air |
| gas composition| Ar   |    |    |
| gas flow rate   | mL/min | 100 | 0  |
| gas consume /mL | 6000 | 3   | 3  |
| repeat times   | 3    | 3   | 3  |

3.2 Experiment (b) involving roasting at different roasting temperatures

In experiment (b), the prepared dust was heated and roasted in air atmosphere at different temperatures, and the weight and compositions of the remaining powders were investigated after the roasting treatment too.

The dust with crucibles were prepared in the same way and roasted at stationary air atmosphere for 60 minutes at temperatures of 750, 800, 850, 900, and 950°C. The operation process was as follows: After the furnace temperature reached the experimental temperature, the prepared dust...
in crucibles were put into the furnace, and the timer was started. When the roasting time was over, the dust with the crucible was removed and covered, and the argon gas was blown for cooling while sealing. The dust was weighed and chemically examined. Every scheme was carried out three times on average. The equipment system and the experimental schemes for experiment (b) are shown in Figure 6 and Table 3.

### Table 3: Schemes for experiment (b) involving at different roasting temperatures

| Temperature /°C | b-1 | b-2 | b-3 | b-4 | b-5 |
|-----------------|-----|-----|-----|-----|-----|
| Dust mass /g    | 750 | 800 | 850 | 900 | 950 |
| Period/min      | 60  | 60  | 60  | 60  | 60  |
| Atmosphere      | stationary air | | | | |
| Repeat times    | 3   | 3   | 3   | 3   | 3   |

4 Experimental results and discussion

In accordance with the schemes of experiment (a), nine experimental dusts were roasted under three different gas environments, and all the residual powders were weighed and chemically examined. The experimental results are shown in Table 4, and the average calculation is shown for each scheme.

Under the three different gas environments, the roasted dusts all dechlorinated completely, and the average dechlorination rate reached 98.51%. The gas environment had little influence on the dechlorination of the steel-making zinc-rich dust. Based on the changes in weight and composition, the dechlorinated mass, the synchronous dezincification, and the actual [Zn] loss were calculated, and the difference between the synchronous dezincification and the actual [Zn] loss represented the mass of [Zn] reclaiming, and the proportion of the [Zn] reclaiming to the synchronous dezincification represented the reclaiming rate of [Zn]. All data are shown in Table 5.

In the experiment of scheme (a-1), argon gas was used to isolate oxygen from the air and accelerate the external diffusion of ZnCl$_2$, and the chemical reaction of ZnCl$_2$ steam in the crucible was eliminated. As a result, all [Zn] in the ZnCl$_2$ steam was lost (2.843 g), and the mass of [Zn] reclaiming was null. In the experiment of scheme (a-2), the experimental condition was consistent with general roasting in an air environment. With the volatilization of ZnCl$_2$ steam, the dechlorination mass and synchronous dezincification are 3.142 g and 2.894 g respectively, and the mass of [Zn] reclaiming is 0.195 g, which represented 6.74%. In the experiment of scheme (a-3), flowing air accelerates the external diffusion of ZnCl$_2$, and gives little impact on the internal diffusion. The dechlorination and synchronous dezincification masses were 3.170 and 2.920 g respectively, and the [Zn] reclaiming mass was only 0.017 g, which represented 0.58%.

The experiment (a) results show that in the three different atmosphere environments, the actual measured masses of [Zn] reclaiming were all very low. The ZnO generated in the gas phase was affected by the gas flow in the crucible, which accelerates the external diffusion of ZnCl$_2$.
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Table 4: Results from experiments (a) involving roasting in different atmosphere environments

| atmosphere | dust weight | residual weight | content of Zn | average weight of Zn | content of Cl | average weight of Cl | average dechlorination rate |
|------------|-------------|-----------------|--------------|----------------------|--------------|----------------------|----------------------------|
| a-1 flowing Argon | 100          | 88.1            | 69.19        | 60.958               | 0.107        | 0.095                | 97.03                      |
|             | 100          | 88.0            | 69.27        | 0.108                |              |                      |                            |
|             | 100          | 87.8            | 69.42        | 0.108                |              |                      |                            |
| a-2 stationary air | 100          | 88.5            | 69.04        | 61.069               | 0.043        | 0.038                | 98.8                       |
|             | 100          | 88.2            | 69.29        | 0.043                |              |                      |                            |
|             | 100          | 87.9            | 69.39        | 0.043                |              |                      |                            |
| a-3 flowing air | 100          | 88.0            | 69.18        | 60.880               | 0.011        | 0.010                | 99.7                       |
|             | 100          | 88.2            | 69.02        | 0.011                |              |                      |                            |
|             | 100          | 87.8            | 69.34        | 0.011                |              |                      |                            |

Table 5: Calculation of dechlorination and [Zn] reclaiming in experiment (a) involving in different atmosphere environments

| atmosphere | dechlorination | synchronous dezincification | actual [Zn] loss | [Zn] reclaiming | Rate of [Zn] reclaiming |
|------------|----------------|-----------------------------|-----------------|----------------|------------------------|
| a-1 flowing Argon | 3.086          | 2.842                       | 2.842           | 0.000          | 0                      |
| a-2 stationary air  | 3.142          | 2.894                       | 2.699           | 0.195          | 6.74                   |
| a-3 flowing air    | 3.170          | 2.920                       | 2.903           | 0.017          | 0.58                   |

steam and is hard to deposit in the crucible. Comparing the experiment results of scheme [a-2] and scheme [a-3], which represent deposition or none, respectively, the mass of [Zn] reclaiming decreased from 0.195 to 0.017 g. According to the most conservative estimation, for the confirmed [Zn] reclaiming reaction, 91.28% of the chemical reaction occurs in the gas environment, compared with 8.72% in the internal gaps of the residual porous media layer. Considering the total mass of zinc that needs to be reclaimed, only 0.58% occurs in the internal gaps of the residual porous media layer. The reaction location of ZnCl₂ reclaiming to generate ZnO mainly occurs in the gas phase, and the reaction characteristics of roasting dechlorination and the [Zn] reclaiming process are consistent with the Hypothesis B.

As verification, the dust was roasted at different temperatures in experiment (b). A total of 15 roasting experiments were conducted under five schemes, and the roasted dust was weighed and assayed. All experimental results are shown in Table 6.

With an increase in roasting temperature, the dechlorination rate rose gradually, and dechlorination was almost complete at temperatures over 800°C. The results of dechlorination and [Zn] reclaiming at different roasting temperatures are shown in Table 7. As the results show, the mass of [Zn] reclaiming slightly increased first and then gradually decreased with an increase of the roasting temperature. The [Zn] reclaiming rate was more representative of the [Zn] reclaiming reaction degree, which decreased with an increase in the reaction temperature, and the [Zn] loss significantly increased (see Figure 7).

According to thermodynamic data, the Gibbs free energy of the [Zn] reclaiming reaction decreases as the reaction temperature increases, which means that the trend of [Zn] reclaiming and the results of the thermal state experiment are contrary to the thermodynamic results. The chemical reaction process is suppressed by the reaction kinetic conditions. According to the Hypothesis A, the ZnCl₂ reclaiming reaction occurs in the layer of residual porous media in which the main constituent is solid ZnO; thus, there is no nucleation problem in the formation of ZnO. The results of experiment (b) contradict with the Hypothesis A.

According to the Hypothesis B that ZnCl₂ steam reacts with O₂ in the gas phase outside of the dust particles, the difficulty of producing a new nucleation ZnO solid phase from gas phase increases with the environmental temperature, and the chemical reaction speed is suppressed. Finally, the ZnO generated and dropped in the crucible de-
Table 6: Results from experiments (b) involving at different roasting temperatures

| Temperature  | dust weight | residual weight | content of Zn | average weight of Zn | content of Cl | average weight of Cl | average dechlorination rate |
|--------------|-------------|-----------------|---------------|----------------------|--------------|----------------------|-----------------------------|
| ∘C           | g           | g               | %             | g                    | %            | g                    | %                          |
| b-1          | 750         | 100             | 91.2          | 68.54                | 62.51        | 0.61                 | 0.556                      | 82.5                       |
|              |             | 100             | 91.0          | 68.71                |              | 0.61                 |                            |
|              |             | 100             | 91.4          | 68.36                |              | 0.61                 |                            |
| b-2          | 800         | 100             | 89.0          | 69.89                | 62.204       | 0.11                 | 0.098                      | 96.9                       |
|              |             | 100             | 89.1          | 68.89                |              | 0.11                 |                            |
|              |             | 100             | 89.0          | 69.89                |              | 0.11                 |                            |
| b-3          | 850         | 100             | 90.0          | 68.12                | 61.312       | 0.074                | 0.067                      | 97.9                       |
|              |             | 100             | 89.0          | 68.89                |              | 0.075                |                            |
|              |             | 100             | 89.0          | 68.89                |              | 0.075                |                            |
| b-4          | 900         | 100             | 88.5          | 69.04                | 61.069       | 0.043                | 0.038                      | 98.8                       |
|              |             | 100             | 88.2          | 69.29                |              | 0.043                |                            |
|              |             | 100             | 87.9          | 69.39                |              | 0.043                |                            |
| b-5          | 950         | 100             | 87.2          | 68.86                | 60.923       | 0.057                | 0.050                      | 98.4                       |
|              |             | 100             | 86.6          | 70.32                |              | 0.057                |                            |
|              |             | 100             | 87.1          | 69.91                |              | 0.057                |                            |

Table 7: Calculation of dechlorination and [Zn] reclaiming in experiment (b) involving at different roasting temperatures

| Temperature  | dechlorination | synchronous dezincification | actual [Zn] loss | [Zn] reclaiming | Rate of [Zn] reclaiming |
|--------------|----------------|----------------------------|------------------|----------------|-------------------------|
| ∘C           | g              | g                          | g                | g              | %                       |
| b-1          | 750            | 2.624                      | 2.416            | 1.295          | 1.121                   | 46.40                     |
| b-2          | 800            | 3.081                      | 2.838            | 1.569          | 1.269                   | 44.71                     |
| b-3          | 850            | 3.113                      | 2.867            | 2.488          | 0.379                   | 13.22                     |
| b-4          | 900            | 3.142                      | 2.894            | 2.699          | 0.195                   | 6.74                      |
| b-5          | 950            | 3.129                      | 2.882            | 2.877          | 0.005                   | 0.17                      |

Figure 7: Results of dechlorination and [Zn] reclaiming with a changing temperature

creases. The results of experiment (b) verify the Hypothesis B.

5 Mechanism model of dechlorination and [Zn] reclaiming

Based on the results of the thermal experiments, the main reaction processes of dechlorination and [Zn] reclaiming are clear: ZnCl₂ is transformed into the gas phase inside the dust particles and spreads out and then diffuses into the surrounding gas phase, where it reacts with O₂ and ZnO is generated. The reaction mechanism mode is shown in Figure 8.
The reaction of dechlorination and [Zn] reclaiming is a multi-step process, and the reaction steps are as follows:

1. When the dust is heated, ZnCl$_2$ boils and becomes steam on the surface of unreacted nuclear matter, and the nonvolatile components form a residual porous media layer at the same time;
2. ZnCl$_2$ steam spreads from the inner part of the dust to the outside. It transmits through the residual porous media layer and the gas boundary layer and, in turn, diffuses into the gas phase;
3. O$_2$ from the air is transmitted to the vicinity of the dust particles;
4. ZnCl$_2$ and O$_2$ encounter and react with each other, and ZnO and Cl$_2$ are generated;
5. The generated ZnO nucleates and grows into solid particles. Under the action of gravity, some ZnO solid particles settle on the surface of dust particles, while other ZnO solid particles remain loose when they are far away from the dust and the crucible;
6. The generated Cl$_2$ diffuses into the gas phase and becomes loose.

According to the reaction mechanism model, the concentration of ZnCl$_2$ steam in the dust particles decreases as the distance from the ZnCl$_2$ boiling interface increases, and it is low in a gas environment, and the reaction may be limited by the dynamics of the new nucleation of ZnO solid. ZnCl$_2$ steam spreads a long distance without reacting, and the generated ZnO from the slow chemical reaction appears in the area, which is far away from the dust and the crucible. It cannot be collected efficiently, resulting in little [Zn] being reclaimed.

If the concentration of O$_2$ is higher in the residual porous media layer, the chemical reaction of [Zn] reclaiming must be unstoppable, and the process of ZnCl$_2$ spreading is blocked, which means more [Zn] is reclaimed. The key reason for the chemical reaction occurring in the external gas environment outside of the dust is that O$_2$ from the air environment cannot be transmitted into the dust particle interior or dust bed efficiently. Accelerated transmission of O$_2$ can change the reaction area and cause more [Zn] reclaiming to occur in the roasting steelmaking zinc-rich dust process.

6 Conclusions

1. The reaction mechanism model of dechlorination and [Zn] reclaiming from steelmaking zinc-rich dust is shown in Figure 8, and the reaction is a multi-step process, as follows: (1) When the dust is heated, ZnCl$_2$ boils and becomes steam on the surface of unreacted nuclear matter, and the nonvolatile com-
ponents form a residual porous media layer at the same time; ② ZnCl₂ steam spreads from the inner part of the dust to the outside. It transmits through the residual porous media layer and the gas boundary layer and, in turn, diffuses into the gas phase; ③ O₂ from the air transmits to the vicinity of the dust particles; ④ ZnCl₂ and O₂ encounter and react with each other, and ZnO and Cl₂ are generated; ⑤ the generated ZnO nucleates and grows into solid particles. Under the action of gravity, some ZnO solid particles settle on the surfaces of dust particles, while other ZnO solid particles remain loose when they are far away from the dust and the crucible; ⑥ the generated Cl₂ diffuses into the gas phase and becomes loose.

2. The key reason that the chemical reaction occurs in the external gas environment outside of the dust is that O₂ from the air environment cannot be transmitted into the dust particle interior or dust bed effectively. Accelerated transmission of O₂ can lead to the solution undergoing efficient [Zn] reclaiming while dechlorinating from the steelmaking zinc-rich dust.

3. Restricted by the reaction mechanism, the reaction rate of [Zn] recalcining is limited, and lots of zinc is lost synchronously without being recovered, so the actual measured mass of [Zn] reclaiming is very low. The reaction of [Zn] recalcining should be limited by the dynamics of new nucleation of ZnO solid, which is more difficult at higher temperatures, although the Gibbs free energy of the [Zn] recalcining reaction is lower.

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