



## Rapid communication

# Study on vacuum carbothermic reduction kinetics of hemimorphite catalyzed by calcium fluoride

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## ABSTRACT

The kinetics of the vacuum carbothermic reduction of hemimorphite was studied with  $\text{CaF}_2$  as catalysis in the temperature range of 1273–1423 K. The results showed that the zinc reduction rate could be enhanced by increasing the adding weight of  $\text{CaF}_2$ , initial moles ratio of  $\text{C}/\text{Zn}_{\text{total}}$  or the reaction temperature. And the zinc reduction rate would decrease with the increasing of either the average particles size of hemimorphite or the system pressure when it was higher than 20 kPa. It could be inferred that the reduction reaction was controlled by the surface reaction with the activation energy of 164.82 kJ/mol by solid–solid reaction model.

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Nonsulphide zinc deposits are generally classified into two categories. One is supergene deposits derived from zinc sulphides. The other is formed by hypogene deposits, recognized as non-sulphide zinc minerals such as hemimorphite, willemite, smithsonite, franklinite, zincite, gahnite, and so on. Among them, hemimorphite or willemite is considered as an attractive substitute for zinc sulfide ores to extract zinc owing to the increasing restriction on sulfur emission all over the world [1]. However, due to the lack of suitable processing methods, this attractive zinc resource is still not widely used up to now. The silicon with high content in hemimorphite usually enters into the aqueous solution in the form of silica gel along with zinc during the hydrometallurgical process, which will result in higher difficulty for filtration [2]. In the pyrometallurgical process, higher temperature is necessary for the reduction of hemimorphite due to the differences of structure and properties between zinc oxide and zinc silicate derived from dehydration of hemimorphite [3]. Based on the advantages of vacuum metallurgy technology [4], such as lower temperature and shorter reaction time, high recovery. In our

previous research, the recovery of zinc is 96.82% by vacuum carbothermic reduction of smithsonite [5], and that of hemimorphite is 93% [6]. Although many studies of lead [4], stibonite [4], zinc [5,6], magnesium [7], aluminum [8,9] have been conducted on carbothermic reduction of their metal oxides in vacuum, the vacuum carbothermic reduction mechanism of hemimorphite in presence of calcium fluoride is not reported, the aim of the present work was to investigate the kinetics and mechanism.

The hemimorphite ore was from Lanping of Yunnan province in China with hemimorphite  $[\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}]$  as major mineral, and zincite  $[\text{ZnO}]$ , franklinite  $[\text{ZnFe}_2\text{O}_4]$  and zinc blende  $[\text{ZnS}]$  as minor minerals. The mass fraction of the main elements in the ore is 49.13% (Zn), 29.29% (O), 12.33% (Si) and 10.38% (Fe), respectively. Coking coal was from Douli Mountain of Liyuan, Hunan province in China. The mass fraction of C, ash and S in the coking coal is 70.28%, 6.39% and 0.75%, respectively. Other chemicals, such as  $\text{CaF}_2$ , are commercially available with analytical purity.

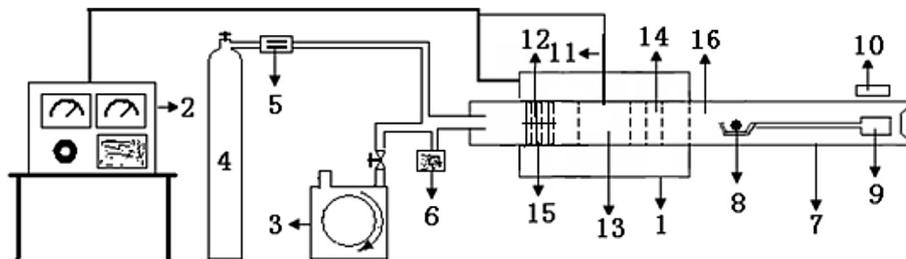
The reduction experiments were carried out by an experimental setup shown in Fig. 1. It is composed of the experimental stove, temperature control system, vacuum acquisition system and gas-supply system.

Hemimorphite with different average particle size and coking coal with average particle size of 30  $\mu\text{m}$  were sifted. Hemimorphite, coking coal, calcium fluoride and water were well mixed and

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**Fig. 1.** Schematic diagram of the experimental setup 1-The experimental stove; 2-Temperature controller; 3-Vacuum pump; 4-Gas containers; 5-Flow meter; 6-Pressure gauge; 7-Alundum tube; 8-Crucible; 9-Handle of iron; 10-Magnet; 11-Thermocouple; 12-Condensator; 13-Flat-temperature zone; 14-Sintering zone; 15-Collecting zone; 16-Cooling zone.

pelletized with the radius of 10 mm. The dried pellets were fed into the crucible and the experimental stove was sealed and quickly heated to the experimental temperature at the required pressure. The crucible was delivered to sintering zone for 30 min to ensure their strength and then to flat-temperature zone for certain time according to the requirement of experiment with magnetic force. In the sintering zone, hemimorphite was decomposed into zinc silicate by dehydration. While in the flat-temperature zone, zinc silicate was reduced to metallic zinc. Vapor of zinc and other volatile substances entered into the collecting zone and were collected there. The crucible was then drawn to the cooling zone and heating was ended. After being cooled completely in the cooling zone, the obtained products and slag were fetched, weighed and analyzed.

The relevant experimental conditions are listed in Table 1. The underlined values are standard operating variables.

Based on our previous study, the interaction between zinc silicate and carbon can be represented by the following reactions [3]:

Direct reduction:



Indirect reduction:



The kinetics of solid–solid reaction is influenced by many factors [10,11]. In this study, the effects of the weight of  $\text{CaF}_2$ , initial moles ratio of  $C/\text{Zn}_{\text{total}}$ , system pressure, average particles size and reaction temperature on the kinetics were investigated.

Zinc reduction rate at  $t = t$  can be calculated according to Eq. (4).

$$a = \frac{m_{\text{sa}}^0 \times C_{\text{Zn}}^0 \times m_{\text{sl}}^t \times C_{\text{Zn}}^t}{m_{\text{sa}}^0 \times C_{\text{Zn}}^0} \quad (4)$$

where  $a$  is the reduction rate of zinc;  $t$  is the reaction time, min;  $m_{\text{sa}}^0$  represents the mass of sample at  $t = 0$ , g;  $m_{\text{sl}}^t$  represents the mass of slag at  $t = t$ , g;  $C_{\text{Zn}}^0$  is the content of Zn in the sample at  $t = 0$ , g/g; and  $C_{\text{Zn}}^t$  is the content of Zn in slag at  $t = t$  min, g/g.

**Table 1**  
Operating variables in the vacuum carbothermic reduction experiments.

Variable	Values
The weight of adding $\text{CaF}_2/\text{wt}\%$	0, 5, <u>10</u> , 15
Initial moles ratio of $C/\text{Zn}_{\text{total}}$	0.5, 1, 1.5, 2, <u>2.5</u> , 3
Pressure of system/kPa	<u>1</u> , 10, 15, 20, 25, 30
Average particles size/ $\mu\text{m}$	8.1, <u>25.6</u> , 49.5, 130.1
Reaction temperature/K	1273, 1323, <u>1373</u> , 1423

Note: Underlined values are standard operating variables.

The content of Zn in the sample and slag was analyzed according to GB/T 8151.1–2000. When the content of Zn in the slag was very low, it was determined by ICP-OES (Intrepid II xsp, American hermo Electron Corporation).

Fig. 2A shows the effect of the weight of  $\text{CaF}_2$  added in the samples on the zinc reduction rate. The higher the weight of  $\text{CaF}_2$ , the faster the reaction occurs.  $\text{CaF}_2$  can act as a catalyst in the reaction between zinc silicate and carbon as reported [6]. More  $\text{CaF}_2$  in the solid sample will provide larger surface area open to zinc silicate and therefore reaction (1) and reaction (2) can be accelerated.

The experimental results of the initial molar ratio of  $C/\text{Zn}_{\text{total}}$  on zinc reduction rate are shown in Fig. 2B.

The zinc reduction rate is greatly affected by  $C/\text{Zn}_{\text{total}}$  when  $C/\text{Zn}_{\text{total}}$  is less than 2.5. The higher the initial molar ratio of  $C/\text{Zn}_{\text{total}}$ , the higher the zinc reduction rate is. Higher carbon content in the solid samples means more contact surface area for C and  $\text{Zn}_2\text{SiO}_4$ . Therefore, reaction (1) can be accelerated with more production of CO to enhance reaction (2) [6]. However, further increase of  $C/\text{Zn}_{\text{total}}$  results in insignificant improvement of zinc reduction rate, probably due to the supersaturation of carbon.

Fig. 2C presents the effect of system pressure on the zinc reduction rate. Although the change of the zinc reduction rate may be ignored when the system pressure is in the range of 1–20 kPa, it is significantly increased when the system pressure is over 20 kPa. There is a critical pressure for zinc evaporation [4,12] at certain temperature. It is obvious from Fig. 2C that the critical pressure for carbothermic reduction of zinc silicate at 1373 K is about 20 kPa.

Generally speaking, smaller particles in solid–solid reaction will have a larger reaction rate. As shown in Fig. 2D, the smaller the size of hemimorphite powders, the faster the reaction occurs. Due to the overdose of coking coal in our experiments, the effect of the average particles size on the reaction rate is small [6,10].

Fig. 2E demonstrates the important effects of reaction temperature on the zinc reduction rate. With the increase of reaction temperature, the zinc reduction rate accelerates significantly, even though it is very low when the temperature is less than 1373 K.

The carbothermic reduction of hemimorphite in the presence of calcium fluoride can be represented by Eqs. (1)–(3). The reaction is a first-order reaction [13] determined by using linear regression method [14]. Assuming that the surface reaction is the rate controlling step, the following expression of the solid–solid reaction model can be tested to describe the reaction kinetics of the process [15]:

$$\left[ (1 - a)^{-2/3} - 1 \right] = kt \quad (5)$$

where  $t$  is the reaction time, min;  $a$  is zinc reduction rate at  $t = t$ ;  $k$  is reaction rate constant. Eq. (5) is use to describe the first-order reaction kinetics of solid–solid reaction when the reactants are spherical in shape [16].

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