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Preparation of metal zinc from hemimorphite by vacuum carbothermic reduction with CaF_2 as catalyst

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Abstract: Zn reduction was investigated by the vacuum carbothermic reduction of hemimorphite with or without CaF_2 as catalyst. Results indicate that CaF_2 can catalyze the carbothermic reduction of zinc silicate, decrease the reaction temperature and time. The lower the reaction temperature and the more the amount of CaF_2, the better the catalytic effect. The optimal process condition is obtained as follows: the addition of about 10% CaF_2, the reaction temperature of 1373 K, the molar ratio of C to Zn_{Total} of 2.5, the pressure of system lower than 20 kPa, the reaction time of about 40 min. Under the optimal process condition, the zinc reduction rate is about 93% from hemimorphite.

Key words: metal zinc; calcium fluoride; catalysis; carbothermic reduction; hemimorphite

1 Introduction

Hemimorphite is one of the most valuable zinc oxide ores as well as the final product when zinc silicate comes into being from sphalerite by weathering over a long period of time. The proportion of hemimorphite to zinc oxide ore is next to that of smithsonite, but the floatability of the former is far less than that of the latter [1]. Due to changeable surface properties and complicated structure, it is difficult to extract metal zinc from hemimorphite. There were few researches on zinc silicate such as hemimorphite. There were different opinions on hemimorphite leaching behaviors. Many researchers [2,3] held that hemimorphite can not be dissolved, which makes the low leaching ratio of zinc oxide ore. Some researchers [4] thought that the silica with high content usually entered solution as silica gel with zinc when hydrometallurgical method was used, and the formation of silica gel made filtration difficult. In pyrometallurgical process, due to the differences of structure and properties between zinc oxide and zinc silicate formed from the dehydration of hemimorphite [5], the reduction of hemimorphite needs high temperature, thus the energy consumption increases greatly. Consequently, it is urgent to find an effective method to exploit and utilize hemimorphite. Vacuum metallurgical technology has high-efficiency on improving metal recovery and shortening process flow, and meets the environmentally-friendly and resource-saving requirements [6−8]. On the basis of the advantages of vacuum metallurgy technology, CaF_2 is added as catalyst to cut down energy consumption and increase the Zn recovery.

2 Experimental

2.1 Materials

Hemimorphite from Lanping of Yunnan Province, China, was employed. Tables 1 and 2 show chemical composition and phases of the original mineral, respectively.

The content of zinc is 49.13% and the major mineral is hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) in the original mineral. Coking coal from Douli Mountain of Lianyuan, Hunan Province in China，was used as not only the reductant but also the binder in this study. The chemical composition of coal is shown in Table 3. Other

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chemical reagents such as CaO, CaF_2 and NaF are analytically pure.

Table 1 Chemical composition of original mineral (mass fraction, %)

Zn	Pb	O	Fe	S	Mg	Si	Al	Ca	P
49.13	0.049	29.9	0.379	0.031	0.287	12.33	1.20	0.189	0.136

Table 2 Zn content in different phases of original mineral

$Zn_4Si_2O_7(OH)_2 \cdot H_2O$	ZnO	ZnS	$ZnO \cdot Fe_2O_3$	Total
44.81	4.02	0.20	0.10	49.13

Table 3 Chemical composition of coking coal

Total moisture as received/%	Moisture in air-dried basis/%	Ash in air-dried basis/%
0.50	1.51	6.39
Volatile in air-dried basis/%	Fixed carbon in air-dried basis/%	Total sulphur as received/%
21.82	70.28	0.75

2.2 Facilities

The reduction was carried out in a vacuum furnace with classification condensation, which was made by Hunan Acme Technology Co., Ltd. The vacuum furnace was designed according to the characteristics of vacuum carbothermic reduction of hemimorphite and utilization of the waste heat for the condensation classification of vapour. It is composed of vacuum furnace (Fig. 1), furnace temperature control system, vacuum acquisition system, water-cooling system and gas-supply system.

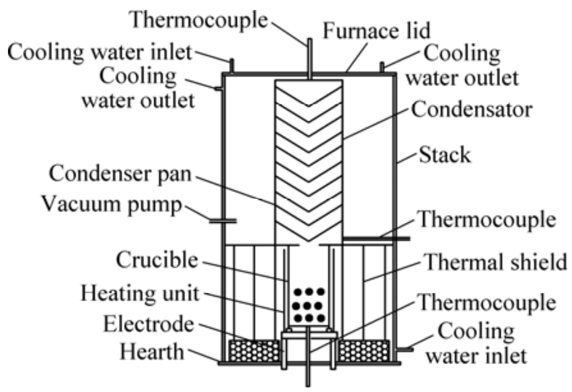
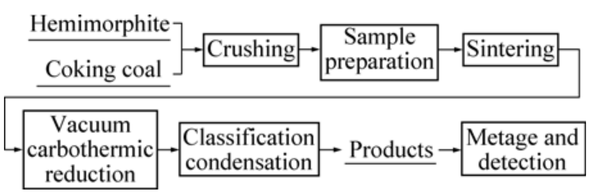


Fig. 1 Sketch map of vacuum furnace with classification condensation

2.3 Experiment process

The experiment process is described as:



Hemimorphite and coking coal were sifted through a sieve with sieve pore size of 0.214 mm (70 mesh). Hemimorphite, coal and water (sometimes adding additive) were well mixed and made into cylinder samples (the radius was 10 mm, the height was 10 mm). The dried samples were sintered at 823 K for 30 min to ensure the sample strength. Then the samples were fed into the crucible of vacuum furnace and quickly heated to the experimental temperature at the required pressure. In this process, zinc silicate was reduced to metal zinc, then vapour of zinc and other volatile substances entered into a classification condenser. The classification condenser consisted of many bottom-up condenser pans where the temperature decreased from 1123 K to 300 K in the experiment process and the substances could be separated, purified and condensed in a suitable place of classification condenser to obtain pure zinc (purity was above 99.95% [9]), pure cadmium and other products. At last, products and slag were weighed and detected. The relevant experimental conditions are listed in Tables 4 and 5.

Table 4 Processing parameters in vacuum carbothermic reduction experiments without catalyst

Parameter	Value
Initial mole ratio of C to Zn_{Total}	2.5
Pressure of system /kPa	0.05
Reaction time/min	10, 20, 30, 40, 50, 60, 70
Reaction temperature/K	1323, 1373, 1423, 1473

Underlined values are standard operating variables.

Table 5 Processing parameters in vacuum carbothermic reduction experiments with catalyst

Parameter	Value
Initial mole ratio of C to Zn_{Total}	1, 1.5, 2, 2.5, 3
Pressure of system/kPa	0.05, 10, 15, 20, 25, 30
Reaction time/min	10, 20, 30，40, 50
Reaction temperature/K	1273, 1323, 1373, 1423

3 Results and discussion

3.1 Calculation of Zn reduction rate and analysis of zinc content

Zinc reduction rate, α, can be calculated according to:

$$\alpha = \frac{m_{sa}^0 \times C_{Zn}^0 - m_{sl} \times C_{Zn}}{m_{sa}^0 \times C_{Zn}^0} \times 100\% \tag{1}$$

where t is the reaction time, min; m_{sa}^0 represents the mass of sample at t=0; m_{sl} is the mass of slag at t; C_{Zn}^0 is the content of Zn in sample at t=0; C_{Zn} is the content of Zn in slag at t, g/g.

The contents of Zn in the samples and slag were