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Reaction mechanism and influence factors analysis for calcium sulfide generation in the process of phosphogypsum decomposition

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ABSTRACT

FactSage6.1 software simulation and experiments had been used to analysis the reaction mechanism and influence factors for CaS generation during the process of phosphogypsum decomposition. Thermodynamic calculation showed that the reaction for CaS generation was very complex and CaS was generated mainly through solid–solid reaction and gas–solid reaction. The proper CO and CO_2 have benefit for improving the decomposition effects of phosphogypsum and reducing the generation of CaS at 1100 °C. Using high sulfur concentration coal as reducer, the proper reaction conditions to control the generation of CaS were: the coal particle size was between 60 mesh and 100 mesh, reaction temperature was above 1100 °C and the heating rate was 5 °C/min. Experimental and theoretical calculation indicated that the concentration of CaS was only ten percents in the solid product at 1100 °C, which is favorable for the further cement producing using solid production.

1. Introduction

Phosphogypsum (PG) is a by-product of wet phosphoric acid during which phosphate rock is reacted with sulfuric acid. It is almost over 40 million tons of PG produced in China each year [1]. Which has become the primary barrier for the development of phosphate fertilizer industry because of its complicated chemical composition, large-tonnage output, and environment harm [2–7]. One of recycling methods for PG is thermal decomposition to reuse sulfur and produce cement [8–11]. Because of its complex components, many middle-products are produced during the process of decomposition [12,13]. Especially the generation of calcium sulfide (CaS), which has disadvantageous effect on the recovery of sulfur dioxide (SO_2) and the further reuse of solid products [14–18]. Oh and Wheelock [19] and Talukdar et al. [20] had done some researches on explaining the generation of CaS. It is important to investigate the mechanism of CaS generation for the reuse of PG.

In the previously research of our group, the decomposition process of phosphogypsum in a nitrogen atmosphere at different conditions had been studied with high sulfur concentration coal as reducer [21,22]. In this study, chemical thermodynamic equilibrium calculation by the Equilibrium model of FactSage6.1 was used to elucidate the possible reaction mechanism and phase transform during the decomposition process of PG at different conditions. As comparing, experiments were taken as the same conditions as in simulation calculation for the decomposition of PG. The purpose of this study is to prove the reaction mechanism of CaS generation and its effect on the decomposition of PG.

2. Mechanism analysis

Because of the complex components of PG, many reactions could take place during the process of PG decomposition. The following reactions about CaS generation and transformation could take place with coal in nitrogen atmosphere:

$$CaSO_4 + 4C \rightarrow CaS + 4CO \tag{1}$$

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \tag{2}$$

$$4CO + CaSO_4 \rightarrow CaS + 4CO_2 \tag{3}$$

$$4CaO + 3S_2(g) \rightarrow 4CaS + 2SO_2 \tag{4}$$

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \tag{5}$$

$$CaSO_4 + 3CaS \rightarrow 4CaO + 4S \tag{6}$$

$$CaS + 3CaSO_4 + 4CO_2 \rightarrow 4CaCO_3 + 4SO_2 \tag{7}$$

$$CaS + 2SO_2 \rightarrow CaSO_4 + 2S \tag{8}$$

$$CaS + 3SO_3 \rightarrow CaO + 4SO_2 \tag{9}$$

The beginning temperature of the possible reactions taking place was listed in Table 1. Thermodynamic results calculated by

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Table 1
ΔrG and ΔrH of reactions at possible beginning temperatures.

Reaction	T (°C)	ΔrG (kJ/mol)	ΔrH (kJ/mol)
(1)	500	−38.135	513.247
(2)	200	−0.093	173.735
(3)	100	−177.036	−172.356
(4)	100	−289.971	−331.996
(5)	1200	−30.996	936.345
(6)	1500	209.079	316.825
(7)	1500	145.735	163.917
(8)	100	−224.302	−364.913
(9)	100	−237.927	−161.925

FactSage6.1 show that all reactions could be occurred theoretically except reactions (6) and (7). CaS is produced by reaction (2). Besides, an important reaction path is $CaSO_4$ reacting with CO (reaction (3)), in which CO is produced by vaporization reaction of coal and reaction (1). During the decomposition process of PG with coal, coal is very easily vaporized to produce CO therefore reaction (3) is easy take place to generate CaS.

The elimination process of CaS is mainly achieved through solid–solid reaction and gas–solid reaction such as reactions (5)–(9). Table 1 indicates that the gas–solid reactions for CaS elimination (reactions (6)–(9)) are exothermic reactions and occurred at very low temperature except reaction (5), which is occurred at 1200 °C and reaction heat is 936.345 kJ/mol. At the high temperature, reactions (8) and (9) are limited while reaction (5) could be happened mostly. This indicates that reaction (5) will be the key reaction of CaS elimination under high temperature.

3. Experimental

3.1. Sample preparation

PG is a chemical compound, which mainly consists of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) and some impurities such as P_2O_5, F^-, organic substances and some trace metals (e.g. Mn, Al, Fe, Na, Ka). The samples of PG used in this study were collected from Yunnan Natural Gas and Chemical Engineering Company; the main chemical compounds were listed in Table 2, the size of PG samples was about 0.074 mm. After drying in tube furnace at 60 °C for 12 h, PG was used in experiment. The high sulfur concentration coal used in the experiment come from Yunnan Chuxiong; the main compounds were detected by standard of Chinese coal classification (GB476-1979) and the results were listed in Table 3. After treatment, coal sample also was crushed into particles with different sizes (200, 160, 100, and 60 mesh) before experiment.

3.2. Experiment methods and equipments

The equipments used in this study were: KTL1600 tube furnace (Nanjing University Experiment Factory), KM9106 complex fuel gas analyzer (KANE Company), D/max-3BPEX-P96 powder X-ray diffract meter (Rigaku).

Decomposition reaction of PG was carried out in a tube furnace at nitrogen atmosphere under different coal particle size, reaction temperature and heating rate. Temperature programming was adopted for heating process, heating rate was 8 °C/min from beginning to 800 °C firstly, above that, using heating rate of 3 °C/min, 5 °C/min, 8 °C/min, and 10 °C/min, respectively. The reaction temperature was controlled at 1000 °C, 1100 °C, and 1200 °C.

The solid products were analyzed by XRD to investigate the composition. The contents of CaS and $CaSO_4$ were examined by chemical methods according to GB/T 16489-1996 and GB/T 5484-2000. Therefore the mass fraction of CaO could be calculated.

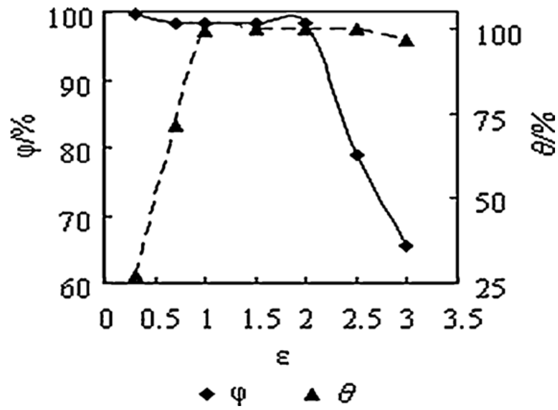

Fig. 1. Result of chemical thermodynamic equilibrium calculation at different molar ratio of $CaSO_4$/C.

3.3. Theoretical calculation

FactSage software, which contains FACT-Win and ChemSage is a powerful calculation software and it could be used to calculate the chemical thermodynamic equilibrium under the limitation of a variety of conditions. In this study, the equilibrium model of FactSage6.1 was used to investigate the influence for CaS generation by different effect factors such as reaction atmosphere (N_2, CO and CO_2), molar ratio of $CaSO_4$/C (ε) and reaction temperature. According to the composition of original PG, initial input components for the reaction equilibrium calculations were $CaSO_4$, SiO_2, Al_2O_3, Fe_2O_3, and the mass was 7.2420 g, 0.943 g, 0.0236 g and 0.0132 g respectively. The inputting composition of high-sulfur coal was C, H, O, N, S and the mass was according to the requirement of ε. The reaction pressure was 1.01×10^5 Pa.

Reactive degrees of PG decomposition were expressed by the decomposition rate (φ) and the desulfurization rate (θ).

$$\varphi = \frac{1.889 m_{CaS} + 1.889 m_{CaS}}{m_{CaSO_4}}$$

$$\theta = \frac{2.125 m_{SO_2}}{m_{CaSO_4}}$$

where m_{CaS} = theoretical yield of CaS, g; m_{CaO} = theoretical yield of CaO, g;

4. Results and discussion

4.1. Theoretical calculations and analysis

4.1.1. Effect of the molar ratio of $CaSO_4$/C

Fig. 1 gives the results calculated by chemical thermodynamic equilibrium of FactSage at different molar ratio of $CaSO_4$/C. It is clear that both decomposition rate and desulphurization rate are very high when ε is between 1.5 and 2.2. That means the reaction for the generation of CaS is hardly to take place under weak reduction condition. While at high ε, it is very difficult for $CaSO_4$ to decompose completely at lacking reducing agent. The decomposition products according to the same calculation at the same conditions are shown in Fig. 2. The mass of CaS is decreased with the increasing of ε, however, the mass of CaO and SO_2 are increased with the increasing of ε. These results confirm the above analysis and are consistent with the results by the research of Ma et al. [14].

4.1.2. Effect of reaction atmosphere

Figs. 3 and 4 are the calculation results of PG decomposition at different amounts of CO and CO_2 under 1100 °C, which indicate that