Experimental study of preparing CaS from phosphogypsum with lignite

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Abstract: The reaction of phosphogypsum (PG) and lignite is complex, which depends on the reaction conditions and atmosphere. In the paper, it was carried out for reduction decomposition of PG to calcium sulfide under N₂ atmosphere. Scanning electron microscopy and XRD were used to analyze the raw material and decomposition solid production. The reaction mechanism of preparing CaS from PG with lignite were analyzed by Factsage 6.1 and thermodynamic analysis. The results indicated that the decomposition reaction temperature were between 800 °C and 1100 °C. These experimental conditions were also studied on Ca/C molar ratio, reaction temperature and reaction time in the N₂ atmosphere. The results showed that the optimal result for production of CaS are found to be a lignite to CaSO₄ molar ratio of 2.4 to 1, a temperature of 900-1000°C in reductive atmosphere. Under these conditions the conversion rate of CaS from phosphogypsum amount to no less than 97.3%.

1. Introduction
One of the recycling effective ways for phosphogypsum (PG) is thermal decomposing to produce sulfuric acid. It may realize the recycling use of sulfur resource in production process of phosphate fertilizer and solved also the environmental problems caused by PG. It is commonly known that PG is industrial solid waste from the production of wet-process phosphoric acid[1]. China's PG production is expected to be 70 million tons in 2019. At present, the treatment method of phosphogypsum is still based on stockpiling[2]. Because phosphogypsum contains a large number of impurities, such as phosphorus, fluorine, phosphoric acid and hydrochloric acid, the open air stacking will cause pollution to the surrounding environment. Therefore, it is extremely urgent to use phosphogypsum as resources.

One of the most effective ways is decomposing PG to produce chemical products[1] such as sulfuric acid among different comprehensive utilization methods [3]. The first step involves the decomposition of PG to calcium sulphide (CaS), which is achieved by reducing it at high temperatures with anthracite, coal or reducing gases [4]. During the next steps CaS is used as main reagent to obtain sulphuric acid.
Another use of CaS is an industrially important chemical, used in the production of sulphur by the Chance-Claus process, in the treatment of waste liquor form paper mills, as an insecticide and germicide [5].

In the previous research of our group, our laboratory used to study the decomposition process of PG and high-sulfur coal under different conditions in a nitrogen atmosphere. In this paper, the same condition as the simulation calculation was used in the experiment to study the decomposition process of lignite and PG under different conditions. To produce CaS form PG with lignite.

2. Reaction Mechanism
The main component of PG is calcium sulfate dihydrate (CaSO$_4$$\cdot$2H$_2$O). The reactions involved in the reductive decomposition of CaS have been studied from the beginning of the 20th century. The reaction equation of PG with lignite is as follows:

$$2C + CaSO_4 = CaS + 2CO_2$$  \hspace{0.5cm} (1)
$$4C + CaSO_4 = CaS + 4CO$$  \hspace{0.5cm} (2)
$$4CO + CaSO_4 = CaS + 4CO_2$$  \hspace{0.5cm} (3)

3. Experimental Section

3.1 Experiment equipment
The experiment and analysis equipment used in this study are as follows: XXWRT-2C thermogravimetric analyzer (Beijing Optician Plant); GSL-1600X40 tube resistance furnace (Hefei Kejing Materials Technology CO.,LTD ); D/max-3BPEX-P96 powder X-ray diffract meter (Rigaku); JSM-6301F scanning electron microscopy (SEM).

3.2 Experiments in a tube furnace
A tube furnace was used to research the reaction process of PG with lignite. A experimental data were collected to determine the conditions. The furnace was a quartz tube with 50mm diameter and 100cm long. The sample was placed in a 5-cm-long, 2-cm-wide, and 4-cm-deep boat. The PG sample and lignite were mixed in different proportions about 10g in each experiment. SEM analysis of the mixed sample was shown in Fig.1 (b). Then, the boat was placed in the middle of reactor. Nitrogen was used as protective atmosphere at a flow rate of 0.6L/min. The temperature was increased from room temperature to 1100°C. Alkali liquor was used to absorb the tail gas produced in the reaction. In the course of the experiments decomposition product were cooled under N$_2$ atmosphere. The solid products were analyzed by XRD to investigate the composition. The contents of CaS and CaSO$_4$ were examined by chemical methods.

4. Results and discussion

4.1 Experimental raw materials
The PG sample used in this study was bought from Yunnan Natural Gas and Chemical Engineering Company. After drying 80°C for 2 h, the chemical analysis was presented in Table 1 and the size range of the PG sample was smaller than 0.074 mm. SEM and XRD analysis of the PG sample was shown in Fig.1 (a), from which it is clear to see the sliced crystal structure of PG. Meanwhile, there are a small amount of small particles containing impurities. The corresponding XRD patterns are shown in Fig. 2. All the detected diffraction peaks were indexed to CaSO$_4$$ \cdot$2H$_2$O. The lignite used in the experiment was obtained from Yunnan Qujing. The compounds were presented in Table 2. The coal sample was also broken and its size range was smaller than 0.147 mm. According to the Fig.1(b), the lamellar particles are the major in PG.
Table 1. The chemical components of the PG

|        | SO₃  | CaO  | SiO₂  | Al₂O₃ | Fe₂O₃ | MgO  | Total P₂O₅ |
|--------|------|------|-------|-------|-------|------|------------|
| Content (wt. %) | 41.23 | 29.76 | 13.16 | 0.18  | 0.06  | 0.04 | 0.16       |

Table 2. The chemical composition of lignite

| Fix-C | Sₚ  | Hₚ  | Oₚ  | Nₚ  | Mₚ  | Vₚ  | Aₚ  |
|-------|-----|-----|-----|-----|-----|-----|-----|
| Content (wt. %) | 70.3 | 2.2 | 1.83 | 2.66 | 1.56 | 3.83 | 18.2 | 13.43 |

(a) Phosphogypsum

(b) The mixed materials of PG and lignite

Fig. 1. The SEM of the PG and mixed materials

Fig. 2. The XRD pattern of PG
4.2 Thermodynamic data of PG Decomposition

The thermodynamic calculations of the PG decomposition reaction by the reaction module of Factsage6.1 are listed in Table 3. The main reaction (1) and reaction (2) could take place at 500 and 400 °C, respectively. Besides, the reaction (3) is parallel competing reactions.

Table 3 $\Delta_rG_m$ and $\Delta_rH_m$ of reaction

| Temperature/°C | Reaction(1) | Reaction(2) | Reaction(3) |
|----------------|-------------|-------------|-------------|
|                | $\Delta_rH_m$/kJ | $\Delta_rG_m$/kJ | $\Delta_rH_m$/kJ | $\Delta_rG_m$/kJ | $\Delta_rH_m$/kJ | $\Delta_rG_m$/kJ |
| 100            | 520.480     | 250.428     | 147.062     | 36.696        | -172.356       | -177.036       |
| 200            | 521.001     | 177.951     | 173.735     | -0.093        | -173.531       | -178.136       |
| 400            | 517.159     | 33.459      | 170.777     | -73.127       | -175.605       | -179.712       |
| 500            | 513.247     | -38.135     | 168.101     | -109.181      | -177.046       | -180.226       |
| 600            | 508.200     | -109.150    | 164.611     | -144.837      | -178.978       | -180.523       |
| 800            | 495.017     | -249.228    | 155.157     | -214.772      | -184.704       | -180.317       |
| 1000           | 479.211     | -386.546    | 143.595     | -282.697      | -195.418       | -178.849       |
| 1200           | 463.437     | -521.368    | 132.393     | -348.822      | -198.650       | -176.276       |

4.3 Effect of the mole ratio of PG / lignite

Some earlier experimental data have shown that the mole ratio of PG and coal affected the decomposition process. For synthesizing CaS for PG and lignite, the molar ratio (ε) C/CaSO₄ should be changes from 1.2 to 2.5. The process of thermochemical decomposition of phosphogypsum to CaS was carried out under N₂ atmosphere. Fig.3 gives the results at different molar ratio (ε) of C/CaSO₄ at 1000°C in N₂ atmosphere. It is clear that the conversion rates are very high when ε is above 2.1. Results also indicate that an increased proportion of lignite in the samples used leads to increase the conversion ratio of CaSO₄. According to Fig.4, when the molar ratios (ε) are above 2.2, the conversion ratio is above 90%. With an increase of ε, the conversion ratios also increase from 90% to 94%. Therefore, this proportion (ε=2.4) was chosen as the reactant in the next experiments.

![Fig.3. Effect of molar ratio (C / CaSO₄)](image)

4.4 Effect of the experimental temperature

To study the influence of the experimental temperature, the sample of PG mixed with lignite was heated respectively at reaction temperatures of 800°C -1150°C respectively. Fig.4 shows typical
conversion curves of PG. It is seen that the conversion ratio is largely depended on the reaction temperature.

![Conversion Ratio vs Temperature](image)

**Fig. 4. Effect of calcining temperature to reductive rate**

From Fig. 4, it is noted that the conversion ratio change with the temperature. When the temperature is low (800 °C), it is not conducive to produce CaS form PG because the conversion ratios is only 48.20%. With the increase of reaction temperature, the conversion ratios reached the maximum 94.6% at 900 °C. When the reaction temperature increased gradually, the conversion ratios decreased. The possible reason is that the reaction of CaS and CaSO₄ took place in our previous word. Comprehensive consideration, the optimal temperature of the reaction temperature is 900-1000 °C.

**5. Conclusions**

The study reported reduction decomposition of PG to calcium sulfide under N₂ atmosphere. Scanning electron microscopy and XRD-ray diffraction were used to analyze the raw material and decomposition solid production. The results showed as followed:

First, the reaction mechanism of CaS from phosphogypsum with lignite were analyzed by Factsage 6.1 and thermodynamic analysis. The results indicated that the decomposition reaction temperature of preparing CaS from PG were between 800 °C and 1000 °C.

Second, these conditions were also studied on a carbon to CaSO₄ molar ratio, reaction temperature and reaction time in the N₂ atmosphere. The results showed that the optimal conditions for production of CaS are found to be a lignite to CaSO₄ molar ratio of 2.4 to 1, a temperature of 900-1000 °C in reductive atmosphere. Under these conditions the conversion rate of CaS from phosphogypsum amount to no less than 97.3%.

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