Phosphogypsum pyrolysis with mineralization agent under weak reducing atmosphere

Hui Feng¹, Rongsheng Xie²*

¹Guangxi Bohuan Environmental Consulting Services Co., Ltd, Nanning, Guangxi, 530007, China;
²Kunming Metallurgical Research Institute, Kunming, Yunnan, 650503, China.
*Corresponding author’s e-mail: xiers90@sina.com

Abstract: Batch experiments of phosphogypsum (PG) pyrolysis were carried out under weak reducing atmosphere, adding coke as reductant and CaF₂ as mineralization agent. As 3 wt% CaF₂ was added to the mixture, the optimal parameters of PG decomposition were mole ratio (C: CaSO₄) 0.7, reaction temperature 950 °C, pyrolysis time 60 min, and 1.9–2.2% oxygen content of inlet gas. Under this condition, the decomposition ratio of CaSO₄ was up to 90.6%, the SO₂ conversion was 70.4%, and the average volume concentration of SO₂ was 11.9%. With the aid of CaF₂, the pyrolysis temperature of CaSO₄ decreased significantly. The surface structure and morphology analysis revealed that CaF₂ was beneficial to the pyrolysis efficiency of CaSO₄. TG curve, XRD analysis and kinetic process have proved that the generation of intermediate substance CaS is the first stage for thermal decomposition of CaSO₄, and CaO is the end product of CaSO₄ pyrolysis under weak reducing atmosphere.

1. Introduction
Phosphogypsum (PG) is a common industrial by-product derived from phosphoric acid by wet process, making phosphate ore react with sulfuric acid [1]. The main ingredients of PG contain CaSO₄·2H₂O, minor amounts of phosphates, fluorides, sulfate ions and other impurities [2]. In China, there are over 55 million tons of PG produced annually [3], but the reuse of PG is lower than 10%. The majority is dumped in large stockpiles without any treatment [4]. The discarded PG occupies huge tracts of land, and it may cause serious environmental pollution due to some of its harmful impurities, so it is urgent to dispose PG and mitigate its adverse effects on environment.

At present, it is regarded as a promising technology for comprehensive utilization of PG to produce cement clinker and sulfuric acid. In order to enhance the effectiveness of PG pyrolysis, a lot of researches [5-11] have been carried out under various conditions, such as using reductive gases CO, CH₄, H₂ or reacting with different types of carbon [12-16]. However, this new technology of PG reuse has been adopted by few enterprises in China, because of the disadvantage of high energy consumption, low SO₂ concentration and low economic profit [17]. Thus, it becomes a hot topic about how to improve the decomposition efficiency of PG at a low temperature, and some researchers have begun to add SiO₂, ZnO, Fe₂O₃ or CaCl₂ as additive for PG decomposition process [18-21].

In view of the fact that CaF₂ has been widely used in steel industry to decrease the sintering temperature, it was initially used as a mineralization agent for PG pyrolysis in this study. The technical parameters such as PG pyrolysis temperature and the proportion of reducing agent were investigated systematically, and the function of mineralization agent CaF₂ was discussed, based on the
2. Materials and Methods

2.1. Sample preparation
The raw phosphogypsum used in the experiments was obtained from a chemical engineering plant in Yunnan, China. The major components of PG were determined as 70.7% CaSO₄, and the main impurities were SiO₂, Fe₂O₃, Al₂O₃, fluoride and insoluble materials, with the maximum amount of silica accounting for 9.43% of impurities. To eliminate the interference from the soluble impurities, the raw phosphogypsum was soaked in distilled water for two hours, and this treatment was repeated for three times. The obtained sediments were dried at 103 °C for 24 h in order to remove moisture, and then they were sieved to obtain the PG samples less than 74 um.

The coke was collected from a coking plant in Yunnan province, and it was grinded to decreased particle size less than 147 um. The main compounds of the prepared coke were analyzed using elemental analyzer (Vario Micro cube, Elementar Co., Ltd., Germany), and the element contents were 82.1% C, 1.00% H, 0.52% N, 1.08% S, respectively.

2.2. Experimental procedure
The experiments of PG pyrolysis were carried out in tube furnace under weak reducing atmosphere. The schematic diagram of the experimental system contained gas feeding, tube furnace, temperature controller, buffer device and gas analysis system (Fig 1). The main unit of the pyrolysis reactor was an electric tube furnace (MXG1400-60, Shanghai Micro-X Furnace Co., Ltd.), and the reaction temperature was controlled by a K-type thermocouple between the tube and the furnace.

For each experiment, mineralization agent CaF₂ was added to the mixture in a proportion (3%) of the total weight. The prepared sample (5 g) was placed in the middle of tube furnace. As the reactor reached the planned temperature, appropriate air was provided during the reaction time to obtain weak reducing atmosphere. During the whole process from programmed heating to the end of experiment, nitrogen was supplied at the flow rate of 50 mL min⁻¹, and the gas flow rate was measured by mass flow controllers. The released gas was sampled from buffer tank to test the concentration of CO, CO₂ and SO₂, then the gas was conducted to an absorption device with sodium hydroxide solution.

3. Results
Different factors such as process conditions or reaction atmosphere could affect the decomposition efficiency of PG, which may make the process of PG pyrolysis uncertain. Some previous researches have confirmed that the reducing atmosphere can affect the PG decomposition, thus this study investigated the effects of oxygen content on pyrolysis process, considering the fact that the reducing agent-carbon can be easily converted to carbon monoxide under low oxygen condition. The experiment condition was following: C:S ratio 0.7, pyrolysis temperature 950 °C, reaction time 60 min, and oxygen content of inlet gas varied from 1.1-2.9%. As showed in Fig.2, both of the PG decomposition and the
SO₂ conversion presented gradual increase before oxygen content was 2.2%, and then dropped moderately. However, the reducing atmosphere (expressed as \( \text{PCO}/\text{PCO}_2 \)) showed continuous decline with the increase of oxygen levels. As the air flow was within the range of 5-6 mL min⁻¹, the oxygen content of inlet gas varied from 1.9% to 2.2%, the ratio of \( \text{PCO}/\text{PCO}_2 \) was 13-18%, and the maximum values of PG decomposition and SO₂ conversion were 90.6% and 70.5% respectively. The results indicated that a suitable \( \text{PCO}/\text{PCO}_2 \) with the value of 13-18% may facilitate PG pyrolysis. This finding is also supported by the existing conclusion that the PG decomposition and SO₂ conversion can achieve a favorable result under an appropriate \( \text{PCO}/\text{PCO}_2 \) ratio of 18-20% in a suspension reactor and that too strong reducing atmosphere could adversely affect the process of PG decomposition [26].

![Figure 2 Decomposition efficiency of phosphogypsum at different oxygen content of inlet gas](image)

**4. Discussion**

4.1. **TG/DTG curves**

In order to observe the variations of the PG sample with the increase of decomposition temperature, TG/DTG analysis was used in this study. The PG sample contained 3wt% CaF₂, and the C:S ratio was 0.7. As shown in Fig.3, three endothermic peaks (presented as E1, E2, and E3) appeared at the temperature of 105 °C, 800 °C, and 950 °C respectively, which were consistent with the mass loss in the temperature range from ambient temperature to 1200 °C. Peak E1 at 105 °C corresponds to the fact that a certain amount of free water was removed. As the temperature reached 800 °C, the sample presented a gradual mass loss and peak E2 appeared, indicating that an intermediate substance may be produced. During the temperature of 900-1000 °C, the mixture showed a rapid mass loss and a remarkable peak E3 showed up. As the temperature was above 1000 °C, there were no distinct changes for. Based on the analysis of TG/DTG curves, the temperature of PG pyrolysis may be in the range of 900-1000 °C. It was also verified in this study that the optimal temperature of PG pyrolysis was 950 °C.
4.2. XRD characterization

Fig. 4 showed the XRD analysis of the raw PG and three reduced samples. With the increase of reaction temperature, the characteristic peak of CaSO$_4$ decreased, whereas the peak of CaO became stronger. As 3wt% CaF$_2$ was added to the mixture containing PG and coke, CaS was the dominant reduced product at 850 °C but disappeared entirely at 950 °C, which demonstrated that producing intermediate substance of CaS should be the first stage for PG decomposition, and reaction temperature may have important effects on PG pyrolysis and the reduced products.

Compared with the condition with no mineralization agent (shown in Fig. 4c), the diffraction peaks of CaSO$_4$ and CaS became insignificant at 950 °C as 3wt% CaF$_2$ was added to the mixture, some probable substances such as Ca$_2$SiO$_4$ and cuspidine (3CaO·2SiO$_2$·CaF$_2$) appeared in the final product (shown in Fig. 4d). The diffraction peaks of the reduced samples revealed that mineralization agent CaF$_2$ facilitate the formation of some fluosilicate complexes, resulting in the PG decomposition at a low temperature under weak reducing atmosphere.
5. Conclusions
CaF$_2$ was initiatively used as a mineralization agent for PG pyrolysis. As a certain amount of CaF$_2$, accounting for 3% of the total mass, was added to the mixture, the optimal parameters for PG decomposition were mole ratio (C: CaSO$_4$) 0.7, reaction temperature 950 °C, pyrolysis time 60 min, and 1.9-2.2% oxygen content of inlet gas. Under the weak reducing atmosphere and with the aid of CaF$_2$, the PG decomposition and SO$_2$ conversion were as high as 90.6% and 70.4% respectively, and the average concentration of SO$_2$ was about 11.9 vol.%, which can meet the requirement of producing sulfuric acid. Keeping a weak reducing atmosphere was necessary for PG pyrolysis. As the ratio of PCO/PCO$_2$ was 13-18%, most of the substance CaSO$_4$ may convert to CaO and SO$_2$, facilitating the decomposition of PG pyrolysis and the release of SO$_2$. This new technology can provide valuable theoretical reference and practical direction for PG pyrolysis to produce sulfuric acid and cement clinker.

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