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Research on thermal decomposing properties of phosphogypsum with Fe addition under multi-atmosphere control

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ABSTRACT

Phosphogypsum (PG) is a by-product of phosphor acid producing, which has become the primary barrier for the development of phosphate fertilizer industry. This paper proposes a series of technical process for the decomposition of PG with Fe addition. The FactSage 7.0 was used as feasibility analysis. Results from the TGA revealed that the initial decomposing temperature of PG was 590 °C, lower 300 °C than without $FeCl_3$ immersion. The decompositions of PG and lignite in multi-atmosphere were performed at different molar ratio in the tube furnace, when the molar ratio of lignite and PG was 1.2:1, the purity of CaO in solid products could reach 90.6%. Fluidized bed experiments were done in a vertical tube furnace, results indicated that after a multi-atmospheres cycles experiment, target production CaO purity could achieve 93.8%. The present research proves that PG with Fe addition decomposed in fluidized bed under multi-atmospheres is feasible.

1. Introduction

In the production of phosphatic fertilizer, 90% phosphoric acid is produced by the reaction between phosphate rock and sulfuric acid. During this process, Phosphogypsum (PG) is generated as one of the waste by-products [1]. The main artificial industrial by-product with major component of $CaSO_4 \cdot 2H_2O$ also include some impurities of phosphorus, fluoride and organic matters. Every year, more than 100–280 million tons of PG produced in the world, and less than 15% has been reused as building materials, soil stabilization, agricultural fertilizers and Portland cement [2–5]. That becomes an urgent task for the government to recycle PG to meet the environmental and economic requirements [6–8].

In China, coal is still the main primary energy at present and in near future, high quality coal resources such as bituminous coal and anthracite has been fully utilized, however, the utilization of lignite in large scale is just beginning [9–12]. Compared with other types of coal, lignite has the characters as: low calorific value, volatile oxygen, high oxygen content, high moisture content, (great difference in ash content and ash melting point); low density; easy to spontaneous combustion. The above characteristics of lignite indicated that it was appropriate used as the reductant in PG decomposition [13,14].

Our team have conducted many research on the optimal conditions and mechanisms of PG's decomposition as well as reducing the temperature of the decomposition reaction by adding addition and reducing atmosphere, which provided a deep insight into this research field [15–18]. Many intermediate products are generated during the process of PG's decomposition because of PG's complexity components, one of the main intermediate is CaS. The study carried the experiment of applying high-sulphur-concentration coal as a reductant to decompose PG and producing CaO and SO_2 in nitrogen atmosphere [19], different decomposition conditions of PG were investigated such as with different decomposition temperatures. In order to get more concentrated CaO, some research have been done in TGA and tubular furnace by applying CO as reductant and switching the reaction atmosphere from a reducing atmosphere to air-support oxidizing atmosphere [20,21]. The previous research also studied the decomposition of PG which was immersed in different concentration $FeCl_3$ in TGA and tubular furnace and its reaction mechanism under CO reducing atmosphere [22,23]. The research results revealed that the optimum concentration of $FeCl_3$ for catalyzing was 0.8 mol/L, $FeCl_3$ catalyst played a vital role in reducing PG's decomposition temperature and increasing the production of SO_2 which had been concluded from the theoretical analysis of FactSage 6.1 and experimental study. However, particles in the TGA and tubular furnace couldn't contact with the gas sufficiently. Many research results showed that the fluidized bed system could improve the physical chemistry character of solid particles distinctly, so fluidization technology had large advantages in PG's decomposition [24–28].

In this study, concluding form the previous research, PG which has been immersed in 0.8 mol/L $FeCl_3$and lignite are mixed proportionally mass ratio. Compared with PG decomposition in TGA, tube furnace and fluidized bed respectively. The research results about PG's

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decomposition reaction process can be a basic theory to apply in the future industrialized fluidized bed reaction.

2. Theory analysis

2.1. FactSage 7.0

FactSage was introduced in 2001 which was developed jointly from both the FACT-Will/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages produced over 30 years ago. The FactSage package contains a series of information, calculation, databases and manipulation modules facilitating the manipulation of databases of pure substances and solutions. FactSage is a powerful tool, which can be applied to perform a wide range of thermochemical calculations by chemical and physical metallurgists, inorganic chemists, chemical engineers, electrochemists, geochemists, environmentalists, and other users. FactSage provides information on the phases formed, their compositions proportions and the activities of individual chemical components and the thermodynamic properties of all components, including pressures and temperatures. FactSage is the largest available thermochemical package and database now [29]. The calculation process was divided into phase diagram calculation and equilibrium calculation stages. In the calculation, the initial calculation pressure was 0.1 MPa and the temperature ranged from 500 to 1100 °C in steps of 20 °C. The results were applied to show the influence of Fe on the system. Fe (+3) was reduced to Fe (+2) by reductant when the temperature was below 500 °C, and the Fe (+2) could be a reducing agent for S (+6). Then there was a new reaction way for PG's decomposition in CO atmosphere (Fig. 1). In this study, a thermodynamic assessment of the ($CaSO_4$—C—N_2-Fe_2O_3) system was conducted, calcium compounds with carbon, oxygen, and/or sulphur were of great industrial importance, and the present study attempt to include all the compositions (Fig. 2).

2.2. Reactive degrees of PG decomposition

Gas sample was analyzed by gas analyzer, the solid sample was collected and analyzed with X-ray fluorescence (XRF) after the experiments. XRF resulted in the form of oxide, the mass fraction of decomposition products was acquired through the normalization processing. Then, the purity of CaO was calculated by Eq. (1) and the yield of CaO was calculated by Eq. (2)

$$\mathrm{Purity} = M_{\mathrm{CaO}}/M_{\mathrm{Total}} \times 100\% \tag{1}$$

$$\mathrm{Yield} = M_{\mathrm{CaO}}/(n_{CaSO4} \times 56) \times 100\% \tag{2}$$

where M_{CaO} is the mass of CaO in the product after experiment, g; M_{Total} is the total mass of solid residue after experiment, g; n_{CaSO4} is the initial molar amount of $CaSO_4$ in the sample, mol; 56 is relative molecular mass of CaO.

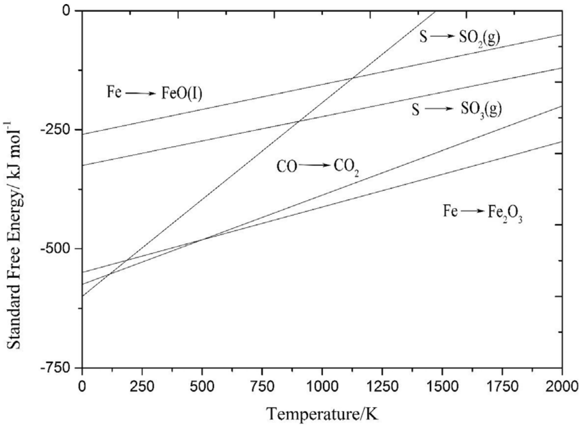

Fig. 1. Ellingham diagram for C, S, Fe [22].

3. Materials and methods

3.1. Sample prepared

PG samples applied in this research were supplied by Yunnan Natural Gas and Chemical Engineering Company; Table 1 shows the main chemical components of PG. According to Table 1, PG mainly consists of $CaSO_4 \cdot 2H_2O$. PG powder was immersed into 0.8 mol/L $FeCl_3$ aqua, stirred by magnetic force at 500 r/min for 12 h, filtered and dried at 120 °Cfor 2 h. The lignite applied in the experiment was taken from Yunnan Chuxiong; the main components were shown in Table 2. Both PG and lignite samples were crushed into particles with the size of 100 mesh.

3.2. Experiment equipment

The experimental equipment and analytical equipment used in this study were: three-dimensional mixer (CH-4132 Switzerland TURBULA), KTL1600 tube furnace (Tianjing Zhonghuan Experiment Stove Company, Ltd.), VTL1400 vertical tube furnace (Boyuntong Instrument technology co., ltd. Nanjing). The furnace was a quartz tube with 5.8 cm in diameter and 100 cm in length. X-ray diffraction system (Rigaku, Model D/max-3BPEX-P96, Japan), X-ray fluorescence (XRF) system (Rigaku, Model ZSX100e, Japan) and KM9106 complex fuel gas analyzer (KANE Company), the experimental system used in this work is shown in Fig. 3.

4. Results and disscussion

4.1. TGA experiments in multi-atmospheres control

4.1.1. Thermogravimetric analysis of PG and lignite reaction mix

In the experiments done in the TGA, Fig. 4 showed the results of a typical TG curve obtained when lignite and the PG were heated up to 1100 °C in multi-atmosphere, using a heating rate of 5 °C/min. Eight thermal events observed were displayed as T1, T2, T3, T4, T5, T6, T7 and T8. T1 began to have mass loss at the temperature of 70 °C, due to the elimination of the hydration water. T2 described the loss of PG's crystal water from 120 °C to 200 °C, which is illustrated in Eq. (3)

$$CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4 \cdot 0.5H_2O \rightarrow \gamma\text{-}CaSO_4(s) + 2H_2O(g) \tag{3}$$

During this period, the samples had 17% in mass loss resulted from the loss of crystal water rather than the oxidation of lignite. Between the temperature range of 400–800 °C, T3 showed the gradually mass loss to approximately 4% because of the oxidation of lignite, which was shown by Eqs. (4) and (5), With adequate O_2/air, lignite was oxidized into CO_2, without adequate O_2/air, lignite was oxidized into CO.

$$C + O_2 = CO_2 \tag{4}$$

$$C + 1/2O_2 = CO \tag{5}$$

T4 occurred during the temperature range of 590–1100 °C, CO and lignite mixture reacted with PG, the reaction can be represented by Eqs. (6)–(9)

$$CaSO_4 + 2C = CaS + 2CO_2 \tag{6}$$

$$CaSO_4 + 4C = CaS + 4CO \tag{7}$$

$$CaSO_4 + CO = CaO + 2CO_2 + SO_2 \tag{8}$$

$$CaSO_4 + 4CO = CaS + 4CO_2 \tag{9}$$

The total mass loss obtained at 1100 °C was 48% of the initial mass. PG reacted with lignite and CO mixture to produce CaS, SO_2 and CO_2, there is generating more than CaS but CaO. When the quality of the solid production no longer changed, the atmosphere was changed from