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# Experimental study of CaS preparation from lignite-reduced phosphogypsum in a fluidized bed

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# Abstract

BACKGROUND: Phosphogypsum (PG) is a solid waste. For a fluidized bed, current research has focused on the preparation of CaO and SO<sub>2</sub> by PG decomposition, while less research has been conducted with calcium sulfide (CaS) as the target product. Therefore, the effect of different conditions on the preparation of CaS by coal reduction of PG was investigated in a fluidized bed. The mechanism of the reaction between coal and PG was revealed through experiments and kinetic calculations.

RESULTS: PG decomposition is a combination of solid-solid reaction (carbon reacting with CaSO<sub>4</sub>) and gas-solid reaction (reducing gas reacting with CaSO<sub>4</sub>), among which the solid-solid reaction plays a major role. A PG decomposition rate of 99.42% and CaS yield of 91.55% are obtained at 850 °C for 60 min when the Ca/C molar ratio is less than 0.25 and coal particle size is less than 0.075 mm. Lignite, bituminous coal and anthracite can promote the decomposition of PG. However, the higher viscosity of bituminous coal can lead to molten coking of the product, while anthracite is less economical, so lignite is the most suitable. Minerals in coal can improve the decomposition rate of PG. A fluidized bed improves the PG decomposition rate compared to a fixed bed.

CONCLUSIONS: CaS is obtained by combined solid-solid and gas-solid reactions. Decreasing the Ca/C ratio and coal particle size as well as controlling the reaction temperature below 850 °C are beneficial for CaS generation. The minerals in coal can reduce the PG decomposition temperature and increase the PG decomposition rate. © 2022 Society of Chemical Industry (SCI).

Supporting information may be found in the online version of this article.

Keywords: phosphogypsum; fluidized bed; lignite; CaS; mechanism

## INTRODUCTION

Phosphogypsum (PG) is a solid waste generated during the wet process of phosphoric acid production in the phosphate fertilizer industry, and its main component is  $CaSO_4 \cdot 2H_2O$  or  $CaSO_4 \cdot 0.5H_2O$ .<sup>1</sup> As piling and burying PG residue not only occupies a large amount of land, but also tends to cause serious pollution to the atmosphere and groundwater, the pressure on environmental protection caused by PG emissions has become one of the important constraints to the development of the phosphate fertilizer industry.<sup>2</sup> Therefore, there is an urgent need for integrated and large-scale utilization of PG to promote the recycling and sustainability of calcium and sulfur.

The reduction of PG to calcium sulfide (CaS) by thermochemical methods is a feasible approach. CaS is an important intermediate product in the preparation of cement and sulfuric acid. It can continue to react with PG to produce CaO and SO<sub>2</sub>.<sup>3</sup> SO<sub>2</sub> can be used to produce sulfuric acid and CaO can be used as raw material for construction materials. On the one hand, such a process can eliminate the pollution of the environment by PG, turn waste into useful products and solve the problem of serious shortage of sulfur resources in China. On the other hand, using the resulting lime slag as a raw material for construction materials can save resources.<sup>4</sup> In addition, CaS is also a widely used chemical raw

material (preparation of fluorescent materials and treatment of heavy metal ions).  $^{\rm 5}$ 

Common reducing agents mainly include low-sulfur coal, highsulfur coal, coke, char, gangue and other solid reducing agents as well as CO, H<sub>2</sub>, H<sub>2</sub>S and other gaseous reducing agents. Xu *et al.*<sup>1</sup> investigated the effects of reaction temperature, reaction atmosphere, reaction time and toner content on the decomposition of PG. It was found that the synergistic effect of coke and CO reducing atmosphere could effectively reduce the decomposition temperature of PG. Antar and Jemal<sup>6</sup> studied the valorization of Tunisian PG and olive processing wastewater (OMW) for the recovery of calcium sulfide. It was found that the use of OMW as a carbon source in pure N<sub>2</sub> significantly reduced the onset reduction temperature and reduction temperature interval, with the PG reduction reaction occurring in the temperature range 600–750 °C (instead of 750–1080 °C for pure carbon),

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resulting in the formation of the intermediate product CaS. Zheng et al.<sup>7</sup> conducted experiments on the production of  $SO_2$ by thermal decomposition of PG under N<sub>2</sub> using high-sulfur coal as reducing agent. It was found that the maximum concentration of SO<sub>2</sub> was 7.6%, the concentration of CaO was 57.13%, the conversion of PG to SO<sub>2</sub> was 92.2% and the desulfurization rate of PG was 95.16% under the optimal conditions. Ma et al.<sup>8</sup> analyzed the reaction mechanism and influencing factors of CaS generation during PG decomposition using high-sulfur coal as the reducing agent. It was found that when the coal particle size was between 60 and 100 mesh, the reaction temperature was at 1100 °C and the heating rate was 5  $^{\circ}$ C mm<sup>-1</sup>, the concentration of CaS in the solid product was only 10%. Zhu et al.<sup>9</sup> studied the reductive decomposition of PG to calcium sulfide under N<sub>2</sub> atmosphere. The results showed that the best result for the production of CaS was a molar ratio of lignite to CaSO₄ of 2.4:1 and a temperature of 900-1000 °C in the reducing atmosphere, and under these conditions, the conversion of CaS in PG was not less than 97.3%. Van der Merwe *et al.*<sup>10</sup> stated that the intermediate product of carbon reduction decomposition of CaSO<sub>4</sub> to CaO was CaS and the formation of intermediate product CaS was observed between 700 and 1100 °C. At low temperatures (1144–1255 K) and high reducing gas concentrations, CaS formation was superior to that of CaO. The mechanism of CaSO<sub>4</sub> decomposition during coal pyrolysis was studied in a small tube furnace by Jia et al.<sup>11</sup> It was found that the presence of coal could significantly promote the decomposition of CaSO<sub>4</sub> during high-temperature pyrolysis. For Xiaolongtan lignite, 87% of CaSO<sub>4</sub> was converted to CaS at 800 °C, which was mainly attributed to a solid-solid reaction  $(2C + CaSO_4 = CaS + 2CO_2)$ , and the CaSO<sub>4</sub> decomposition rate decreased significantly with an increase of coal particle size. However, the studies mentioned above mainly focused on fixed bed reactors.

Due to the strong mixing in a fluidized bed, the bed temperature distribution is uniform, the material suspension is stable and the interference of fine powder escaping and coarse powder settling can be overcome in a certain particle size range. These characteristics provide good external conditions for the decomposition and heat transfer of PG in a fluidized bed, which can ensure a high decomposition rate of PG. Based on the rapid development of fluidization technology, some scholars have used fluidization technology in the process of PG thermal decomposition. Chen et al.<sup>12</sup> investigated the effect of different factors on the decomposition of PG to CaS in a three-phase fluidized bed. It was shown that the three-phase fluidized bed reactor was more favorable for the decomposition of PG to CaS than a tank reactor. After the decomposition of gypsum in a reducing atmosphere, a certain amount of air was passed to make the atmosphere oxidizing and more SO<sub>2</sub> was released. Miao et al.<sup>13</sup> investigated the decomposition characteristics of flue gas desulfurization gypsum in a bubbling fluidized bed. It was found that CO<sub>2</sub> could increase the CaO content by significantly inhibiting CaS. Zheng et al.<sup>14</sup> compared the CaO preparation process by reducing PG from lignite in a fixed bed and a fluidized bed. It was found that when the molar ratio of lignite to PG was 1.2:1, the CaO purity in the fluidized bed was 93.8%, significantly higher than that of 90.6% in the fixed bed after multiple atmosphere cycles. Zheng et al.<sup>15</sup> investigated the possibility of PG production of SO<sub>2</sub> and lime in a pilot-scale circulating fluidized bed. It was found that the optimal reaction conditions were two cycles of nitrogen and air atmosphere at 1100 °C. Chen et al.<sup>16</sup> studied the reaction of hydrogen reduction decomposition of PG in a vibrating fluidized bed. It was found that increasing the H<sub>2</sub> concentration and increasing the temperature were beneficial for the decomposition of PG. When the reduction decomposition temperature was 1050 °C, the hydrogen volume fraction was 5% and the reaction time was 60 min, the decomposition rate and desulfurization rate of PG could reach 98.78% and 84.24%, respectively. Liu et al.<sup>17</sup> investigated the reduction of PG by CO in a lowspeed vibrating fluidized bed. It was found that the decomposition rate and desulfurization rate of PG were significantly improved in the vibrating fluidized state. The decomposition characteristics of PG in the dispersed state were investigated with fluidized bed experiments by Ying.<sup>18</sup> It was found that the decomposition time was only 15-30 s under fluidized conditions, and the decomposition rate of PG could reach 95% with a desulfurization rate of 85%. Guo et al.<sup>19</sup> conducted a study on the coupling of PG decomposition and coke combustion reaction in a vibrating fluidized bed. It was found that the decomposition rate, desulfurization rate and SO<sub>2</sub> mass fraction of PG were significantly improved under energy coupling conditions.

In summary, for fluidized bed reactors, current studies have focused on examining the effects of different process conditions on the yield of CaO and SO<sub>2</sub> prepared by PG decomposition, while fewer studies have identified CaS as the target product. Moreover, concerning the effects of reductant selection, ratio, reaction temperature, reaction time and impurities in the reductant on CaS yield as well as PG decomposition rate, there is a lack of in-depth studies using fluidized beds with CaS as the target product. Therefore, the work reported in this paper systematically investigated the effects of PG-to-lignite ratio, reaction temperature, reaction time, coal type and minerals in coal on the decomposition behavior of PG in a fluidized bed with lignite as reducing agent, and revealed the mechanism of the reaction of coal and PG by combining with kinetic calculations.

# **EXPERIMENTAL**

## Materials

PG was obtained from Yuntian International Chemical Co. Ltd and dried at 105 °C for 12 h to remove some of the crystalline water, and then sealed and stored for use. The dried PG was analyzed for chemical composition and the results are presented in Table 1. The particle size of PG was determined using a Malvern Zetasizer Nano S90 nanoparticle size analyzer and the results are shown in Fig. S1. The average bulk particle size of PG powder was 40.8  $\mu$ m.

Two typical Chinese lignite coals, AnNing (AN) and LuLiang (LL), two typical bituminous coals, ShanXi (SX) and HaMi (HM), and two typical anthracite coals, XiaoFaLu (XFL) and ZunYi (ZY), were

Table 1. Analysis of PG composition (wt%)								
SiO <sub>2</sub>	$AI_2O_3$	SO <sub>3</sub>	$Fe_2O_3$	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	
17.25	0.51	47.87	0.54	33.51	0.25	0.23	0.16	

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crushed and sieved to provide raw coal samples (referred to as Raw). Among them, AN was sieved using 20 mesh (0.83 mm), 40 mesh (0.38 mm), 100 mesh (0.15 mm) and 200 mesh (0.075 mm) sieves, and the coal samples with particle size distributions of 0–0.075, 0.075–0.15, 0.15–0.38 and 0.38–0.83 mm were taken as raw coal samples. The particle size distribution of the remaining coal types was 0–0.075 mm. AN deash coal (referred to as Dem) was prepared according to the literature.<sup>20</sup> Both Raw and Dem were dried at 105 °C for 12 h and then stored in a sealed state. Char was obtained by pyrolysis in N<sub>2</sub> atmosphere at 900 °C for 2 h. Tables 2 and 3 summarize the industrial analysis of Raw, elemental analysis and sulfur morphology of the samples and the ash composition of AN prepared at 900 °C, respectively.

Different ratios of PG to coal were prepared by mechanical mixing. PG and coal were weighed according to the Ca/C molar ratio. In this study, the molar ratios of PG to coal were 2, 0.5, 0.25 and 0.125, and the mixtures were defined as Ca/C = 2, Ca/C = 0.5, Ca/C = 0.25 and Ca/C = 0.125, respectively.

#### Fluidized bed experiments

The experiments were carried out in a small fluidized bed reactor, as shown in Fig. 1. The quartz tube reactor has an inner diameter of 50 mm and a guartz filter element with a filtration accuracy of 20 µm in the middle to prevent PG powder from falling into the bottom of the reactor and blocking the air inlet. To prevent the material from being taken out of the reactor, there is a valve system at the top of the charging funnel, which can form a memory for storing the reaction particles. The quartz tube is placed vertically in the middle of an electric heating furnace, and the temperature of the reaction process is precisely controlled using the temperature control system of the electric heating furnace. The reaction gas flow is precisely controlled using a mass flow meter (Beijing Seven Star, CS200). Before the experiment started, the mixture of coal and PG was placed in a bin with a screen at the bottom, and then the bin was placed into the top of the reactor (the top temperature was lower and did not reach the coal pyrolysis temperature). The reactor was first warmed to a predetermined temperature, and then the bins were quickly extended into the center of the reactor and the N<sub>2</sub> flow rate was adjusted to 4 L min<sup>-1</sup> to allow for uniform fluidization of the material in the reactor. It was found that when the gas flow rate exceeded  $0.1 \text{ Lmin}^{-1}$ , the mass transfer resistance generated by the gas film around the particles could be neglected.<sup>21</sup>

#### **Fixed bed experiments**

The experiments were carried out using a rapidly heating tube furnace, and the operation procedure was as follows. (i) The reactants were placed in a quartz boat, and placed in the low-temperature section of the quartz tube (the temperature was lower than 200 °C, and no reaction would occur). N<sub>2</sub> at 500 mL min<sup>-1</sup> was passed through for 30 min to remove air from the tube, and then heating was started. (ii) When the required temperature was reached, the quartz boat with the reactants was quickly pushed to the constant temperature section. The tar produced during the reduction process was removed by cold hydrazine and the gas was collected by a gas bag. (iii) After the reaction was completed, the quartz boat was pulled to the low-temperature section and then began to cool. After it was reduced to room temperature, the product was weighed and stored for analysis.

#### **Coal reactivity testing**

The coal reactivity experiments were completed using a micro fluidized bed multi-stage gas-solid reaction analyzer with a mass spectrometer for online measurement of the gas produced by the reaction. The device can realize online instantaneous sample feeding, rapid temperature rise, fast and smooth switching of reaction atmosphere and high accuracy of measurement results. Meanwhile, the quartz sand inside the quartz reactor was used as fluidization medium to strengthen heat and mass transfer, which can eliminate the inhibition effect of external diffusion. The micro fluidized bed system is shown in Fig. 2. The experiments to determine the reactivity of coal species were carried out by fluidization under CO<sub>2</sub> atmosphere with an apparent gas flow rate of 400 mL min<sup>-1</sup> and a sample feed of about 10 mg. The experimental temperatures were chosen to be 800, 850 and 900 °C, and the system re-mixing degree was small, so that the reacted gas composition and its content could be measured more accurately.

#### **Determination of product composition**

After the experiments were completed, the solid samples were immediately collected and stored in dry containers to prevent the reaction of CaS and CaO with oxygen and water vapor in the air. The composition of PG decomposition products was determined by chemical methods. The decomposition rate of PG was calculated by the determination of SO<sub>3</sub> content (GB/T

	Ultimate analysis (wt%)		Elemental analysis (wt%, d)			Sulfur forms (wt%, d)					
Sample	Mad	Ad	Vd	С	н	O <sup>a</sup>	Ν	St	Ss	Sp	So <sup>a</sup>
AN	5.07	18.84	46.62	54.10	4.45	20.72	1.33	0.56	0.06	0.06	0.44
LL	4.76	34.25	32.40	44.07	3.35	16.87	1.15	0.31	0.03	0.13	0.15
SX	1.46	6.62	40.68	76.42	4.66	10.73	1.01	0.56	0.05	0.21	0.3
НМ	4.20	6.01	42.05	70.01	4.77	17.96	0.91	0.34	0.05	0.03	0.26
XFL	0.31	2.46	7.46	87.98	4.53	3.47	0.80	0.76	0.12	0.23	0.41
ZY	0.56	18.95	7.59	76.57	2.13	0.83	1.10	0.42	0.06	0.18	0.18
Dem	6.27	2.23	56.13	65.47	5.16	24.94	1.61	0.59	0.07	0.07	0.45
Char	3.0	26.61	2.86	69.14	0.37	2.63	0.96	0.29	0.04	0.13	0.12

S<sub>t</sub>, total sulfur; S<sub>p</sub>, pyritic sulfur; S<sub>s</sub>, sulfate sulfur; S<sub>o</sub>, organic sulfur. <sup>a</sup> By difference.

" By differen

Table 3. Analysis

Compound

<sup>a</sup> By difference.

AN

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 $K_2O$ 

2.24

Na<sub>2</sub>O

0.49

Gas outlet



Others

1.70

of ash comp	ositions in raw	coals (wt%)				
SiO <sub>2</sub>	$AI_2O_3$	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> (
51.17	23.98	3.67	9.09	2.57	5.09	2.2
	₽		Contro	○ ○ ○ • • ○ L cabinet	uartz filter	
	MF					
N2						



Figure 1. Schematic diagram of fluidized bed reactor.



N2

Figure 2. Schematic diagram of micro fluidized bed reactor.

5484-2000). CaS was determined by the methylene blue spectrophotometric method (GB/T 16489-1996). CaO was purified using sucrose-CO<sub>2</sub> to decompose calcium oxide in the slag, and the content of calcium oxide in the solid-phase product was determined by the EDTA volumetric method (cement chemical analysis method GB/T 176-2008).

The carbon content of coal and char was determined by elemental analysis. The sulfate sulfur content in coal and char was determined according to GB/T 215-2003. The analysis revealed that the sulfate sulfur content in coal was low (<0.06%) compared to CaSO<sub>4</sub> in PG, so the decomposition of  $SO_4^{\ 2-}$  in coal was ignored. X-ray diffraction (XRD) was used for the determination of the product composition. Scanning electron microscopy (SEM) was used for the determination of the product surface morphology.

## **Calculation method**

$$m_{t,\text{CaSO}_4} = \frac{m_{o,\text{CaSO}_4} \times x_{t,\text{CaSO}_4}}{x_{t,\text{CaSO}_4} + \frac{x_{t,\text{CaSO}_4} \times M_{\text{CaSO}_4}}{M_{\text{CaSO}_4}} + \frac{x_{t,\text{CaSO}_4} \times M_{\text{CaSO}_4}}{M_{\text{CaSO}_4}}$$
(1)

$$m_{t,\text{CaS}} = \frac{m_{o,\text{CaSO}_4} \times x_{t,\text{CaS}}}{x_{t,\text{CaSO}_4} + \frac{x_{t,\text{CaS}} \times M_{\text{CaSO}_4}}{M_{\text{CaO}}} + \frac{x_{t,\text{CaS}} \times M_{\text{CaSO}_4}}{M_{\text{CaS}}}}$$
(2)

$$m_{t,CaO} = \frac{m_{o,CaSO_4} \times x_{t,CaO}}{x_{t,CaSO_4} + \frac{x_{t,CaO} \times M_{CaSO_4}}{M_{CaO}} + \frac{x_{t,CaS} \times M_{CaSO_4}}{M_{CaS}}}$$
(3)

$$\varphi_{CaSO_4} = \frac{m_{o,CaSO_4} - m_{t,CaSO_4}}{m_{o,CaSO_4}} \times 100\%$$
(4)

$$\phi_{CaSO_4} = \frac{m_{t,CaSO_4}}{m_{t,CaSO_4} + m_{t,CaS} + m_{t,CaO}} \times 100\%$$
(5)

$$\phi_{\text{CaS}} = \frac{m_{t,\text{CaS}}}{m_{t,\text{CaSO}_4} + m_{t,\text{CaS}} + m_{t,\text{CaO}}} \times 100\%$$
(6)

$$\phi_{CaO} = \frac{m_{t,CaO}}{m_{t,CaSO_4} + m_{t,CaS} + m_{t,CaO}} \times 100\%$$
(7)

Here,  $\varphi_{CaSO_4}$  represents the decomposition rate of PG, %;  $\phi_{CaO}$ ,  $\phi_{CaS}$ ,  $\phi_{CaSO_4}$  represent the percentage of calcium-based products, %;  $m_{t,CaSO_4}$ ,  $m_{t,CaS}$ ,  $m_{t,CaO}$  represent the mass of CaSO<sub>4</sub>, CaS, CaO in the products, respectively, g;  $m_{o,CaSO_4}$  represents the mass of CaSO<sub>4</sub> in PG, %;  $x_{t,CaSO_4}$ ,  $x_{t,CaS}$ ,  $x_{t,CaO}$  represent the percentage of CaSO<sub>4</sub>, CaS, CaO in the products, respectively, %;  $M_{CaSO_4}$ ,  $M_{CaS}$ ,  $M_{CaO}$  represent the relative molecular masses of CaSO<sub>4</sub>, CaS, CaO, respectively.

To investigate the mechanism of  $CaSO_4$  decomposition in PG and the effect of operating parameters on  $CaSO_4$  decomposition, a series of six experiments were conducted. Table 4 summarizes the experimental conditions used in this study.

# **RESULTS AND DISCUSSION**

## Thermodynamic calculations

Thermodynamic calculations of the chemical reactions occurring during the reduction of PG from lignite were carried out with HSC software, and the specific reactions are presented in Table 5. As can be seen from Table 5, R15 is the decomposition reaction of pure CaSO<sub>4</sub> at about 1662 °C. R1–R14 are the reactions after the addition of carbon source. The addition of carbon source can reduce the decomposition temperature of CaSO<sub>4</sub>. From Figs 3 (a), (b), it can be seen that in the reaction of lignite reduction of PG,  $\Delta G$  of R1–R6 and R9–R11 decreases and log *K* increases with an increase of temperature. Therefore, CaS is formed more easily

than CaO at the same temperature with an increase of carbon content as well as the amount of reducing gas.

# **Reaction mechanism**

The decomposition mechanism of PG was investigated using AN with particle size <0.075 mm as an example. Figure 4 shows the effects of different Ca/C molar ratio and temperature on the decomposition rate of PG. As can be seen from Fig. 4(a), when the Ca/C molar ratio is 0.25, the PG decomposition rate increases rapidly from 74.77% to 99.55% as the temperature increases from 800 to 1000 °C. When the fixed temperature is 850 °C, the decomposition rate of PG also increases rapidly from 35.64% to 99.42% as the Ca/C molar ratio decreases from 2 to 0.125. It can be seen that the decomposition of PG strongly depends on the temperature and Ca/C ratio, and an increase of temperature as well as an increase of carbon content are favorable for the decomposition of PG. The distribution of PG decomposition products in Figs 4 (b)-(f) also shows that the relative CaS content in the products gradually increases and the relative CaSO<sub>4</sub> and CaO content gradually decreases as the Ca/C ratio decreases. For example, when the temperature is 850°C, as the Ca/C ratio decreases from 2 to 0.125, the CaS content in the decomposition products increases from 12.49% to 93.94%, CaSO<sub>4</sub> content decreases from 78.44% to 1.09% and CaO content decreases from 9.06% to 4.95%, indicating that the decrease of Ca/C ratio is favorable for the generation of CaS.

Secondly, when the Ca/C molar ratio is constant, the CaS content first increases and then decreases with an increase of temperature. For example, when Ca/C is 0.25, the CaS content first increases from 58.50% to 91.55% and then decreases to 74.36% as the temperature increases from 800 to 1000 °C. The CaS content reaches a maximum value at 850 °C. This is mainly because

No.	Proportion	Temperature (°C)	Coal particle size (mm)	Reaction time (min)	Coal type
1	PG:Coal = 2:1	850-1000	0–0.075	60	AN
	PG:Coal = 1:2	850-1000	0-0.075	60	AN
	PG:Coal = 1:4	850-1000	0–0.075	60	AN
	PG:Coal = 1:8	850-1000	0-0.075	60	AN
2	PG:Char = 2:1	850	0–0.075	60	AN
	PG:Char = 1:2	850	0-0.075	60	AN
	PG:Char = 1:4	850	0-0.075	60	AN
	PG:Char = 1:8	850	0-0.075	60	AN
3	PG:Dem-Coal = 2:1	850	0–0.075	60	AN
	PG:Dem-Coal = 1:2	850	0-0.075	60	AN
	PG:Dem-Coal = 1:4	850	0–0.075	60	AN
	PG:Dem-Coal = 1:8	850	0-0.075	60	AN
4	PG:Coal = 1:4	850	0-0.075	60	AN
	PG:Coal = 1:4	850	0.075-0.15	60	AN
	PG:Coal = 1:4	850	0.15-0.38	60	AN
	PG:Coal = 1:4	850	0.38-0.83	60	AN
5	PG:Coal = 1:4	850	0–0.075	20-80	AN
6	PG:Coal = 1:4	850	0–0.075	60	AN
	PG:Coal = 1:4	850	0-0.075	60	LL
	PG:Coal = 1:4	850	0-0.075	60	SX
	PG:Coal = 1:4	850	0-0.075	60	НМ
	PG:Coal = 1:4	850	0-0.075	60	XFL
	PG:Coal = 1:4	850	0-0.075	60	ZY

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Table 5.	Possible chemical reactions of PG with lignite		
No.	Equation	<i>T</i> (°C)	$\Delta G$
R1	$CaSO_4 + (1/2)C = CaO + SO_2 + (1/2)CO_2$	849.05	<0
R2	$CaSO_4 + C = CaO + CO + SO_2$	811.55	<0
R3	$CaSO_4 + (3/2)C = CaO + S + (3/2)CO_2$	485.55	<0
R4	$CaSO_4 + 2C = CaS + 2CO_2$	207.18	<0
R5	$CaSO_4 + (5/2)C = CaS + (3/2)CO_2 + CO$	304.19	<0
R6	$CaSO_4 + 4C = CaS + 4CO$	451.64	<0
R7	$CaSO_4 + CO = CaO + CO_2 + SO_2$	924.60	<0
R8	$CaSO_4 + 4CO = CaS + 4CO_2$	0	<0
R9	$CaSO_4 + CH_4 = CaS + 2H_2O + CO_2$	286.39	<0
R10	$CaSO_4 + (1/4)CH_4 = CaO + SO_2 + (1/2)H_2O + (1/4)CO_2$	949.40	<0
R11	$CaSO_4 + H_2 = CaO + SO_2 + H_2O$	1225.15	<0
R12	$CaSO_4 + 4H_2 = CaS + 4H_2O$	0	<0
R13	$3CaSO_4 + CaS = 4CaO + 4SO_2$	1179.11	<0
R14	$CaSO_4 + 3CaS = 4CaO + 4S$	1585.80	<0
R15	$CaSO_4 = CaO + SO_2 + (1/2)O_2$	1661.92	<0
R16	$C + CO_2 = 2CO$	699.91	<0



**Figure 3.** CaSO<sub>4</sub>–C reaction system:  $\Delta G$  and log *K versus* temperature.

at 800 °C, the solid-solid reactions of R1, R2 and R13 have not yet occurred, so CaO is not detected. When the temperature reaches 850 °C, the solid-solid reactions of R1 and R2 intensify, reaction R13 occurs and CaO starts to be generated. It is found that the initial temperature of the occurrence of reaction R13 is 825 °C.<sup>22</sup> Meanwhile, as the temperature increases, coal pyrolysis will produce more reducing gases, resulting in the relative content of CaS still increasing. Continuing to increase the temperature to 900 °C, R13 becomes more and more intense, leading to a gradual increase in the CaO content and a gradual decrease in the CaS content. The XRD results in Fig. 5 also confirm this conclusion. From Fig. 5(a), it can be seen that the CaSO<sub>4</sub> peak gradually decreases with an increase of temperature, and the CaS peak first increases and then decreases, and the characteristic peak of CaO appears when the temperature reaches 850 °C. As seen in Fig. 5 (b), with a decrease of Ca/C ratio from 2 to 0.25, the CaSO<sub>4</sub> characteristic peak decreases, CaS characteristic peak increases and CaO characteristic peak decreases, and the XRD pattern for Ca/C of



0.125 is not much different from that for 0.25. This result verifies the product distribution results in Fig. 4.

For the solid–solid reaction mechanism, the C element in coal is directly involved in the decomposition reaction of PG as a solid reductant, while for the gas–solid reaction mechanism, the CO produced by coal pyrolysis and gasification reaction is the main cause of PG decomposition as a gaseous reductant. To date, there is no unified understanding of the two reaction mechanisms. For this, further experimental studies were carried out in the study reported here.

It can be seen from Fig. 6(a) that the addition of char significantly promotes the reduction of PG and the reduction rate increases rapidly with a decrease of Ca/C molar ratio. For example, when Ca/C is reduced from 2 to 0.5, the reduction rate increases from 29.14% to 93.48% for char–PG and from 35.65% to 98.32% for coal–PG. The difference between the two is not significant. The result is inconsistent with the gassolid reaction mechanism, since no  $CO_2$  is produced during



Figure 4. Effect of different Ca/C molar ratio and temperature on PG decomposition rate.

pyrolysis of char, and R16 does not occur under N<sub>2</sub> atmosphere due to the lack of CO<sub>2</sub>. Therefore, neither the pyrolysis nor the gasification reaction of char will produce CO, resulting in the reaction of CO with CaSO<sub>4</sub> also not taking place. Therefore, based on the gas-solid reaction mechanism, the addition of char does not lead to a large amount of PG decomposition, so the gas-solid reaction mechanism does not explain well the decomposition characteristics of PG when char is added. Zheng *et al.* also verified this result by thermogravimetric experiments. They concluded that below 1100 °C, when C/CaSO<sub>4</sub> = 2, mainly the solid–solid reaction plays a major role, and the solid–solid interaction becomes more intense with an increase of C/CaSO<sub>4</sub>.<sup>23</sup> It can be seen from Fig. 6(b) that the reduction rates of CaSO<sub>4</sub> by char and raw coal do not differ much when the

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Figure 5. XRD analysis results of products under different process conditions: (a) temperature; (b) Ca/C molar ratio (experimental conditions: AN particle size: 0–0.075 mm; N<sub>2</sub> atmosphere).



Figure 6. Effect of raw coal and char on PG decomposition rate under different process conditions: (a) Ca/C molar ratio; (b) temperature (experimental conditions: AN particle size: 0–0.075 mm; N<sub>2</sub> atmosphere).

reaction temperature is below 1000 °C. Although it is inferred from common sense that the solid-solid reaction is more difficult to occur compared with the gas-solid reaction, the PG

particle size used in this experiment is <0.075 mm, and the two are mixed strongly in the fluidized bed, which provides good conditions for the solid–solid reaction to occur.

#### **Kinetic analysis**

When the Ca/C molar ratio is 0.25, the thermogravimetric (TG) and differential TG (DTG) curves of the material are shown in Fig. 7. As can be seen from Fig. 7, the TG and DTG curves move towards higher temperatures as the heating rate increases. Due to the faster heating rate, the heat transfer time between the inner and outer surfaces of the sample is shortened, alleviating the 'heat delay' phenomenon to some extent. At the same time, the maximum rate of mass change of the material increases as the heating rate increases. This is because at high heating rates, the amount of heat absorbed from the external environment per unit time increases, which increases the activity of the pyrolysis reaction.<sup>24</sup>

To investigate the reaction mechanism of PG reduction, the Flynn–Wall–Ozawa (FWO) method and the Kissinger–Akahira–Sunose (KAS) method were used to calculate  $f(\alpha)$ , activation energy ( $E_a$ ) and finger front factor (A) for PG decomposition at different rates of warming, and the results are shown in Fig. 8. Figure 8(a) shows a non-isothermal plot of  $\ln(\beta)$  versus 1/T calculated by the FWO method, and Fig. 8(b) shows the ratio of  $\ln(\beta/T^2)$  versus 1/T calculated by the KAS equation. The linear correlation coefficients for the two models are  $R^2 = 0.978-0.999$  and  $R^2 = 0.963-0.999$ , respectively, and the fit is satisfactory. On this basis,  $E_a$  and A are calculated for different conversion rates, and the results are presented in Table 6 and Fig. 9.

As can be seen from Fig. 9, the activation energies calculated by the FWO and KAS models have similar trends with conversion, but fluctuate considerably, indicating that the PG reduction process is a complex reaction process.<sup>25</sup> As evident from Table 6,  $E_a$  calculated by the FWO method is slightly higher than that calculated by the KAS method. The different approximation formulas chosen for the temperature integration function P(x) are the reason for the deviation of  $E_a$  calculated by the two methods from  $A^{26}$ . According to Fig. 9, E<sub>a</sub> can be divided into three stages. The first stage has an  $\alpha$  conversion between 0.05 and 0.2 and a temperature range of 329 to 515 °C. The  $E_{\rm a}$  values in this stage are small, averaging 157.53 kJ mol<sup>-1</sup>, and the reaction is fast and easy to occur. In this conversion rate interval, the reaction mainly corresponds to lignite undergoing primary pyrolysis to produce tar and gas.  $E_a$  shows a trend of increasing and then decreasing. This is due to the transient dynamic changes in the material reaction process as the pyrolysis reaction process proceeds, while involving numerous mutually coupled and interacting chemical reactions, and also this may be due to different types of diffusion effects such as interparticle, intraparticle and external diffusion.<sup>27</sup> The second stage has an  $\alpha$  conversion between 0.2 and 0.6, a temperature range of 515 to 875 °C and a gradual increase in  $E_a$ . This stage mainly corresponds to the solid–solid and gas–solid reactions between PG and lignite to produce CaS, CO<sub>2</sub> and CO, which is a complex reaction process. In the third stage, the conversion rate increases from 0.6 to 0.95, corresponding to the temperature range of 875–924 °C, with a slowly decreasing trend of  $E_a$ . This stage corresponds mainly to the reaction of PG with CaS to form CaO.

As can be seen in Fig. 9, the  $E_a$  values during PG decomposition fluctuate considerably, indicating that a single kinetic mechanism cannot describe the entire conversion rate range ( $\alpha = 0.05$  to 0.95). The decomposition process is divided into three intervals based on the variation of  $E_{\rm a}$ , and the conversion rate interval values  $\alpha$ 1 of 0.15, 0.4 and 0.8 are selected as the reference points for the three intervals, respectively. Using the integral master curve method, the average  $E_a$  in each conversion rate range is brought into different solid integral function equations (Table S1) and empirical equations (supporting information, kinetic theory analysis Eqn (10)) to obtain  $q(\alpha)/q(\alpha)$ . In the present case, 30 common kinetic mechanism functions  $q(\alpha)$  are selected for solid-state thermal decomposition, as presented in Table S1 of the supporting information.<sup>28</sup> A series of theoretical master plots can be obtained by plotting  $q(\alpha)/q(\alpha 1)$  versus  $\alpha$ . Substituting the average  $E_a$  for each conversion rate range into the equation (see Eqn (12) in the kinetic theory analysis in Appendix S1), the left-hand side of the equation becomes the function  $q(\alpha)/q(\alpha 1)$  versus  $\alpha$  forming the standard curve, and the right-hand side of the equation is  $P(X\alpha)/P(\alpha 1)$  versus  $\alpha$ , forming the experimental curve.<sup>29</sup> The corresponding theoretical and experimental curves of  $P(X\alpha)/P(\alpha 1)$  are shown in Fig. 10. By comparing the deviations between the two curves, the most probable mechanistic function  $q(\alpha)$  is determined for each kinetic stage of lignite reduction of PG.

As can be seen from Fig. 10, the experimental and standard curves at different rates of warming are essentially the same, indicating that all stages of PG decomposition can be described by a kinetic model. As can be seen from Fig. 10(a), in the low



Figure 7. (a) TG and (b) DTG curves with heating rates of 5, 10 and 15 K min<sup>-1</sup>.

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0.05

0.1

0.15

0.2

3.0

(a)





**Figure 8.** Plots of (a)  $\ln(\beta)$  versus 1/T calculated by the FWO method and (b)  $\ln(\beta/T^2)$  versus 1/T calculated by the KAS method.

0.25

0.3

<b>Table 6.</b> Values of $E_{a}$ , ln A and $R^2$ calculated by FWO and KAS methods								
Conversion		OFW method		KAS method				
α	$\ln A (min^{-1})$	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	$R^2$	$\ln A (\mathrm{min}^{-1})$	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	R <sup>2</sup>		
0.05	30.38	174.77	0.97846	30.10	173.60	0.96389		
0.1	30.13	185.73	0.99698	29.96	185.01	0.99681		
0.15	26.02	171.87	0.99999	25.47	169.03	0.95351		
0.2	14.19	109.93	0.99441	12.42	102.49	0.99876		
0.25	8.02	110.65	0.99416	5.89	100.75	0.99317		
0.3	17.21	197.99	0.99891	16.12	191.11	0.99778		
0.35	29.08	311.32	0.99988	28.82	309.43	0.99088		
0.4	30.86	330.83	0.99952	30.69	329.61	0.99776		
0.45	31.09	334.63	0.99493	30.92	333.386	0.99612		
0.5	31.06	335.15	0.99955	30.87	333.76	0.99834		
0.55	31.04	335.53	0.99997	30.84	334.02	0.99588		
0.6	30.82	333.83	0.99923	30.60	332.10	0.99503		
0.65	33.22	331.29	0.99801	32.97	329.31	0.99127		
0.7	33.05	330.84	0.99684	32.78	328.72	0.99523		
0.75	32.64	327.96	0.99600	32.34	325.59	0.99746		
0.8	32.45	327.02	0.99527	32.13	324.49	0.99915		
0.85	31.97	323.28	0.99491	31.61	320.45	0.99987		
0.9	31.69	321.35	0.99573	31.31	318.30	0.99578		
0.95	31.77	322.71	0.99664	31.39	319.59	0.99563		

conversion range (0.05  $\leq \alpha \leq$  0.2), the experimental master diagram agrees with the theoretical master diagram F2. Diagram F2 belongs to the type of secondary solid-phase chemical reaction, corresponding to the mechanistic functional equation  $q(\alpha) = (1$  $(-\alpha)^{-1}$  – 1. At temperatures between 329 and 515 °C, the liquite undergoes a primary reaction, where the breakage of reactive functional groups such as methoxy and phenolic hydroxyl groups in the benzene ring of the molecule produces tar and gas, and a lower activation energy needs to be overcome, so  $E_a$  of the system at this stage is low. As can be seen from Fig. 10(b), the conversion is in the range  $0.2 \le \alpha \le 0.6$ , corresponding to a pyrolysis temperature of 515-875 °C. In this interval, the experimental master diagram is consistent with the theoretical master diagram D4, which belongs to the three-dimensional diffusion reaction mechanism (Ginstlinge-Brounshtein model), corresponding the to

mechanism function  $g(\alpha) = (1 - 2/3\alpha) - (1 - \alpha)^{2/3}$ . In this temperature interval, as the temperature increases, PG and lignite undergo vigorous solid–solid and gas–solid reactions, which need to overcome large activation energy, generating large amounts of CO<sub>2</sub>, CO and other gases, and a sharp decrease in mass, leading to a sharp increase in  $E_a$ . Further progress of the solid-phase reaction depends on the migration and change processes of the particles within the reacting material, resulting in a three-dimensional diffusion process controlling the reaction mechanism at this stage. As can be seen in Fig. 10(c), the conversions are in the range 0.6 to 0.95, corresponding to temperatures of 875 to 924 °C. In this interval, the experimental master diagram is consistent with the theoretical master diagram A6, which belongs to the nucleation and growth model and corresponds to the mechanism function  $g(\alpha) = [-\ln(1 - \alpha)]^{2/3}$ . Although reaction R13 is



**Figure 9.** Variation of activation energy with conversion rate calculated by the FWO and KAS methods.

thermodynamically more difficult to occur, CaS and CaSO<sub>4</sub> can occur at 850–900 °C according to the liquid-phase eutectic model proposed by previous authors,<sup>30,31</sup> and coupled with the fact that PG contains impurities such as iron which can significantly reduce the temperature of the reaction.<sup>32</sup> In addition the products underwent significant bonding, as evident from the SEM images shown in Fig. 11. Comparing before and after the reaction, the particles melt into a glassy enamel-like substance, the surface becomes uneven and the surface of the material is a mixture of pores of different sizes and dense structures. It is believed that there is liquid-phase cocrystallization during the solid–solid reaction of CaS and PG. At this stage as the reaction proceeds, the unreacted CaSO<sub>4</sub> particles shrink and become encapsulated in the center by the CaS product layer, and the SO<sub>2</sub> generated needs to diffuse outwards through the gradually thickening product layer to form a pore structure.

#### Effect of reaction time

The effect of reaction time on the decomposition efficiency of PG was examined, and the experimental results are shown in Fig. 12. From Fig. 12(a), it can be seen that the decomposition rate of PG







Figure 11. SEM images of reactants and products: (a) full view of PG original appearance; (b) partial view of PG original appearance; (c) full view of product appearance at 900 °C; (d) partial view of product appearance at 900 °C.



Figure 12. Effect of reaction time on PG decomposition characteristics: (a) PG decomposition rate; (b) calcium-based product composition (experimental conditions: 850 °C; AN particle size: 0–0.075 mm; N<sub>2</sub> atmosphere).

gradually increases with an increase of reaction time. For example, when the reaction time is extended from 20 to 60 min, the decomposition rate of PG rapidly increases from 81.37% to 98.32%, and the decomposition rate does not change much when the time continues to 80 min, indicating that the decomposition

of PG is almost complete at 60 min. From Fig. 12(b), it can be seen that as the reaction time is extended from 20 to 60 min, the amount of  $CaSO_4$  rapidly decreases from 25.36% to 3.18% and that of CaS rapidly increases from 73.63% to 91.55%, with a smaller increase in CaO content. Therefore, for economic reasons,



a reaction time of 60 min is chosen as appropriate to obtain the target product CaS.

## Effect of coal particle size

The particle size of coal is one of the most important parameters influencing the decomposition of PG. The experiments kept the PG particle size constant (average particle size of 40.8  $\mu$ m), and the effect of coal particle size (0–0.075, 0.075–0.15, 0.15–0.38 and 0.38–0.83 mm) on the decomposition characteristics of PG was investigated. The results are shown in Fig. 13. When the particle size of coal increases from 0–0.075 to 0.38–0.83 mm, the decomposition rate of PG decreases sharply from 98.32% to 74.59%. Also, as can be seen from Fig. 13(b), as the coal particle size increases from 0–0.075 to 0.38–0.83 mm, the proportion of CaSO<sub>4</sub> in the product increases from 3.18% to 31.87%, CaS decreases from 91.55% to 66.32% and CaO decreases from 5.25% to 1.81%. CaS is formed mainly by solid–solid reaction between CaSO<sub>4</sub> and CaSO<sub>4</sub> according to the liquid-phase

eutectic model. The reaction degree of solid–solid reaction depends mainly on the contact area. As the particle size of coal increases, the contact area between coal and PG decreases, and the decomposition rate of PG decreases.

## Effect of coal type

The effect of different coal types on the decomposition rate of PG was experimentally examined and the results are shown in Fig. 14. From Fig. 14(a), it can be seen that for a Ca/C molar ratio of 0.25, after 60 min, the reduction rates of PG for SX, HM, XFL and ZY are 99.15%, 99.63%, 99.99% and 99.65%, respectively. The decomposition rates of PG for LL and AN are 94.43% and 98.32%, respectively. Except for LL, the decomposition rates of PG for the other five coal types do not differ much from each other. As seen in Fig. 14(b), when Ca/C remains the same, there is little difference in the composition of PG decomposition products. This is mainly due to the fact that the Ca/C molar ratio is consistent, and it is clear from the solid–solid reaction mechanism that the carbon content plays a major role in PG decomposition. The reason for



Figure 13. Effect of coal particle size on PG decomposition characteristics: (a) PG decomposition rate; (b) calcium-based product composition (experimental conditions: 850 °C; AN; reaction time:60 min; N<sub>2</sub> atmosphere).



Figure 14. Effect of different coal types on PG decomposition characteristics: (a) PG decomposition rate; (b) calcium-based product composition (experimental conditions: 850 °C; particle size: 0–0.075 mm; reaction time: 60 min; N<sub>2</sub> atmosphere).

897

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Figure 15. Effect of minerals in coal on PG decomposition rate: (a) effect of temperature; (b) effect of Ca/C molar ratio (experimental conditions: particle size: 0–0.075 mm; reaction time: 60 min; N<sub>2</sub> atmosphere).



Figure 16. Reactivity of Raw and Dem at different temperatures: (a) 800 °C; (b) 850 °C; (c) 900 °C.



Figure 17. (a) TG curves and (b) DTG curves for the reaction of Raw and Dem with PG.

the low reduction rate of LL towards PG may be that the volatile fraction in LL is low, and the levels of reducing gases produced by pyrolysis under the same conditions, such as CO, are low,

which can also reduce PG to some extent, so the reduction rate of PG by LL is lower than for the other four coal types. However, due to the strong bonding of bituminous coal, the colloidal



Figure 18. Effect of reaction time on PG decomposition characteristics: (a) PG decomposition rate; calcium-based product composition in (b) fluidized bed and (c) fixed bed (experimental conditions: 850 °C; particle size: 0–0.075 mm; N<sub>2</sub> atmosphere).

components precipitated from coal particles during pyrolysis and gasification tend to bond the solid particles in the bed, thus rapidly forming low-temperature coke leading to lower fluidization quality, resulting in poor local fluidization and the overtemperature phenomenon, which eventually leads to molten coking of PG ash. The anthracite coal is less economically applicable due to its higher price, so from practical considerations, it is advisable to use AN as the reducing agent for PG.

#### Effect of minerals in coal

Minerals such as  $Fe_2O_3$ ,  $Al_2O_3$  and  $SiO_2$  in PG play an important role in the PG decomposition process, not only by reducing the PG decomposition temperature, but also by influencing the composition of PG decomposition products. The effect of minerals in coal on the decomposition characteristics of PG was investigated by comparing Dem + PG and Raw+PG as raw materials, and the experimental results are shown in Fig. 15. As can be seen from Fig. 15(a), the decomposition rate of PG is significantly higher for Raw than for Dem at all temperatures. As the temperature increases from 800 to 900 °C, the decomposition rate of PG from Raw increases from 74.77% to 98.32% and that from Dem increases from 69.64% to 90.28%. This is due to the fact that the acid washing treatment removes a significant amount of catalytic alkali metal ash from the coal,<sup>33</sup> making it significantly less reactive. Figure 16 shows the reactivity results of Raw and Dem at different temperatures (800, 850, 900 °C). From Fig. 16, it can be seen that as the temperature increases from 800 to 900 °C, the gap between Dem and Raw is gradually decreasing with an increase of temperature. This is due to the fact that the catalytic alkali materials in Raw, such as  $Al_2O_3$  and  $Fe_2O_3$ ,<sup>34</sup> react with calcium-based substances to form various salts as the temperature increases,<sup>35</sup> making the reduction-promoting effect on PG somewhat weaker. This shows that the minerals in the coal play an important role in the decomposition of PG.

As can be seen in Fig. 15(b), the reduction rate of PG from Dem is significantly lower than that from Raw for the same Ca/C ratio, but this gap is diminishing as the Ca/C ratio decreases. For example, when Ca/C is increased from 0.5 to 0.125, the decomposition rate of Raw to PG increases from 73.40% to 99.42%, and the decomposition rate of Dem to PG increases from 58.13% to 96.15%, the gap between the two decreasing with a decrease of Ca/C ratio, this result is consistent with the results of the TG experiment shown in Fig. 17. The reason is that as the carbon content increases, the concentration of reducing gases from coal pyrolysis increases and the reducing atmosphere is enhanced. The solid–solid and gas–solid reactions intensify, resulting in a smaller gap between the two.

## **Reactor comparison**

The effects of different reactors on the decomposition behavior of PG were investigated, and the results are shown in Fig. 18. From

Fig. 18(a), it can be seen that the PG decomposition rate in the fluidized bed is significantly higher than that in a fixed bed for the same time. For example, when the reaction time is 40 min, the PG decomposition rate in the fluidized bed is 91.13%, much higher than the 79.89% in the fixed bed. In addition, Figs 18(b), (c) show that the content of CaS in the fluidized bed is significantly higher than that in the fixed bed under the same conditions. The reason is mainly that the mass and heat transfer efficiency of the fluidized bed is significantly higher than that of the fixed bed, resulting in more complete reaction of PG with lignite for the same reaction time.

# CONCLUSIONS

In order to convert PG to CaS, the effect of different process conditions on the coal reduction of PG was investigated in a fluidized bed. The mechanism of the reaction between coal and PG was revealed by experiments and kinetic calculations. PG decomposition is a combination of solid-solid reaction and gas-solid reaction, among which the solid-solid reaction plays a major role. Kinetic calculations find that the reaction can be divided into three stages when the temperature is between 200 and 1000 °C. The first stage is a secondary solid-phase chemical reaction type with temperatures between 329 and 515 °C, where the primary reaction occurs mainly in lignite. The second stage corresponds to a temperature between 515 and 875 °C and corresponds to a three-dimensional diffusion reaction mechanism, which mainly involves vigorous solid-solid and gas-solid reactions between PG and lignite to produce CaS. The third stage corresponds to a nucleation and growth model with a temperature between 875 and 924 °C, which mainly involves CaS and CaSO<sub>4</sub> to produce CaO through a liquid-phase eutectic model. A PG decomposition rate of 99.42% and CaS yield of 91.55% are obtained at 850 °C for 60 min when the Ca/C molar ratio is less than 0.25 and coal particle size is less than 0.075 mm. Lignite, bituminous coal and anthracite can significantly promote the decomposition of PG, but lignite is the most suitable. Minerals in coal can significantly improve the decomposition rate of PG. A fluidized bed improves the PG decomposition rate compared to a fixed bed.

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# **CONFLICT OF INTEREST**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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