

Preparation of calcium oxide by decomposition of phosphogypsum under CO and water vapor atmosphere

Dong Ma* and Qinhui Wang

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China

Abstract. Phosphogypsum (PG) is an industrial solid waste, and the production of CaO by CO reduction of PG can not only solve the environmental problems caused by PG, but also turn waste into treasure to generate CaO. However, the current yield of CaO production by CO reduction of PG is low. To further improve the yield of CaO, a technical method of CaO preparation by CO-H₂O synergistic reduction of PG is proposed. The impacts of CO concentration, P(H₂O)/P(CO) ratio and reaction temperature are examined in this work together with FactSage thermodynamic simulations in order to determine the ideal reaction conditions and reaction mechanism. It is found that the CaO yield could reach 96.78% at 1100 °C of 3% CO and P(H₂O)/P(CO) of 10. The mechanism study shows that when the CO atmosphere contains H₂O, the reductive decomposition of PG by CO is actually the result of the joint action of CO, H₂ and CO₂. Overall, this research will help to enhance a novel technological strategy for preparing CaO by decomposition of PG.

1 Introduction

Phosphogypsum (PG) is a byproduct of the phosphate fertilizer industry, and its accumulation can lead to environmental concerns such as radioactivity and soil acidification[1]. PG contains large amounts of calcium sulphate, which can be decomposed by thermal reduction to produce calcium oxide. This process offers a sustainable and economically viable approach to produce calcium oxide while also addressing the environmental concerns associated with PG disposal.

Commonly used reducing agents for the preparation of CaO by PG decomposition mainly include carbon based (coal[2], CO[3]) and sulphur based (H₂S[4], high sulfur coal[5]). By comparison, the use of CO as a reducing agent for the decomposition of calcium sulfate offers a promising approach for the sustainable management of PG. Its low energy consumption and high efficiency make it an attractive option for large-scale operations, while also reducing the environmental impact of waste management practices. Miao et al.[6] found that CO concentration significantly affected the decomposition rate and product composition of PG. Lower CO content favored the production of more CaO products and more SO₂. Xia et al.[7] found that the yield of calcium oxide was 80.3% at 1150 °C and CO concentration of 2%. In addition, the addition of partial CO₂ and O₂ to the CO atmosphere can further improve the CaO yield. Based on theoretical calculations, Zhang et al.[8] found that the main product of CaSO₄ decomposition is CaS when the molar ratio of CaSO₄ to CO is 0.25. However, increasing the reaction temperature and decreasing the CO/CaSO₄ molar ratio, the product was mainly CaO. Okumure et al. [9] found that the highest yield of CaO during CaSO₄ decomposition was 91% at

1000 °C of 2% CO-30% CO₂. However, in CO-N₂ atmosphere, the main product was CaS. Xiao et al.[10] found by thermogravimetric experiments that there was a competitive reaction between CaS and CaO in CaSO₄ decomposition products, and the CaO content increased with the decrease of CO volume fraction and the increase of temperature. Zhu et al.[11] also proved this conclusion by thermogravimetric experiments.

In summary, most of the above literature is based on thermogravimetric experiments qualitatively describing the decomposition process of CaSO₄ in CO. However, the CaO and CaS produced by the reaction of PG with CO has not been quantified. In addition, CaO yield can be further enhanced. Therefore, this paper presents a new method for the preparation of CaO by PG decomposition by adding water vapor to the CO atmosphere in order to improve the CaO yield. The decomposition processes of PG in CO-N₂ and CO-H₂O-N₂ atmospheres are studied in this work, and the effects of CaO preparation by PG decomposition under various process circumstances are investigated using FactSage thermodynamic simulations. This study will provide a theoretical reference for the preparation of CaO by PG decomposition.

2 Experimental part

2.1 Raw materials

PG is taken from a phosphorus chemical enterprise in Yunnan. After sieving the PG, any particles with a size less than 0.075 mm are dried at 105 °C for 6 hours. By using an X-ray fluorescence spectrometer (XRF), the chemical composition of dried PG can be determined, as indicated in Table 1. According to Table 1, the primary chemical

*dongma@zju.edu.cn

components of PG are CaO and SO₃, and it also includes 5.42% SiO₂, 0.15% Al₂O₃, 0.61% P₂O₅, 0.22% F, and trace quantities of organic materials.

Table 1 Chemical composition of PG (wt.%)

SiO ₂	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	Total F	Organic matter
5.42	0.15	51.40	--	35.94	0.09	0.21	0.20	0.61	0.22	0.31

2.2 Fluidized bed experiments

As shown in Fig.1, the tests are conducted in a small fluidized bed reactor. In the middle of the electrically heated furnace, the quartz tube is positioned vertically with the inner diameter of 50 mm. Furthermore, in the center of the quartz tube, a air cloth plate with the hole diameter of 20 μm has been inserted. At this aperture size, the material does not fall to the bottom of the reactor. To stop material from leaving the reactor, a valve has been installed at the top of it. The reaction temperature is regulated using a temperature control system. The flow rates of CO and N₂

are controlled by flow meters. Water vapor is prepared using a steam generator. Before starting the experiment, PG is placed on the air distribution plate. To ensure that the material in the reactor could be equally fluidized, the total gas flow rate is set to 2 L/min. The temperature is then raised to the specified temperature at 20 °C/min under N₂ and thermostated for 10 min. The water vapor pump switch and CO pressure reducing valve are then turned on and the reaction is carried out under a certain water vapor and CO flow rate for 1 h and then cooled to room temperature. The solid products are collected for subsequent analysis, and the exhaust gas is collected by gas bag.

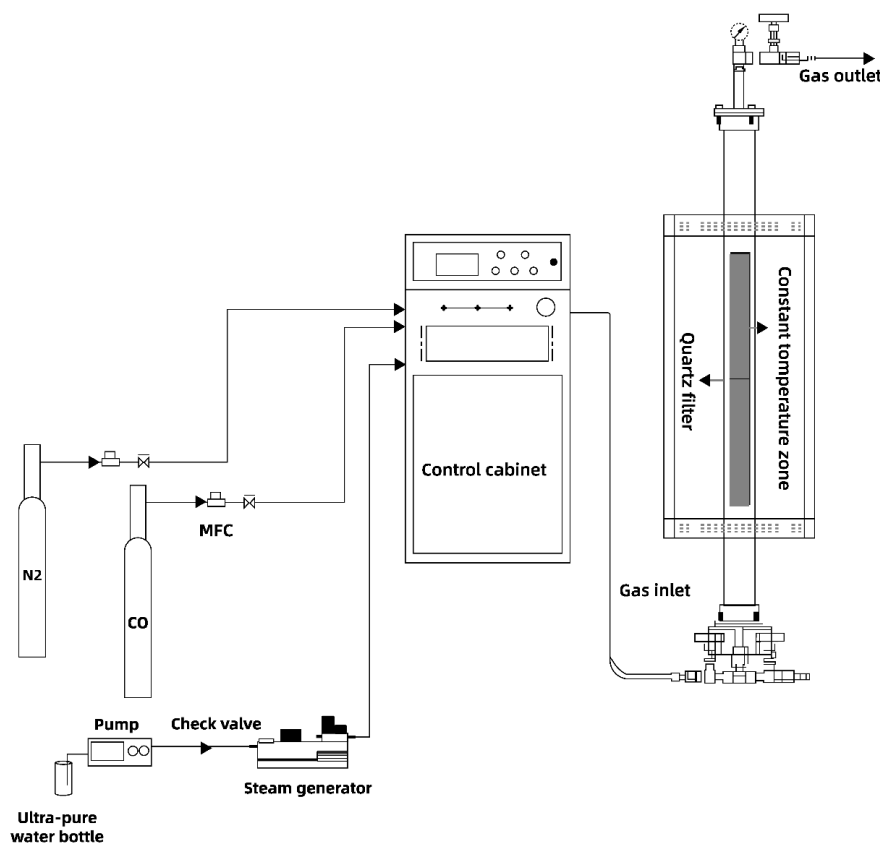


Fig.1 Schematic diagram of small fluidized bed reactor

2.3 Determination of product composition

The solid samples are collected and kept when the tests are done. The barium sulfate precipitation technique (GB/T 5484-2012) is employed to calculate the PG decomposition rate. CaS is identified by spectrophotometric method (HJ 1226-2021). The CaO content is determined by sucrose method (HG-T/4205-2011). X-ray diffractometer (XRD) is used to determine the composition of a product.

The specific calculation process is shown in Equation (1)-(3).

$$\phi_{CaSO_4} = \frac{m_{o,CaSO_4} - m_{t,CaSO_4}}{m_{o,CaSO_4}} \times 100\% \quad (1)$$

$$\phi_{CaS} = \frac{m_{t,CaS}}{Q_{CaS}} \times 100\% \quad (2)$$

$$\phi_{CaO} = \frac{m_{t,CaO}}{Q_{CaO}} \times 100\% \quad (3)$$

φ_{CaSO_4} denotes the PG decomposition rate, %.
 ϕ_{CaO} 、 ϕ_{CaS} denotes CaO and CaS yield respectively, %.
 $m_{t,CaSO_4}$ 、 $m_{t,CaS}$ 、 $m_{t,CaO}$ denote the quality of $CaSO_4$,
 CaS and CaO in the product respectively, g. $m_{o,CaSO_4}$ de-
 notes the quality of $CaSO_4$ in PG, %. Q_{CaS} denotes the
 theoretical quality of $CaSO_4$ converted to CaS completely,
 g; Q_{CaO} denotes the theoretical quality of $CaSO_4$ con-
 verted to CaO completely, g.

2.4 Thermodynamic calculations

Based on the idea of the minimal Gibbs function, FactSage software calculates thermodynamic equilibrium and offers a vast database of chemical processes and thermodynamics. In this work, the phase diagram module is used in order to understand the PG decomposition product composition. The setting compound type is gas and solid, the starting pressure is 0.1 MPa, and the reaction temperature is 1100 °C.

3 Results and discussion

3.1 Equilibrium phase diagram analysis

The equilibrium phase diagram of the reduced decomposition products of $CaSO_4$ under CO is explored with the

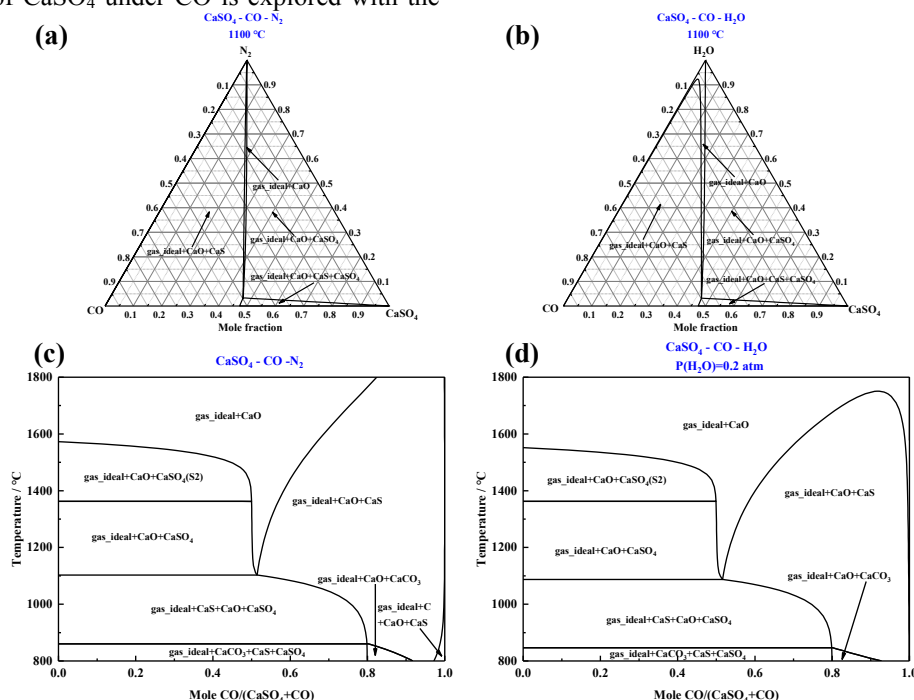


Fig.2 (a) $CaSO_4$ -CO- N_2 ternary equilibrium phase diagram; (b) $CaSO_4$ -CO- H_2O ternary equilibrium phase diagram; (c) $CaSO_4$ -CO- N_2 binary equilibrium phase diagram; (d) $CaSO_4$ -CO- H_2O -0.2atm binary equilibrium phase diagram.

3.2 Influence of CO concentration

Firstly, as shown in Fig.3, the influence of CO concentration on PG decomposition process under CO- N_2 and CO- H_2O - N_2 was studied. According to Fig.3(a), when the CO concentration rises from 1% to 3% under CO- N_2 at

phase diagram module in Factsage 6.0 as shown in Fig. 2. Figs. 2(a)-(b) investigate the effect of adding water vapor to the CO atmosphere on the decomposition products of $CaSO_4$ at 1100 °C and a system pressure of 1 atm. Comparison of Fig. 2c and Fig. 2d shows that the area of the pure CaO phase increases significantly at this temperature and pressure when water vapor is added. This finding suggests that the presence of water vapor in the CO atmosphere promotes the formation of CaO in $CaSO_4$ decomposition process.

Fig.2(c) depicts the influence of the molar ratio of CO/(CO+ $CaSO_4$) on the $CaSO_4$ decomposition products when the temperature ranges from 800 °C to 1800 °C at 1 atm. It can be seen that the reaction equilibrium products are influenced not only by the reaction temperature but also by the molar ratio of the reaction between CO and $CaSO_4$. During the reductive decomposition of $CaSO_4$ by CO, the lowest temperature at which the pure CaO phase appears is about 1100 °C and the lowest CO/(CO+ $CaSO_4$) molar ratio is slightly greater than 0.5. In the temperature range of 800 °C to 1800 °C at 1 atm, Fig.2(d) investigates the effects of 20% water vapor addition to the reaction atmosphere on the decomposition products of $CaSO_4$. As can be observed, when 20% water vapor is added to the CO, the region occupied by pure CaO in the equilibrium phase diagram increases in comparison to water vapor not added. This discovery provides more evidence that the production of CaO benefits from the addition of water vapor to CO atmosphere.

As the CO concentration rises from 1% to 5% under CO-N₂, it can be observed from Fig.3(b) that the CaS yield increases from 16.43% to 51.87% and the CaO yield falls from 66.78% to 46.44%. The findings are consistent with earlier research findings[10]. Furthermore, the sum of CaS yield and CaO yield is lower than the PG decomposition rate probably due to the measurement error and the

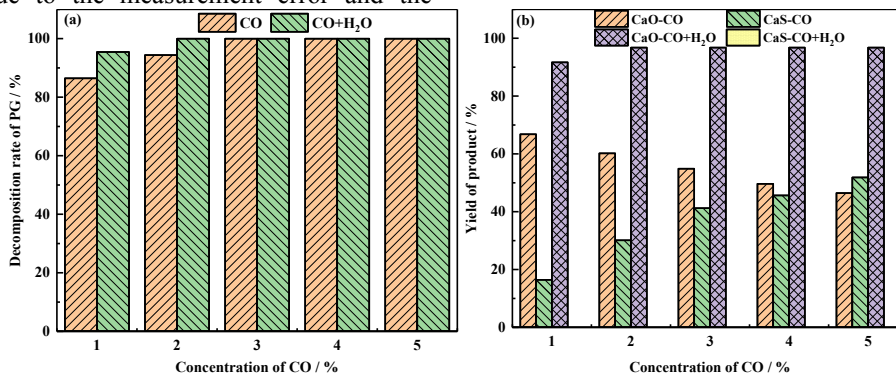


Fig.3 (a) Influence of CO concentration on PG decomposition rate in the CO-N₂ and CO-H₂O-N₂; (b) Influence of CO concentration on CaO and CaS yield in the CO-N₂ and CO-H₂O-N₂

3.3 Influence of P(H₂O)/P(CO) ratio

The influence of varied P(H₂O)/P(CO) ratios on PG decomposition process was examined at 1100 °C of 3% CO concentration as shown in Fig.4. From Fig.4(a), the addition of water vapor can significantly increase the PG decomposition rate. The rate of PG decomposition rises from

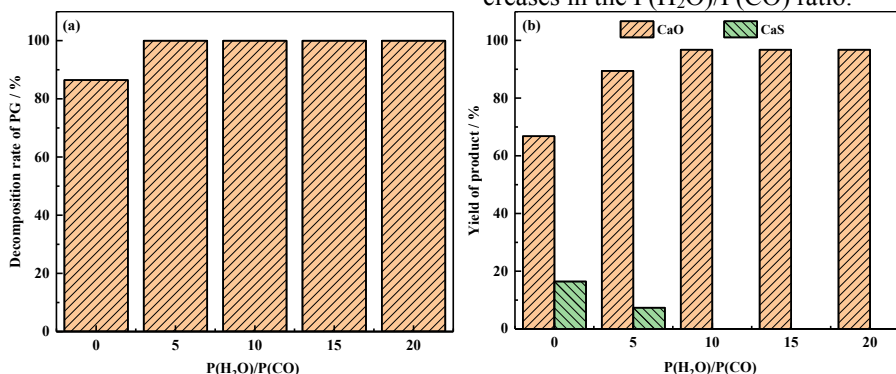


Fig.4 (a) Influence of P(H₂O)/P(CO) ratio on PG decomposition rate in the CO-H₂O-N₂; (b) Influence of P(H₂O)/P(CO) ratio on CaO and CaS yield in the CO-H₂O-N₂

3.4 Influence of temperature

The influence of temperature on the PG decomposition process was studied at temperatures between 950 and 1150 °C in the presence of 3%CO-N₂ and 3%CO-30%H₂O-N₂ as shown in Fig.5.

The influence of reaction temperature on PG decomposition rate in CO-N₂ and CO-H₂O-N₂ is depicted in Fig.5(a). The PG decomposition rate rises as temperature rises, as seen in the figure. The PG decomposition rate in CO-N₂ and CO-H₂O-N₂ are 94.67% and 99.99%, respectively at 950 °C. The PG decomposition rate in both

reaction of CaO with SiO₂ in PG to form Ca₂SiO₄[12]. However, when water vapor is added to the CO-N₂ atmosphere it is seen that CaS disappears completely and CaO yield reaches 96.78%. This suggests that the CaO yield can be significantly increased by include water vapor in the CO-N₂ atmosphere.

86.45% to 99.99% as (H₂O)/P(CO) goes from 0 to 5. The yield of CaO during PG decomposition is significantly influenced by the partial pressure ratio, as illustrated in Fig.4(b). As P(H₂O)/P(CO) increases, the CaO yield steadily rises. The CaO yield rises from 66.72% to 96.78% when P(H₂O)/P(CO) increases from 0 to 10. The yield of CaO is stabilized at around 96.7% with additional increases in the P(H₂O)/P(CO) ratio.

atmospheres are almost 100% when the temperature surpasses 1000 °C.

The impact of temperature on the product composition is depicted in Fig.5(b). As the temperature rises from 950 °C to 1150 °C in CO-N₂, the CaO yield rises from 23.38% to 54.87% while the CaS yield falls from 62.11% to 41.23%. This conclusion is consistent with the results of the FactSage simulation discussed above and suggests that raising the temperature encourages an increase in CaO yield. It can be seen from comparing the decomposition properties of PG in 3% CO-30% H₂O-N₂ that the presence of water vapor may greatly boost the CaO yield, reaching a high of 96.78% at 1100 °C.

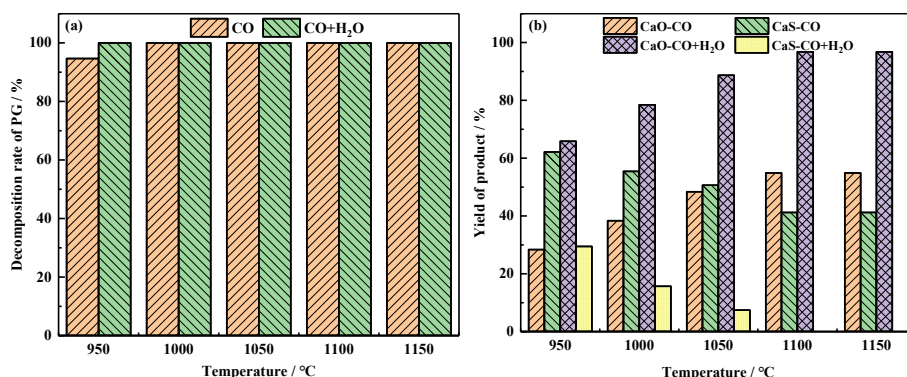


Fig.5 (a) Influence of temperature on PG decomposition rate in CO-N₂ and CO-H₂O-N₂; (b) Influence of temperature on CaO and CaS yield in the CO-N₂ and CO-H₂O-N₂

3.5 Reaction mechanisms

Since CO and H₂O can react to form H₂ and CO₂ at high temperature as shown in Equation (4), the composition analysis of the reacted gas was carried out by gas chromatography. The characteristic peak of hydrogen appears in the gas, indicating that when water vapor is added to the reaction atmosphere, CO and water vapor reacts to form H₂ and CO₂. Therefore, the PG decomposition process is the result of the joint action of H₂, CO and CO₂.

The decomposition products of PG in 3%CO-30%H₂O-N₂ is examined by XRD at a reaction temperature of 1100 °C for every 5 minutes to explore the reaction mechanism of PG decomposition by CO and water vapor to produce CaO. The distribution of each ingredient in the solid product at each reaction time point is depicted in Fig.6(a). The figure shows that a little quantity of CaS is first detected in the solid sample of PG decomposition, and that this CaS content rapidly diminishes until it vanishes as the reaction moves forward. It demonstrates that CaS is a byproduct of the CO-reduction process. It may be suggested that during the CO reductive decomposition of PG to create CaO, both CaO and CaS are generated. As the reaction proceeds, CaS will undergo a secondary reaction to form CaO. This conclusion is also supported by Fig.6(b). As the reaction period grows, the typical peaks of CaSO₄ in the product progressively decrease and are

replaced by the characteristic peaks of CaS and CaO. When the reaction reaches 60 minutes, the product contains only the characteristic peaks of CaO, Ca₂SiO₄, and Ca(OH)₂. Ca(OH)₂ is generated when CaO and water vapor combine. Ca₂SiO₄ is generated when CaO and SiO₂ react at high temperatures. According to the foregoing data, CaS is an intermediate product of the reaction that will continue to react with CaSO₄ and CO₂ to generate CaO as time passes.

In conclusion, the following describes the reaction process of the conversion of PG to CaO in CO-H₂O-N₂. Firstly, part of CO and H₂O in the reaction atmosphere react to form H₂ and CO₂. Secondly, CaSO₄ decomposes to CaO and CaS simultaneously in the presence of H₂ and CO as shown in Eqs.(5)-(8). Finally, CaO is formed when CaS interacts with unreacted CaSO₄ and CO₂ as shown in Eqs.(9)-(10)[13, 14].

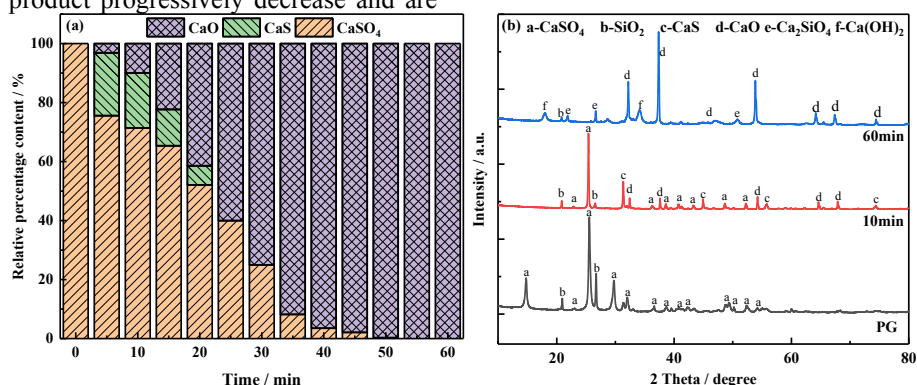
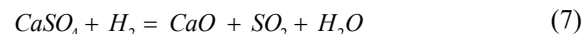
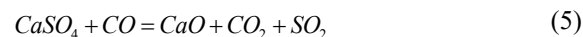


Fig.6 (a) Variation of the percentage of decomposition products with time; (b) XRD pattern of the product decomposition process of PG. PG will be completely decomposed to CaO at 1100 °C of 3% CO concentration and P(H₂O)/P(CO) of 10.

4 Conclusion

By analyzing the equilibrium phase diagram, it is found that the addition of H₂O to CO facilitates the decomposition of PG to CaO. The CO concentration, P(H₂O)/P(CO) and reaction temperature significantly affect the

The following describes the reaction process of the conversion of PG to CaO in CO-H₂O-N₂. First, part of CO and H₂O react at high temperatures to generate H₂ and CO₂. Second, CaSO₄ in PG reacts with H₂ and CO to form CaO

and CaS, respectively. Finally, CaO is formed when CaS interacts with unreacted CaSO₄ and CO₂. This study will improve a new technical approach for the preparation of CaO by PG decomposition.

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