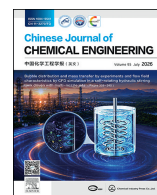




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Full Length Article

Influence mechanism and regulation strategy of atmospheric conditions on the thermal decomposition of phosphogypsum

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ABSTRACT

Phosphogypsum, a large-volume phosphoric acid production by-product with significant environmental risks, demands urgent resource and high-value utilization. Reductive decomposition to high-activity quicklime is effective for this purpose. For high-quality products, improving CaO yield and inhibiting CaS formation enhances added value. Based on this, this study systematically investigates the reaction mechanism and regulation strategy of phosphogypsum decomposition to CaO under different atmospheric conditions. Special focus is placed on analyzing the effects of CO concentration, CO₂ concentration, and $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio on the reductive decomposition pathway and the products obtained from phosphogypsum. The results show that introducing CO₂ into the CO reducing atmosphere can effectively promote the conversion of CaSO₄·2H₂O to CaO, increasing the decomposition mass loss rate from 43.10% to 63.83%, indicating that adding CO₂ to the reducing atmosphere achieves directional regulation of CaO formation. When the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio increases from 0.15 to 15, the mass loss rate of CaSO₄·2H₂O rises from 55.66% to 62.50%, demonstrating that a higher $P_{\text{CO}_2}/P_{\text{CO}}$ ratio not only promotes the reaction between CaSO₄ and CO to form CaO but also facilitates the conversion of generated CaS to CaO. Under the CO–CO₂–N₂ mixed atmosphere, the initial reaction temperature of phosphogypsum reductive decomposition decreases by approximately 300 °C, while the formation of CaS is inhibited, significantly increasing the CaO content in the products and realizing directional regulation of the thermal decomposition products of phosphogypsum.

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1. Introduction

Phosphogypsum is a bulk industrial solid waste generated during the wet-process production of phosphoric acid in phosphorus chemical enterprises. Typically, 4–5 tons of phosphogypsum are produced for per ton of phosphoric acid, with its main chemical component being CaSO₄·2H₂O [1,2]. Currently, the primary disposal method of phosphogypsum is open-air stockpiling, which not only occupies a large amount of land resources but also poses environmental risks of soil and groundwater pollution by leachate [3,4]. Extensive research on the resource utilization of phosphogypsum has been conducted worldwide. Among various

approaches, converting phosphogypsum into basic raw materials such as CaO and SO₂ under high-temperature conditions is an effective way to achieve its high-value utilization [5–7]. Most existing processes use coal powder as a single reducing agent. Although the technology is mature, it has problems such as high decomposition temperature, coexistence of CaS and CaO in the products, and low purity, which limit its high-value application [8–11].

Existing studies have shown that reducing gases such as CO and H₂ can promote the thermal decomposition of phosphogypsum to a certain extent [12,13]. However, most current studies focus on single atmospheric conditions, with shallow interpretation of the reaction mechanism and a lack of systematic research on product selective regulation. This leads to insufficient theoretical guidance for process parameter optimization, making industrial application become difficult [14–16]. In recent years, reaction systems

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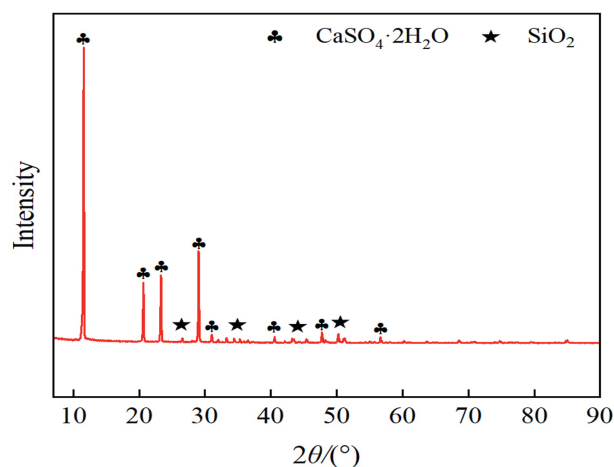


Fig. 1. XRD pattern of the phosphogypsum.

involving multi-atmosphere synergy, reducing agents, and catalysts have become research hot topic. Compared with single reduction conditions, they can significantly improve the decomposition rate of phosphogypsum and the yield of the target product CaO [17–22]. Notably, metallurgical flue gas is rich in CO and CO₂. Using it as the atmosphere source for the reductive decomposition of phosphogypsum not only realizes the resource treatment of solid waste but also provides a new technical idea for cross-industry synergistic emission reduction and resource recycling between metallurgy and chemical engineering. Moreover, compared with traditional industrial-grade CO raw materials, it can greatly reduce costs and carbon emissions, achieving remarkable environmental and economic benefits.

Based on aforementioned analysis, this study aims to achieve high selectivity in the preparation of target product CaO through the reductive decomposition of phosphogypsum. It systematically investigates the influence of different atmospheric conditions on the reductive decomposition pathway and product selection of phosphogypsum. The reaction mechanism is revealed through thermogravimetric analysis (TGA) and X-ray diffraction (XRD) phase characterization, and the regulation mechanism of product selectivity is clarified. This provides a theoretical basis for the directional conversion of phosphogypsum to CaO and SO₂, and lays a technical foundation for the industrial application of collaborative treatment of solid waste with metallurgical flue gas.

2. Experimental

2.1. Experimental materials and equipment

The industrial solid waste phosphogypsum used in the experiment was provided by Hubei Yihua Environmental Protection Technology Co., Ltd., located in Hubei Province, China. The XRD pattern of phosphogypsum is shown in Fig. 1, with its main component being CaSO₄·2H₂O. Its main chemical and mass composition is presented in Table 1, including CaO: 32.19%; SO₃:

40.62%; SiO₂: 5.18%, and small amounts of P₂O₅, Al₂O₃, Fe₂O₃, and F. The analytical-grade CaSO₄·2H₂O used in the experiment was purchased from Shanghai Macklin Biochemical Technology Co., Ltd., China, with a purity of 99%, and the graphite powder had a purity of 99%. The reaction gases N₂, CO, and H₂ were purchased from Wuhan Xiangyun Gas Co., Ltd., China, with a purity of ≥99.999%.

2.2. Experimental methods

First, the industrial solid waste phosphogypsum sample was placed in a blast drying oven and dried to constant mass at (60 ± 2) °C to remove free water. Subsequently, to obtain key parameters (e.g., initial reaction temperature, reaction time, and mass loss) via TGA, (100 ± 0.5) mg of analytical grade CaSO₄·2H₂O reagent or pretreated phosphogypsum was accurately weighed using an electronic analytical balance (recorded as m_1) and placed in a crucible of the TGA instrument. The heating rate was set to 10 °C·min⁻¹, and the total gas flow rate was controlled at 100 ml·min⁻¹. The reaction atmosphere was configured as required by the experiment, and after the gas blending system stabilized for 5 min, the gas path was switched to introduce the reaction gas into the TGA instrument. Literature research indicates the solid sample is stable in the temperature range of room temperature to 1200 °C under N₂ atmosphere, thus N₂ was used as the protective gas to prevent unwanted reactions of the sample from reacting during the programmed heating process, which would affect the subsequent experimental results [15]. After the reaction, to avoid reactions between the products and H₂O/CO₂ in the air which might interfere with subsequent characterization results, the gas path was switched back to N₂ atmosphere. Once the sample was naturally cooled to room temperature. The solid product obtained from the reaction was weighed (recorded as m_2) and stored in a dry container under N₂ protection.

The mass loss rate ω was calculated by the formula: $\omega = (m_1 - m_2)/m_1 \times 100\%$

2.3. Analytical methods

The thermal decomposition behavior of samples (e.g., mass loss rate, initial reaction temperature, and reaction duration) was analyzed using a TGA (HJ-HCT5S, Beijing Hengjiu Instrument Co., Ltd., China). An electronic analytical balance (CP210, OHAUS, USA) was employed for accurate weighing of raw materials and reaction products (precision: ±0.5 mg). A blast drying oven (DHG-9076A, Shanghai Jinghong Experimental Equipment Co., Ltd., China) was used to dry phosphogypsum samples at (60 ± 2) °C to remove free water.

The chemical compositions of phosphogypsum and reaction products were determined via an X-ray fluorescence spectrometer (XRF, ZSXPrimus IV, Hitachi, Japan), and the reaction products were quantified via this technique. Subsequently, the content of CaO in the products was accurately determined using the EDTA titration method [23]. The crystalline phases of raw materials and products were identified using an XRD (D/MAX 2000, Hitachi, Japan). The microscopic morphology and elemental distribution of

Table 1
Main chemical composition of phosphogypsum.

Component	CaO	SO ₃	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Fe ₂ O ₃	F	H ₂ O [⊙]	Others
Mass content/%	32.19	40.62	0.49	5.18	0.79	0.25	0.62	19.25	0.61

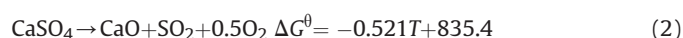
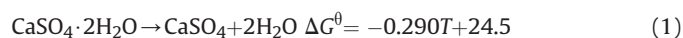
[⊙] H₂O content here refers to crystal water.

the samples were characterized by a scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDS-SEM, ApreoS, Thermo Fisher Scientific (FEI), Netherlands) detector.

2.4. Theoretical analysis

Under the condition of using N_2 as the carrier and introducing a mixed atmosphere of CO and CO_2 , the possible reactions in the system are as follows (unit: $\text{kJ} \cdot \text{mol}^{-1}$). The calculated variation of ΔG^θ with temperature in different reactions are shown in Fig. 2.

Thermal decomposition reactions of $CaSO_4$:



Possible reactions of $CaSO_4$ under carbon-containing conditions:

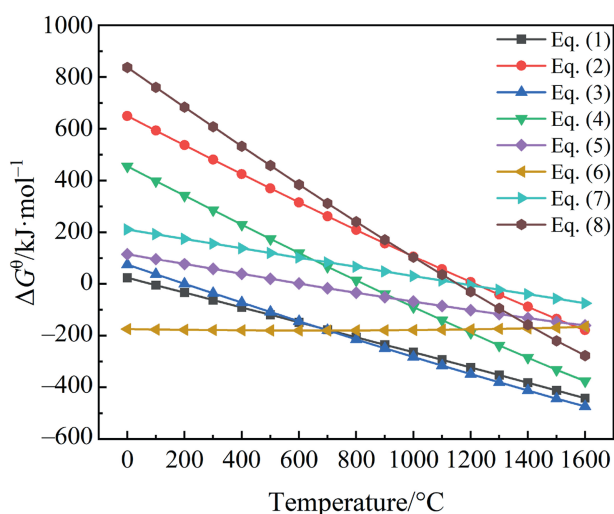
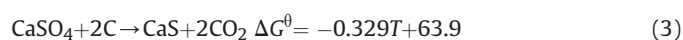
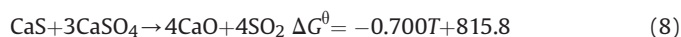
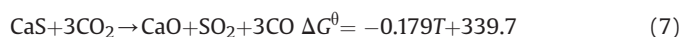
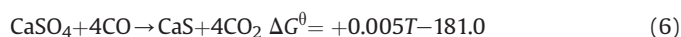
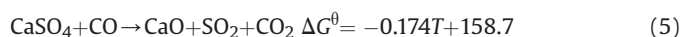


Fig. 2. Variation of ΔG^θ with temperature in different reactions.

Possible reactions of $CaSO_4$ under CO reducing atmosphere:



3. Results and Discussion

3.1. Thermal decomposition process of $CaSO_4 \cdot 2H_2O$

The thermal decomposition process of $CaSO_4 \cdot 2H_2O$ was systematically studied using a thermogravimetric analyzer, based on thermodynamic calculations and literature investigations, $CaSO_4 \cdot 2H_2O$ samples exhibit stable properties within 1200°C under an N_2 atmosphere. Thus, the final reaction temperature was set at 1400°C in the experiments to ensure the complete thermal decomposition of $CaSO_4 \cdot 2H_2O$ and the results are shown in Fig. 3(a). From the TG-DTG curves, the thermal decomposition process can be clearly divided into two mass loss stages with significant differences in thermodynamic properties, and the mass loss of each stage strictly corresponds to the reaction mechanism. The first mass loss stage is concentrated in the range of $40\text{--}120^\circ\text{C}$, with an actual mass loss rate of 19.55%, which is highly consistent with the theoretical crystal water content of $CaSO_4 \cdot 2H_2O$, indicating high purity of the raw material. From the DTG curve, the temperature corresponding to the maximum mass loss rate in this stage is approximately 85°C , reflecting that the coordination bond energy between crystal water and Ca^{2+} is low, and the reaction can occur at a relatively low temperature [24,25].

The initial temperature of the second mass loss stage is approximately 1150°C , and the final temperature is approximately 1350°C . The entire reaction process lasts for about 20 min, with a stage mass loss rate of 43.00%, which corresponds to the thermal decomposition process of $CaSO_4$. According to thermodynamic calculations, the ΔG of the self-decomposition reaction of $CaSO_4$ (Eq. (2)) is close to 0 at 1150°C , indicating that this temperature is the critical temperature for the spontaneous occurrence of the reaction.

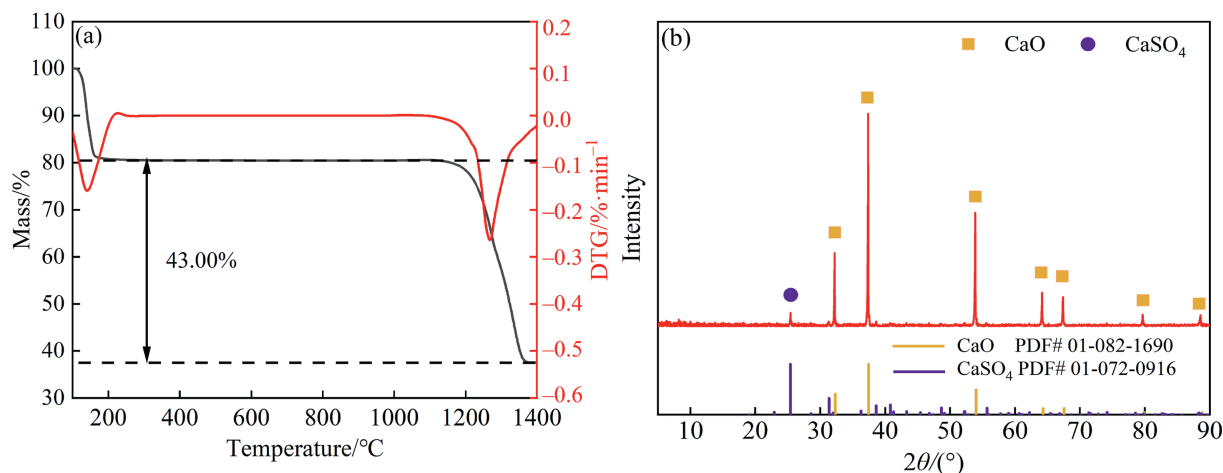


Fig. 3. Decomposition reactions of $CaSO_4 \cdot 2H_2O$ under N_2 atmosphere: (a) non-isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

The XRD pattern of the final decomposition product is shown in Fig. 3(b). The main phase of the decomposition product is CaO, with sharp and high-intensity characteristic diffraction peaks, indicating good crystallinity of the generated CaO crystals. Meanwhile, weak characteristic diffraction peaks of CaSO_4 ($2\theta = 25.4^\circ$) can still be detected in the pattern, indicating that CaSO_4 is not completely decomposed. No other impurity phases such as CaS are observed, suggesting that the thermal decomposition of CaSO_4 under N_2 atmosphere only follows the self-decomposition reaction without other side reactions.

3.2. Decomposition process of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under different reduction conditions

Given the high self-decomposition temperature of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under inert atmosphere, to effectively reduce the decomposition temperature of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, subsequent experiments used graphite powder and CO as reducing agents respectively to systematically investigate the reductive decomposition process of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under two different reduction conditions.

3.2.1. Graphite powder as reducing agent

When graphite powder is used as the reducing agent, under the condition of $n_{\text{C}}/n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = 2$ (where n denotes molar, and the ratio represents the molar ratio of C to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), the thermal decomposition behavior of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ changes significantly. The thermogravimetric analysis results are shown in Fig. 4(a). Compared with N_2 atmosphere, the initial reaction temperature decreases from 1150°C to 900°C , indicating that graphite powder, as a reducing agent, undergoes a redox reaction with CaSO_4 . According to thermodynamic calculations, the ΔG of Eqs. (3) and (4) is much less than 0 at 900°C , while the ΔG of Eq. (2) is close to 0, indicating that the decomposition of CaSO_4 at this temperature is dominated by reduction reactions rather than self-decomposition reactions.

From the TG curve, the entire decomposition process lasts for about 15 min and basically ends at around 1050°C . The second mass loss rate is 41.98%, which is slightly less than 43.00% under N_2 atmosphere. According to molar mass calculation, the theoretical mass loss rate of CaSO_4 completely decomposed into CaO is 46.51%, while the actual mass loss rate under N_2 atmosphere is only 43.00%, indicating that CaSO_4 is not completely decomposed under this condition. In the carbon reduction system, CaO and CaS are generated simultaneously. For the same molar amount of

CaSO_4 , the theoretical mass loss rate when decomposed into CaS is 37.21%, which is much lower than 46.51% when decomposed into CaO. This is because the formation of CaS in the system leads to a decrease in the overall mass loss rate.

The XRD results of the reduced product are shown in Fig. 4(b). Obvious characteristic peaks of CaO ($2\theta = 32.3^\circ, 37.4^\circ, 54.0^\circ$) and CaS ($2\theta = 31.5^\circ, 45.0^\circ, 56.0^\circ, 74.6^\circ$) coexist in the pattern, indicating that there are two competitive reactions in the carbon reduction system. From the reaction mechanism, the reaction between C and CaSO_4 first occurs at the particle contact interface. The generated CaS has high reactivity and can further undergo a secondary reaction with unreacted CaSO_4 . The relative contents of CaO and CaS in the product depend on the competitive balance of the above reactions. When carbon is excessive, the rate of CaS formation via Eq. (3) is relatively fast, leading to a high CaS content in the product. If the carbon ratio is reduced, the proportion of CaO formation via Eq. (2) will increase accordingly. This rule provides a theoretical basis for regulating the product composition. The decomposition process of CaSO_4 is carried out in a strong reducing environment, resulting in a higher CaS content than CaO in the product.

3.2.2. CO as reducing agent

Compared with the solid–solid reaction system of carbon powder, CO as a gaseous reducing agent can form a gas–solid reaction system with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which has the advantages of high mass transfer efficiency and sufficient contact at the reaction interface. Its thermal decomposition curve is shown in Fig. 5(a). The experimental results show that the initial reaction temperature is further reduced to 800°C , which is about 100°C lower than that of the carbon reduction system. This is because gaseous CO molecules have a high diffusion coefficient and can quickly reach the surface of CaSO_4 particles, adsorb on active sites, and undergo interface reactions with CaSO_4 . Therefore, the CO reduction system has a lower initial reaction temperature and better reaction kinetic performance.

From the TG curve, the entire reaction process lasts for about 15 min and basically ends at around 950°C , with the reaction temperature about 100°C lower than that of the carbon system. Although low temperature will lead to a decrease in reaction rate, the gas–solid reaction system has a higher mass transfer rate, which can offset this impact. Therefore, the reaction completion time is basically the same as that of the carbon reduction system. From the mass loss data, the total mass loss rate of the reaction is

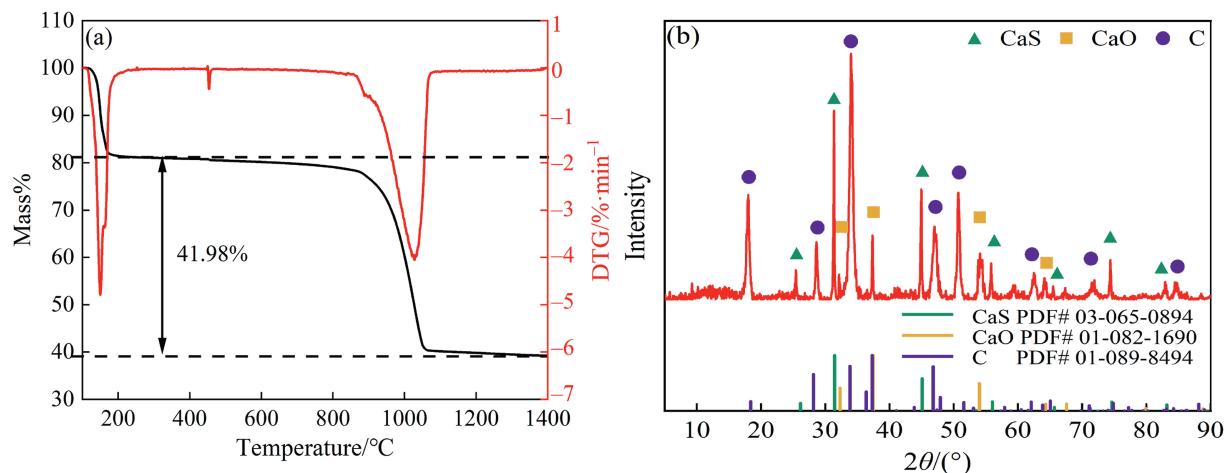


Fig. 4. Decomposition reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under carbon-added condition: (a) non-isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

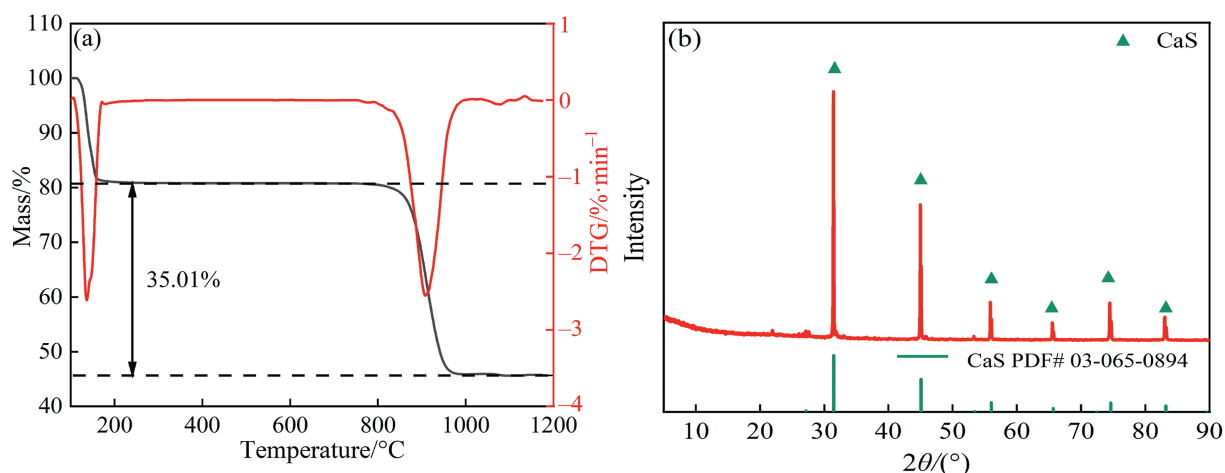


Fig. 5. Decomposition reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under CO atmosphere: (a) non-isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

about 55%, which is slightly lower than that of the carbon reduction system. Combined with the theoretical calculation of molar mass, it can be inferred that the reaction product is mainly CaS.

The XRD analysis results of the reduced product are shown in Fig. 5(b). Only obvious characteristic diffraction peaks of CaS are detected in the product, and no characteristic peaks of CaO are found. This indicates that the reductive decomposition of CaSO_4 under pure CO atmosphere mainly follows the pathway of Eq. (6), and the final product is dominated by CaS, which is consistent with the analysis results of the TG curve. It shows that at 800 °C, Eq. (6) has a stronger spontaneous tendency and is the dominant reaction in the system.

3.3. Regulation of thermal decomposition products of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under different reducing atmospheres

Under a single CO atmosphere, the reduced product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is only CaS, which is difficult to achieve high-value utilization. To directionally regulate the yield of CaO in the product and improve the product added value, the thermal decomposition process of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and its product regulation mechanism under different reducing atmospheres were further studied.

3.3.1. Influence of CO concentration on the thermal decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

At 1050 °C, the decomposition reaction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in CO-N_2 atmosphere with CO volume fraction of 5% to 50% was studied, and the results are shown in Fig. 6(a). The results indicate that under different CO concentrations, the decomposition rate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is stably around 56%, showing that CO concentration has no significant effect on the decomposition degree and product at this temperature. As the CO concentration increases from 5% to 50%, the time to reach reaction equilibrium shortens, indicating that the reaction rate increases with the increase of CO concentration. This is because the adsorption amount of CO molecules on the surface of CaSO_4 particles increases with the increase of CO concentration, thereby improving the reaction rate. However, the TG curve shows that as the CO concentration increases, the mass loss rate at equilibrium decreases from 56.90% to 54.66%, with an insignificant change. This indicates that although high CO concentration is more conducive to CaS formation, leading to a decrease in mass loss rate, the impact is limited. It is difficult to effectively regulate the type of CaSO_4 decomposition products only by adjusting the CO concentration in the atmosphere.

Subsequently, CO_2 was introduced under the above conditions, with the atmosphere composition controlled as 5% CO –5% CO_2 –90% N_2 , to investigate the influence of CO_2 on the reduced

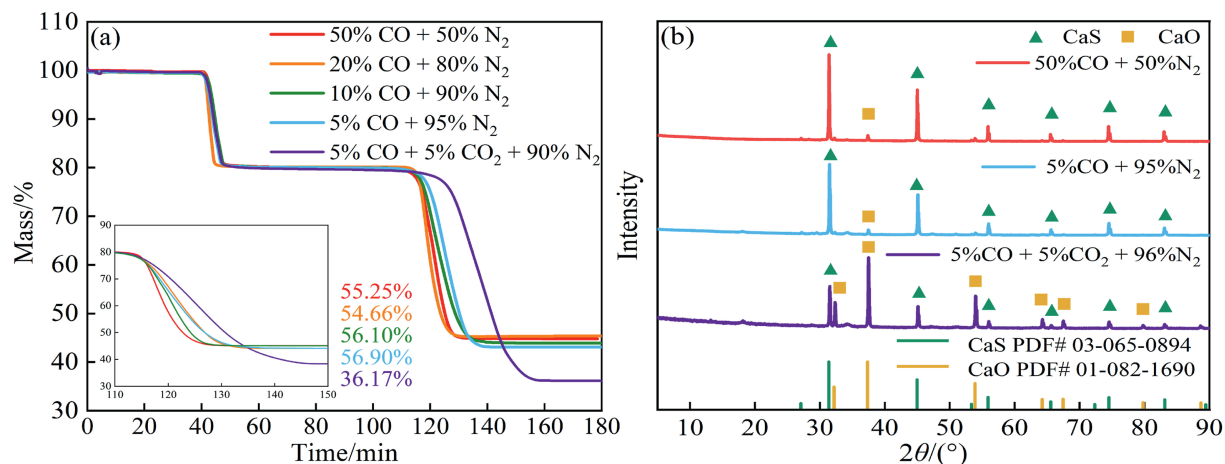


Fig. 6. Decomposition reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under different CO concentration atmospheres at 1050 °C: (a) isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

product. The results are shown in Fig. 6(a) and (b). In comparison, after introducing CO_2 , the mass loss rate of the second reaction stage increases significantly from 56% to 62%. Combined with the corresponding relationship between mass loss rate and product composition mentioned above, this indicates a substantial increase in the proportion of CaO in the product. The XRD analysis results show that obvious characteristic diffraction peaks of CaO appear in the product, while the intensity of CaS characteristic peaks is significantly weakened, confirming the regulatory effect of CO_2 on product selectivity. From the reaction mechanism, the introduction of CO_2 mainly increases the yield of CaO by promoting the progress of Eq. (7). The generated CaS undergoes a secondary reaction with CO_2 to form CaO, thereby improving the selectivity of CaO [26].

However, the TG curve shows that the time to reach reaction equilibrium increases from 20 min to 40 min after introducing CO_2 , indicating that CO_2 has an inhibitory effect on the overall reaction rate. This is because CO_2 and CO have competitive adsorption on the active sites of CaSO_4 particles. The adsorption of CO_2 will occupy some active sites, reducing the contact opportunity between CO and active sites, thereby decreasing the rates of Eqs. (5) and (6). Meanwhile, Eq. (7) is an endothermic reaction that consumes heat in the system, leading to a decrease in local reaction temperature and further slowing down the reaction rate [27,28]. In summary, CO_2 exhibits dual effects of promoting CaO formation and inhibiting reaction rate in this system, which provides a key basis for the subsequent optimization of atmosphere composition.

3.3.2. Influence of CO_2 concentration on the thermal decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

At 1050 °C with a fixed CO volume fraction of 5%, the influence of CO_2 volume fraction (5% to 30%) on the decomposition behavior of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in CO– CO_2 – N_2 mixed atmosphere was investigated, and the results are shown in Fig. 7(a). The experimental data indicate that under different CO_2 concentrations, the total mass loss rate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is stably around 62%, showing that CO_2 concentration has no significant effect on the reductive decomposition degree. From the perspective of thermodynamic equilibrium, there is a thermodynamic equilibrium of Eqs. (5)–(7) in the system at this temperature. Although changes in CO_2 concentration will cause shifts in the reaction equilibrium, a dynamic balance is achieved between the reactions, ultimately maintaining the overall reductive decomposition degree of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ stable.

As the CO_2 concentration increases from 5% to 30%, the reaction completion time prolongs from 20 min to 40 min, indicating that the reaction rate decreases significantly with the increase of CO_2 concentration. This phenomenon verifies the competitive adsorption mechanism between CO_2 and CO on the active sites of CaSO_4 . A higher CO_2 concentration makes it easier to occupy active sites and affect the thermodynamic equilibrium of Eqs. (5) and (6), leading to a decrease in their reaction rates. Although the rate of Eq. (7) increases with the increase of CO_2 concentration, it is much lower than that of Eqs. (5) and (6), so the overall reaction rate still shows a downward trend.

The XRD analysis results of the reduced product are shown in Fig. 7(b). It can be seen that as the CO_2 concentration increases from 5% to 30%, the intensity of the characteristic diffraction peaks of CaO increases, while the intensity of the characteristic diffraction peaks of CaS gradually weakens, indicating that increasing CO_2 concentration increases the yield of CaO in the product. A high CO_2 concentration provides sufficient reactants for Eq. (7), promoting the conversion of CaS to CaO, thereby increasing the proportion of CaO and inhibiting the progress of Eq. (6), reducing the yield of CaS. However, the change range of XRD peak intensity is relatively small, and further increasing CO_2 concentration cannot promote the conversion of CaS, indicating that Eq. (7) has reached equilibrium, and the regulatory effect of CO_2 on product selectivity has an upper limit.

3.3.3. Influence of $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio on the thermal decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

At 1050 °C with a fixed N_2 volume fraction of 20%, the influence of $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio on the decomposition process of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was investigated by adjusting the concentration ratio of CO and CO_2 . The results are shown in Fig. 8(a). When the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio increases from 0.15 to 15, the mass loss rate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ increases significantly from 55.66% to 62.50%, indicating that the yield of CaO in the product increases significantly with the increase of the partial pressure ratio. The core reason is that the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio is a key parameter affecting the equilibrium of Eqs. (5)–(7). According to the equilibrium constant $K_5 = P_{\text{SO}_2} \times P_{\text{CO}_2}/P_{\text{CO}}$ of Eq. (5), an increase in the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio will shift Eq. (5) to the forward direction, promoting the formation of CaO. At the same time, it promotes the forward progress of Eq. (7), further facilitating the conversion of CaS to CaO. In contrast, Eq. (6) will shift to the reverse direction with the increase of the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio, reducing

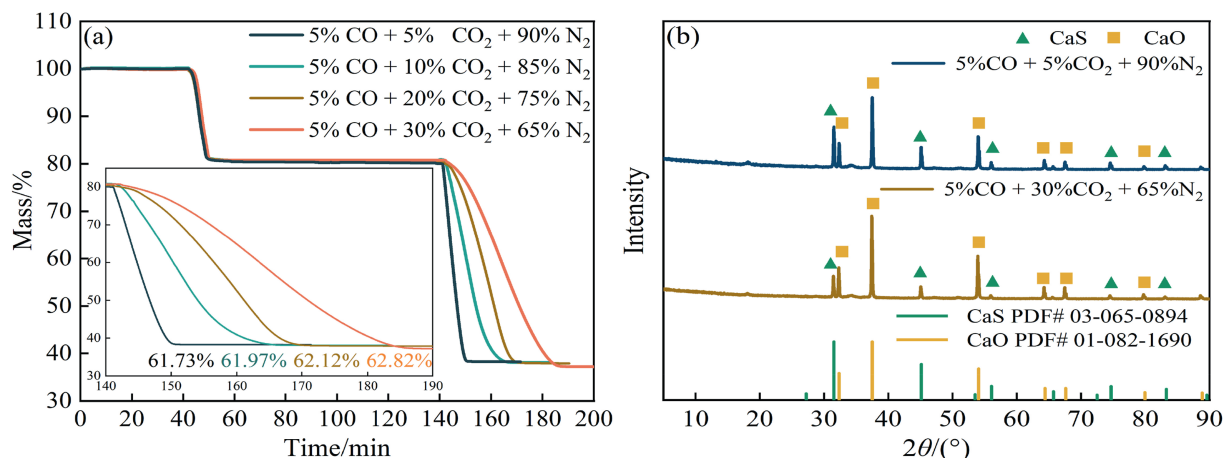


Fig. 7. Decomposition reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under different CO_2 concentration atmospheres at 1050 °C (with 5% CO): (a) isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

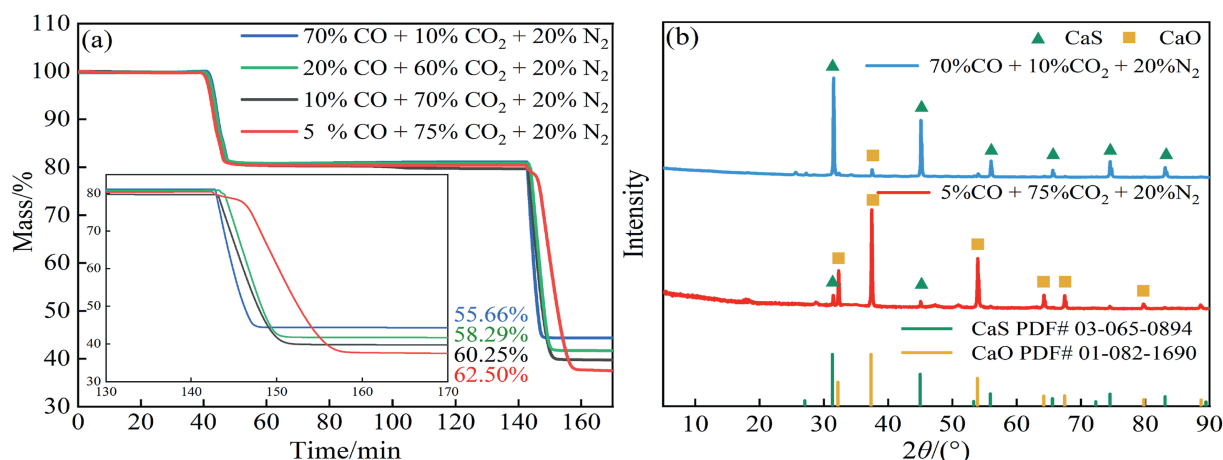


Fig. 8. Decomposition reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under different $P_{\text{CO}_2}/P_{\text{CO}}$ atmospheres at 1050 °C: (a) isothermal thermal decomposition TG curve; (b) XRD pattern of the product.

the formation of CaS. Therefore, a high $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio significantly increases the yield of CaO by synergistically promoting Eqs. (5) and (7) and inhibiting Eq. (6).

When the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio increases from 0.15 to 15, the time of the second reaction stage prolongs from 10 min to 20 min, indicating that the reaction rate decreases with the increase of the partial pressure ratio. This phenomenon is consistent with the competitive adsorption mechanism of CO₂, i.e., as the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio increases, the adsorption proportion of CO₂ on the active sites of CaSO_4 becomes higher, and the overall reaction rate shows a downward trend.

The XRD analysis results of the reduced product (Fig. 8(b)) show that as the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio increases from 0.15 to 15, the intensity of the characteristic diffraction peaks of CaO increases significantly, while the intensity of the CaS characteristic peaks decreases correspondingly. This confirms that the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio is a key parameter for regulating product selectivity. By accurately adjusting this ratio, directional control of the product from CaS-dominated to CaO-dominated can be achieved. This rule is of great significance for industrial applications. Flue gas generated from different metallurgical processes can be used as the reducing agent, and its ratio can be adjusted to modify the atmospheric composition, thereby realizing the directional conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to high-purity CaO.

3.4. Analysis of the reduction process of phosphogypsum

To verify the actual regulatory effect of the mixed atmosphere on the reductive decomposition of real phosphogypsum, a tube furnace was used to simulate the industrial reaction environment. Reductive experiments of phosphogypsum were conducted at 1050 °C under the atmosphere of 5% CO–75% CO₂–20% N₂. The microscopic morphology and phase composition of the products were analyzed through SEM-EDS and XRD characterizations.

The SEM characterization results are shown in Fig. 9(a). The SEM image of the phosphogypsum reduction product reveals that its microscopic structure retains the flaky structure of raw phosphogypsum and consists of numerous scaly small particles. EDS point scan analysis detected three elements: Ca, O, and S. The content of S is close to 0, confirming that CaS in the product has been almost completely converted without accumulation of sulfur-containing impurities. The XRD analysis results of the reduction product, presented in Fig. 9(b), show sharp and high-intensity characteristic diffraction peaks of CaO. There is no obvious diffraction peaks of CaS are detected. This indicates that under this atmosphere condition, the core product is high-purity CaO.

In summary, the 5% CO–75% CO₂–20% N₂ mixed atmosphere can effectively reproduce the directional conversion law of pure reagent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. By inhibiting the formation of CaS and promoting the conversion of CaS, it achieves the directional

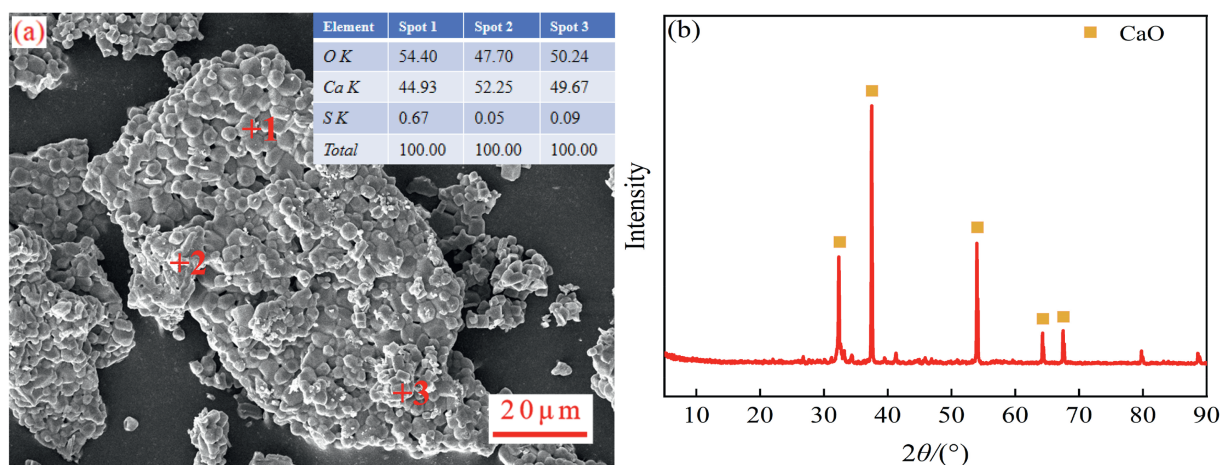


Fig. 9. Decomposition reactions of phosphogypsum under 5% CO–75% CO₂–20% N₂ atmosphere at 1050 °C: (a) SEM-EDS images; (b) XRD pattern of the product.

Table 2

Key parameters of phosphogypsum reductive decomposition under different conditions.

Reaction condition	Temperature/°C	Time/min	Reaction product	Literature source
C	850	60	91.55% CaS	[8]
S	800	20	Almost CaS	[13]
H ₂	900	120	81.1% CaO	[23]
CO–N ₂ (1:99)	—	60	63.43% CaO	[27]
CO–N ₂ (50:50)	950	15	Almost CaS	[12]
CO–CO ₂ –N ₂ (5%:75%:20%)	850	20	99.0% CaO	The present research

preparation of high-purity CaO from real phosphogypsum, providing direct data support for the industrial application of synergistic treatment of phosphogypsum with metallurgical flue gas.

To the best of our knowledge, the relevant studies conducted worldwide have been reviewed. The key experimental parameters and results pertaining to the reductive decomposition of phosphogypsum under single reducing atmospheres, including the onset reaction temperature, reaction duration and product distribution, are presented in Table 2. Under reduction with coke and sulfur, CaS is consistently the dominant reaction product. Notably, the onset reaction temperature of gaseous reducing atmospheres is 100 °C higher than that in the reduction systems using coke and sulfur as solid reducing agents. Furthermore, under H₂ reducing atmosphere, the maximum yield of CaO derived from the reductive decomposition of phosphogypsum is merely 81.1%. Under a CO reducing atmosphere, CaS becomes the dominant product when the CO concentration exceeds 50%; at the CO concentration of 1%, the maximum CaO yield is only 63.43%, with effective inhibition of CaS formation proving elusive. In contrast, the CO–CO₂–N₂ mixed atmosphere employed in this study not only lowers the onset temperature of phosphogypsum reductive decomposition to a level close to that in the reduction systems using coke and sulfur, but also elevates the CaO yield to over 99%, alongside the near-total elimination of CaS, thereby enabling the selective preparation of high-purity CaO.

3.5. Reaction mechanism

In summary, the reaction mechanism of this process is illustrated in Fig. 10, consisting of three core stages: (1) In a CO

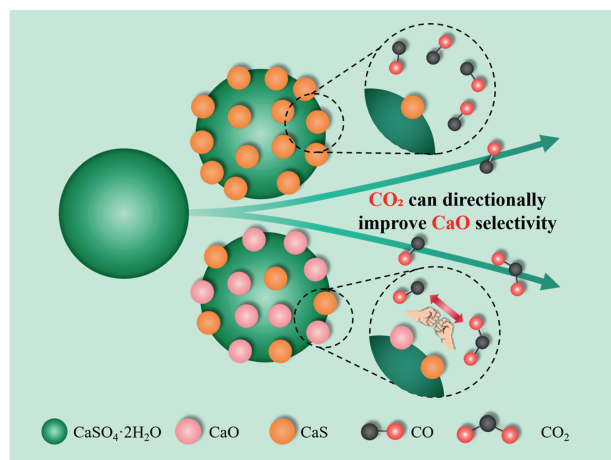


Fig. 10. Reaction mechanism of reductive decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under CO – CO_2 mixed atmosphere.

atmosphere, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in phosphogypsum is mainly reduced to the product CaS. (2) In the CO – CO_2 mixed atmosphere, CO_2 promotes the secondary conversion of CaS to CaO, enabling the directional transformation of CaS into the target product. (3) By adjusting the $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio, the competitive adsorption mechanism between CO and CO_2 is regulated, which further suppresses CaS formation and enhances CaO selectivity.

4. Conclusions

This study systematically investigates the reductive decomposition process and characteristics of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ under various atmospheric conditions. By comparing the mass loss rates of samples under typical reaction conditions and combining with XRD phase characterization, the reaction mechanism and regulation strategy of preparing CaO via $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reductive decomposition are revealed. The main research conclusions are as follows.

- (1) The decomposition characteristics of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in N_2 and pure CO atmospheres are significantly different. Under N_2 atmosphere, it undergoes two-step mass loss to form CaO as the main product. Under CO atmosphere, the initial decomposition temperature decreases to 800 °C with CaS as the sole product. The CO volume fraction in the range of 5% to 50% has no significant effect on product composition.
- (2) CO_2 can directionally improve CaO selectivity but significantly inhibits the reaction rate. The introduction of CO_2 promotes the secondary reaction between CaS and CO_2 , thereby enabling the directional regulation of the reductive decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to form CaO without affecting the overall decomposition degree. With fixed CO concentration, increasing CO_2 concentration from 5% to 30% prolongs the reaction completion time, due to competitive adsorption between CO_2 and CO on CaSO_4 active sites.
- (3) The $P_{\text{CO}_2}/P_{\text{CO}}$ partial pressure ratio is the core parameter for directional product regulation. Increasing the ratio from 0.15 to 15, the reductive decomposition mass loss rate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ rises from 55.66% to 62.50%, the CaO yield increases significantly. This confirms that an increase in the partial pressure ratio can promote the conversion of CaS to CaO, increase the CaO content in the product, and ultimately achieve directional product control.
- (4) Under the conditions of 1050 °C and 5% CO –75% CO_2 –20% N_2 mixed atmosphere, high-purity CaO can be directionally prepared through phosphogypsum reduction experiments simulated in an industrial environment using a tube furnace. EDS analysis shows that the atomic ratio of S element is close to 0, indicating the almost complete conversion of CaS, and thus providing a reliable experimental basis for the industrialization of synergistic treatment of phosphogypsum with metallurgical flue gas.

CRedit Authorship Contribution Statement

Weizhe Jie: Writing – original draft, Data curation. Tong Wang: Funding acquisition. Yi Su: Visualization, Formal analysis. Wu Zhou: Conceptualization. Yubo Zeng: Methodology. Yang Li: Writing – review & editing, Supervision, Project administration, Funding acquisition. Hua Zhang: Project administration, Funding acquisition. Hongwei Ni: Project administration.

Declaration of Competing 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.

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References

- [1] F. Mohammed, W.K. Biswas, H.M. Yao, M. Tadó, Sustainability assessment of symbiotic processes for the reuse of phosphogypsum, *J. Clean. Prod.* 188 (2018) 497–507.
- [2] S. Bisone, M. Gautier, V. Chatain, D. Blanc, Spatial distribution and leaching behavior of pollutants from phosphogypsum stocked in a gypstack: Geochemical characterization and modeling, *J. Environ. Manag.* 193 (2017) 567–575.
- [3] Q.S. Chen, Q.L. Zhang, C.C. Qi, A. Fourie, C.C. Xiao, Recycling phosphogypsum and construction demolition waste for cemented paste backfill and its environmental impact, *J. Clean. Prod.* 186 (2018) 418–429.
- [4] Y. Chernysh, O. Yakhnenko, V. Chubur, H. Roubík, Phosphogypsum recycling: A review of environmental issues, current trends, and prospects, *Appl. Sci.* 11 (4) (2021) 1575.
- [5] Y. Maierdan, M.A. Haque, B. Chen, M. Maimaitiyming, M.R. Ahmad, Recycling of waste river sludge into unfired green bricks stabilized by a combination of phosphogypsum, slag, and cement, *Constr. Build. Mater.* 260 (2020) 120666.
- [6] S.H. Liu, J.Y. Ouyang, J. Ren, Mechanism of calcination modification of phosphogypsum and its effect on the hydration properties of phosphogypsum-based supersulfated cement, *Constr. Build. Mater.* 243 (2020) 118226.
- [7] Y. Shen, J.S. Qian, J.Q. Chai, Y.Y. Fan, Calcium sulphoaluminate cements made with phosphogypsum: Production issues and material properties, *Cem. Concr. Compos.* 48 (2014) 67–74.
- [8] D. Ma, Q.H. Wang, Experimental study of CaS preparation from lignite-reduced phosphogypsum in a fluidized bed, *J. Chem. Technol. Biotechnol.* 98 (3) (2023) 756–772.
- [9] Y. Cui, J.D. Bai, I.S. Chang, J. Wu, A systematic review of phosphogypsum recycling industry based on the survey data in China—applications, drivers, obstacles, and solutions, *Environ. Impact Assess. Rev.* 105 (2024) 107405.
- [10] Q. Liu, X.Q. Ao, Q.L. Chen, Y. Xie, Y. Cao, Reaction characteristics and kinetics of phosphogypsum decomposition via synergistic reduction effect of composite reducing agent, *J. Mater. Cycles Waste Manag.* 24 (2) (2022) 595–605.
- [11] X. Jia, Q.H. Wang, K.F. Cen, L.M. Chen, An experimental study of CaSO₄ decomposition during coal pyrolysis, *Fuel* 163 (2016) 157–165.
- [12] F. Laasri, A. Carrillo Garcia, M. Latifi, J. Chaouki, Reaction mechanism of thermal decomposition of phosphogypsum, *Waste Manag.* 171 (2023) 482–490.
- [13] X.S. Yang, Z.Y. Zhang, X.L. Wang, L. Yang, B.H. Zhong, J.F. Liu, Thermodynamic study of phosphogypsum decomposition by sulfur, *J. Chem. Thermodyn.* 57 (2013) 39–45.
- [14] L.J. Zhao, T.M. Wan, X.S. Yang, L. Yang, X.J. Kong, Z.Y. Zhang, X.L. Wang, Effects of kaolinite addition on the melting characteristics of the reaction between phosphogypsum and CaS, *J. Therm. Anal. Calorim.* 119 (3) (2015) 2119–2126.
- [15] K. Antar, M. Jemal, A thermogravimetric study into the effects of additives and water vapor on the reduction of gypsum and Tunisian phosphogypsum with graphite or coke in a nitrogen atmosphere, *J. Therm. Anal. Calorim.* 132 (1) (2018) 113–125.
- [16] K.G. Gorbovskiy, A.I. Ryashko, A.I. Kazakov, A.M. Norov, A.I. Mikhaylichenko, The influence of water-soluble impurities on thermal dehydration kinetics of phosphogypsum in self-generated atmosphere, *J. Therm. Anal. Calorim.* 133 (3) (2018) 1549–1562.
- [17] D.L. Zheng, L.P. Ma, R.M. Wang, J. Yang, Q.X. Dai, Research on thermal decomposing properties of phosphogypsum with Fe addition under multi-atmosphere control, *Thermochim. Acta* 661 (2018) 59–66.
- [18] N. Mihara, D. Kuchar, Y. Kojima, H. Matsuda, Reductive decomposition of waste gypsum with SiO₂, Al₂O₃, and Fe₂O₃ additives, *J. Mater. Cycles Waste Manag.* 9 (1) (2007) 21–26.
- [19] Y. Wang, J.Z. Wang, Z.Y. Zhang, L. Yang, X.S. Yang, B.H. Zhong, X.J. Kong, X.L. Wang, Investigation of the fusion characteristics of ash in the reduction of pyrite and phosphogypsum, *J. Sustain. Metall.* 3 (4) (2017) 737–752.
- [20] S.R. Pinto, C. Angulski da Luz, G.S. Munhoz, R.A. Medeiros-Junior, Durability of phosphogypsum-based supersulfated cement mortar against external attack by sodium and magnesium sulfate, *Cement Concr. Res.* 136 (2020) 106172.
- [21] S. Zemni, M. Hajji, M. Triki, A. M'Nif, A.H. Hamzaoui, Study of phosphogypsum transformation into calcium silicate and sodium sulfate and their physicochemical characterization, *J. Clean. Prod.* 198 (2018) 874–881.
- [22] X. Xia, A.Q. Xia, Y.L. Qiao, G.B. Duan, Z.M. Liu, Insight into the reaction characteristics of H₂-reduction decomposition of gypsum: Experimental and isothermal kinetic analysis, *Int. J. Hydrogen Energy* 49 (2024) 1344–1360.
- [23] H.A. Foner, S. Ehrlich, Simple method for the determination of gypsum, with some observations on the solubilities of gypsum, anhydrite, calcite and dolomite, *Analyst* 108 (1286) (1983) 615–620.
- [24] P.J. Xu, W.H. Liu, H. Li, Y.X. Chen, Thermal decomposition mechanism and characterization of phosphogypsum in suspension under multifactor coupling effect, *Case Stud. Constr. Mater.* 20 (2024) e02861.
- [25] Z.Q. Yan, Z.A. Wang, X.F. Wang, H. Liu, J.R. Qiu, Kinetic model for calcium sulfate decomposition at high temperature, *Trans. Nonferrous Met. Soc. China* 25 (10) (2015) 3490–3497.
- [26] H.W. He, L.F. Hao, C.G. Fan, S.G. Li, W.G. Lin, A two-step approach to phosphogypsum decomposition: Oxidation of CaS with CO₂, *Thermochim. Acta* 708 (2022) 179122.
- [27] H.J. Tian, Q.J. Guo, X.H. Yue, Y.Z. Liu, Investigation into sulfur release in reductive decomposition of calcium sulfate oxygen carrier by hydrogen and carbon monoxide, *Fuel Process. Technol.* 91 (11) (2010) 1640–1649.
- [28] X. Xia, L.Q. Zhang, Z.Y. Li, X.L. Yuan, C.Y. Ma, Z.L. Song, G.F. Chen, Recovery of CaO from CaSO₄ via CO reduction decomposition under different atmospheres, *J. Environ. Manag.* 301 (2022) 113855.