

# Advances in Phosphogypsum Calcination and Decomposition Processes in Circulating Fluidized Beds

Pengxing Yuan, Meng Li, Shiyi Chen,\* and Wenguo Xiang\*

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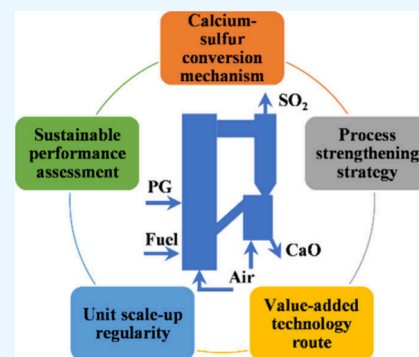
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**ABSTRACT:** Phosphogypsum (PG) is an industrial hazardous waste product discharged during wet-process phosphoric acid production. Once crystallized, the byproduct PG is filtered and separated from the liquid-phase product and sluiced to the disposal area near the production site for storage, seriously threatening the harmonious symbiosis between humans and nature. Therefore, devising effective solid waste management and cleaner production programs to contain and eliminate PG is of interest to researchers. In this study, the utilization status of PG is comprehensively reviewed, and a feasibility pathway for resourceful recovery of PG is proposed. The key challenges and countermeasures for the high-temperature calcination and decomposition of PG are analyzed and discussed. The visualization analysis based on bibliometrics reveals that the maximum recovery of abundant calcium (as CaO) and sulfur (as SO<sub>2</sub>) in PG and their utilization for the copreparation of calcium-based materials and sulfuric acid are the most suitable solutions for the large-scale application of PG. Five challenges that restrict the commercial promotion of PG calcination and decomposition processes are perfecting the calcium–sulfur conversion mechanism, establishing a process strengthening strategy, developing value-added technology routes, mastering unit scale-up regularity, and conducting sustainable performance assessment. Industrial applications are expected within 10–15 years.



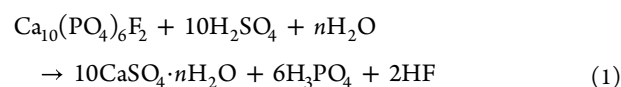
## 1. INTRODUCTION

Although the Industrial Revolution resulted in considerable development, it also created two environmental governance challenges that constrain the sustainable development of all humanity: global climate change and industrial waste management.

### 1.1. Sources and Hazards of Phosphogypsum.

Phosphogypsum (PG) is a solid waste product generated by the phosphate fertilizer chemical industry.<sup>1–3</sup> More precisely, PG originates from the production process of phosphoric acid, which is a basic raw material for producing phosphate fertilizers.<sup>4,5</sup> Two industrially mature processes are available for preparing phosphoric acid:<sup>1,6,7</sup> (1) The electric furnace method utilizes high-temperature carbon to first reduce phosphate rock (an effective component containing P<sub>2</sub>O<sub>5</sub> after beneficiation treatment<sup>6</sup>) to yellow phosphorus and then oxidize yellow phosphorus to produce phosphoric acid. The process employs electric heating, resulting in high energy and electricity consumption.<sup>7</sup> (2) The sulfuric acid method,<sup>1</sup> in which phosphoric acid is extracted by decomposing phosphate rock with sulfuric acid, is more widely known as the wet process for producing phosphoric acid.<sup>3,8,9</sup> The most prominent feature of this method is that liquid phosphoric acid is produced after the decomposition of phosphate rock, while calcium sulfate is produced as crystals with low solubility.<sup>1</sup> Compared with the electric furnace method, the simple liquid–solid separation in the wet process is more

advantageous. Therefore, more than 90% of phosphoric acid is produced by the wet process.<sup>1,6</sup> The main chemical reactions involved in the process can be expressed as follows:



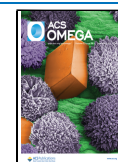
The value of  $n$  in eq 1 determines the form of calcium sulfate crystallization. Depending on the phosphoric acid concentration and operating temperature,<sup>1</sup>  $n$  may take the value 0, 1/2, or 2 to produce anhydrous calcium sulfate (CaSO<sub>4</sub>), hemihydrate calcium sulfate (CaSO<sub>4</sub>·1/2H<sub>2</sub>O), or dihydrate calcium sulfate (CaSO<sub>4</sub>·2H<sub>2</sub>O), respectively. Among them, CaSO<sub>4</sub>·2H<sub>2</sub>O is the most common component of PG, contributing 70%–80% and sometimes exceeding 90%.<sup>3,10</sup> In addition, impurities such as small amounts of oxides (e.g., oxides of Si and Al), heavy metals (e.g., Fe and Cu), products of radioactivity (e.g., U-238 and Ra-266 decay series), and trace elements (e.g., P and K) are present.<sup>3,10,11</sup>

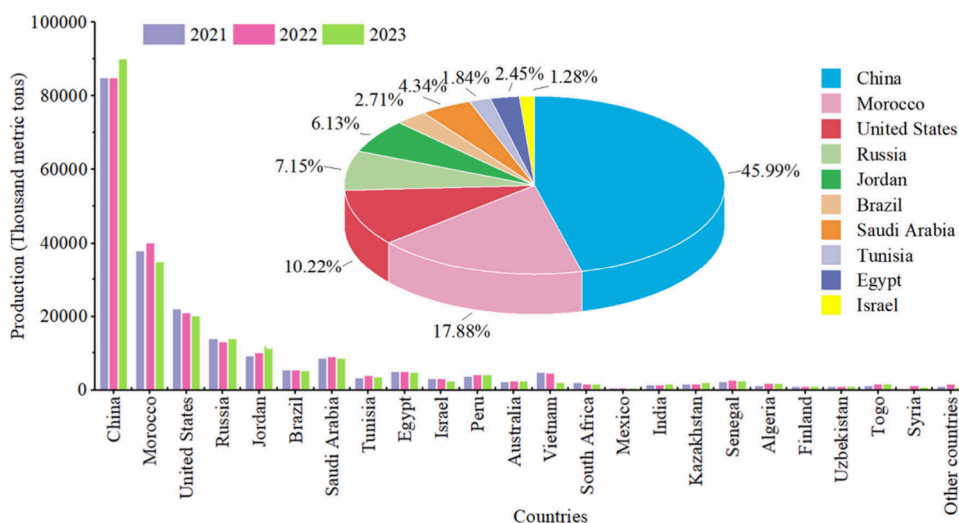
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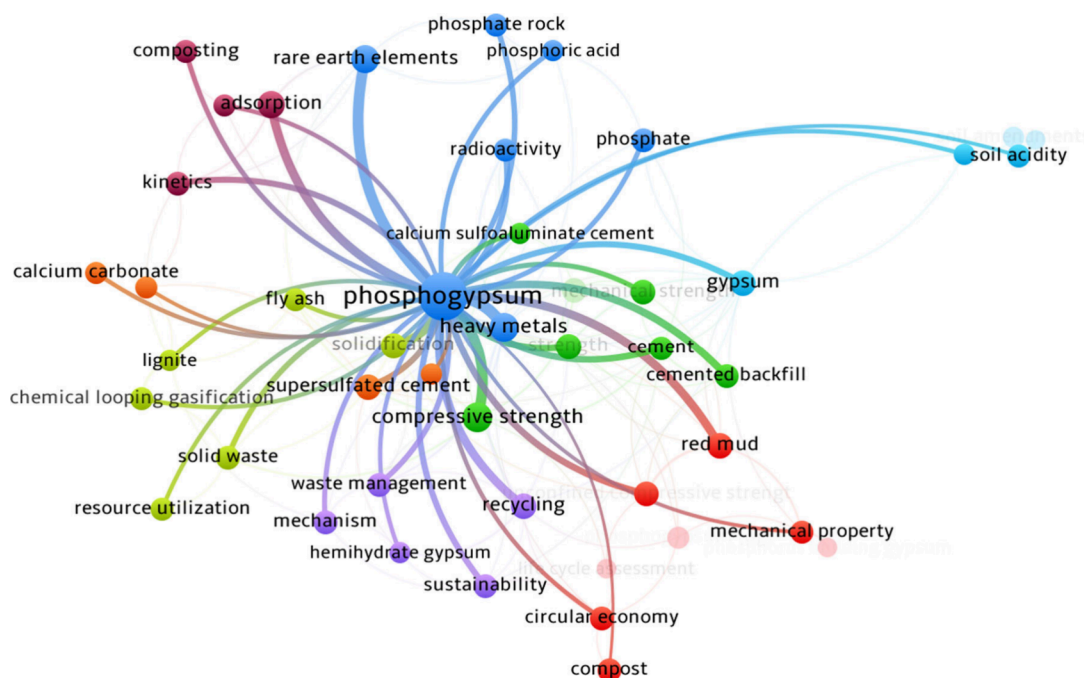
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**Figure 1.** Overview of world phosphate production from 2021 to 2023 and the top 10 phosphate producing countries.

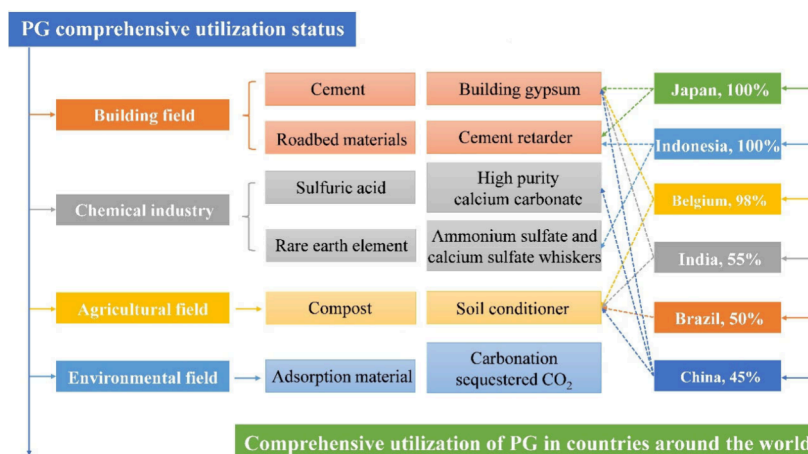


**Figure 2.** Co-occurrence analysis of keywords in comprehensive utilization of PG from 2020 to 2024.

Calculations have shown that only 0.2–0.3 tons of phosphoric acid are produced per ton of phosphate rock decomposed, but 4.5–6.0 tons of PG are generated per ton of phosphoric acid prepared.<sup>3,5,6,8</sup> That is, 1–3 tons of PG are obtained as byproducts for every ton of phosphate rock consumed.<sup>12,13</sup> An overview of phosphate production capacity (bar chart) worldwide in the past three years (2021–2023) and the proportion of phosphate production capacity of China (pie chart) are shown in Figure 1.<sup>14</sup> China is the largest producer of phosphate in the world, followed by Morocco and the United States, and produces nearly 85–90 million tons of phosphate annually, accounting for 45.99% of the total production of the 10 largest phosphate producing countries. The United States Geological Survey statistics claim that<sup>14</sup> more than 300 billion tons of phosphate rock are available worldwide. No imminent shortages of phosphate rock are expected. The global phosphate production capacity, in terms

of the  $P_2O_5$  content, is projected to increase to 69.1 million tons by 2027 compared with 63.6 million tons in 2023.

The purpose of the phosphate rock mined is for the manufacture of phosphoric acid and elemental phosphorus, which are used to produce phosphorus fertilizers and phosphorus compounds for agricultural<sup>9</sup> and industrial applications, primarily fertilizers.<sup>1,2,14</sup> There are no substitutes for phosphorus in agriculture.<sup>14</sup> The production, sales, imports, and consumption of phosphoric acid and fertilizers are expected to increase, driven by economic globalization and industrial and agricultural demands.  $P_2O_5$  consumption in the global fertilizer industry is projected to increase to 50 million tons by 2027 compared with 45.7 million tons consumed in 2023. Asia and South America are expected to be the leading regions for growth. The big data<sup>14</sup> indicate that PG production cannot be effectively curbed in a short time and may continue to increase.<sup>2,11,13</sup>



**Figure 3.** Strategy of PG comprehensive utilization and comprehensive utilization rate of PG in some countries around the world.

Currently, 280–300 million tons of PG are produced annually worldwide,<sup>8,11,15</sup> with China contributing close to 75–80 million tons.<sup>3,13</sup> Once PG crystallizes in large quantities, it is separated from the liquid-phase product via filtration.<sup>6</sup> According to Bilal et al.,<sup>11</sup> about 58% of the PG crystals mixed with water are sluiced to prepared storage areas near the production site for stacking;<sup>13</sup> about 28% are directly discharged into waters such as oceans; and only 14% are recycled. PG is stored on the surface or discharged into water bodies without treatment, and the numerous impurities present in it may pose a threat to the surrounding ecological environment.<sup>8</sup> The leaching of heavy metal elements, leakage of fluoride, emission of radiation by radionuclides, and release of nanoparticles from the PG pose long-term and irreversible pollution risks to the soil, water, and atmosphere,<sup>2,6,8</sup> affecting the sustainability of the local ecology. Meanwhile, the area required to build PG treatment areas often exceeds the land area of industrial production bases.<sup>2</sup> Therefore, PG can result in wastage of land resources, destruction of soil functions, changes in hydrological environment, disturbance of atmospheric ecology, and, ultimately, the complete distortion of natural landscapes.<sup>2,16</sup>

**1.2. Comprehensive Utilization Status of Phosphogypsum.** This study presents a cluster interconnection visualization analysis of the comprehensive utilization status of PG by the bibliometrics method with the help of the VOSviewer software program.<sup>10,16,17</sup> Based on the Web of Science (WoS) core database developed by Thomson Scientific, the Science Citation Index Expanded (SCIE) collection is used as the data source because the WoS is considered the most comprehensive and influential database.<sup>10</sup> The topic and time span for searching were set, and literature results were obtained from the SCIE. Finally, the full record and cited reference content of relevant literature are exported in the form of the tab-delimited file as basic data.

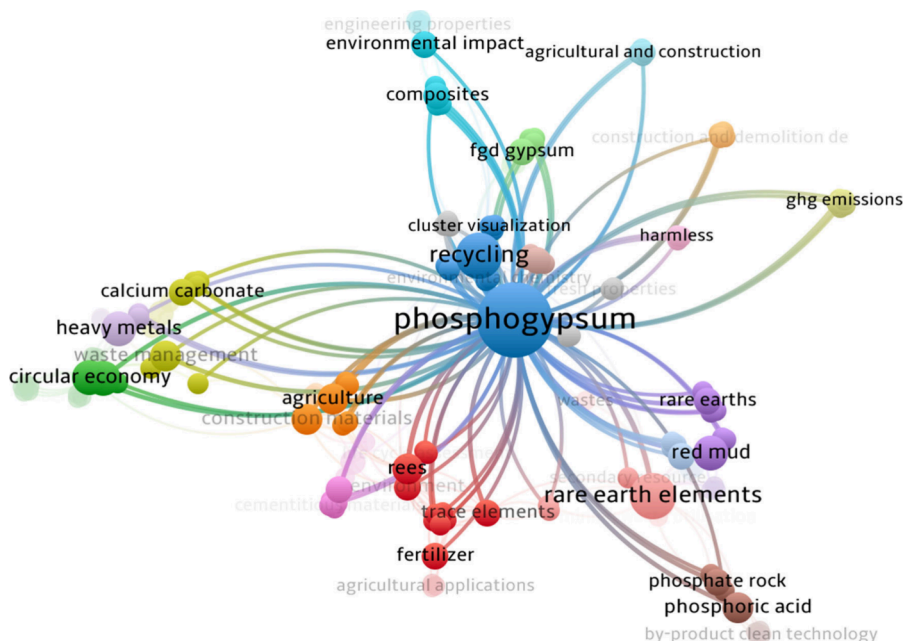
Figure 2 shows the search for 1040 articles from 2020 to 2024 with the topic “Phosphogypsum”; it shows the generation of a visualization network of keyword co-occurrence through VOSviewer. The nodes of the cluster interconnection network represent specific keywords. The larger the nodes, the higher the frequency of keyword occurrence; the thicker the chain, the stronger the connection between the keywords.<sup>10,16</sup>

High-frequency keywords can intuitively reflect the hot areas and development trends of comprehensive PG comprehensive utilization. Combined with the cluster relationship of keyword

co-occurrence shown in Figure 2, the research directions of comprehensive PG utilization in the past five years can be summarized considering four aspects: (1) The first aspect is the reuse of PG in the building industry with “gypsum”, “hemihydrate gypsum”, “cement”, “supersulfated cement”, “calcium sulfoaluminate cement”, “cemented backfill”, “compressive strength”, and “mechanical property” as the main keywords. More than 40% of PG is used in the preparation of building materials such as construction gypsum, cement, and mining fillers.<sup>12</sup> The technical challenge in the preparation of cement by PG lies in the effect of impurities on the compressive strength and mechanical properties of cement.<sup>8,15</sup> (2) The second aspect is the reuse of PG in the chemical industry with “phosphate rock”, “phosphoric acid”, “rare earth elements”, and “calcium carbonate” as keywords and recycling the calcium and sulfur elements in PG to prepare high-purity calcium carbonate and sulfuric acid,<sup>18,19</sup> while efficiently recovering rare earth resources.<sup>20,21</sup> (3) The third aspect is the reuse of PG in the field of agriculture with “composting”, “soil acidity”, and “heavy metals” as the keywords and preparing compost and soil conditioners, improving soil physicochemical properties (salinity and PH, etc.) and elemental content, providing nutrients such as P, K, and Si that promote plant growth, and preventing soil heavy metal pollution.<sup>2,8,9</sup> (4) The fourth aspect is the reuse of PG in the environmental field with “adsorption” as a keyword and preparing pollutant adsorption materials, achieving carbon capture and sequestration.<sup>12,18</sup>

In summary, the recognized strategy for the comprehensive utilization of PG is to use it as a secondary raw material for preparing high value-added chemicals and calcium-based materials,<sup>12,22,23</sup> as shown in Figure 3. Japan, Indonesia, and Belgium have formed mature PG recycling modes with a comprehensive PG utilization rate of nearly 100%, and the recycling modes are mainly concentrated in the building field. The average comprehensive utilization rates of PG in countries such as China, India, and Brazil are around 50%, concentrating on building and agriculture, in line with the national characteristics of developing countries.

**1.3. Review Objective.** From the perspective of short-term benefits, the building industry offers effective ways to absorb PG rapidly, thereby solving and eliminating environmental hazards. However, the application of PG in the building industry may stagnate due to overcapacity in the cement industry.<sup>24</sup> Meanwhile, the CO<sub>2</sub>, nitrogen oxides, and



**Figure 4.** Co-occurrence analysis of keywords in PG related review articles from 1985 to 2024.

particulate pollutants emitted by cement production have adverse environmental impacts,<sup>25,26</sup> which contradicts the development concept of the green chemistry industry. Therefore, utilization in the building industry is not a permanent solution for recycling PG. On the other hand, the occurrence mechanism, migration, and transformation laws of toxic and harmful impurities in PG, such as heavy metals and radioactive elements, restrict the large-scale preparation of soil conditioners (compost) and adsorption materials because of the potential of secondary pollution and high treatment costs.<sup>12</sup> Therefore, the comprehensive utilization efficiency of PG in agricultural and environmental fields is poor. In the future, the efficient and low-energy recovery of calcium, sulfur, and rare earth elements from PG may be the most efficient mode of reusing PG, especially as a resource of calcium and sulfur.

Figure 4 shows the co-occurrence visualization network of keywords for 70 review articles searched with the topic “Phosphogypsum” from 1985 to 2024. The bibliometric results show that the research hotspots of past reviews focused on fields such as building, agriculture, and environment, and the main keywords include “environmental impact”, “agricultural” and “construction”, “composites”, “ghg emissions”, “heavy metals”, “trace elements”, “fertilizer”, “phosphate rock”, “phosphoric acid”, and “circular economy”. Except for high-frequency keywords pertaining to the chemical industry, such as “rare earths” and “calcium carbonate”, few studies conducted a systematic and comprehensive examination of the PG calcination and decomposition processes to recover calcium and sulfur resources.

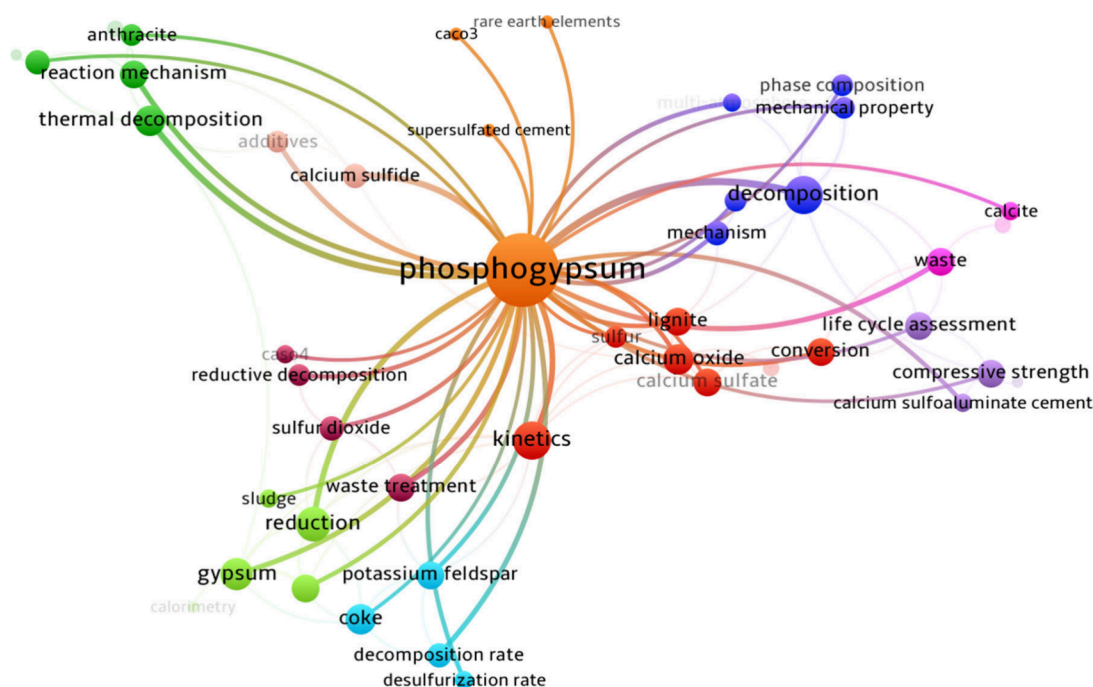
The problems of environmental deterioration and resource waste caused by PG storage have become a common concern of governments and society alike. One of the environmental governance challenges that constrains sustainable human development in the 21st century is industrial solid waste management. Therefore, the development and rapid industrialization of new key technologies is an urgent need to absorb PG and solve the problems caused by PG. This study analyzes

the comprehensive utilization status of PG using bibliometric methods and proposes potential strategies for resourceful recycling of PG with focus on the research progress of PG calcination and decomposition for recovering calcium and sulfur, the key scientific issues faced by the process scale-up, and the response methodology and insights. This review provides a basis and reference for the large-scale utilization of PG and the industrial application of calcination and decomposition processes.

## 2. PHOSPHOGYPSUM CALCINATION AND DECOMPOSITION PROCESS

The decomposition of calcium sulfate has been studied for over 120 years. The first valuable publications were published at the beginning of the last century.<sup>19</sup> In 1903, Lunge first proposed that calcium sulfate can be directly decomposed into SO<sub>2</sub> when heated together with clay in shaft kilns, yielding cement clinker as the byproduct. However, at that time, the temperature at which decomposition occurred was too high to achieve. In 1908, Hofman and Mostowitsch<sup>27</sup> published a study on the effect of temperature on the rate at which additives decompose calcium sulfate. They found that the rate of decomposition of calcium sulfate is dependent on the amount and performance of the additive. In the absence of additives, calcium sulfate begins decomposing at 1473 K and is completely decomposed at 1673 K in a molten state.

The decomposition technology matured further during the First World War. A process for producing sulfuric acid using calcium sulfate instead of elemental sulfur, pyrite, or other raw materials was developed in Germany.<sup>19</sup> The war hindered the shipping of pyrite, imported from Spain for acid production, to Germany. In 1915, Mueller studied the decomposition of calcium sulfate and coke in his laboratory in Leverkusen and set up a small pilot plant with two small cement kilns, which did not operate successfully. In early 1916, with Kuhne joining Leverkusen, the process gradually progressed. In 1918, when Kuhne established the correct reaction formula  $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2$ , followed by  $\text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2$ , he



**Figure 5.** Co-occurrence analysis of keywords in the literature related to the PG calcination decomposition from 1985 to 2024.

overcame the difficulties that prevented the production of raw  $\text{SO}_2$  gas in standard concentrations and high-quality cement clinker. Thus, the actual molar ratios required for the operation of industrial plants were established. The Leverkusen plant was closed after 1931 because of economic reasons as the Hartz District lacked any sources of hard gypsum sources.<sup>19</sup>

In fact, the current understanding of the PG calcination and decomposition process by researchers has largely inherited the technical development ideas from the research conducted in Germany. Figure 5 shows the co-occurrence visualization network of keywords for PG decomposition, with the topic “Phosphogypsum” and “Decomposition”, and a total of 160 published papers searched from 1985 to 2024. The high-frequency keywords can be classified considering seven categories: (1) calcium sulfate reductive decomposition into CaS, CaO, and  $\text{SO}_2$ ; (2) the reaction mechanism and kinetic model; (3) the solid-phase reducing agent, mainly coal; (4) admixtures, kaolinite, potassium feldspar, etc.; (5) evaluation parameters, including the decomposition and desulfurization rates; (6) cement preparation; and (7) life cycle assessment.

**2.1. Thermodynamic Reaction Mechanism of Phosphogypsum Decomposition.** Thermodynamic properties serve as the basic elements to judge the progress of a chemical reaction.<sup>28</sup> In other words, a chemical reaction is feasible kinetically only if it is thermodynamically possible.

PG decomposition conditions are harsh, and the reaction process is complex. The thermal decomposition temperature of PG in an inert atmosphere usually exceeds 1623 K.<sup>23,29</sup> A reducing atmosphere can accelerate the decomposition of PG and reduce its initial decomposition temperature to 1073–1473 K.<sup>30–32</sup> Meanwhile, the chemical reactions involved in PG decomposition and desulfurization will vary depending on the reaction atmosphere and the impurity content. Specifically, when coal is used for PG decomposition, more than 30 chemical reactions may occur simultaneously in the same system,<sup>33</sup> as summarized in Table 1. This will reduce the system efficiency, making the process difficult to control.

Further, another important fact is that the occurrence of a side reaction will promote the production of intermediate products CaS and eutectics such as  $\text{Ca}_2\text{SiO}_4$ <sup>34–36</sup> and reduce the yields of the target products CaO and  $\text{SO}_2$ .<sup>23,37,38</sup> A high reaction temperature and low-value decomposition products are not conducive to the large-scale recovery and utilization of PG. Therefore, it is necessary to select the key chemical reaction processes that control the PG reductive decomposition process in an appropriate temperature range and systematically elucidate the thermodynamic evolution characteristics and reaction mechanism of the whole process of the reductive decomposition of PG to recover calcium and sulfur.

Sun et al.<sup>33</sup> studied the high-temperature decomposition mechanism of Fe–P slag and PG and reported that CaS is the key intermediate product in the PG decomposition process. Ma et al.<sup>32,39</sup> examined the mechanism of Ca generation during the reductive decomposition of PG using high-sulfur coal and CO in a  $\text{N}_2$  atmosphere. They found that Ca conversion was mainly accomplished through solid–solid (R15 and R22) and gas–solid (R3) reactions and that an appropriate amount of CO and  $\text{CO}_2$  helps reduce CaS production. Ma et al.<sup>40,41</sup> experimentally studied the catalytic decomposition of PG from lignite to prepare CaS (in a  $\text{N}_2$  atmosphere) and CaO (in a  $\text{CO}_2$  atmosphere). CaS is formed by the interaction of carbon and reducing gases with  $\text{CaSO}_4$ , wherein solid–solid reactions (R13–15) play a major role. CaO generation involves two stages.  $\text{CaSO}_4$  is reduced to CaS and CaO, and some CaS and  $\text{CaSO}_4$  undergo a solid–solid reaction (R22) to generate CaO. Then the remaining CaS is oxidized by  $\text{CO}_2$  to CaO (R18). Xia et al.<sup>30</sup> described an approximate reaction mechanism for the decomposition of pure  $\text{CaSO}_4$  using CO as a reducing agent to produce CaO (in  $\text{CO}_2$  and  $\text{O}_2$  atmospheres). They also noted that the reaction of CaS and  $\text{CaSO}_4$  with  $\text{CO}_2$  helps to improve the CaO yields, but the effect of  $\text{O}_2$  is more pronounced. The study of the thermal decomposition mechanism of PG by Laasri et al.<sup>42</sup> concluded that the PG decomposition products depend on the

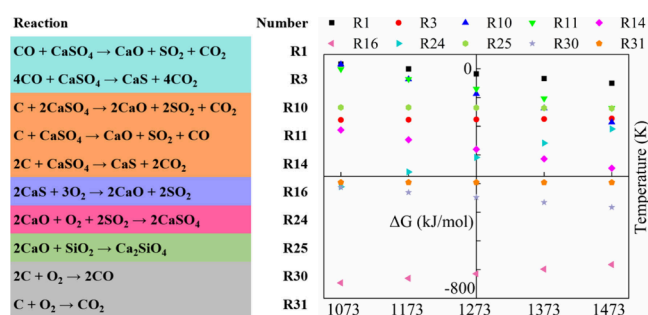
**Table 1. Possible Chemical Reactions during the PG Decomposition and Desulfurization and Their Thermodynamic Parameters in the Standard State**

Number Reaction	$\Delta H$ (kJ/mol)	$\Delta S$ (J/K-mol)	$\Delta G$ (kJ/mol)	ln K
Gas–solid reductive decomposition reactions of reducing gases and CaSO <sub>4</sub>				
CO + CaSO <sub>4</sub> → CaO + SO <sub>2</sub> + CO <sub>2</sub> (R1)	219.24	195.71	160.92	−64.95
4CO + CaSO <sub>4</sub> → CaO + COS + 3CO <sub>2</sub> (R2)	−77.74	13.63	−81.80	33.02
4CO + CaSO <sub>4</sub> → CaS + 4CO <sub>2</sub> (R3)	−170.96	14.35	−175.23	70.73
H <sub>2</sub> + CaSO <sub>4</sub> → CaO + SO <sub>2</sub> + H <sub>2</sub> O (R4)	260.38	237.88	189.49	−76.48
4H <sub>2</sub> + CaSO <sub>4</sub> → CaO + H <sub>2</sub> S + 3H <sub>2</sub> O (R5)	53.04	181.29	−0.99	0.40
4H <sub>2</sub> + CaSO <sub>4</sub> → CaS + 4H <sub>2</sub> O (R6)	−6.41	183.03	−60.95	24.60
CH <sub>4</sub> + 4CaSO <sub>4</sub> → 4CaO + 4SO <sub>2</sub> + CO <sub>2</sub> + 2H <sub>2</sub> O (R7)	722.89	1501.80	275.35	−111.13
CH <sub>4</sub> + CaSO <sub>4</sub> → CaO + COS + 2H <sub>2</sub> O (R8)	251.83	354.67	146.14	−58.99
CH <sub>4</sub> + CaSO <sub>4</sub> → CaS + CO <sub>2</sub> + 2H <sub>2</sub> O (R9)	158.61	541.60	−2.78	1.12
Solid–solid reductive decomposition reactions of C and CaSO <sub>4</sub>				
C + 2CaSO <sub>4</sub> → 2CaO + 2SO <sub>2</sub> + CO <sub>2</sub> (R10)	610.91	567.23	441.87	−178.35
C + CaSO <sub>4</sub> → CaO + SO <sub>2</sub> + CO (R11)	391.67	371.52	280.95	−113.40
2C + CaSO <sub>4</sub> → CaO + COS + CO <sub>2</sub> (R12)	267.11	365.25	158.26	−63.88
5C + 2CaSO <sub>4</sub> → 2CaS + 3CO <sub>2</sub> + 2CO (R13)	520.20	907.75	249.69	−100.78
2C + CaSO <sub>4</sub> → CaS + 2CO <sub>2</sub> (R14)	173.89	365.97	64.83	−26.17
4C + CaSO <sub>4</sub> → CaS + 4CO (R15)	518.73	717.59	304.89	−123.06
Gas–solid reactions of oxidizing atmosphere and intermediate product CaS				
2CaS + 3O <sub>2</sub> → 2CaO + 2SO <sub>2</sub> (R16)	−917.38	−156.05	−870.88	351.51
CaS + 2O <sub>2</sub> → CaSO <sub>4</sub> (R17)	−960.90	−360.20	−853.56	344.51
CaS + 3CO <sub>2</sub> → CaO + SO <sub>2</sub> + 3CO (R18)	390.20	181.37	336.15	−135.68
CaS + 4CO <sub>2</sub> → CaSO <sub>4</sub> + 4CO (R19)	170.96	−14.358	175.23	−70.73
CaS + 4CO <sub>2</sub> → CaCO <sub>3</sub> + 3CO + SO <sub>2</sub> (R20)	211.87	22.43	205.19	−82.82
CaS + 3CaSO <sub>4</sub> + 4CO <sub>2</sub> → 4CaCO <sub>3</sub> + 4SO <sub>2</sub> (R21)	334.62	132.74	295.06	−119.09
Other reactions of calcium containing substances				
CaS + 3CaSO <sub>4</sub> → 4CaO + 4SO <sub>2</sub> (R22)	1047.93	768.50	818.91	−330.53
CaS + 3SO <sub>3</sub> → CaO + 4SO <sub>2</sub> (R23)	−161.84	204.04	−222.64	89.86
2CaO + O <sub>2</sub> + 2SO <sub>2</sub> → 2CaSO <sub>4</sub> (R24)	−1004.41	−564.35	−836.23	337.52
Solid phase reaction of SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , and calcium containing substances				
2CaO + SiO <sub>2</sub> → Ca <sub>2</sub> SiO <sub>4</sub> (R25)	−134.18	3.18	−135.13	54.54
CaO + SiO <sub>2</sub> → CaSiO <sub>3</sub> (R26)	−82.45	7.83	−84.79	34.22
6CaSO <sub>4</sub> + 4SiO <sub>2</sub> → 2CaSiO <sub>3</sub> + 2Ca <sub>2</sub> SiO <sub>4</sub> + 6SO <sub>2</sub> + 3O <sub>2</sub> (R27)	2579.97	1715.07	2068.87	−835.04
CaO + Al <sub>2</sub> O <sub>3</sub> → CaAl <sub>2</sub> O <sub>4</sub> (R28)	−15.52	25.21	−23.04	9.30
2CaSO <sub>4</sub> + 2Al <sub>2</sub> O <sub>3</sub> → 2CaAl <sub>2</sub> O <sub>4</sub> + 2SO <sub>2</sub> + O <sub>2</sub> (R29)	973.37	614.78	790.16	−318.93
Relevant reactions of C				
2C + O <sub>2</sub> → 2CO (R30)	−221.08	178.70	−274.33	110.73
C + O <sub>2</sub> → CO <sub>2</sub> (R31)	−393.51	2.88	−394.36	159.17
C + CO <sub>2</sub> → 2CO (R32)	172.42	175.81	120.03	−48.45

reaction temperature and CO partial pressure. The results of a thermogravimetric test revealed that the initial decomposition temperature of PG was 873 K. The products were dominated by CaS when the CO partial pressure exceeded 50% and by CaO when it was lower than 20%. After 1373 K, the decomposition products of PG mainly consisted of a mixture of CaS and CaO and a few byproducts.

At present, a generally accepted conclusion is that PG tends to produce CaS in strongly reducing atmospheres (R3 and R13–15), while weakly reducing atmospheres tend to form CaO (R1 and R10–12). The key reaction steps for controlling

PG decomposition and desulfurization can be summarized by 10 chemical eqs (Figure 6). From the scatter plot in Figure 6, it can be seen that R1, R3, R10, R11, R14, R16, R24, R25, R30, and R31 all proceed positively and spontaneously at 1173–1473 K. However, the rise in ambient temperature increases the complexity of the PG decomposition and desulfurization system. At 1173–1273 K, the order of reaction spontaneity is R16 > R30 > R31 > R24 > R14 > R3 > R25 > R10 > R11 > R1. This indicates that the spontaneity of oxidation reactions such as R16, R30, and R31 is higher than that of the other reactions, implying that the CaS and C oxidation process plays



**Figure 6.** Thermodynamic properties of critical chemical reactions in the process of coal reductive decomposition of PG to prepare CaO and  $\text{SO}_2$ .

an important role in the initial stage of PG reductive decomposition. At 1273–1473 K, the above oxidation reactions occur, and the spontaneous order of R1, R3, R10, R11, R14, R24, and R25 is unclear and difficult to judge accurately. Therefore, maintaining the ambient temperature at 1173–1273 K may be conducive to control the PG decomposition and desulfurization reaction process and the production unit operation.

In summary, based on previous research work, a thermodynamic reaction mechanism was devised for recovering calcium and sulfur by PG calcination and decomposition in a  $\text{CO}_2$  atmosphere. Under the action of  $\text{O}_2$ , the incomplete and complete combustion of solid fuel produces CO and  $\text{CO}_2$  (R30 and R31). High concentrations of CO and coke rapidly reduce  $\text{CaSO}_4$  to CaS and CaO (R1, R3, R10, R11, and R14); as the reducing atmosphere weakens, CaO generation may be enhanced (R1, R10, and R11). Meanwhile, CaO and  $\text{SiO}_2$  combine to form a  $\text{Ca}_2\text{SiO}_4$  eutectic (R25). Because of the excellent spontaneity of R16, CaS is oxidized to CaO and  $\text{SO}_2$  by  $\text{O}_2$  immediately after it is produced. The reaction of CaO,  $\text{SO}_2$ , and  $\text{O}_2$  to generate  $\text{CaSO}_4$  (R24) involves a whole process until the end of the reaction. All the above-mentioned chemical reactions are in a parallel competitive relationship, and the oxidation reactions take relative priority over other reaction processes.

**2.2. Phosphogypsum Decomposes into CaS.** CaS is an important chemical raw material,<sup>40,43</sup> and a  $\text{CaH}_2\text{S}_2$  solution can be obtained by leaching with  $\text{H}_2\text{S}$  solution; further carbonization can extract  $\text{H}_2\text{S}$  and  $\text{CaCO}_3$ . Finally,  $\text{H}_2\text{S}$  can be used to prepare sulfuric acid and thiourea. Second, CaS can be used as a vulcanizing agent<sup>44</sup> to extract Ni–Fe–S metallurgical raw materials from sapropelic laterite ores and prepare metal Ni after purification. In addition, the reaction of carbon reductive decomposition  $\text{CaSO}_4$  to generate CaS can be performed at lower temperatures,<sup>39,45</sup> and the  $\text{CO}_2$  flue gas produced by the reaction is rich in high heat. Therefore, the drying of PG in the early stage and calcination in the later stage can be integrated to realize process integration, shorten the process flow, and improve the thermal recovery rate of the system. Therefore, it is important to clarify the generation mechanism and reaction rules of CaS for developing the PG decomposition process and theory.

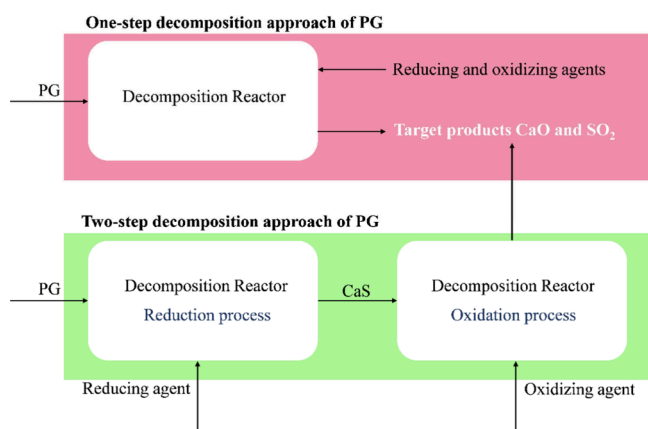
Many studies have indicated that CaS is inevitably produced during PG decomposition. Zhu et al.<sup>46</sup> analyzed the experimental process of reductive decomposition of PG from lignite using thermogravimetry. The results showed that under the optimal conditions of a lignite/ $\text{CaSO}_4$  molar ratio of 2.4:1 and a reduction temperature of 1173–1273 K more than

97.3% of PG is converted to produce CaS. Jia et al.<sup>47</sup> studied the sulfur conversion behavior during the thermal decomposition of coal and  $\text{CaSO}_4$  in a fixed bed reactor. When the temperature is higher than 873 K, the sulfide sulfur content increases rapidly with the addition of  $\text{CaSO}_4$  because the conversion of  $\text{CaSO}_4$  to CaS produces sulfur-containing gases. Liu et al.<sup>43</sup> investigated the effect of composite reducing agents prepared from coal gangue and coke on the decomposition reaction characteristics of PG using a thermogravimetric method. The results showed that when the coal gangue/coke/PG mass ratio is 1:2:10 the decomposition rate of PG reaches as high as 99% at a reaction temperature of 1273 K, and the solid phase products are mainly CaS and  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ . Fang et al.<sup>48</sup> studied the high-temperature reaction properties of PG decomposition catalyzed by iron additives and carbon by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). They found that the decomposition temperature of  $\text{CaSO}_4$  and the amount of CaS produced decrease with an increase in the dosage of iron additives. However, researchers should note that CaS is not the end product of PG decomposition because the formation of CaS reduces the PG desulfurization rate.

Furthermore, the conversion behavior of PG to the intermediate product CaS may have some reference value for chemical looping technology (CLT).<sup>49–51</sup> CLT provides a new way of energy thermal conversion and utilization and achieves the efficient combustion and gasification of fuels through the oxygen-carrying and oxygen-releasing characteristics of the intermediate circulating medium, i.e., oxygen carriers,<sup>52</sup> during the redox process. The redox reactions (R15 and R7) between PG after high-temperature dehydration (mainly yielding  $\text{CaSO}_4$ ) and CaS meet this standard. Ma et al.<sup>53</sup> studied the preparation of sulfuric acid by the chemical looping combustion (CLC) of sulfur paste (mainly containing elemental sulfur) using PG as an oxygen carrier. Yang et al.<sup>54–57</sup> from the Kunming University of Science and Technology in China investigated the reaction properties of syngas and the mechanism of syngas production from lignite by chemical looping gasification (CLG) using PG and NiO– $\text{CaSO}_4$ -based (prepared from NiO and PG) oxygen carriers, respectively. These studies demonstrated that PG has excellent oxygen-carrying/releasing capacity. At present, technologies such as CLC/CLG have reached the megawatt-scale of the pilot and demonstration<sup>58–61</sup> and have potential for industrial production. Therefore, the application of PG as an oxygen carrier to CLT, such as CLC-based capture of high-concentration  $\text{CO}_2$  and power generation<sup>49</sup> and CLG-based production of high-quality syngas,<sup>60,61</sup> may be a feasible pathway to absorb PG on a large scale.

**2.3. Phosphogypsum Decomposes into CaO and  $\text{SO}_2$ .** For the successful PG decomposition and desulfurization process, the decomposition and desulfurization rates should remain consistent. That is, the maximum possible conversion of PG to the target products CaO and  $\text{SO}_2$  should be achieved for the maximum recovery of the rich calcium and sulfur resources in PG. Currently, there are two main pathways for PG to decompose into CaO and  $\text{SO}_2$ , as shown in Figure 7.

The one-step decomposition approach involves the one-time reductive decomposition of PG into CaO and  $\text{SO}_2$  in a single reactor using a reducing agent. Meanwhile, to increase the product yield and reduce the reaction temperature, a suitable oxidizing atmosphere and additives should be introduced to assist the PG decomposition during the process. Zheng et al.<sup>62</sup>



**Figure 7.** Decomposition scheme of one- and two-step approaches for PG.

and Ma et al.<sup>39</sup> studied the reductive decomposition of PG from high-sulfur coal in a N<sub>2</sub> atmosphere; the former obtained SO<sub>2</sub> (7.6% concentration) at 1273 K that met the production standard of sulfuric acid, while the latter obtained a large amount of CaO at the optimal coal particle size (~0.25 mm). Zheng et al.<sup>63</sup> and Bi et al.<sup>64</sup> investigated the high-temperature reaction characteristics of gypsum and PG, respectively, obtained by reductive decomposition and desulfurization from anthracite in a N<sub>2</sub> atmosphere; the former found that increasing the molar ratio of C/CaSO<sub>4</sub> and reaction temperature to appropriate values favors CaO formation, while the latter reported that the high-activity anthracite accelerated PG decomposition and yielded a solid-phase mixture of CaS, CaO, and Ca<sub>2</sub>SiO<sub>4</sub>. Ma et al.<sup>41</sup> and Xia et al.<sup>30</sup> studied the catalytic decomposition of PG by lignite in a CO<sub>2</sub> atmosphere and reductive decomposition of pure CaSO<sub>4</sub> by CO in a CO<sub>2</sub>/O<sub>2</sub> atmosphere, respectively, to prepare CaO. Under optimal conditions, the PG decomposition rate and CaO yield of both exceed 99%. Yan et al.<sup>65</sup> explored the effect of Fe additives on the process of reductive decomposition of PG by CO. The results indicated that Fe additives are a suitable catalyst for promoting PG decomposition and can reduce the initial decomposition temperature of PG to 883 K.

A two-step decomposition approach involves the efficient decomposition of PG into CaO and SO<sub>2</sub> in a single reactor via the flexible switching of reducing and oxidizing atmospheres. Specifically, PG is first decomposed in a reducing atmosphere, completing the conversion of CaSO<sub>4</sub> to the intermediate product CaS. During this period, CaS and CaSO<sub>4</sub> may also react to form CaO and SO<sub>2</sub>. Then, CaS is maximally converted into the target product CaO in a weakly oxidizing atmosphere, achieving further desulfurization. The reduction and oxidation steps involve isothermal switching, and the reaction temperature is generally 1273–1373 K. Air/O<sub>2</sub> and CO<sub>2</sub> are the two most widely used weak oxidizing agents. Yan et al.<sup>66</sup> and Qian et al.<sup>67</sup> investigated a two-step reductive decomposition of PG by CO and lignite/CH<sub>4</sub>, respectively, with air as a weak oxidizing agent. In the former study, the main decomposition product of PG was CaO at 1372 K. In the latter study, CH<sub>4</sub> was found to be more suitable than lignite for PG decomposition. He et al.<sup>68</sup> proposed using CO<sub>2</sub> as an oxidizing agent for the two-step decomposition of PG and found that more than 96.2% of CaSO<sub>4</sub> in PG can be converted into CaO. Zheng et al.<sup>69</sup> studied the two-step PG decomposition characteristics under the action of iron additives, with lignite

and air serving as reducing and oxidizing agents, respectively. The results showed that the Fe additive can further reduce the initial decomposition temperature of PG to 863 K, and the purity of the CaO product in the tube furnace can reach 93.8% after multiple cycles.

Theoretically, the cyclic switching of weakly reducing and oxidizing atmospheres is beneficial to simplifying the complexity of the chemical reaction system in the PG decomposition and desulfurization and helps maximize the yield of the target products CaO and SO<sub>2</sub>. However, the two-step decomposition process is more cumbersome, and the operating conditions are more stringent, especially the requirement regarding the reaction atmosphere and temperature. Because of the very high concentration of weak oxidants, CaS will be overoxidized to CaSO<sub>4</sub>,<sup>45,70</sup> resulting in a decrease in the PG decomposition rate. Meanwhile, the conversion of CaSO<sub>4</sub> to CaS can be completed at temperatures below 1273 K;<sup>39,45,71</sup> currently, both reduction and oxidation processes are carried out under isothermal conditions, raising the energy consumption. Two important reasons limit the product yield of the two-step decomposition method. Although the one-step decomposition method is simpler to operate, the weak oxidizing agent and reducing atmosphere are introduced into the reactor together at the initial moment of PG decomposition,<sup>23,66</sup> increasing the difficulty of controlling the process. Therefore, for the orderly manipulation of the reaction process and the efficient operation of the production unit, a reasonable regulation mechanism for the reaction atmosphere and temperature must be established, and the comparative relationship of PG decomposition and desulfurization efficiency and energy consumption of the one-step and two-step processes should be clarified.

**2.4. Kinetic Reaction Model of Phosphogypsum Decomposition.** The kinetic characteristics of chemical reactions are important for the design, operation, and optimization of PG decomposition processes and industrial units. The nonisothermal kinetic method realizes the separation of reaction rate constants and mechanism functions, improving the accuracy of kinetic parameters while simplifying the calculation process. This method provides a reliable way for the kinetic analysis of PG decomposition and the desulfurization process. Currently, the study of PG decomposition kinetics mainly focuses on two aspects: the reductive decomposition of PG by C/CO and the oxidation of CaS by O<sub>2</sub>/CO<sub>2</sub>.

Ma et al.<sup>72</sup> and Zheng et al.<sup>63</sup> explored the kinetic reaction characteristics of the reductive decomposition of PG by high-sulfur coal and the catalytic decomposition desulfurization gypsum by anthracite coal, respectively. The former found that the PG decomposition process conforms to the characteristics of the Avrami nucleation and growth model and involves an activation energy of 475.99 kJ/mol. The latter suggested that the process of converting CaSO<sub>4</sub> to CaO follows a two-stage decomposition mechanism. The first stage is reproduced by a three-dimensional diffusion model and an activation energy of 225.28 kJ/mol and the second by the Avrami nucleation and growth model and an activation energy of 262.13 kJ/mol. Gruncharov et al.<sup>73,74</sup> successively derived the activation energies of the PG decomposition reaction using the Arrhenius kinetic equation in CO–CO<sub>2</sub>–Ar and H<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>O–Ar atmospheres as 113.88 and 84.99 kJ/mol, respectively, and noted that diffusion is the key factor determining the rate of PG decomposition. Xia et al.<sup>75</sup> also concluded that the PG



decomposition process is controlled by the Avrami nucleation and growth model in a kinetic study of the catalytic decomposition of  $\text{CaSO}_4$  by  $\text{H}_2$  to prepare  $\text{CaO}$  with an activation energy of 49.34 kJ/mol. In addition, Ma et al.<sup>32</sup> studied the effect of the  $\text{CaCl}_2$  additive on the kinetic behavior of reductive decomposition of PG by  $\text{CO}$ . The results showed that the catalytic effect of additives reduces the activation energy of the PG decomposition reaction to 150–200 kJ/mol (after introducing  $\text{CaCl}_2$ ), which is half that for pure PG decomposition (300–400 kJ/mol).

Yan et al.<sup>66</sup> investigated the oxidation kinetics of  $\text{CaS}$  in an air ( $\text{O}_2$ ) atmosphere. The results showed that the  $\text{CaS}$  oxidation mechanism is complex and that the temperature significantly influences the reaction products. The activation energy for  $\text{CaS}$  oxidation was determined to be 257.35 kJ/mol by the Coats–Redfern method. He et al.<sup>45</sup> analyzed the oxidation reaction mechanism of  $\text{CaS}$  in a  $\text{CO}_2$  atmosphere and found that the  $\text{CaS}$  oxidation process conforms to a single reaction kinetics model. Compared with pure  $\text{CaS}$ , the  $\text{CaS}$  samples prepared using PG had higher reactivity, and the activation energy of  $\text{CaS}$  oxidation fitted by the Arrhenius equation was 135.0 kJ/mol.

In summary, the kinetic mechanism of reductive decomposition of PG by  $\text{C}/\text{CO}$  mainly follows the Avrami nucleation and growth model and the diffusion model. In addition, Meng et al.<sup>76</sup> reviewed the works of Oh et al.<sup>77</sup> and Yan et al.<sup>71</sup> and revealed that these works indicated the possibility of a contraction kernel model for the decomposition kinetics of PG but did not provide a systematic and reasonable explanation for this model. The current understanding of and insights into the  $\text{CaS}$  oxidation mechanism are relatively limited. There is a lack of consensus among researchers about the kinetic reaction model of the PG decomposition and desulfurization process. Further, the products of PG decomposition and  $\text{CaS}$  oxidation depend on the coordinated cooperation of the reaction atmosphere and temperature. Therefore, it is necessary to analyze the key reaction steps controlling the PG reductive decomposition to recover calcium and sulfur in combination with the kinetic factors, establish the priority order of key chemical reactions under dual standards of thermodynamics and kinetics, and finally construct a redox kinetic reaction model and thermal-kinetic linkage mechanism for PG decomposition and desulfurization.

### 3. CONVERSION OF PHOSPHOGYPSUM INTO TARGET PRODUCTS $\text{CAO}$ AND $\text{SO}_2$

As mentioned earlier, the main objective of PG calcination and decomposition is to recover the calcium and sulfur resources contained therein, and the reaction temperature and atmosphere greatly determine the phase composition of the PG decomposition products. Therefore, this section summarizes the effects of operational factors such as PG decomposition temperature, reducing and oxidizing atmospheres, additive catalytic effect, and mult catalyst synergy on the process and performance of PG decomposition and desulfurization and proposes a process strengthening strategy for converting PG to target products  $\text{CaO}$  and  $\text{SO}_2$ .

#### 3.1. Phosphogypsum Decomposition Temperature.

The process of pure PG decomposition is long and consumes a lot of heat. Sebbahi et al.<sup>78</sup> investigated the thermal decomposition behavior of Moroccan PG by the thermogravimetric analysis–differential thermal analysis (TGA-DTA) coupled method, without adding any auxiliary agent during

the process. The mass loss of PG was summarized into five stages: (1) At 339–406 K, the surface water wet of PG is removed by thermal evaporation. (2) At 406–701 K, the crystalline water in PG is completely removed, forming type III anhydrite (a hexagonal system). (3) At 701–1421 K, type III anhydrite is transformed into type II anhydrite (an orthorhombic system). (4) At 1421–1573 K, type II anhydrite transforms into type I anhydrite (an orthorhombic system). (5) Finally, above 1573 K,  $\text{CaSO}_4$  decomposes into  $\text{CaO}$ ,  $\text{SO}_2$ , and  $\text{O}_2$ .

The reducing atmosphere helps to reduce the initial decomposition temperature of PG and accelerates its decomposition rate. Carbon was introduced as an auxiliary agent by van der Merwe et al.<sup>79</sup> to explore the thermal decomposition reaction characteristics of PG, synthetic gypsum, and pure  $\text{CaSO}_4$  in a  $\text{N}_2$  atmosphere. The reductive decomposition of PG by carbon involves four obvious weight loss zones: (1) At 353–473 K, the hydrated water is removed. (2) At 873–1023 K, the carbon is oxidized, and the degree of oxidation depends on the availability of  $\text{O}_2$  in the ambient. (3) At 1023–1353 K, the carbon reacts with  $\text{CaSO}_4$  to generate  $\text{CaS}$  and  $\text{CO}_2$ . (4) At 1353–1573 K,  $\text{CaSO}_4$  decomposes to produce  $\text{CaO}$  and sulfur-containing gases.

The type of reducing atmosphere affects the decomposition temperature of PG. Yang et al.<sup>80</sup> found that for PG decomposition sulfur is preferable over coke as a reducing agent because the former requires a lower reaction temperature (823–1073 K) compared with the latter (1023–1373 K). Bi et al.<sup>64</sup> studied PG decomposition by anthracite and reported that at a reaction temperature of 1123–1223 K the PG decomposition rate increases with temperature; when the temperature exceeds 1273 K, the PG decomposition rate is close to 100% and remains stable. Xia et al.<sup>30</sup> studied the reaction performance of decomposition of pure  $\text{CaSO}_4$  by  $\text{CO}$ ; the  $\text{CaSO}_4$  decomposition rate was only 77.61% at a reaction temperature of 1223 K but reaches 99.5% as the temperature exceeds 1272 K. Xia et al.<sup>75</sup> examined the reductive decomposition of industrial byproduct gypsum by  $\text{H}_2$  in an atmosphere of 2% $\text{H}_2$  +  $\text{N}_2$  and found that the decomposition rate of  $\text{CaSO}_4$  is only 65% at a reaction temperature of 1173 K, but at a temperature of 1273 K, the  $\text{CaSO}_4$  is completely decomposed. Ji et al.<sup>81</sup> analyzed the feasibility of reductive decomposition of industrial byproduct gypsum by  $\text{CH}_4$  and found that the initial temperature of decomposition of PG from  $\text{CH}_4$  is 1173 K, and the conversion efficiency of  $\text{CH}_4$  increases from 37% to 60% as the reaction temperature increases from 1223 to 1273 K.

**3.2. Reducing and Oxidizing Atmospheres.** A reducing atmosphere promotes PG decomposition, as manifested in the lowered reaction temperature, accelerated reaction process, and improved conversion efficiency. An oxidizing atmosphere improves the phase distribution of PG decomposition products to induce secondary desulfurization and conversion of intermediate product  $\text{CaS}$  into  $\text{CaO}$  and  $\text{SO}_2$ , thereby increasing the target product yield. Many materials have been tested for their potential as reducing agents. They can be classified depending on the material states into the following three categories: (1) solid-phase reducing agents, including coal,<sup>41</sup> coke,<sup>82,83</sup> sulfur,<sup>80</sup> biomass,<sup>84</sup> sludge,<sup>84</sup> oil shale,<sup>85</sup> and industrial waste slag (Fe–P slag,<sup>33</sup> coal gangue,<sup>43</sup> converter dust,<sup>82</sup> and copper slag<sup>83</sup>); (2) gas-phase reducing agents, including  $\text{CO}$ ,<sup>75</sup>  $\text{H}_2\text{S}$ ,<sup>81</sup>  $\text{H}_2$ ,<sup>75</sup> and  $\text{CH}_4$ ,<sup>81</sup> (3) liquid-phase reducing agents that are either solutions such as ammonia,<sup>12</sup>

ammonium chloride,<sup>86</sup> and hydrochloric acid<sup>87</sup> used to extract  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  from PG, or aqueous solutions of ammonium carbonate and potassium chloride<sup>18</sup> used as leaching agents;  $\text{Ca}^{2+}$  is used to prepare calcium carbonate, and  $\text{SO}_4^{2-}$  is used to produce agricultural fertilizers such as ammonium sulfate and potassium sulfate. Further, solid- and gas-phase reducing agents are related to the theme of this study. Unfortunately, solid-phase reducing agents such as coke and sulfur and almost all gas-phase reducing agents are limited to varying degrees by factors such as economic costs and material sources. Therefore, from the perspective of industrial applications, solid-phase reducing agents, such as coal and biomass, with abundant reserves and wide sources are more suitable for the large-scale calcination and decomposition of PG, and other reducing agents can be used as auxiliaries. In addition, the currently discussed oxidizing atmospheres are mainly air ( $\text{O}_2$ ) and  $\text{CO}_2$ .<sup>45,66</sup>

Ma et al.<sup>40</sup> examined the reductive decomposition of PG by coal to produce CaS in a small-scale fluidized bed and found that lignite is more suitable than bituminous coal with higher viscosity and anthracite with poor economy for PG decomposition and desulfurization. Qian et al.<sup>67</sup> reported a similar inference in their study on the two-step method decomposition of PG and noted that the  $\text{CaSO}_4$  decomposition rate (83.19%) and  $\text{SO}_2$  concentration (31.42 g/m<sup>3</sup>) achieved with lignite as the reducing agent are higher than those for coke and activated carbon. The reason for this is that the minerals and organic sulfides in lignite improve the conversion efficiency of  $\text{CaSO}_4$ . Meanwhile, they also compared the effects of  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$  on the decomposition performance of  $\text{CaSO}_4$ , and the  $\text{CaSO}_4$  decomposition rate (98.55%) and  $\text{SO}_2$  concentration (38.14 g/m<sup>3</sup>) corresponding to  $\text{CH}_4$  are higher than those of  $\text{CO}$  and  $\text{H}_2\text{S}$ .

Miao et al.<sup>29</sup> explored the feasibility of the multiatmosphere decomposition of PG. The thermogravimetric results showed that some CaS is converted to CaO when the reducing atmosphere with  $\text{CO}$  (concentration: 2%) is replaced by an oxidizing atmosphere with  $\text{O}_2$  (concentration: 0.6%), and the CaO mass fraction in the PG decomposition products is as high as 91.6%. The laboratory-level bubbling fluidization tests showed that when a 5% air atmosphere is used to replace a 2%  $\text{CO}$  atmosphere the oxidant inevitably causes the regeneration of  $\text{CaSO}_4$ , but the CaO content in the solid phase product and the  $\text{SO}_2$  concentration at the reactor outlet increased. Qian et al.<sup>67</sup> found that the  $\text{CaSO}_4$  decomposition rate first increased and then decreased with the increase in the air flow rate when discussing the effect of air flow rate on PG decomposition, and the optimal air flow rate was 15 mL/g/min.

Bi et al.<sup>64</sup> and Ma et al.<sup>41</sup> experimentally studied CaO recovery by PG decomposition in small fluidized beds with diameters of 20 and 50 mm, respectively. The difference between their studies is that  $\text{CO}_2$  was used as both the fluidized gas and oxidizing gas in the former study, while in the latter study,  $\text{CO}_2$  was used as only an oxidizing atmosphere. In the former work, a 96.2% PG conversion rate was obtained under the optimal conditions of a reaction temperature of 1273 K and a C/ $\text{CaSO}_4$  molar ratio of 1. In the latter work, the  $\text{CaSO}_4$  decomposition rate and CaO yield reached 99.63% and 99.28%, respectively, under the optimal conditions of a reaction temperature of 1373 K, a C/Ca molar ratio of 1.75, and a  $\text{CO}_2$  concentration of 7.5%. Xia et al.<sup>30</sup> studied the decomposition of pure  $\text{CaSO}_4$  to prepare CaO in  $\text{O}_2$ - $\text{CO}$ - $\text{N}_2$

and  $\text{O}_2$ - $\text{CO}$ - $\text{CO}_2$ - $\text{N}_2$  atmospheres. The  $\text{O}_2$  concentration in both atmospheres did not significantly affect the decomposition rate of  $\text{CaSO}_4$ . In the  $\text{O}_2$ - $\text{CO}$ - $\text{CO}_2$ - $\text{N}_2$  atmosphere, the CaO yield was unaffected by the  $\text{O}_2$  concentration and remained stable at 100%. In the  $\text{O}_2$ - $\text{CO}$ - $\text{N}_2$  atmosphere, the CaO yield increased from 80.4% to 99.8% with an increase in the  $\text{O}_2$  concentration from 1% to 7%.

**3.3. Additive Catalytic Effect.** The introduction of additives to further strengthen the decomposition and desulfurization processes of PG is the subject of current research. Some additives exhibit efficient catalytic effects, which are beneficial for promoting the reaction process and reducing reaction energy consumption. Effective additives can be summarized into the following four categories: (1) the Fe additives,<sup>65,67,71</sup> including  $\text{FeCl}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{NO}_3)_3$ , and pyrite ( $\text{FeS}$ ); (2) the Ca additives,<sup>1,34</sup> mainly  $\text{CaCl}_2$ ; (3) the metal oxides,<sup>79,88</sup> such as  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Co}_2\text{O}_3/\text{Co}_3\text{O}_4$ ; and (4) other additives,<sup>89,90</sup> such as hydrocarbons (e.g., asphalt) and nitrogenous compounds (e.g., ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) and urea ( $\text{CO}(\text{NH}_2)_2$ )).

Yan et al.<sup>65,71</sup> conducted a series of experimental studies on  $\text{FeCl}_3$ -catalyzed PG decomposition. The impregnation of PG and different concentrations of  $\text{FeCl}_3$  favor the process, and the ion exchange of  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  and a phase change of  $\text{FeCl}_3$ - $\text{FeO}$ - $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{O}_3$  during the decomposition process improves the selectivity of the reduction reaction and increases the formation rate of  $\text{SO}_2$  gases. In addition, another important phenomenon is the partial transformation of  $\text{CaSO}_4$  into  $\text{CaCl}_2$  as the  $\text{FeCl}_3$  content increases. Ma et al.<sup>32</sup> and Gruncharov et al.<sup>34</sup> added  $\text{CaCl}_2$  during the reductive decomposition of PG by carbon, and both noted that the additives can affect the decomposition temperature and mass loss of PG. In the former case,  $\text{CaSO}_4$  is almost completely decomposed after the addition of 5%  $\text{CaCl}_2$ . In the latter case, the time required for the complete decomposition of PG after the addition of 0.4%  $\text{CaCl}_2$  is effectively shortened. Meanwhile, Gruncharov et al.<sup>89</sup> found that the additives strengthen the process only in a temperature range of 1223–1298 K because the kinetics determines PG decomposition in this interval, and the reaction activation energy is 185 kJ/mol with added  $\text{CaCl}_2$  and 203 kJ/mol without the additives. A study of the effect of additives on the reductive decomposition  $\text{CaSO}_4$  by carbon by van der Merwe et al.<sup>79</sup> showed that the addition of 5%  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  as catalysts can reduce the activation energy and reaction temperature of PG decomposition. Antar et al.<sup>88</sup> evaluated the effect of a series of metal oxides on the reductive decomposition of Tunisian PG by coke in a  $\text{N}_2$  atmosphere. They found that additives such as  $\text{Co}_2\text{O}_3/\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Cr}_2\text{O}_3$  reduced the PG decomposition temperature and activation energy, but the effect of  $\text{Co}_2\text{O}_3/\text{Co}_3\text{O}_4$  was more significant. Thus, metals with two oxidation states may have superior catalytic properties.

**3.4. Multicatalyst Synergy.** When auxiliary agents are introduced to assist PG decomposition, it must be considered that reducing agents and additives should have practical application value for industrial production. However, currently widely studied auxiliary materials, such as Fe additives and gas phase reducing agents, are not aligned with this principle because their acquisition involves high processing costs. Therefore, developing conventional catalysts that are economical and environmentally friendly can help accelerate the

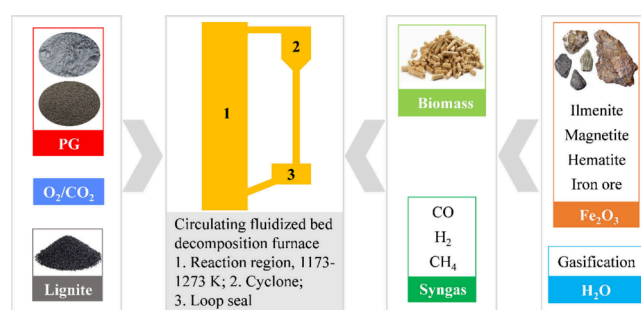
resource utilization process of PG. Some efforts have been made, but research in this area is still lacking.

Ma et al.<sup>82–84</sup> conducted a series of studies on the decomposition of PG by additives in collaboration with reducing agents. In a study on the reductive decomposition of PG by sludge-assisted rice husk,<sup>84</sup> they found a synergistic mechanism between sludge and rice husk, and  $\text{Fe}_2\text{O}_3$  in sludge and sludge ash promoted tar cracking into monocyclic aromatic hydrocarbons and aliphatic hydrocarbons while producing  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CH}_4$  to promote  $\text{CaSO}_4$  decomposition. When 20% sludge and 40% rice husk were reacted at 1173 K for 30 min, the PG decomposition rate was as high as 99.99%, and the CaS yield was 98.38%. Their study<sup>82</sup> on the catalytic decomposition of PG by converter dust-assisted lignite coke showed that the kinetic reaction mechanism of converter dust and coke conforms to the nucleation and growth model. The  $\text{Fe}_3\text{O}_4$  synergistic coke first converts  $\text{CaSO}_4$  to CaS, while  $\text{Fe}_3\text{O}_4$  is oxidized to  $\text{Fe}_2\text{O}_3$ . Then CaS and  $\text{CaSO}_4$  react with  $\text{Fe}_2\text{O}_3$  to form  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{SO}_2$ . The initial decomposition temperature of PG decreases from 1248 to 1187 K upon the introduction of converter dust. The PG was calcined for 24 min under the optimal conditions of  $\text{Fe}_3\text{O}_4/\text{Ca}$  molar ratio of 0.6, C/Ca molar ratio of 0.4, and reaction temperature of 1373 K. The decomposition rate reached 99.56%, and  $\text{SO}_2$  mass yield was 97.64%. In addition, they also studied<sup>83</sup> the decomposition performance of synergistic catalytic PG by copper slag and coke. The results showed that under the optimal conditions (a copper slag/PG mass ratio of 1, coke/PG mass ratio of 0.06, and reaction temperature of 1373 K for 20 min) the PG decomposition rate reaches 99.35%, and the  $\text{SO}_2$  yield is 96.81%.

**3.5. Process Strengthening Strategy.** Overall, factors such as calcination time, sample form, ambient nature, heating rate, PG origin,  $\text{CaSO}_4$  content, and impurity components can affect PG thermal decomposition, and the reaction temperature and atmosphere (reducing agents, oxidizing agents, and additives) are noteworthy.

The characteristic temperature range of PG decomposition is 1273–1373 K, and lignite is the preferred reducing atmosphere for the PG decomposition and desulfurization process. The thermodynamic properties indicate that it is necessary to lower the decomposition temperature of PG to 1173–1273 K (Figure 6) since the low temperature facilitates the efficient regulation of the decomposition process and the safe operation of the reaction unit. In a study comparing the decomposition of PG by grapefruit peel and coke, Luo et al.<sup>91</sup> found that biochar has a stronger effect on reducing the decomposition temperature of PG than coke, but the decomposition rate of PG is still higher when using coke than when using biochar. Therefore, adding biomass as an auxiliary reducing agent may help reduce the decomposition temperature of PG without affecting its conversion rate. In addition, gas-phase reducing agents perform slightly better than solid-phase reducing agents because of higher gas–solid reaction rates. The studies of Zhao et al.<sup>92</sup> and Ji et al.<sup>81</sup> showed that the synergistic effect of  $\text{H}_2\text{S}$  and  $\text{CH}_4$  helps reduce the initial temperature of PG decomposition and enhances the reaction efficiency. Therefore,  $\text{CO}/\text{H}_2/\text{CH}_4$  can also be considered to achieve the above goals. However, directly introducing  $\text{CO}/\text{H}_2/\text{CH}_4$  will reduce the economics of the process. Antar et al.<sup>88</sup> found that  $\text{H}_2\text{O}$  has no effect on the initial temperature of PG decomposition, implying that the passage of  $\text{H}_2\text{O}$  may not affect the process autothermally, but

further verification is still needed. Therefore, the  $\text{H}_2\text{O}$  can be selectively introduced to provide carbon and hydrogen sources for the decomposition process of PG. On the other hand, both  $\text{O}_2$  and  $\text{CO}_2$  can serve as oxidizing atmospheres to regulate product distribution. The thermodynamic data of He et al.<sup>45</sup> showed that the reaction spontaneous temperature of  $\text{CO}_2$  oxidation of CaS is higher than 2073 K, but experimental studies proved that the process can proceed normally at 1273–1373 K. Therefore, the reasons for the huge difference between thermodynamic and experimental temperatures must be deeply explored. Fe additives are more suitable for PG decomposition and desulfurization but are influenced by economic factors. Therefore, Fe-containing ores can be preferred as a catalyst to achieve the efficient decomposition of PG through the redox reaction of  $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--FeO}$ . The CLT has considerable experience in the research and application of Fe-containing ores.<sup>52,93,94</sup> The final construction of a PG cyclic decomposition system with PG reduction by Fe synergistic coal– $\text{CO}/\text{H}_2$  and oxidation of CaS by  $\text{O}_2/\text{CO}_2$  in a single reactor is shown in Figure 8.



**Figure 8.** Process strengthening strategy for PG conversion to CaO and  $\text{SO}_2$ .

#### 4. TECHNICAL ROUTE FOR COPRODUCING CALCIUM-BASED MATERIALS AND SULFURIC ACID

High-temperature reductive decomposition promotes the opportunity for the high-value utilization of the abundant calcium and sulfur resources in PG. The mineral clinker formed by the reaction of solid CaO with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , etc., can produce cement after mixing, roasting, blending, and grinding.<sup>95,96</sup> The  $\text{SO}_2$  gas can be purified, dried, converted, and absorbed to prepare sulfuric acid.<sup>19</sup> In addition, with the help of the liquid-phase reducing agents<sup>12,18</sup> mentioned earlier, the high purity calcium carbonate can be obtained from the aqueous solution for PG decomposition for capturing  $\text{CO}_2$ . Qian et al.<sup>97</sup> also proposed that phosphoric acid can be produced by the adsorption of  $\text{SO}_2$  released during PG decomposition using phosphorus slurry.

The PG decomposition to sulfuric acid coproduction cement in a hollow rotary kiln is a mature technical route. In the early and middle 20th century (1916–1955), nearly 10 modern production plants<sup>19</sup> for the coproduction of sulfuric acid and cement through the decomposition of anhydrite were built and operated in European countries, mainly, Germany and the United Kingdom. From 1952 to 1955, Solway Chemical Co., Ltd.<sup>19</sup> built a sulfuric acid plant with an annual production capacity of 100,000 tons of sulfuric acid and an equivalent amount of Portland cement; the capacity of the plant could be doubled if necessary. In the early 1950s, China

also began to explore this technology. By the beginning of 1990, Lubei Chemical Group<sup>98</sup> had built the first industrial demonstration unit for the comprehensive utilization of PG with an annual output of 30,000 tons of ammonium phosphate, 40,000 tons of sulfuric acid, and 60,000 tons of cement in the phosphorus compound fertilizer industry. The unit has been in good operation so far.

**4.1. Melting Characteristics of the Reaction between Phosphogypsum and CaS.** The solid–solid reaction (R22) between  $\text{CaSO}_4$  and CaS is an important step in PG decomposition to sulfuric acid cogeneration cement technology,<sup>35,36</sup> achieving the maximum recovery of CaO and  $\text{SO}_2$ . However, both  $\text{CaSO}_4$  and CaS are low melting point compounds. They can easily form a liquid phase melt in the reaction process, resulting in ring formation and blockage of the rotary kiln, and furthermore, they can cause discontinuous production and unstable product quality. Gruncharov et al.<sup>34</sup> investigated the thermochemical decomposition behavior of a pure  $\text{CaSO}_4$ –CaS–CaO system. They observed the presence of a liquid phase at 1223–1273 K, and the production of eutectic compounds was pronounced when the contents of  $\text{CaSO}_4$  and CaS approached 10% of the total mass of the system. Davies et al.<sup>99</sup> also considered that the liquid phase melts of CaS and  $\text{CaSO}_4$  are formed in this temperature range. Shi et al.<sup>100</sup> and Wang et al.<sup>36</sup> analyzed the phase evolution characteristics of  $\text{CaSO}_4$ –CaS–CaO in the PG decomposition system. They pointed out that the gas phase is generated at 1423 K, and the liquid phase is formed at 1573 K. Specifically, no reaction occurs at 1373–1423 K. As the temperature increases to 1423–1473 K, the equilibrium system of  $\text{CaSO}_4$ –CaS–CaO is broken, and three regions of Gas–CaS– $\text{CaSO}_4$ , Gas–CaO, and Gas–CaS–CaO appear, indicating that  $\text{CaSO}_4$  and CaS react. At 1473–1573 K, the Gas–CaO zone is further expanded, implying that a high temperature is conducive to promoting the reaction of  $\text{CaSO}_4$  and CaS to generate CaO and  $\text{SO}_2$ . The liquid phase is obtained when the temperature exceeds 1573 K.

The melting temperature of a PG decomposition system is 473–573 K higher than that of a pure material system. The reason behind this was explained by Gruncharov et al.<sup>34</sup> as follows: Impurity compounds such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  in PG can participate in the reaction of  $\text{CaSO}_4$  and CaS, during which the formation of minerals with high melting points, such as silicates, aluminates, ferrites, and aluminosilicates,<sup>37,38</sup> increases the melting temperature of the ash. Therefore, a batch of admixtures such as potassium feldspar and kaolinite with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as the main components are used to strengthen the reaction process of  $\text{CaSO}_4$  and CaS.<sup>101,102</sup> Gan et al.<sup>103</sup> proposed to use the coreaction of potassium feldspar and PG to extract soluble potassium salts and recover  $\text{SO}_2$ . Their results showed that the mineralization reaction between potassium feldspar and PG promotes the formation of CaO and silicates, reducing process energy consumption and  $\text{CO}_2$  emissions. Lu et al.<sup>35</sup> discussed the effect of potassium feldspar on the decomposition rate of PG. Under the optimal conditions of a coke/PG mass ratio of 0.07, potassium feldspar/PG mass ratio of 0.43, and reaction temperature of 1423 K for 25 min, the PG decomposition rate increased from 64% when only coke was added to 99.40%. Zhao et al.<sup>104</sup> investigated the effect of kaolinite on the melting characteristics of the reaction between  $\text{CaSO}_4$  and CaS. When the content of kaolinite was less than 5%, the liquid phase gradually decreased with an increase in kaolinite content,

indicating that kaolinite helped increase the melting temperature. The reason is that the crystal skeleton composed of ionic and hydrogen bonds inside kaolinite has the characteristics of a strong structure and high melting point.

**4.2. Research on Phosphogypsum to Sulfuric Acid Coproduction Cement.** The PG decomposition to sulfuric acid coproduction cement in a hollow rotary kiln has become the conventional technology, and the most representative of this process is the Portland cement production process.<sup>19</sup> Therefore, this section focuses on two aspects: the introduction of the conventional cement production process and the potential application of PG in the development of new cementitious materials.

Cement production includes three basic steps:<sup>105,106</sup> raw meal preparation, hot treatment to produce cement clinker, and clinker compounding and grinding. The raw materials transported from the mine are first crushed, ground, and mixed to achieve a homogenized cement raw meal that meets production standards, typically with a particle size of 0.05 mm. Then it is fed to the preheater for the first stage of hot treatment; the heat is derived from a stream of circulating flue gas generated by the calcination furnace. The preheated material enters the calcination furnace at a higher temperature for a second hot processing. Thereafter, it is roasted in a kiln for calcination to form a cement clinker. The rotary kiln is the main equipment, and the temperature inside the kiln can reach 1723 K. Finally, the clinker pellets are fed into the grinder to obtain cement products.

According to conservative estimates, every 1.5 tons of raw material consumed can produce approximately 1.0 ton of cement but will emit 0.9 tons of  $\text{CO}_2$ .<sup>25,26,106</sup> Researchers are working to develop new cementitious materials to replace Portland cement, which has a high energy consumption and carbon emissions. The alkali-activated high-performance binders widely studied in the 1960s<sup>107,108</sup> and the calcium sulfoaluminate cement developed by China National Building Materials Research Institute in the 1970s<sup>25,109</sup> have played an excellent demonstration role in reducing the amount of Portland cement. Both have lower energy consumption and  $\text{CO}_2$  emissions than those of Portland cement. Rashad et al.<sup>110</sup> carried out a series of studies on the preparation of alkali-activated binders using calcined PG instead of partial fly ash. The results indicated that alkali-activated calcined PG has great potential for application, and after addition of 5% and 10% calcined PG, the compressive strength of fly ash-based binders before and after calcination improved. Shen et al.<sup>111</sup> and Zhang et al.<sup>112</sup> evaluated the process potential of using PG to produce calcium sulfoaluminate cement. The former infers that the decomposition of PG has a positive effect on the formation of calcium sulfoaluminate and that the optimal firing temperature is 1523–1573 K. The latter reports that the compressive strength of calcium sulfoaluminate cement will exceed 50 MPa when roasted at an optimal calcination temperature of 1523 K for 45 min. However, the cementitious materials are not the most ideal materials to utilize PG and its decomposition product CaO because in addition to energy consumption and production costs recycling and reuse in the cement industry are indispensable in many countries.<sup>108,113</sup>

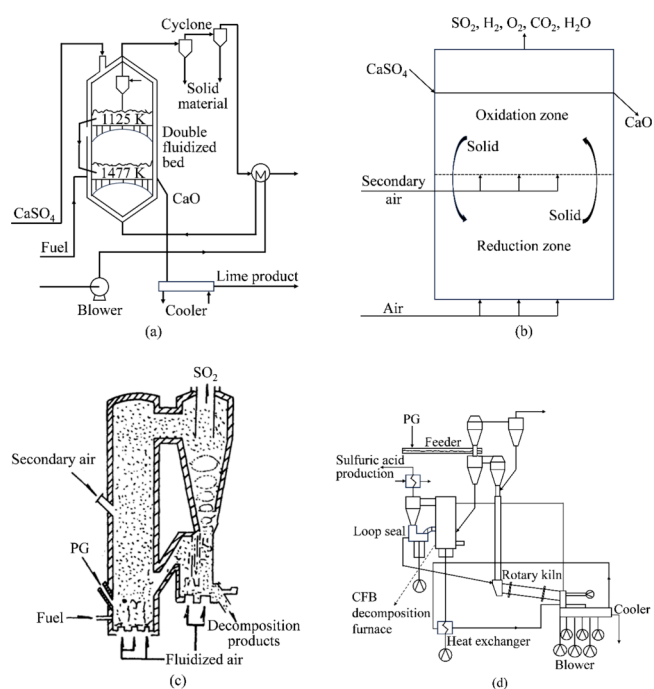
## 5. CIRCULATING FLUIDIZED BED REACTOR DESIGN AND PILOT SCALE-UP TESTS

The rotary kiln is the main unit of PG decomposition to sulfuric acid coproduction cement and consists of an inclined

cylinder mounted on a supporting device.<sup>29,106</sup> The kiln body rotates during operation, and the materials inside the kiln roll in the circumferential direction while moving from high to low in the axial direction, allowing the materials to flow slowly through the entire cylinder. During this period, three reaction stages were sequentially experienced:<sup>98</sup> (1) the reductive decomposition of PG by coke to produce CaS (1073–1273 K); (2) the reaction of CaSO<sub>4</sub> with CaS to generate CaO and SO<sub>2</sub> (1273–1523 K); and (3) the CaO and admixtures such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, firing the cement clinker (1273–1723 K). Subsequently, the cement clinker is transported from the end of the kiln into the cooling system and cooled to 373 K. Since the PG decomposition and clinker firing take place in the same kiln, there are some practical production problems:<sup>36,98</sup> (1) The high thermal stability of PG leads to a high demand for decomposition heat and crusting and blockage of the kiln. The temperatures of the complete decomposition of CaSO<sub>4</sub> in PG and the firing of most cement clinker are higher than 1473 K, which makes the system prone to producing a molten liquid phase. (2) The complexity of the PG thermal decomposition mechanism leads to difficulties in process control and low product quality. PG decomposition is accompanied by the main reaction of generating CaO and SO<sub>2</sub> and the side reaction of forming CaS, silicates, aluminates, ferrites, etc. Meanwhile, the concentration of SO<sub>2</sub> (7%–8%) in the kiln gas is low, and the quality of cement is not easy to ensure.

**5.1. Reactor Conceptual Design.** The feasible approach for the test is to separate the PG decomposition process from the rotary kiln and perform it in the fluidized bed, thereby establishing an external kiln decomposition system to obtain two columns of gas: rotary kiln exhaust gas and fluidized bed rich gas (rich in SO<sub>2</sub>).<sup>114</sup> In 1968, Iowa State University in the United States and KEET FEEDS jointly developed a new process for the decomposition of PG in a fluidized bed, as shown in Figure 9 (a). The fluidized bed decomposition furnace was divided into two bed layers; during the operation stage, CaSO<sub>4</sub> is sent to the upper fluidized bed (1125 K) for preheating; after completion, it is sent to the lower fluidized bed (1477 K) for decomposition through the interlayer overflow pipe; and the product is discharged through the lower overflow pipe. The combustion of natural gas in an insufficient air atmosphere provides a reducing atmosphere for PG decomposition. The decomposition of PG by the double-layer fluidized bed requires strict control of the reaction temperature and concentration of the reducing gas to prevent the generation of liquid phases and excess CaS. Meanwhile, the reaction rate in a single atmosphere is relatively low, and the bed material needs to stay in the furnace for 60–120 min with a SO<sub>2</sub> gas concentration of 12.6%.

To overcome the disadvantages of a single-atmosphere decomposition mode, Wheelock et al. at Iowa State University proposed a novel dual-atmosphere decomposition of PG, as shown in Figure 9 (b). The whole process is performed in a single fluidized bed decomposition furnace. The temperature inside the furnace is maintained at 1373–1473 K. In this furnace, one part of the region maintains a reducing atmosphere (the reduction zone), while the other part simultaneously maintains an oxidizing atmosphere (the oxidation zone). PG decomposes into CaO and SO<sub>2</sub> in the reduction zone, accompanied by the production of CaS. Since the bed material circulates in the furnace, the byproduct CaS can be oxidized into CaO and SO<sub>2</sub> on entering the oxidation zone. The particles converted to CaSO<sub>4</sub> can be recycled back



**Figure 9.** Design of PG decomposition furnace in CFB.<sup>114</sup> (a) The double decomposition furnace at Iowa State University, (b) the reaction mechanism of double atmosphere PG decomposition furnace, (c) the CFB PG decomposition furnace from Lurgi company, and (d) the pilot process for PG decomposition at Lurgi company.

to the reduction zone for decomposition. After multiple cycles in the reducing and oxidizing atmospheres, the PG decomposition rate reaches 97%, and the SO<sub>2</sub> concentration is as high as 16% after waste heat recovery and utilization. The dual-atmosphere decomposition mode does not need to consider CaS generation, so a high concentration of reducing atmosphere can be used to accelerate PG decomposition while also avoiding particle melting due to high temperature.

With the rise of fast fluidized bed technology in the 1980s, coupled with economic and raw material radioactivity and other reasons, PG decomposition by single- and dual-atmosphere low-speed fluidization was not widely promoted in the industry. In 1985, the Lurgi Company of Germany introduced a new type of reactor for PG decomposition, namely, a circulating fluidized bed (CFB), and completed a pilot test for processing 10 tons of PG per day. The structure of the CFB decomposition furnace and the pilot process of PG decomposition are shown in Figure 9 (c) and (d), respectively. The CFB PG decomposition furnace adopts a dual-atmosphere reaction mode, and the operating temperature is 1273 K. In addition to the reduction and oxidation cycles of the bed material in the furnace, the external circulation of the material is realized through a loop seal. During the test, air blowing in causes the incomplete combustion of coal powder to provide a reducing atmosphere for PG decomposition. The oxidizing atmosphere is achieved by adding secondary air, and the finished CaO product is discharged by a loop seal. The operation results showed that the PG decomposition rate is as high as 99%, and the SO<sub>2</sub> concentration reaches 15%.

**5.2. Scale-up Tests at a Hundred Tons and Ten Thousand Tons Scale.** Although fluidized PG decomposition technology has been developing and advancing, it failed to achieve industrial applications. The valuable experience of its

predecessor has motivated research to achieve more benefits. Miao et al.<sup>29</sup> proposed the production of CaO and SO<sub>2</sub> by the decomposition desulfurization of gypsum using a multistage fluidized bed with multiple atmospheres and verified the feasibility of the new process using thermogravimetric and laboratory-scale bubbling beds. The thermogravimetric analysis showed that multiatmosphere cycling helps to improve the conversion rate of CaSO<sub>4</sub>, and the mass fraction of CaO in the decomposition products can reach 91.6%. However, because of the low surface–gas velocity of the initial test, the fluidization state of the bubbling reactor is poor, and hence, further experiments are needed. Zhao et al.<sup>115</sup> conducted experimental research on PG decomposition and CO<sub>2</sub> adsorption using a tube furnace and a three-phase fluidized bed coupling unit. The results showed that the C-based adsorbent (CaS) prepared by the decomposition of PG from lignite captures CO<sub>2</sub>, and the H<sub>2</sub>S generated from the carbonation process then acts as a reducing atmosphere to assist PG decomposition by lignite, which is conducive to establishing the sulfur cycle system of CaSO<sub>4</sub>–CaS–H<sub>2</sub>S.

Using the new process of decomposition of CaSO<sub>4</sub> by sulfur gas in a suspended reduction furnace outside a kiln developed by Xi'an University of Architecture and Technology, Chen et al.<sup>116</sup> discussed the effects of the molar ratio of CaSO<sub>4</sub>/S<sub>2</sub>, particle residence time, and flue gas temperature at the kiln tail on the performance of the reduction furnace by using computational fluid dynamics. The simulation studies showed that the optimal combination of the operating parameters is as follows: a CaSO<sub>4</sub>/S<sub>2</sub> molar ratio of 3.04, a particle residence time of 8.90 s, and a flue gas temperature of 1265.39 K at the kiln tail. Li et al.<sup>117</sup> also reported a method of using a new suspension preheating technology to decompose PG for producing sulfuric acid and cement and studied the adaptability of PG decomposition temperature to a predecomposition furnace. The results indicated that the initial decomposition temperature of PG is 1273–1303 K, and the maximum decomposition rate is achieved at 1453 K. Even when a reducing or oxidizing atmosphere is involved, the temperature of PG complete decomposition is still higher than 1473 K, meaning that the predecomposition furnace still faces the risk of crusting and blockage.

Wang et al.<sup>118,119</sup> performed a series of studies on the low-temperature decomposition of PG by sulfur to produce sulfuric acid and built a small-scale and pilot demonstration unit of a spouted fluidized bed to process 400 and 10,000 tons of PG per year in 2013 and 2015, respectively. The small-scale test study showed that the two-stage decomposition of PG in rotary kilns is feasible. When the reaction temperature of the first stage (S<sub>2</sub> + CaSO<sub>4</sub> → CaS + 2SO<sub>2</sub>) is higher than 923 K, the decomposition rate of PG reaches 60%, which meets the material ratio requirement of the second stage reaction (CaS + 3CaSO<sub>4</sub> → 4CaO + 4SO<sub>2</sub>). After the material is kept at an operating temperature of 1373 K for 1 h, the main PG decomposition product obtained is CaO. The 10,000 ton scale test was operated continuously for 72 h at a temperature of 1323 K, achieving the technical indicators of a PG conversion rate of 99% and SO<sub>2</sub> gas concentration of 12.2%.

The flexible switching of reducing and oxidizing atmospheres to recover CaO and SO<sub>2</sub> by PG calcination and decomposition in the CFB has great potential for industrial application. This method not only reduces the energy consumption and cost of the production process but also enhances the stability and efficiency of the equipment

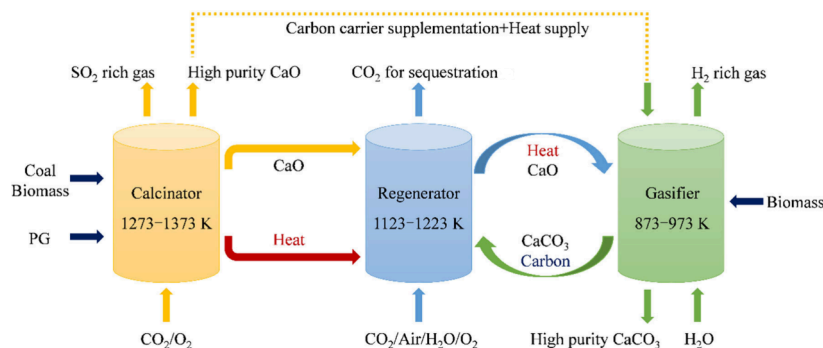
operation and, more importantly, increases the gas concentration (12%–16%) of the raw material SO<sub>2</sub> for acid production. Currently, research on PG decomposition in fluidized beds is still at the laboratory level, and the operational experience of the pilot scale and larger scales needs to be enriched urgently. The successful start-up and operation of industrial production units are inseparable from the testing and demonstrations of intermediate-scale plants. Therefore, the key to promote the commercial application of fluidization PG decomposition technology is to design and develop a new reactor type for the CFB PG decomposition in the hundred tons/ten thousand tons scale with autothermal operation and to master the unit scale-up regularity of its autothermal state.

## 6. SUSTAINABILITY ASSESSMENT OF PHOSPHOGYPSUM TO CAO AND SO<sub>2</sub>

The faster an industrial chemical plant is built and put into operation, the longer its operating cycle, and the greater its social, economic, and ecological benefits. At the social level, a large-scale plant for PG decomposition can increase employment opportunities for people in the surrounding areas. At least 18 staff members are required to ensure the normal operation of the plant,<sup>120</sup> including nine technical positions (six operators and three supervisors, working three shifts) and nine administrative positions (one administrator, one accountant, one receptionist, and six security guards). At the economic level, secondary utilization helps to reduce the storage cost of PG and achieves maximum profitability for the phosphate fertilizer industry. It is estimated that the processing and storage cost of PG is about \$1.5 per ton,<sup>2</sup> and the lifetime storage cost will continue to increase with the stockpile years. At the ecological level, the reuse of PG can effectively avoid land waste and prevent environmental pollution. The treatment of every 25,000 tons of PG (with a stockpile height of 1 m and a density of 2320 kg/m<sup>3</sup>) is expected to recover 12,000 m<sup>2</sup> of land.<sup>120</sup>

**6.1. Life Cycle Assessment.** The life cycle assessment (LCA)<sup>121</sup> was performed to comprehensively examine the environmental impact of a process or product throughout the entire activity period. The LCA consists of four basic steps: establishing research objectives and scope, creating a life cycle inventory, environmental impact and assessment, and discussion of results and further improvement, with the aim of reducing or preventing potential environmental problems from the source.

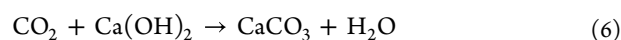
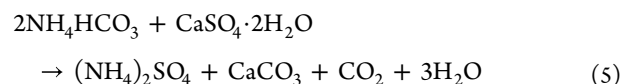
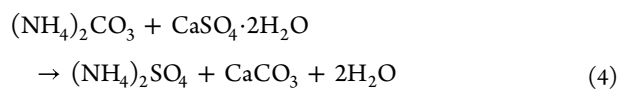
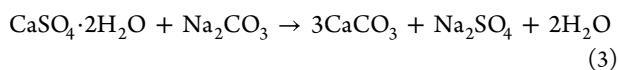
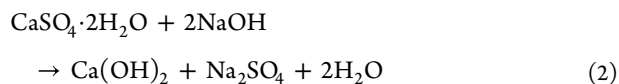
Suárez et al.<sup>122</sup> investigated the environmental impacts of gypsum waste recycling and Portland cement production processes using the LCA method. They showed that when the gypsum waste is no more than 30 km from the recycling plant the energy consumption and CO<sub>2</sub> emissions of the recycling process are less than 65% of those of obtaining natural gypsum. Meanwhile, the use of recycled gypsum waste to prepare Portland cement in all assessed categories has a lower environmental impact than natural gypsum. Wu et al.<sup>123</sup> analyzed the environmental impact of the coproduction of sulfuric acid (0.476 tons) and calcium sulfoaluminate cement (1 ton) from industrial byproduct gypsum. The results showed that the impacts of the new cogeneration process on 18 environmental categories are lower than those of the conventional production process, especially in terms of human toxicity, particulate matter formation, and agricultural land use. Mohammed et al.<sup>120</sup> evaluated the life cycle characteristics of PG and sodium salts (Na<sub>2</sub>CO<sub>3</sub> and NaOH)



**Figure 10.** Integrated process principle of sulfur and hydrogen ( $\text{SO}_2\text{--H}_2$ ) coproduction and  $\text{CO}_2$  capture in three reactors (CFB).

converted to  $\text{Na}_2\text{SO}_4$  and  $\text{CaCO}_3$  by precipitation reactions.  $\text{Na}_2\text{SO}_4$  formed during the process can be used for papermaking, and  $\text{CaCO}_3$  can be used for cement production; however, neither has significant advantages economically and environmentally. Meanwhile, compared to  $\text{Na}_2\text{CO}_3$ , the energy requirements for using  $\text{NaOH}$  are higher. Although the  $\text{Ca}(\text{OH})_2$  solution produced by the reaction of 1 ton of PG with  $\text{NaOH}$  can absorb 0.26 tons of  $\text{CO}_2$ ,<sup>121,124</sup> the high cost of the  $\text{NaOH}$  reagent may offset the sales gains of the product. Monat et al.<sup>124</sup> proposed a bipolar membrane electrodialysis method to further convert  $\text{Na}_2\text{SO}_4$  into  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$  to improve the economic benefits of the PG reuse process.  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$  can be used to dissolve PG and produce phosphoric acid, respectively. Compared to directly purchasing  $\text{NaOH}$ , the use of the bipolar membrane electrodialysis process can reduce the costs of chemicals by 50%.

**6.2. New Process Concept.** Extraction of Ca from PG for capturing and storing of  $\text{CO}_2$  will be the most promising value-added pathway. There is a strong demand for  $\text{CaCO}_3$  in the construction and paper industries, which generate substantial economic income. The use of calcium-containing products to absorb  $\text{CO}_2$  is in line with the energy conversion concept of clean and efficient technology, and the dual-carbon (carbon peaking and carbon neutrality) strategy requires low-carbon recycling, which is conducive to the sustainable development of humanity in the future. At present, the preparation of  $\text{CaCO}_3$  by PG mainly relies on a batch of liquid-phase reducing agents, such as the aqueous solutions of sodium and ammonium salts. The typical chemical process is shown in eqs 2–6.<sup>18,120,125</sup> Unfortunately, economic and environmental factors such as high costs, global warming, and eutrophication potential limit the use of chemical reagents in large quantities, in turn restricting the chemical conversion of large tonnage PG. The most suitable approach is to find inexpensive reagents for substitution or to develop technically, economically, and environmentally feasible symbiotic pathways.



The calcium looping (CaL)<sup>126</sup> process utilizes carbon carriers to enhance the absorption of  $\text{CO}_2$  for hydrogen production. CaL has the advantages and potential of CLT, but an important challenge limiting its commercial application is the degradation of adsorbent performance during  $\text{CO}_2$  capture and  $\text{CaO}$  regeneration cycles.<sup>127</sup> The feasibility of PG for CLT has been confirmed.<sup>53–57</sup> Therefore, realizing the integration and coupling of the CFB PG calcination and decomposition and CaL hydrogen production processes and establishing a new integrated process for sulfur–hydrogen ( $\text{SO}_2\text{--H}_2$ ) cogeneration and  $\text{CO}_2$  capture in three reactors will be a promising pathway for PG resource recovery with industrial applications. The process principle is shown in Figure 10.

The integrated system consists of three CFB reactors: a calcinator, a regenerator, and a gasifier. The operating temperature of the calcinator is 1273–1373 K, and the reductive decomposition of PG by coal/biomass yields high-purity  $\text{CaO}$  and a  $\text{SO}_2$ -rich sulfuric acid feed gas. The solid-phase heat-carrying  $\text{CaO}$  stream is first introduced into the regenerator, because  $\text{CaO}$  regeneration is an endothermic process, and the system requires an additional heat supply. The operating temperature of the regenerator is 1123–1223 K, and  $\text{CaCO}_3$  decomposes and produces high-concentration  $\text{CO}_2$ , as shown in reaction 7. Next, the  $\text{CaO}$  heat carriers are circulated to the gasifier to provide sensible heat<sup>128</sup> for biomass gasification. The operating temperature of the gasifier is 873–973 K; the biomass and steam gasification produce  $\text{H}_2$ -rich gas; and  $\text{CO}_2$  is captured by  $\text{CaO}$  and carbonated to form  $\text{CaCO}_3$ , as shown in reaction 8. The  $\text{CaO}$  stream from the calcinator can be directly transported into the gasifier to supplement the carbon carriers and maintain the mass and heat balance of the system.<sup>60,94</sup>



The process initially has the following advantages: (1) The temperature of the three reactors is distributed along a gradient, and the heat is highly concentrated and complementary. The system can realize autothermal operation.<sup>60,94</sup> (2) The CFB operates efficiently and stably and enables the parallel production of sulfuric acid feed gas  $\text{SO}_2$ , green  $\text{H}_2$ , and high-concentration  $\text{CO}_2$ . (3) The calcinator acts as an

adsorbent and a heat source for the CaL system, while coproduction sulfuric acid and calcium-based materials. (4) The CLT has completed the commissioning and operation stages of the pilot and demonstration plants,<sup>58–61</sup> reducing the economic coast of rebuilding a reactor unit.

The economic, environmental, and technological limitations have increased the difficulty of large-scale utilization of PG. The potential secondary pollution caused by various new PG reuse processes should be evaluated. A comprehensive sustainability assessment of PG calcination and decomposition with subsequent value-added conversion pathways of CaO and SO<sub>2</sub> from the perspectives of energy consumption, economy, environment, society, and safety is recommended.

## 7. CONCLUSION

A feasible approach for the resource utilization of PG is the large-scale recovery of calcium and sulfur elements that are abundant in PG. Although the CFB PG calcination and decomposition processes have been studied for nearly 60 years, they have not been applied industrially. This reflects, to some extent, the technical difficulty associated with recycling and using PG itself. The ultimate goal of PG decomposition is to maximize the availability of CaO and SO<sub>2</sub> and use them to coproduce calcium-based materials and sulfuric acid. At present, there is an urgent need for the test results of pilot and demonstration plants at the scale of hundred tons and ten thousand tons to assess the sustainability of PG calcination and decomposition with subsequent high-value utilization routes, thereby helping governments and the society to build the prospect and confidence of large-scale utilization of PG and to provide policy-based and financial incentives and support. The five main technical challenges to the current and future PG calcination and decomposition processes are as follows: perfecting the calcium–sulfur conversion mechanism, establishing a process strengthening strategy, developing value-added technology routes, mastering unit scale-up regularity, and conducting sustainable performance assessment. The commercial production of fluidization PG calcination and decomposition processes is expected to be achieved in the next 10–15 years.

## AUTHOR INFORMATION

### Corresponding Authors

**Wenguo Xiang** – Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 211189, China; [orcid.org/0000-0001-9989-0936](https://orcid.org/0000-0001-9989-0936); Email: [wxian@seu.edu.cn](mailto:wgxian@seu.edu.cn)

**Shiyi Chen** – Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 211189, China; [orcid.org/0000-0002-2155-9167](https://orcid.org/0000-0002-2155-9167); Email: [sychen@seu.edu.cn](mailto:sychen@seu.edu.cn)

### Authors

**Pengxing Yuan** – Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 211189, China; [orcid.org/0009-0007-9411-8737](https://orcid.org/0009-0007-9411-8737)

**Meng Li** – SINOPEC Nanjing Engineering & Construction Incorporation, Nanjing 210049, China; College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, China

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.4c05475>

## Author Contributions

Pengxing Yuan: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing—original draft, Writing—review and editing. Meng Li: Validation. Shiyi Chen: Validation. Wenguo Xiang: Funding acquisition, Project administration, Resources, Supervision, Validation, Writing—review and editing.

## Notes

The authors declare no competing financial interest.

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## NOMENCLATURE

PG, Phosphogypsum; WoS, Web of Science; SCIE, Science Citation Index Expanded; CLT, Chemical looping technology; CLC, Chemical looping combustion; CLG, Chemical looping gasification; XRD, X-ray diffraction; SEM, Scanning electron microscopy; TGA-DTA, Thermogravimetric analysis-differential thermal analysis; CFB, Circulating fluidized bed; LCA, Life cycle assessment; CaL, Calcium looping

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