



Review on high-value utilization of phosphogypsum: Utilization of calcium and oxygen resources present in phosphogypsum



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ARTICLE INFO

Editor: G. Chen

Keywords:

Utilization of phosphogypsum
Oxygen carrier
Calcium oxide
CO₂ capture

ABSTRACT

The world's annual production of phosphogypsum (PG) is up to 200 million tons at present. It was found that 15 % of PG produced worldwide is recycled. Therefore, it is imperative to seek a new pathway to recycle PG. This work provides an overview of the state-of-the-art scheme for high-value utilization of PG. Compared with previously published works, this review focuses on the utilization of oxygen (O) and calcium (Ca) resources. The state-of-the-art technology of utilizing O in PG consists of lignite's chemical looping gasification (CLG) with PG-based oxygen carrier. The state-of-the-art technology for utilizing Ca in PG is the low-temperature decomposition of PG for producing CaO and CaCO₃ from the reductive decomposition of PG. The process and the reaction mechanism of state-of-the-art technology for application of O and Ca in PG are summarized. Based on current research status, it is suggested to apply two or more solid wastes in cement, bricks and other aspects of large-scale. When utilizing PG, the migration transformation of impurities in PG and their reaction mechanisms at the molecular level deserve to be focused on. The key to solving the problems caused by PG large consumption, high value-added utilization and the introduction of policies providing incentives to this end. This research provides guidance for new engineering techniques for PG to achieve high-value and efficient use of resources in the large-scale utilisation of PG.

1. Introduction

China produces and consumes significant quantities of phosphate fertilizer [1–4]. Phosphoric acid is an important raw material for preparing the phosphoric fertilizer [1,5–8]. The preparation of wet phosphoric acid is one of the main sources of producing phosphoric acid [9–11]. In this process, industrial solid waste of phosphogypsum (PG) is produced [12–15]. Every ton of phosphoric acid produces around 4.5–5 ton of PG [16–19]. In order to bring high yield and economic benefits to crops, a huge number of by-products PG generates via the wet production of phosphoric acid [20–25]. At present, the world's annual production of PG was up to 200 million tons [26–28], whereas the amount of PG produced has continued to increase over the past decade [29–31]. Nearly 300 million tons of PG is produced annually globally [32]. To date, more than 7 billion tons of PG has been produced worldwide [33],

out of which, 58 % is dry or wet stockpiled [34], whereas 28 % is discharged into coastal waters [35]. According to a previous study, 15 % of PG produced worldwide is recycled [36]. In 2010–2022, the average annual production and the average annual utilization of PG were around 7.3 million tons and 2.5 million tons in China, respectively (Fig. 1) [37,38]. For a long time, the recycling of PG has been slowly increasing for protecting the ecological environment based on Chinese ‘The Yangtze River ‘three phosphorus’ special investigation and remedial action implementation plan’ and other laws and regulations [39–41]. China's 14th Five-Year Plan provides guidance on the comprehensive utilization of bulk solid waste [42–44]. Chinese researchers should pay more attention to improving the rate of reuse of solid wastes (such as PG) and expanding the application pathways of PG [42,45–48]. According to the “Environmental Protection Tax Law”, China has levied a solid waste tax (\$25/ton) since 2018, and no new storage sites have been approved. Many areas in Southwest China even “set production based on

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Nomenclature			
α (wt.%)	the conversion rate of reactants	CLG	chemical looping gasification
t (s)	the reaction time	XRD	X-ray diffraction
R (J/mol/K)	the natural constant	XRF	X Ray Fluorescence
T (K)	the reaction temperature	SEM	scanning electron microscopy
Abbreviations		Ce/PG	compound oxygen carrier of Ce with PG
PG	phosphogypsum	Fe/PG	compound oxygen carrier of Fe with PG
O	oxygen resource in phosphogypsum	Ni/PG	compound oxygen carrier of Ni with PG
Ca	calcium resource in phosphogypsum	Cu/PG	compound oxygen carrier of Cu with PG
“863”Program	National High Technology Research and Development Program	G-CuFe ₂ O ₄	compound oxygen carrier of Cu and Fe with PG
NSFC	Natural Science Foundation of China	GB-SCM	Ginstling-Brounshtein Shrinking Core Model
		TGA	thermo-gravimetric analysis
		Δ TG	weight loss

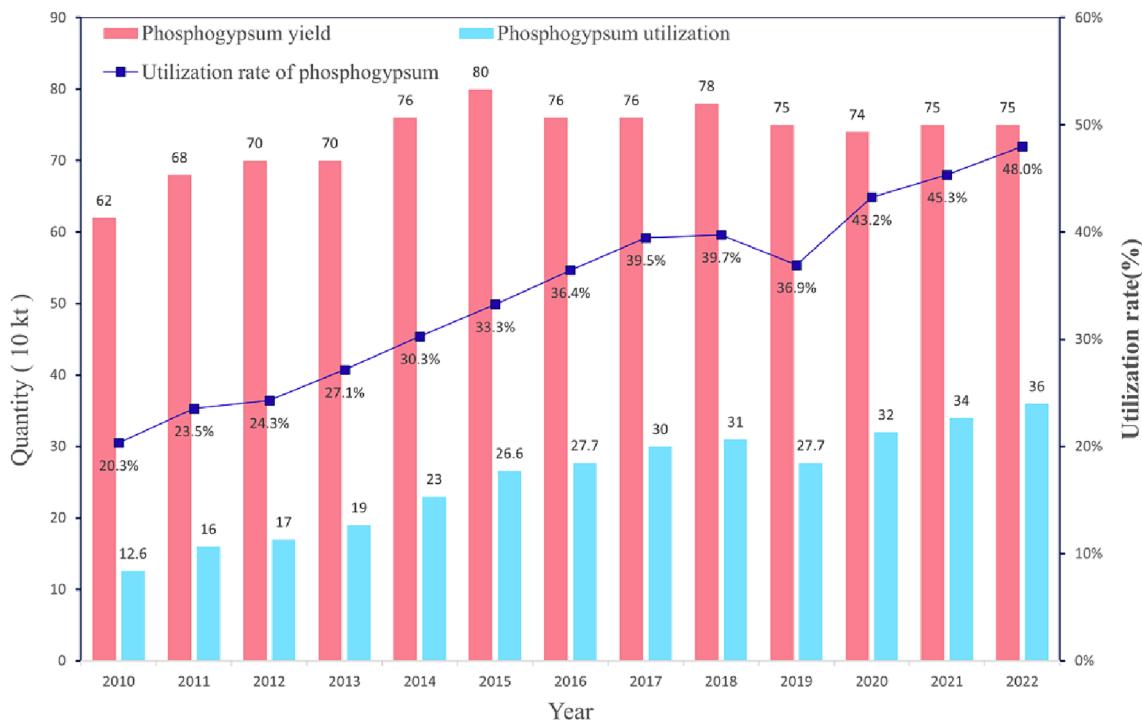


Fig. 1. Production and utilization of PG in China from 2010 to 2022 [37,38].

slag" [49].

In recent years, although the overcapacity in the domestic phosphate fertilizer industry has been plagued by the upstream and downstream markets, the contradiction between supply and demand is still prominent [50–53]. A large amount of PG is still produced, which is stored in the form of large slag mountains in the surrounding ecological environment, posing a serious threat to human health and the ecosystem [54]. At the same time, more and more PG is produced worldwide, due to which, the sustainable development of the entire phosphate fertilizer industry faces severe challenges [55–57]. The massive accumulation of PG is not only a waste of land resources but also a waste of oxygen and calcium resources [58–63]. Particularly, in order to build a resource-saving and environment-friendly society and to increase citizens' environmental awareness, people have higher and higher requirements for the recycling of resources, environmental protection and sustainable development [64–66]. As a kind of misplaced resource, it is necessary to recycle PG [57,67–70]. Its resource utilization is related to the sustainable development of China's phosphorus industry. The increasing

emphasis of practitioners and academics on the circular economy has put pressure on extractive industries to move from a linear economic model to a more circular one [71–73]. The nature of mining clearly makes this challenging, with circular economy considerations often focusing on minimizing the extraction of natural resources and residual waste, and focusing on waste, by-products or mine tailings [74–83].

Research on PG began in Japan in the 1970s [84]. Then, the United States and Germany also began to study it. In the 1980s, the utilization of PG as a resource gradually began and spread around the world. At present, PG is used in the remediation of soil [85–88] and the production of cement [89–93], in non-insulating materials [94,95] and so on. Even with all these applications, a significant amount of PG still remains that needs to be used in a sustainable fashion [96–98]. There are three main aspects of the comprehensive utilization of PG. One is the use of PG as a building material [99–101]. The second is the use of PG in agriculture [49,102,103]. The third is the decomposition of PG to produce sulfuric acid for the co-production of cement [104–108]. Among them, the third has become the main focus for the utilization of PG. It has attracted

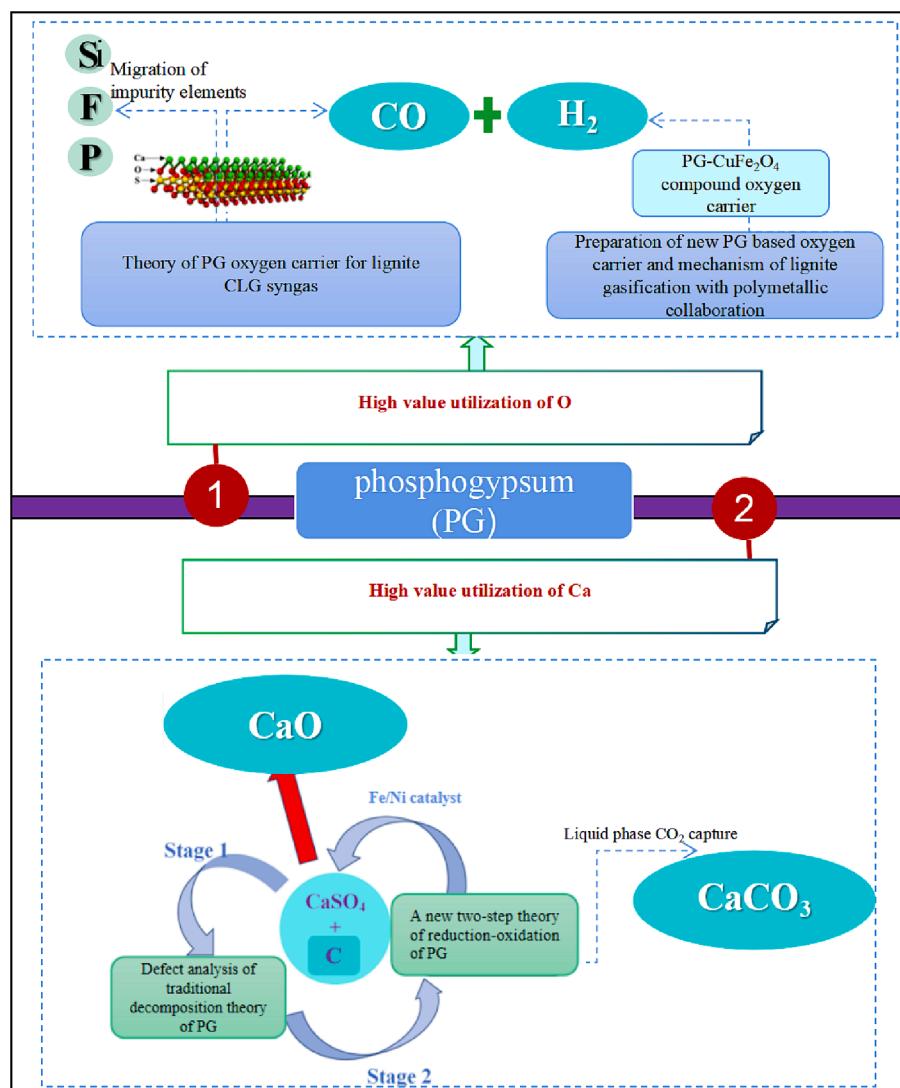


Fig. 2. Research framework of high-value utilization of O and Ca resources in PG.

much attention because of the advantages of large consumption of PG and achieving zero emissions. As early as 1916, Muller and Kuhne of Germany developed the decomposition of natural gypsum during the co-production of sulfuric acid and cement [109–111]. Then UK, France, Poland, South Africa and other countries successively developed natural gypsum, hard gypsum and PG as the raw material for the co-production of sulfuric acid and cement [76,112–114]. In China, the research on the decomposition of gypsum for the co-production of sulfuric acid and cement started in the 1950s [115]. However, due to the high decomposition temperature and the long-term failure to effectively resolve the key equipment problems, it is difficult to promote its application [63,116–118]. To address the theoretical bottlenecks in the development of key technologies for the sustainable use of PG, the basic theoretical research on the reconstruction of the physical phase of PG and the recycling of valuable elements from PG was conducted with support from the National High Technology Research and Development Program (“863” Program) and the Natural Science Foundation of China (NSFC) projects [119–124]. These research works put forward the relevant basic theories to break through the bottlenecks of PG’s resource utilization.

It is worth noticing that, although a large number of reviews on the PG resource utilization have appeared in recent years, they have mainly included applications in cement retarders, building materials, cement raw materials, concrete raw materials, cementitious materials, and fillers and modifiers road-base. Relevant review papers have focused on

the preparation of materials, reaction mechanisms, and the potential impact of the prepared materials on environmental pollution. Up till now, various research results have shown that the O in PG can be used as an oxygen carrier in chemical looping gasification (CLG), whereas the Ca in PG can be used as the CaCO₃ and CaO, which can open up a new way of PG resource utilization. The reviews related to PG’s resource utilization have not yet addressed high-value utilization of O and Ca in PG. This review focuses on the utilization of O and Ca resources (Fig. 2). Additionally, according to the current situation of O and Ca resources in PG, in order to improve the resource utilization of PG on a large scale, corresponding recommendations are made. The research work is of great significance for improving the basic theory of efficient resource utilization of PG and providing guidance to the related engineering applications.

2. Physical and chemical properties of PG

2.1. Physical properties of PG

The physical properties of PG are shown in Fig. 3. PG is usually a grayish black or grayish white material obtained from USA and China [125]. The color of the PG depends on the phosphate ore [126–128]. The particle diameter of PG is generally 100–300 μm [129].

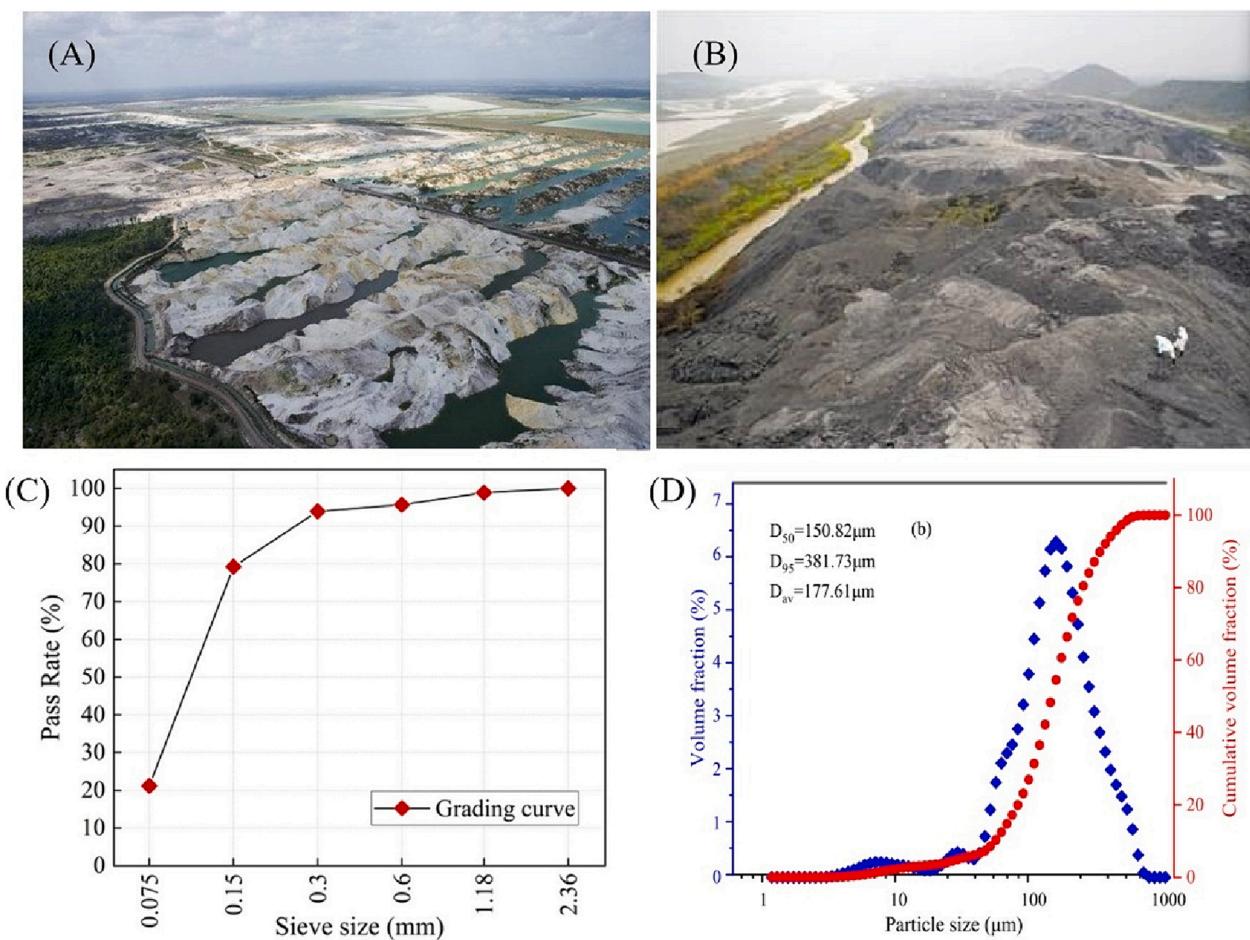


Fig. 3. Physical properties of PG: (A) Storage condition of PG in USA; (B) Storage condition of PG in China; (C) Gradation of PG; (D) Particle size distribution of PG [125,129].

Table 1
Chemical composition of PG (wt.%) [130].

Composition	SO ₃	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Total P ₂ O ₅	Hydrotropic P ₂ O ₅
Content (%)	40.86	29.82	9.43	0.236	0.132	0.005	1.17	0.87
Composition	Total F	Hydrotropic F	Na ₂ O	K ₂ O	MnO	Free water	Crystal water	Acid-insoluble
Content (%)	0.52	0.12	0.043	0.086	0.002	5.38	4.27	8.42

Table 2
Main impurities in PG [141].

Impurity type	Primary form	Solubility
Phosphoric acid,	H ₃ PO ₄ , H ₃ PO ₄ ⁴⁻ , HPO ₄ ²⁻ CaHPO ₄ ·2H ₂ O	Soluble Eutecticum
Fluoride	Phosphate complex, Apatite SiF ₆ ²⁻ , F ⁻ , CaF ₂ , CaSiF ₆ , NaAlF ₆	Insoluble Soluble Insoluble
Organisms	Rotting plant organic impurities contained in phosphate rock	Insoluble
Other impurities	Na ⁺ , K ⁺ SiO ₂ , Metal and phosphate complex, Radio-active elements	Soluble Insoluble

2.2. Chemical properties of PG

Based upon the X-ray diffraction (XRD) and X Ray fluorescence (XRF) analyses (see Table 1), it can be seen that the main physical phase of PG obtained from Yunnan (China) was calcium sulfate [130]. Calcium sulfate in PG was more than 80 % [130]. It is worth noting that the

composition of PG may vary greatly depending on the phosphate ore. Impurities in PG consist of various components other than the calcium sulphate dihydrate. They include a small amount of incompletely decomposed phosphorite, residual phosphoric acid [128], as well as fluoride [127,131], acid insoluble matter [126], iron and aluminum compounds [132], organic matter [133] and certain other components [133–137] (see Table 2). According to the physical properties of the impurities in PG, the impurities can be divided into four categories. The first category consists of the phosphoric acid and phosphate [128,138]. The second category consists of fluoride [127,138]. The third category consists of organisms [133]. The fourth category consists of other impurities [133–137,139]. The crystalline form of PG has four forms [140]: acicular, monodisperse plate, polycrystalline nuclei and dense. Among them, the plate crystals are the dominant form [141] (see Fig. 4 [130]).

3. High value utilization of O in PG

Chemical looping gasification (CLG) is a new type of gasification technology [43,142–145]. The highly active oxygen carrier should be applied to oxidize carbon-containing feedstock [146–148]. The common

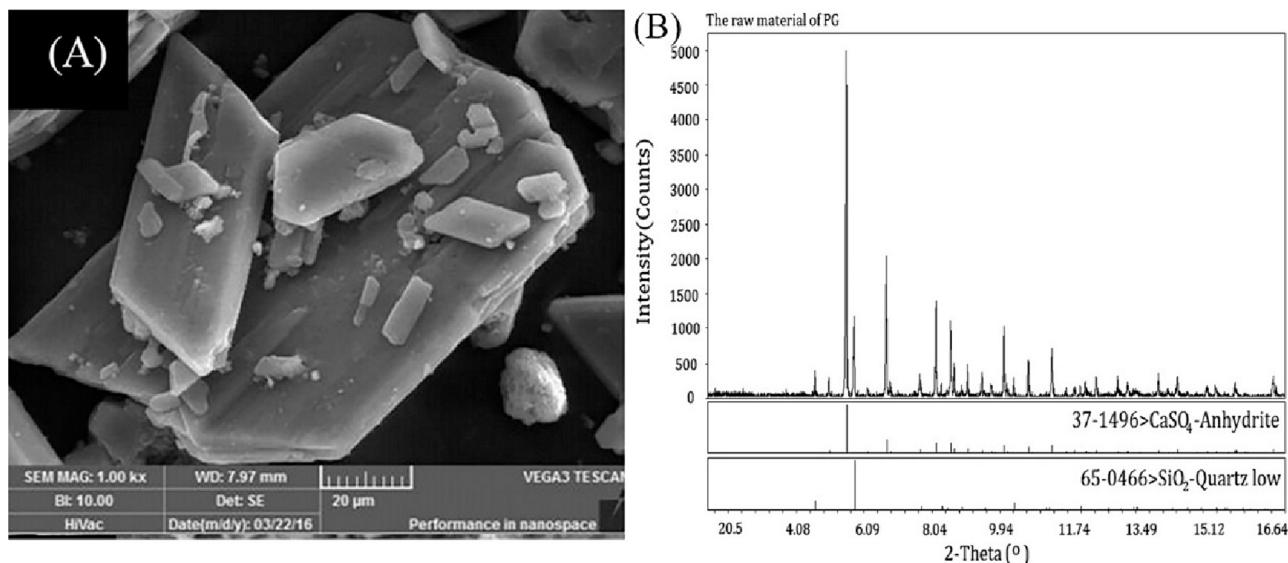


Fig. 4. Characterization of PG: (A) scanning electron microscopy (SEM); (B) XRD [130].

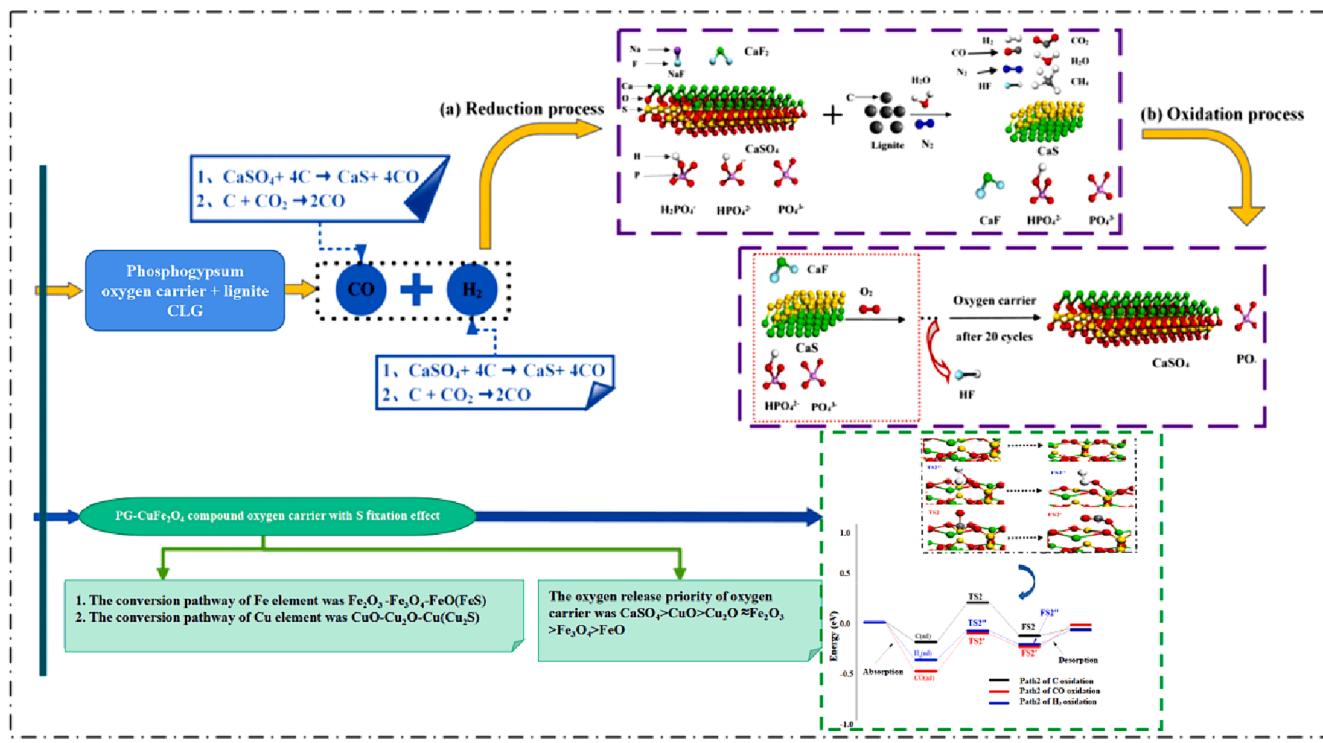


Fig. 5. Utilization of oxygen resources in PG.

typical oxygen carriers are Fe, Mn, and Ca [149–154]. In contrast, CaSO_4 has emerged as a promising oxygen carrier for the CLG process [155–160]. Researchers found that the production of syngas using CaSO_4 as an oxygen carrier showed good thermal properties and high syngas selectivity [161–164]. This is due to the reason that PG contains a large amount of CaSO_4 , which has a high oxygen-carrying capacity. Therefore, Yang et al. proposed the direct generation of syngas using PG-based materials as the oxygen carrier in low-grade lignite CLG process [130,162,165,166]. The results revealed the synergistic mechanism of multiple metals combined with PG in the CLG of lignite [121,162,167–169]. The results also elucidated the migration and changes in phosphorus, sulfur, fluorine, silicon and other elements. A new technology for the gasification of low-rank lignite was established

by determining the heterogeneous structure–activity relationship among oxygen carrier, lignite and water vapors. This technology opened up a new way for the development of clean energy based upon the usage of low-rank lignite coupled with the disposal of PG (Fig. 5).

3.1. Theory of PG oxygen carrier used for chemical looping gasification of low-order lignite to produce syngas

Yang et al. used PG as an oxygen carrier to produce syngas during the CLG of lignite [166]. The results illustrated the mechanism for the release of oxygen from PG through adsorption-diffusion-desorption process during the gasification of lignite [166]. In the CLG process where PG was directly used as an oxygen carrier and lignite was used as

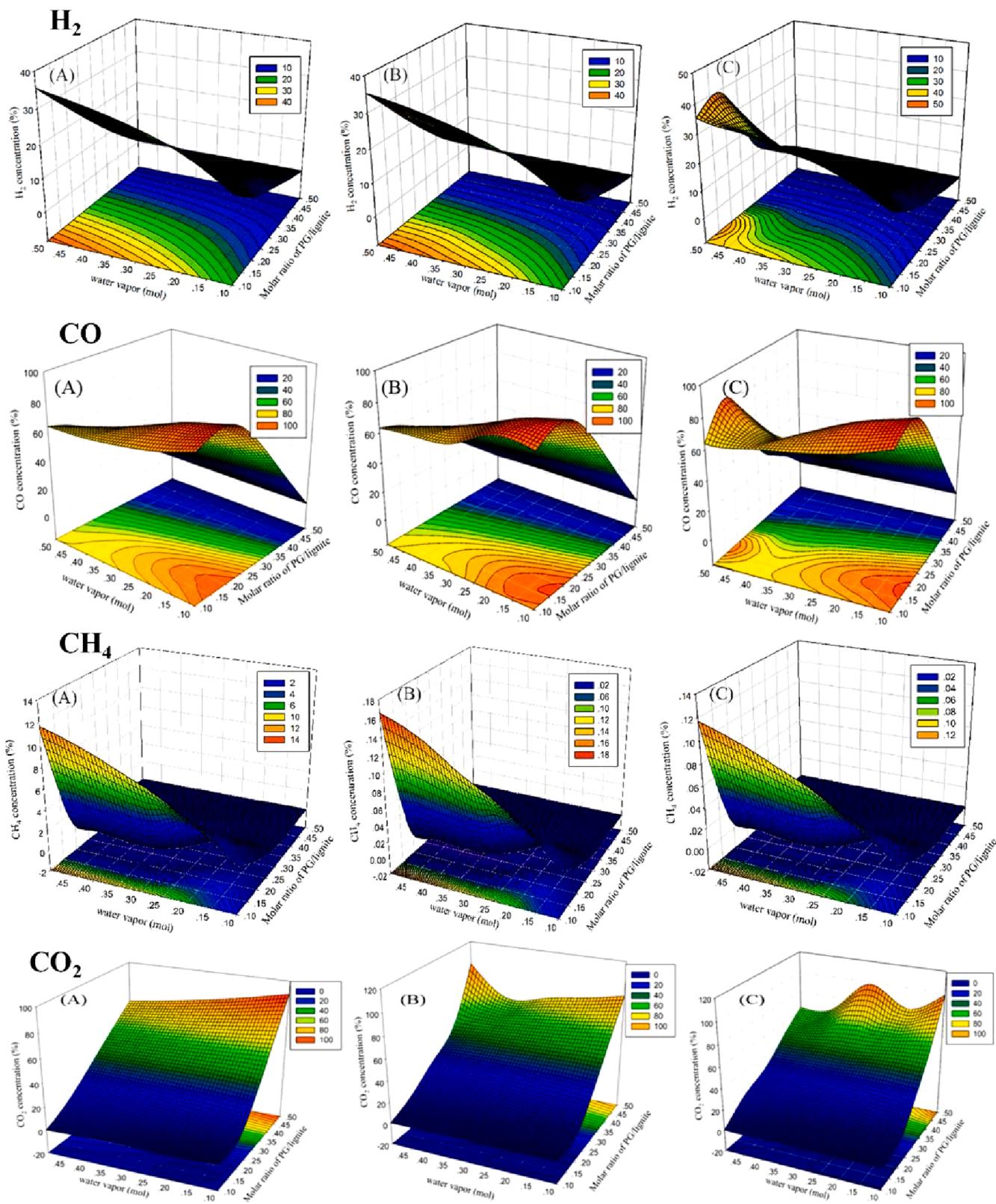


Fig. 6. Effect of reaction factors on composition of syngas [166].

the fuel, the following conclusions were obtained using the ANOVA analysis [166]. The reaction temperature, molar ratio of PG/lignite and water vapors had a significant influence on the production of syngas [166]. The production of H_2 and CH_4 was strongly dependent on the amount of water vapors [166]. Moreover, the strength of the influence of

various factors affecting the production of CO followed the descending order of: PG/lignite molar ratio > temperature > water vapor. The effect of reaction temperature on the production of CO_2 was less pronounced than the other factors [166]. The molar ratio of PG/lignite and reaction temperature had a significant effect on the decomposition of lignite

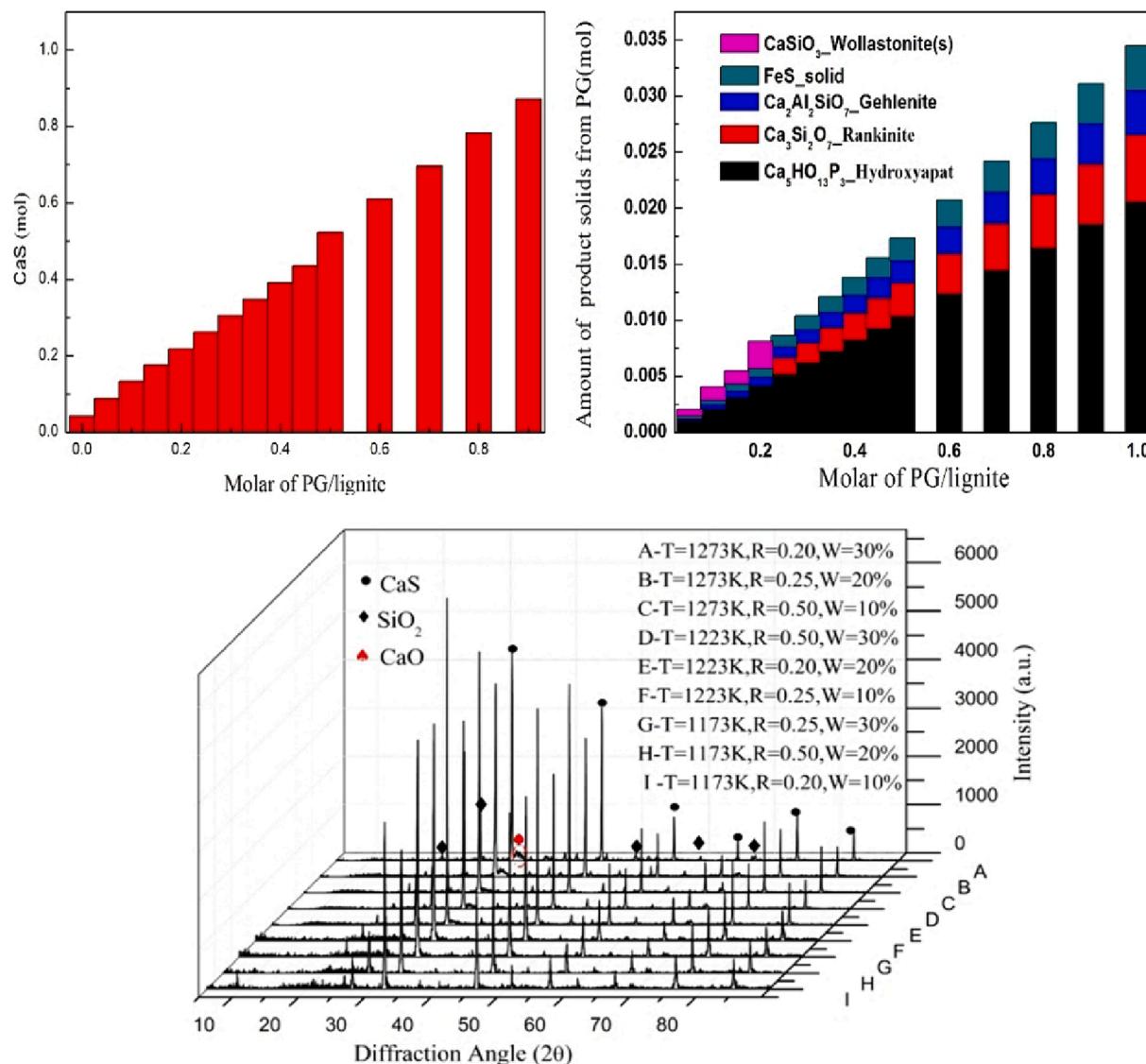


Fig. 7. Solid phase products during the CLG of low-rank lignite using PG as the oxygen carrier to produce syngas [130,166].

(Fig. 6) [166].

The research results revealed the changes of solid products of PG that was used as the oxygen carrier for the CLG of low-rank lignite to produce syngas (Fig. 7) [130]. The PG sample was mainly composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Moreover, SiO_2 , Al_2O_3 , Fe_2O_3 and other impurities were also present in the system. After the CLG process, the solid phase was dominated by CaS. Meanwhile, there were small amounts of FeS, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, $\text{Ca}_3\text{Si}_2\text{O}_7$, CaSiO_3 and $\text{Ca}_5\text{HO}_{13}\text{P}$ [130]. These solid products increased with the addition of PG. With the addition of PG, the amount of CaSiO_3 decreased and finally approached zero. However, high temperatures (950 °C and 1000 °C) and high content of water vapors (30 % and 20 %) partially converted CaSO_4 to CaO [166].

The results of the study revealed that the reaction mechanism of the non-homogeneous system of PG-lignite-water vapors was dominated by gas-solid reaction and solid-solid reaction (Fig. 8) [166]. The main reactions for the production of CO were $\text{CaSO}_4 + 4\text{C} \rightarrow \text{CaS} + 4\text{CO}$ and $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$. The main reactions for the production of H₂ were $\text{CO}_2 + \text{H}_2\text{O(g)} + 2\text{CH}_4 \rightarrow 3\text{CO} + 5\text{H}_2$ and $\text{C} + \text{H}_2\text{O(g)} \rightarrow \text{CO} + \text{H}_2$ [166]. The main reactions for the production of H₂ using CH₄ were mainly derived from the volatile components of lignite through gasification. The production of CO₂ mainly consisted of the reaction: $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2$ [166].

Based on the results of the above analyses, the mechanism of the influence of the amount of material in the non-homogeneous system of PG-lignite-water vapor on the composition of gaseous products and solid products was obtained.

PG contains a variety of impurities, of which the evolution of silicon, phosphorus, fluorine and sulphur has significant impacts on the quality of gasification products [99,123,124,170–174]. In order to clarify the changes of impurities during the reaction process, the change of the elements throughout the non-homogeneous system was analyzed [175,176].

The tracking of Si revealed that SiO_2 in PG was used as an inert scaffold between the CaSO_4 particles [177]. On the other hand, it participated in CLG through a series of reactions at high temperatures (conversion from SiO_2 to CaSiO_3 , $\text{Ca}_3\text{Si}_2\text{O}_7$ and Ca_2SiO_4) (Fig. 9) [177].

The interaction mechanism between SiO_2 and CaSO_4 in PG was investigated using the Zener effect theory [177]. The results revealed that SiO_2 in PG facilitated the maintenance of stable oxygen-carrying properties of PG by inhibiting the growth of PG grains during the CLG process. The maximum resistance (F_D) per unit area of the grain boundary to grain boundary motion was given by Equation E(1) [178,179]:

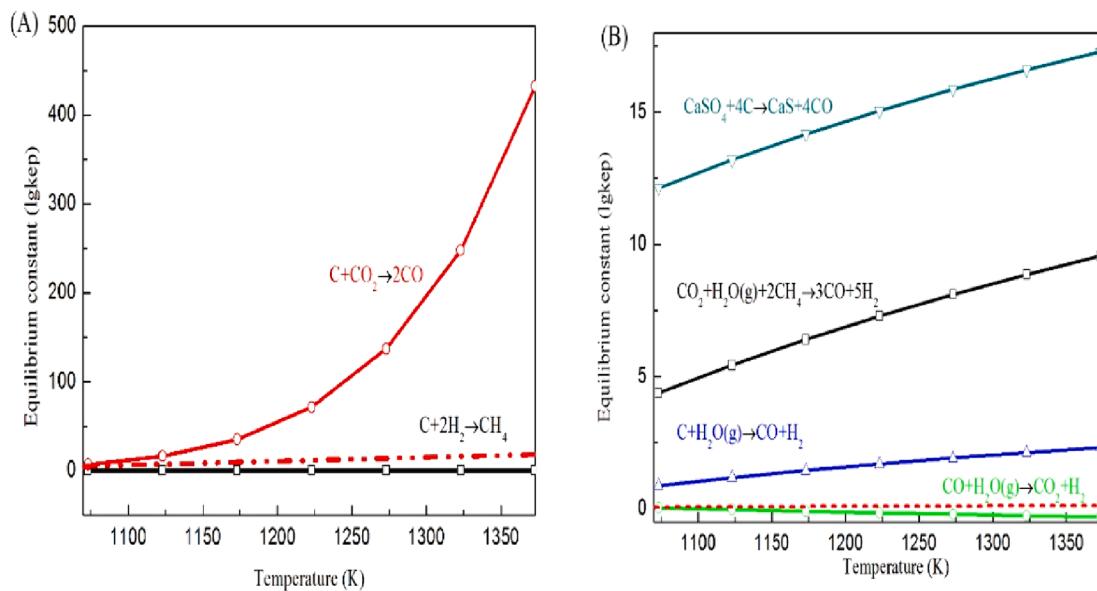


Fig. 8. Changes in the equilibrium constant with temperature in the non-homogeneous CLG process of PG-lignite-water vapor [166].

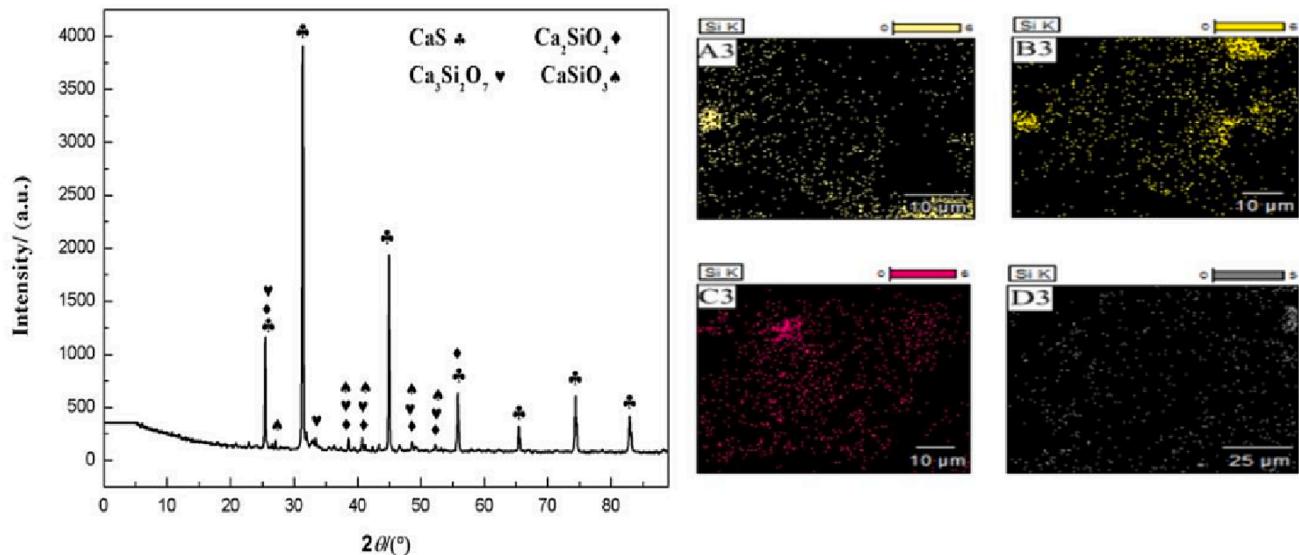


Fig. 9. XRD results and the EDS patterns of the distribution of Si in the solid-phase products [177].

$$F_p = \frac{3f\gamma_b}{2r} \quad (E1)$$

where f is the fraction of inert carrier material, γ_b is the surface energy of the oxygen carrier and r is the radius of the inert carrier material.

Taking into account the effect of the drag force of the inert support material (SiO₂), the kinetics of the growth of oxygen carrier's grains can be given by Equation E(2) [180,181].

$$\frac{dG_{oc}}{dt} = aM \left[\frac{2\gamma_b}{G_{oc}} - \left(\frac{3f\gamma_b}{2r} \right) \right] \quad (E2)$$

where f is the proportion of SiO₂, r is the radius of SiO₂, γ_b is the surface energy of the CaSO₄ grain of the oxygen carrier and G_{OC} is the particle radius of the oxygen carrier.

From Equation E(2), it can be found that the proportion of the inert support material (SiO₂) has an important influence on the oxygen-carrying performance of the oxygen carrier grains. The addition of SiO₂ was conducive to the inhibition of the growth of oxygen carrier's

grains during the reaction process, which stabilized the cyclic oxygen-carrying performance of the oxygen carrier particles. The larger the proportion of SiO₂, the greater the drag force, leading to better inhibition. Based on the thermodynamic, this was due to the fact that the second phase grains occupied the boundary, while the inert support material with small total grain boundary energy produced less drag [177].

Theoretical calculations were used to analyze the transformation and migration of F and P elements during the CLG process in which PG was used as an oxygen carrier under optimum conditions [182,183]. It was found that F existed in the form of solid-phase CaF₂ (80.02 %) and solid-phase Ca₁₀(PO₄)₆F₂ (19.98 %) at 100–400 °C [183]. When the temperature was gradually increased from 400 °C to 500 °C, the solid phase CaF₂ was converted to solid phase Ca₄Si₂F₂O₇ [183]. At the temperature of 500 °C, the F element was in the form of solid phase Ca₄Si₂F₂O₇ (80.02 %) and solid phase Ca₁₀(PO₄)₆F₂ (19.98 %) [183]. When the temperature reached the value of 600 °C, the gas phase HF started to appear. When the temperature was further increased to about 1000 °C,

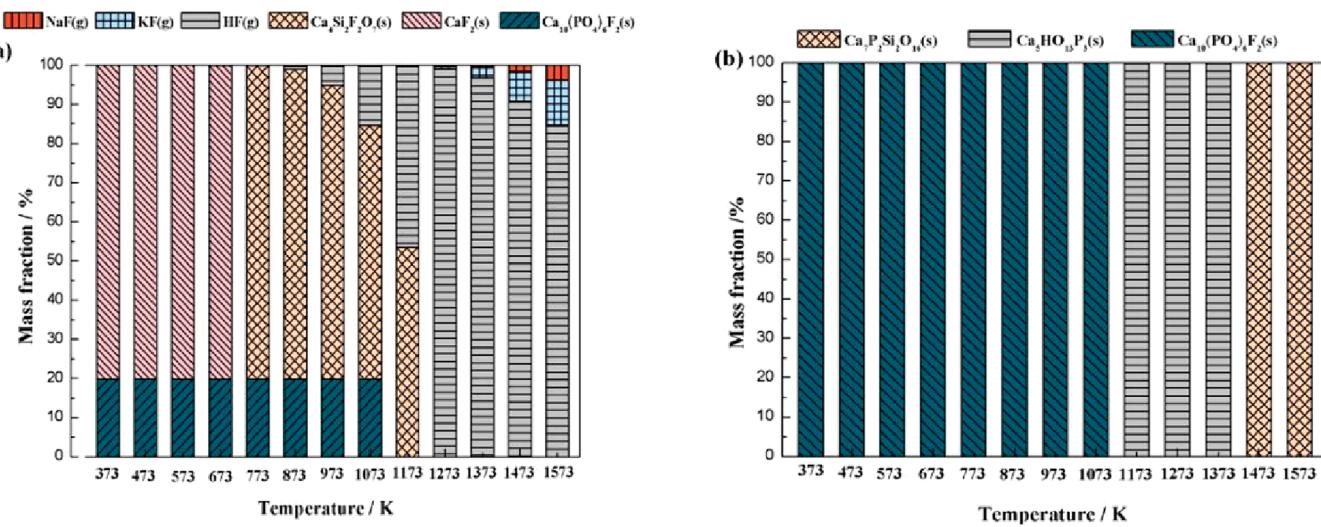


Fig. 10. Existence patterns of F and P elements of PG at different temperatures during the CLG process: (a) F of PG; (b) P of PG [182].

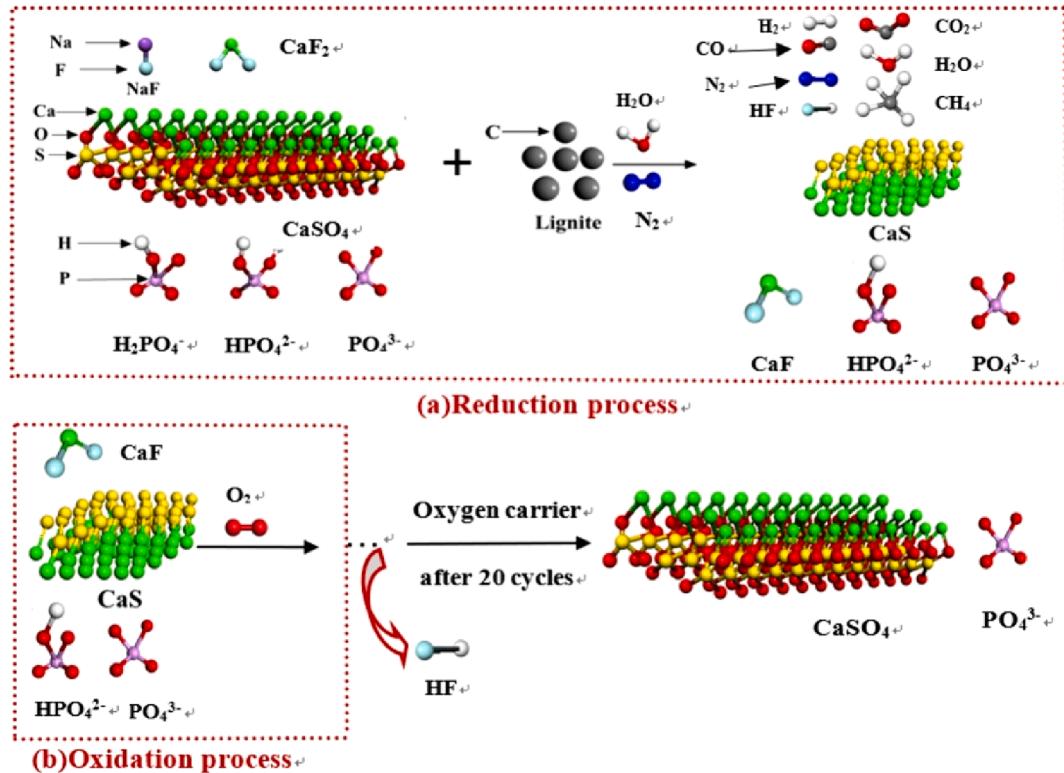


Fig. 11. Migration and transformation pathways of F and P during the CLG process, in which PG has been used as the oxygen carrier [183].

the solid phase Ca₄Si₂F₂O₇ and solid phase Ca₁₀(PO₄)₆F₂ disappeared completely, and the products gradually transformed into gas phase HF with small quantities of KF. During the increase of temperature from 1200 °C to 1300 °C, the F element began to appear in the form of a new gas phase of NaF. With the increase of temperature, the content of gas phase KF and NaF tended to increase. At the temperature of 900 °C, the F element existed in the form of solid-phase Ca₄Si₂F₂O₇ (53.2 %) and gas-phase HF (46.8 %) (Fig. 10) [182].

The migration and transformation pathways of F and P elements during the CLG process in which PG was used as the oxygen carrier were further investigated using experiments [183]. The corresponding results are shown in Fig. 11. The F element in PG mainly existed in the form of water-soluble NaF and insoluble CaF₂ during the reaction [183]. The

water-soluble NaF was gradually transformed into HF [183]. However, the insoluble solid-phase CaF₂ was attached to the surface of oxygen carrier and did not participate in the reaction process [183]. Eventually, most of the F element in PG would overflow to the gas phase. Only some of it would be present in the solid-phase residue in the form of Na₂SbF₅, KF, NaF, and CaF₂ [183]. For elemental P in PG, the P element was sequentially converted to Ca₃(PO₄)₂ by Ca(H₂PO₄)₂ and Ca(HPO₄), completing the phase transition of P element. Subsequently, PO₄³⁻ and free Ca²⁺ reacted to form insoluble Ca₃(PO₄)₂ [183]. A layer of Ca₃(PO₄)₂ particles was periodically presented in the middle of the oxygen particles, which acted as an adhesive between the oxygen carrier's particles [183]. As the reaction proceeded, most of the phosphorus would eventually be present in the solid phase residue as Ca(H₂PO₄)₂.

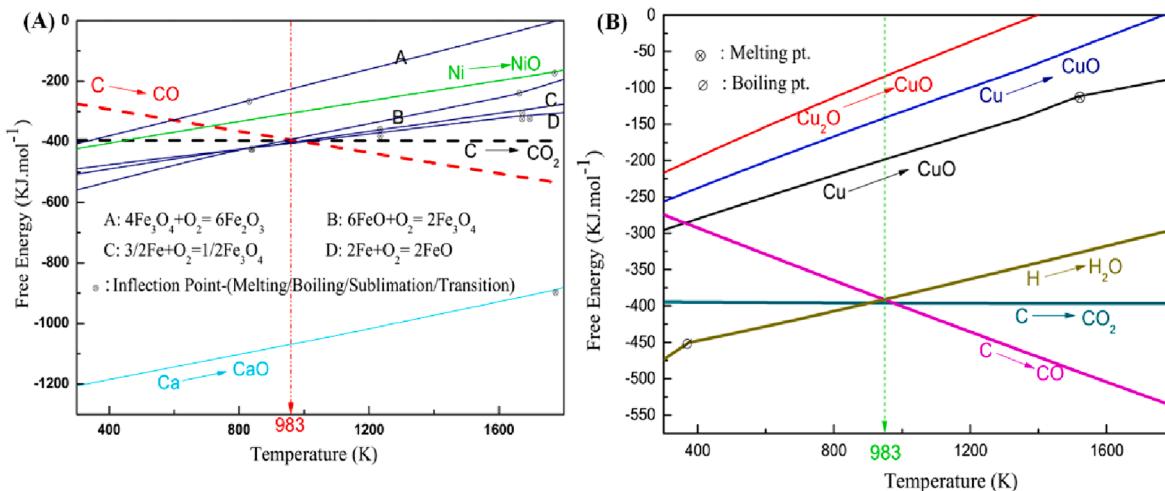


Fig. 12. Ellingham diagram: (A) Ellingham diagram of Fe-Ni-C-Ca; (B) Ellingham diagram of Cu-C-H [184].

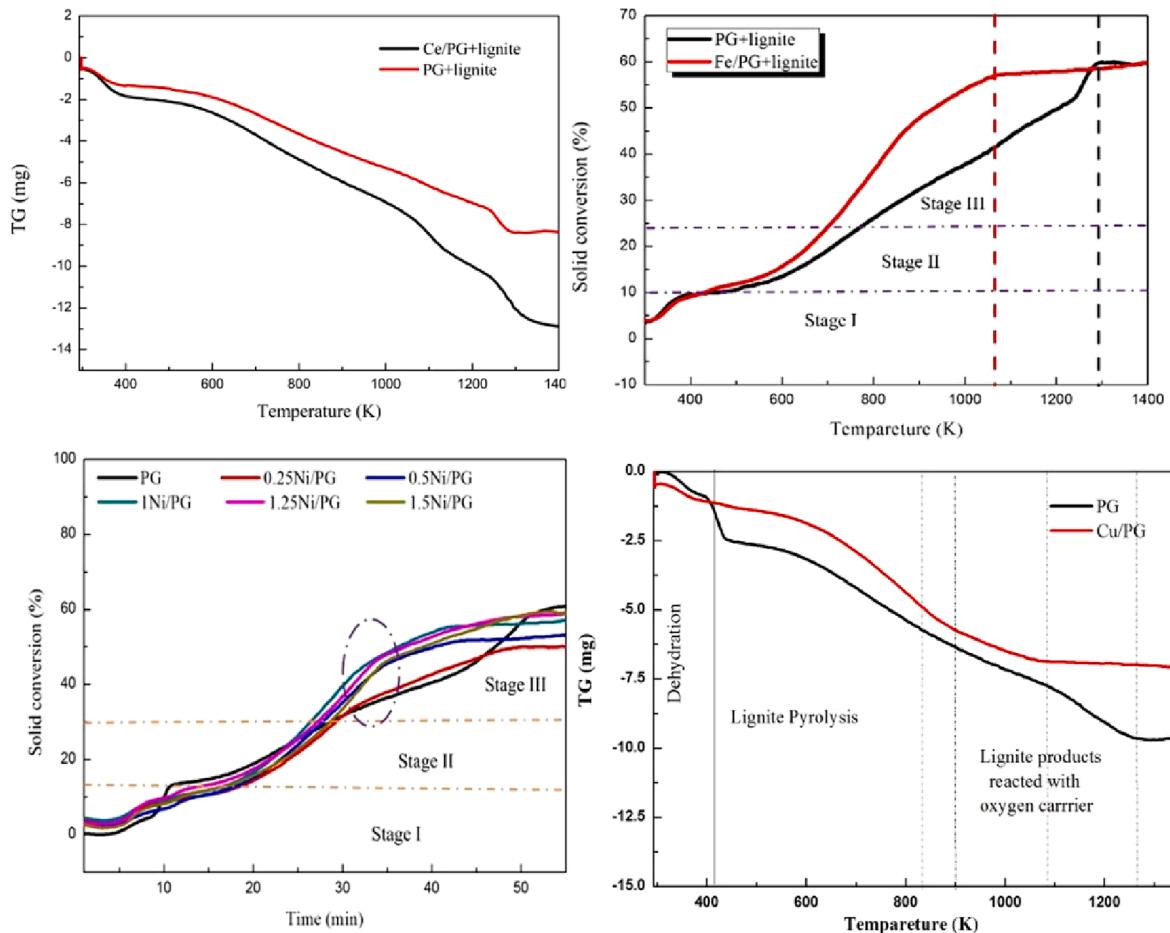


Fig. 13. TG analysis of compound oxygen carriers [167,184,185].

and $\text{Ca}_3(\text{PO}_4)_2$ [183].

The main component of PG (CaSO_4) has strong oxygen carrying capacity, whereas Al and Fe of PG can reduce the decomposition temperature. Moreover, Si of PG can improve the anti-agglomeration capability of the oxygen carrier. Based on theoretical research and some experimental works, PG is found to be an excellent oxygen carrier for the production of syngas during lignite's CLG process.

3.2. Preparation of new PG-based oxygen carrier and the mechanism of lignite's gasification with polymetallic collaboration

Aiming at energy-savings and efficient output, oxygen carriers consisting of calcium-based compounds with the ability to reduce the reaction temperature of lignite's CLG were developed. Compound oxygen carriers (Ce/PG, Fe/PG, Ni/PG, Cu/PG) were prepared using the Ellingham diagram, which helped screen cerium, iron, nickel, and

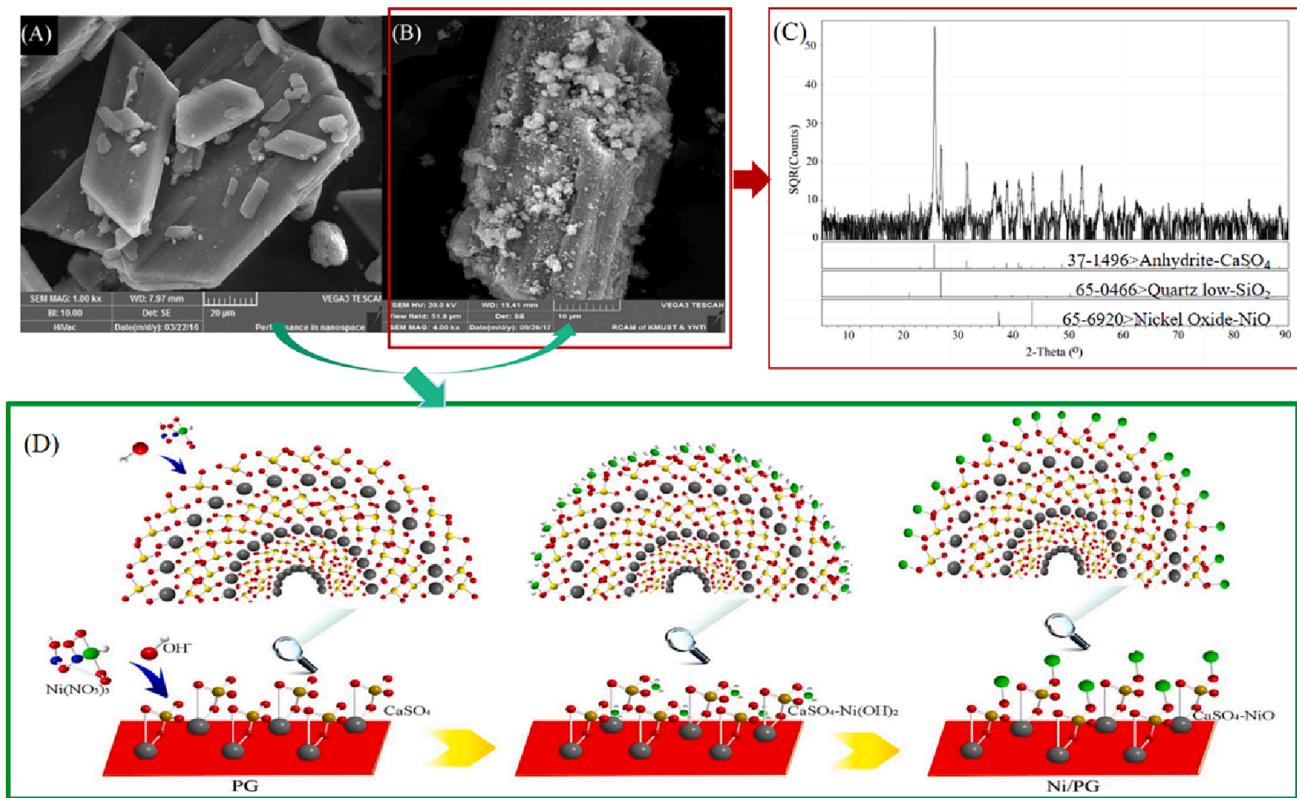


Fig. 14. Ni/PG compound oxygen carrier and PG: (A) SEM of PG; (B) SEM of Ni/PG; (C) XRD of Ni/PG; (D) Preparation mechanism of Ni/PG.

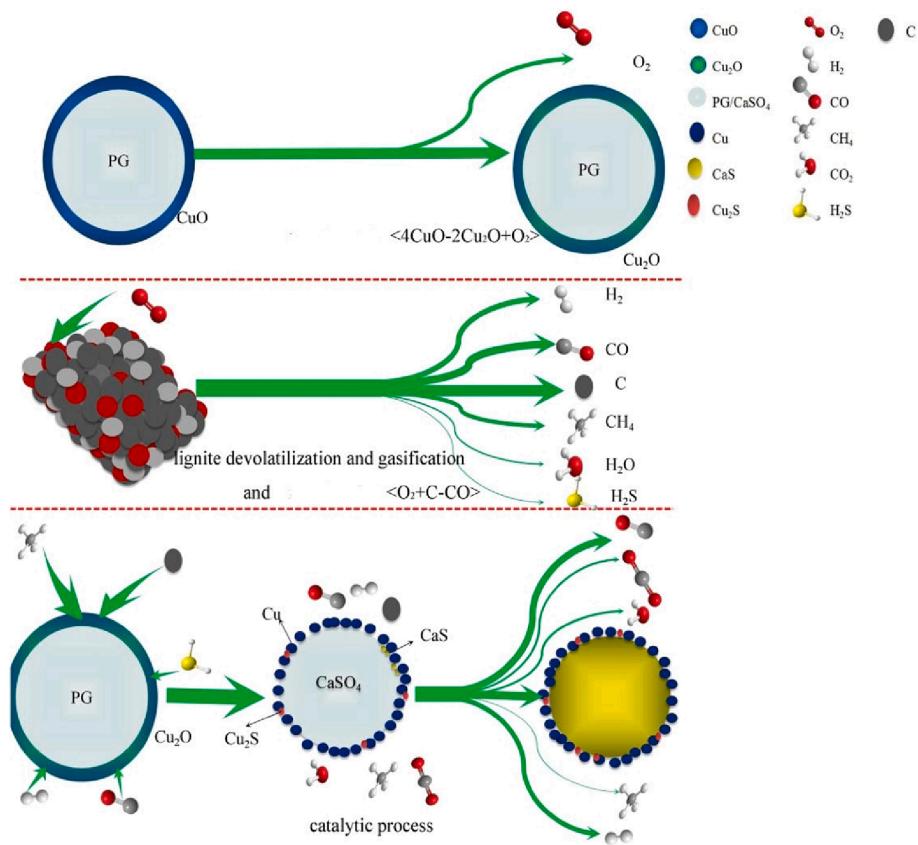


Fig. 15. Mechanism of the production of syngas from lignite's CLG using the oxygen carrier of Cu/PG [184].

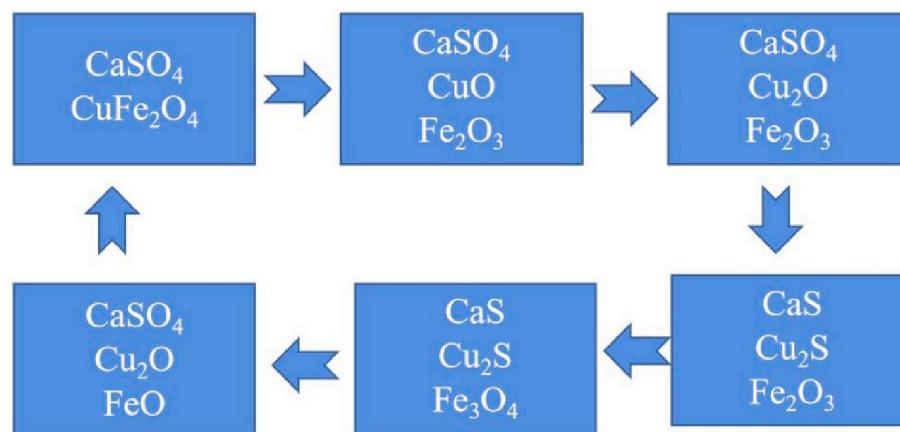


Fig. 16. Oxygen release mechanism of PG-CuFe₂O₄ compound oxygen carrier [186].

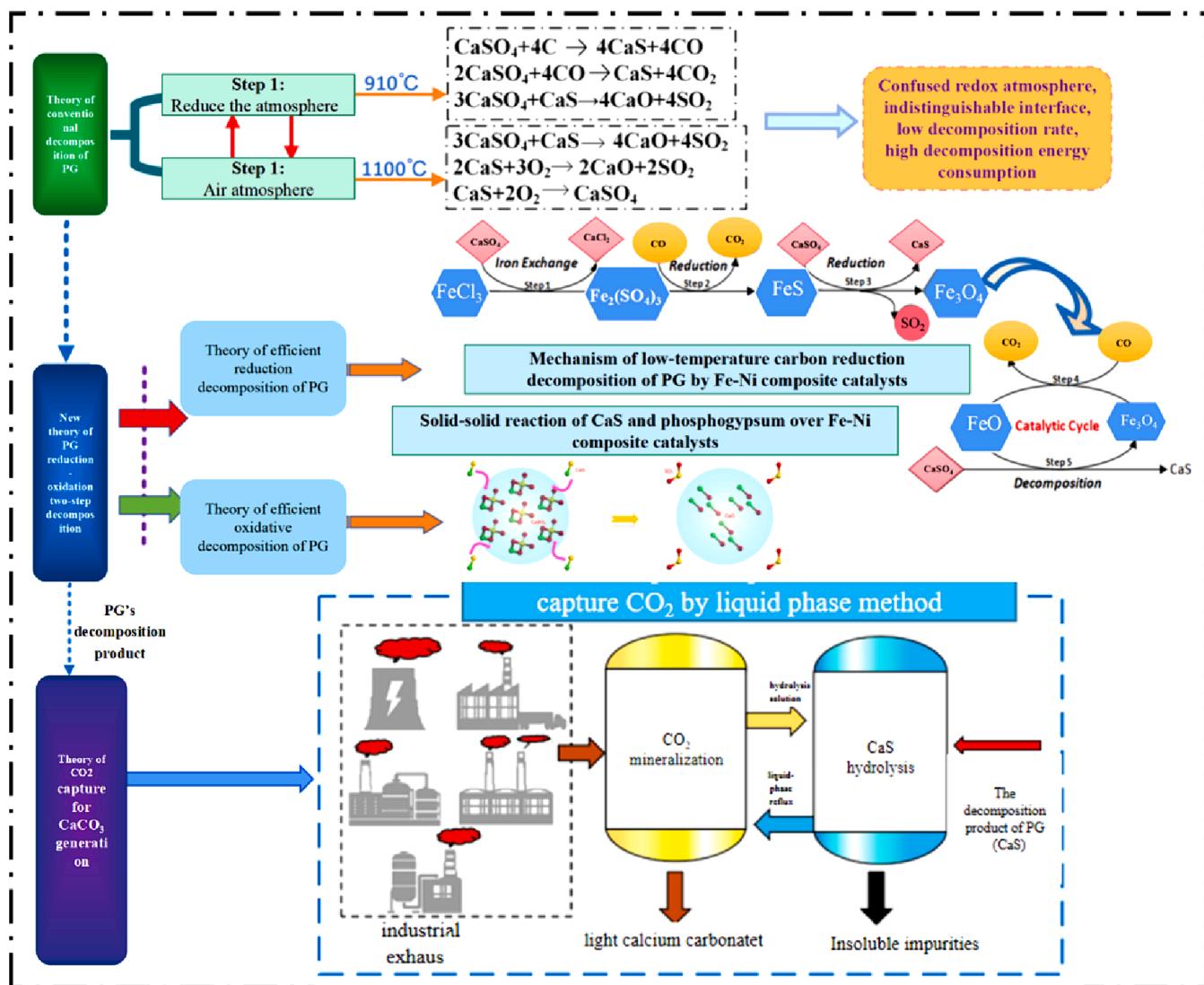


Fig. 17. Utilization of Ca resources in PG.

copper for use with PG (Fig. 12) [184].

It was found that, except for Ce/PG compound oxygen carriers, other PG-based compound oxygen carriers (Fe/PG, Ni/PG, and Cu/PG) were able to reduce the temperature of the CLG process (Fig. 13)

[167,184,185]. The temperature of lignite's decomposition by Ce/PG compound oxygen carrier was higher than that of lignite's decomposition by PG. The main reason was that CeO₂ was loaded on the surface of PG, which on the one hand required higher energy to react with lignite,

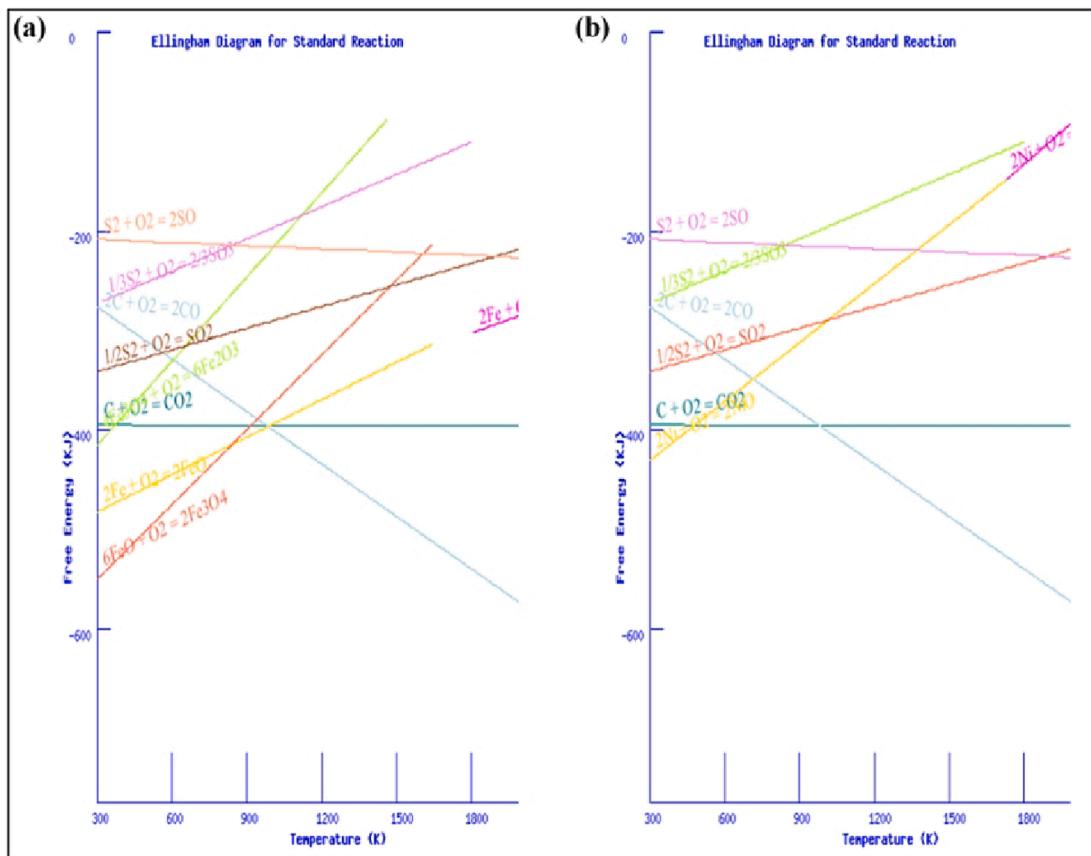


Fig. 18. Analysis of the Ellingham diagrams: (a) C-S-Fe and (b) C-S-Ni [123].

and on the other hand, the loading of CeO_2 hindered the reaction of CaSO_4 with lignite [184]. The slopes of the second and third phases of the reaction of Cu/PG, Fe/PG, and Ni/PG compound oxygen carriers were comparatively larger. The decomposition termination temperature of PG-based compound carrier was lower than that of PG alone during CLG process.

The preparation mechanism of Cu/PG, Fe/PG, and Ni/PG compound oxygen carriers was investigated. It was found that Cu/Fe/Ni elements existed as small crystals of oxides on the surface of the compound oxygen carrier such as in Ni/PG (see Fig. 14).

[168]. In the preparation process of the compound oxygen carrier, Ni element was loaded onto the surface of PG in the form of hydroxides in the presence of ammonia. Meanwhile, the oxygen atoms of the hydroxide fused with the oxygen atoms in PG to form the chemical bonds of H-Ni-O-S-Ca. After further calcination, the chemical bonds of H-Ni-O-S-Ca lost their water molecules to form Ni-O-S-Ca. This way, Ni/PG compound oxygen carrier was obtained.

The reaction mechanism of Cu/PG in the lignite's CLG process was investigated [184]. It was found that CuO released molecular oxygen at high temperature during the CLG process of lignite using Cu/PG as the oxygen carrier. The loading of Cu during the reaction provided more active sites, and thus, reduced the reaction temperature during the gasification process (Fig. 15) [184]. The preparation of syngas from lignite's CLG with Cu/PG changed the original lignite's CLG reaction process with PG as an oxygen carrier. The pathways of lignite's CLG with Cu/PG were as follows. First, the decomposition of CuO released O_2 at the high temperature. Then, the gasification of lignite and the reaction of O_2 with carbon occurred. Next, the gasification products reacted with Cu_2O , CaSO_4 , and water vapors. Additionally, the oxygen carrier could trap S in the syngas. Among them, the O_2 released from the decomposition of CuO promoted the conversion of lignite to CO and also induced the whole process of CLG.

Based on the excellent reaction properties of Cu/PG, the reaction kinetics of the CLG process using Cu/PG was further explored for industrial applications. The results revealed that the mass transfer of lignite's CLG using Cu/PG was in accordance with the Ginstling-Brounshtein Shrinking Core Model (GB-SCM) [169]. The reacting materials must overcome the following resistance until the reaction took place: film transfer, diffusion through the interstices among the grains (the pores), diffusion through the product layer around the grain and the chemical reactions on the interface in the grain. The kinetic equation for the reaction of the process is given by Equation E(3) [169].

$$\frac{d\alpha}{dt} = 181.6716 \times \exp\left(\frac{88.1700}{R\Gamma}\right) \times \frac{2}{3} \times 3 \left[(1 - \alpha)^{-1/3} - 1 \right]^{-1} \quad (\text{E3})$$

where α (wt.%) is the conversion rate of reactants, t (s) is the reaction time, R (J/mol/K) is the natural gas constant and T (K) is the reaction temperature.

In order to harness the respective advantages of PG, Fe and Cu, the compound oxygen carrier of PG-Cu Fe_2O_4 was prepared. The reaction properties of PG-Cu Fe_2O_4 of lignite's CLG were investigated [186]. It was found that the optimum temperature range of the reaction was 750–850 °C. The CO selectivity was 70.3 %, whereas the CO_2 selectivity was 23.8 %. Moreover, the H_2/CO value was 0.78, with the highest carbon conversion efficiency of 91.9 % [186]. The results of the study revealed the oxygen release pathway of the composite oxygen carrier. The oxygen release pathway of Fe in the composite oxygen carrier was $\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4-\text{FeO}$ (FeS). The oxygen release pathway of Cu was $\text{CuO}-\text{Cu}_2\text{O}-\text{Cu}$ (Cu_2S). The oxygen release priority of the compound oxygen carrier was found to lie in the following descending order: $\text{CaSO}_4 > \text{CuO} > \text{Cu}_2\text{O} \approx \text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{FeO}$ (Fig. 16) (Fig. 16) [186].

Based on the above findings, the oxygen release mechanism of multi-metal PG-based compound oxygen carriers and the influencing

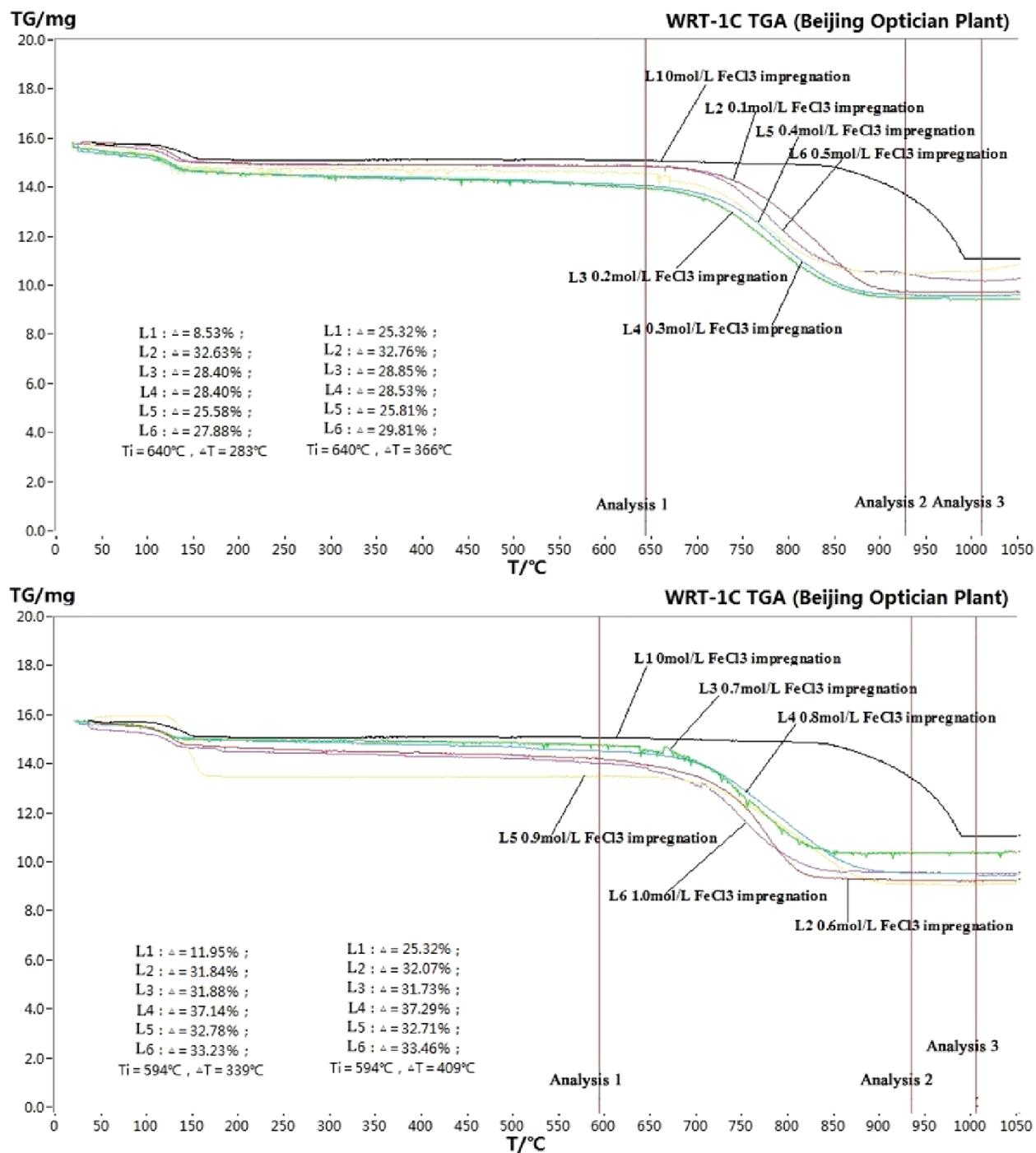


Fig. 19. TGA analysis of catalytic decomposition of PG impregnated with different concentrations of FeCl₃ solution [122].

mechanism on lignite's CLG process were explored. PG combined with other metals to prepare compound oxygen carriers can increase the rate of reaction and decrease the reaction temperature. However, the cost of metals is high, whereas the industrial solid waste containing these elements is a good alternative to using pure metals of compound OCs. This provides a theoretical basis for PG to be combined with other potential solid wastes and used as an oxygen carrier.

4. High-value utilization of Ca in PG

PG is rich in Ca resources. This section summarizes two aspects of PG's high-quality Ca resources. The first aspect is the decomposition of PG to prepare CaO and SO₂. The disadvantages of traditional

decomposition of PG for producing CaO were summarized, and the advantages of two-step process for the production of CaO were put forward. The reaction mechanism for the preparation of CaO using two-step method was summarized and analyzed. Moreover, high quality CaCO₃ was prepared by mineralizing and capturing CO₂ from the decomposition slag of PG. The mass transfer process of the decomposition slag of PG was studied and a population equilibrium model was established. This provides guidance for the high-quality utilization of Ca resources present in PG (see Fig. 17).

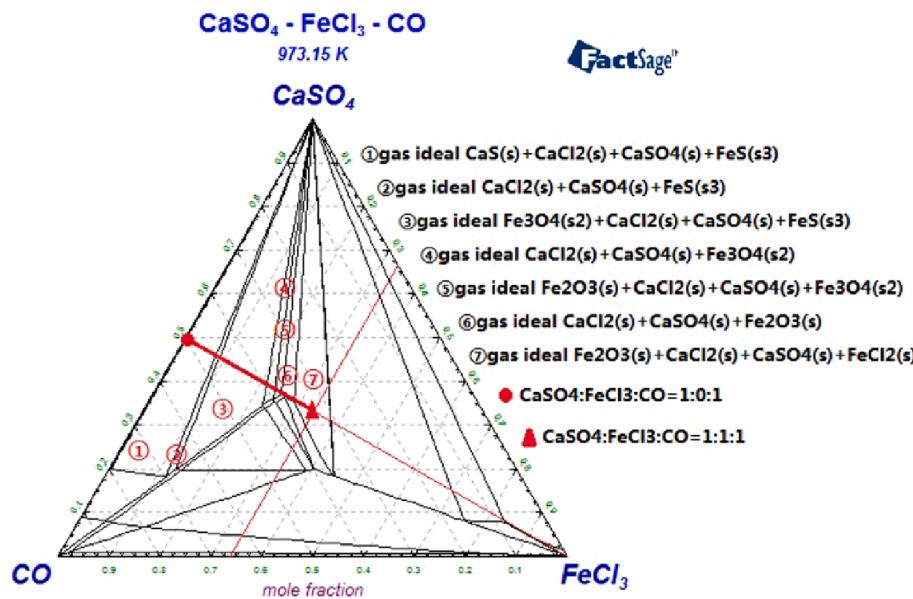


Fig. 20. Ternary phase diagram of $\text{CaSO}_4\text{-FeCl}_3\text{-CO}$ at 700 °C [122].

4.1. Mechanism of two-step low-temperature decomposition for preparing CaO

The Ca source in PG can be decomposed at high temperature to prepare CaO [187,188]. CaO prepared from PG was used as cement clinker in construction industry [129,189–191]. The study of the traditional method for the decomposition of PG yielded the following findings. Under the reducing atmosphere, the decomposition reaction between C and CaSO_4 in PG occurred slowly during the decomposition process of PG [192,193]. Small amounts of CaS and SO_2 were produced during this reaction [170]. When the temperature was increased to 910 °C, the production of CaS and the reaction between CaS and PG were carried out simultaneously [124]. At the end of this composite reaction, CaSO_4 , CaS and CaO appeared simultaneously in the solid product [124]. When switching to the oxidizing atmosphere, the reaction temperature reached more than 1100 °C, and the following three reaction systems existed in the system: (1) the oxidation of CaS to CaO , (2) the oxidation of CaS to CaSO_4 , and (3) the solid-solid reaction of CaS with CaSO_4 [171]. After four cycles, it was found that CaS exhibited the third stage of reaction characteristics at 1100 °C, which means that the weight loss tended to stabilize [171]. The overall mass of the reactants increased due to the coupling of multiple reactions, where the rate of the solid-solid reaction remained constant. The rate of the oxidation of CaS to CaSO_4 decreased, leading to further production of CaO . Due to the diffusion resistance of the product layer to the reaction gas, it was difficult for CaS to be completely converted into CaSO_4 and CaO . As a result, the reaction eventually stabilized in the third stage.

The above study revealed the theoretical defects in the traditional one-step PG, which were as follows: confusion of redox atmosphere, indistinguishable interfaces, low decomposition rate, and high energy consumption for the decomposition process. Therefore, the theory of PG reduction-oxidation two-step decomposition was proposed [172].

4.1.1. Efficient reduction and decomposition theory of PG

Based on the problems of the previous study, the addition of catalysts in the reduction stage of PG was proposed to improve the decomposition efficiency of PG [173,174]. The main component of PG is calcium sulfate dihydrate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), which undergoes gas-solid and solid-solid redox reactions with reducing agents to achieve the reconstruction of calcium sulfate along with the participation of metal catalysts such as Al/Mg/Fe/Ni [123,176,194,195]. Through the Ellingham diagram of

Al/Mg/Fe/Ni/PG, it was found that, due to the existence of many oxides with different valence states of elemental Fe, the Fe element exists in many different valence states. Moreover, there are several intersections of Fe with S, C and other oxides in a straight line, indicating that the oxides of Fe can be involved in the redox reaction system of PG with CO [196]. The Ni element exists in three basic valence states such as 0, +1 and + 2, and intersects with the oxides of both S and C. It suggests that Ni has the potential to be a catalyst for the redox reaction of PG with CO. Therefore, the Fe-Ni catalyst was obtained as a low-temperature decomposition catalyst for PG with excellent catalytic reduction properties (Fig. 18) [123].

The effect of Fe-based and Ni-based catalysts on the reductive decomposition of PG was investigated [194,197]. The results showed that the weight loss of PG was divided into three stages: (1) the removal of free water from PG at a temperature of 100–150 °C; (2) the removal of crystalline water from PG at a temperature of 400–550 °C. and (3) the catalytic decomposition stage of PG at 590–1000 °C (Fig. 19) [122]. The corresponding starting decomposition temperature of PG was 590 °C at an FeCl_3 impregnation concentration of 0.8 mol/L, thus demonstrating that Fe and its oxides play a significant role in this process (Fig. 19). As shown in Fig. 19, when the FeCl_3 impregnation concentration was 0.8 mol/L, the corresponding temperature for the onset of PG's decomposition was 590 °C, indicating the significant role of Fe and its oxides in reducing the decomposition temperature of PG. After thermodynamic calculations, it was found that the presence of Cl element in FeCl_3 provided a new reaction pathway for the decomposition of PG to produce CaCl_2 (Fig. 20) [122]. Compared with CaO ($\Delta H(25^\circ\text{C}) = -635.09 \text{ kJ/mol}$ and $\Delta H(25^\circ\text{C}) = -604.3 \text{ kJ/mol}$), CaCl_2 ($\Delta H(25^\circ\text{C}) = -795.8 \text{ kJ/mol}$ and $\Delta H(25^\circ\text{C}) = -748.1 \text{ kJ/mol}$) was easier to be generated, which also greatly facilitated the decomposition of PG. In addition, Fe and its oxides were involved in the series of gas-solid and solid-solid reactions of PG's reduction through $\text{Fe}(+3)\text{-Fe}(+2)\text{-Fe}(+3)$. It significantly reduced the decomposition temperature of PG and increased the rate of decomposition of PG. When NiCl_2 impregnation concentration was 0.4 mol/L, PG began to decompose at a temperature of 644 °C with a maximum weight loss of 38.86 % (Fig. 21) [173]. According to the results of the thermodynamic calculations (Fig. 22) [173], at the beginning of the low-temperature decomposition of PG, Fe had a limiting effect on the production of $\text{S}(-2, \text{CaS})$. However, it could facilitate the production of SO_2 [195]. Due to the constant production of FeCl_2 , too much Fe was limiting the production of SO_2 . Furthermore, Ni was able to

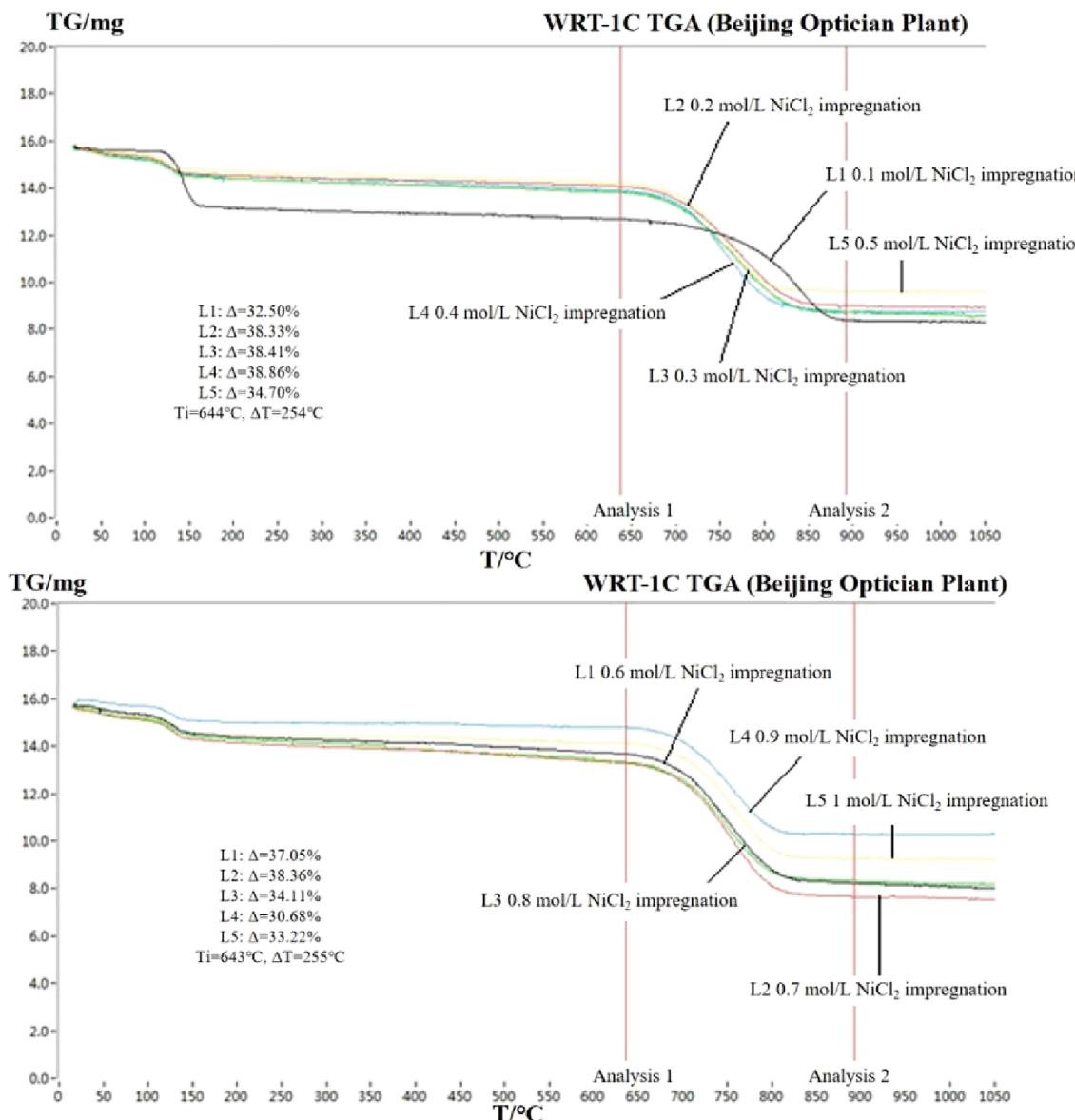


Fig. 21. Thermo-gravimetric analysis (TGA) of catalytic decomposition of PG impregnated with different concentrations of NiCl_2 solution [173].

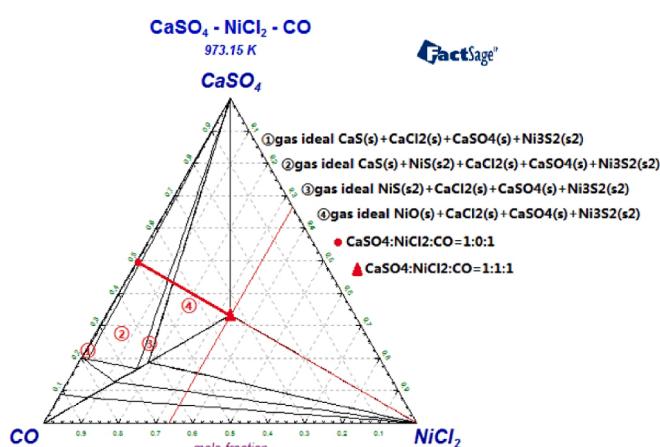


Fig. 22. Ternary phase diagram of < CaSO₄-NiCl₂-CO > at 700 °C [173].

limit the production of S (-2, CaS) while combining very easily with Fe oxides to produce conjugates such as $\text{NiO}\text{-Fe}_2\text{O}_3$. It limited the production of Fe (+2). However, it improved the reduction selectivity of CO, and produced more SO_2 .

Comparing the effects of Fe and Ni in the low-temperature catalytic decomposition of PG, it was found that Fe and its oxides were effective in reducing the onset of the decomposition temperature of PG. On the other hand, Ni and its oxides played a dominant role in increasing the rate of decomposition of PG and recovering S and Ca resources. Therefore, the addition of Fe-Ni composite catalyst in the decomposition process of PG was investigated to obtain maximum weight loss (ΔTG) and reduce the temperature of the decomposition of PG. The catalytic reaction system of PG under Fe-Ni compound catalysis was constructed through the characterization of the decomposition products of PG under Fe-Ni composite catalysis and the Boren-Haber reaction cycle (Figs. 7 and 8). Based on the above results, the mechanisms of the combination of Fe-Ni compound catalyst, the amount of the catalyst and the catalytic pathway for the reduction in the decomposition temperature of PG and the improvement of its decomposition efficiency were summarized. The result can be found as follows [173]:

Step 1: PG's impregnation (iron salt solution). PG impregnated

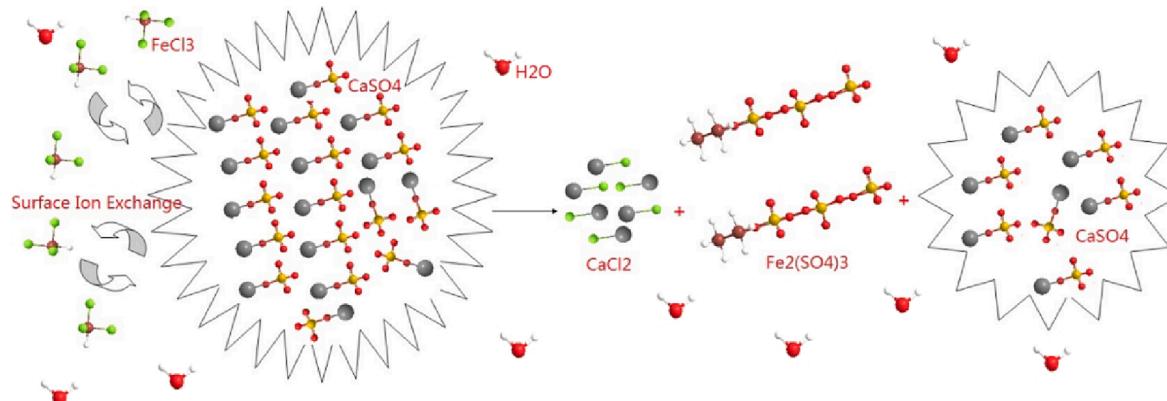


Fig. 23. Step 1: PG's impregnation (iron salt solution).

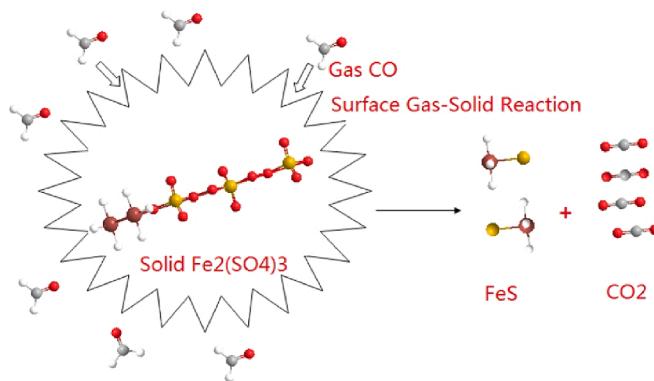
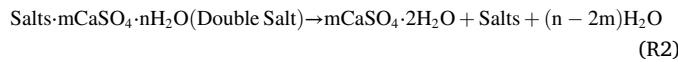


Fig. 24. Step 2: Reduction of Fe₂(SO₄)₃ by CO to form FeS.

surfaces underwent an ion exchange reaction with CaCl₂ and Fe₂(SO₄)₃ as the reaction products (Fig. 23). At this stage, the formation and transformation of CaSO₄ complex salts happened through R1 and R2.



Step 2: Reduction of Fe₂(SO₄)₃ by CO to form FeS (Fig. 24). This reaction was a gas–solid reaction occurring on the surface of PG. This reaction could proceed spontaneously due to ΔH (727 °C) = −2545.93

kJ/mol. It was highly amenable to forward progression between the temperature range of 700–800 °C.

Step 3: Reduction of CaSO₄ by FeS (Fig. 25). This solid–solid reaction occurred on the surface and in the interstices of PG with Gibbs' free energy of −332.68 kJ/mol at 727 °C. Its reduction products were CaS, SO₂ and Fe₃O₄.

Step 4: Reduction of Fe₃O₄ to FeO by CO (Fig. 26). The gas–solid reaction occurred on the surface and in the interstices of PG with the Gibbs' free energy of −2556.63 kJ/mol at 727 °C.

Step 5: Reduction of CaSO₄ by FeO (Fig. 27). This reaction was a solid–solid reaction that occurred on the surface and in the interstices of PG with the Gibbs' free energy of −115.78 kJ/mol at 727 °C. Its reduction products were CaS and Fe₃O₄.

According to the above analysis, Steps 2 and 4 in the low-temperature catalytic decomposition system of PG were gas–solid reactions. Steps 3 and 5 were solid–solid reactions, and both of them occurred on the surface of PG and within the interstitial space. Step 1 contained the ion exchange process between CaSO₄ and Fe salts, and the CaSO₄ complex salt effect.

As shown in Fig. 28, Step 1 was the initiating reaction for the catalytic reduction. In Steps 2 and 3, Fe₃O₄ was produced, which was the key substance. Steps 4 and 5 constituted the catalytic reduction cycle of PG, resulting in the continuous and rapid decomposition of PG until complete decomposition of PG.

4.1.2. Theory of efficient oxidative decomposition of PG

The effects of different reaction atmospheres and reaction temperatures on the morphological changes of Ca and S in PG during

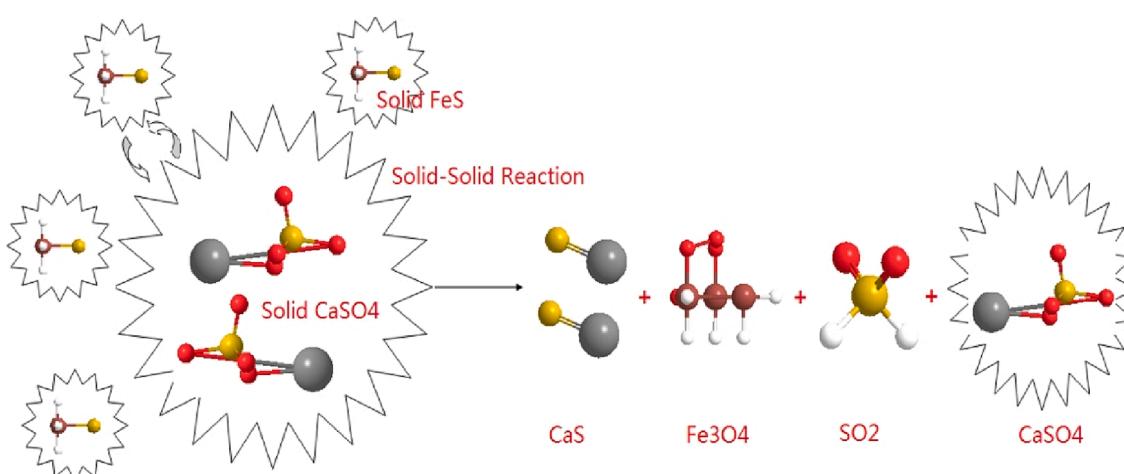


Fig. 25. Step 3: Reduction of CaSO₄ by FeS.

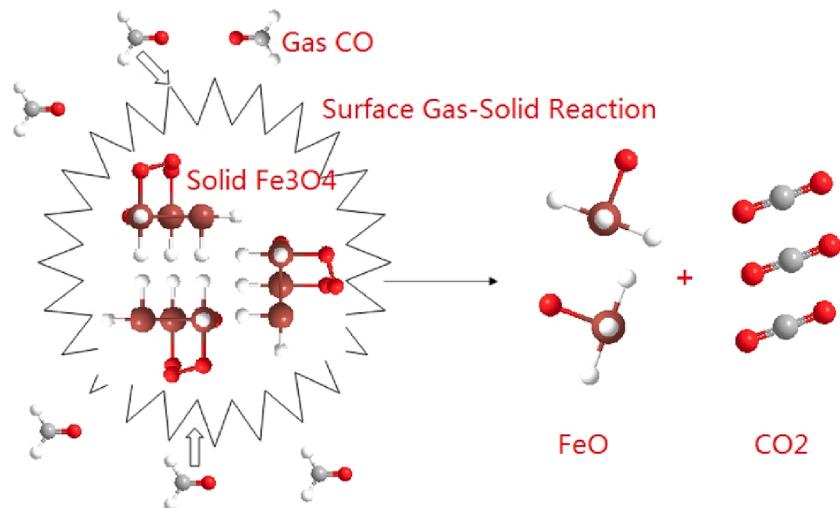
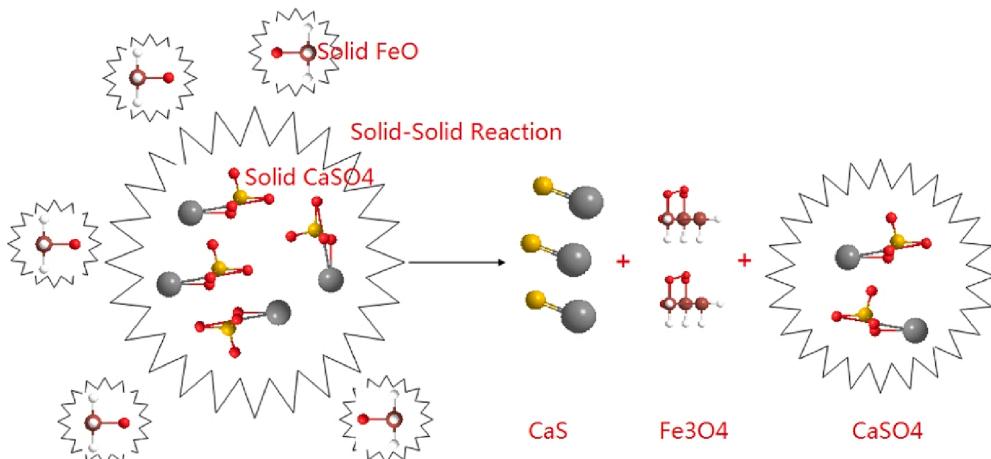
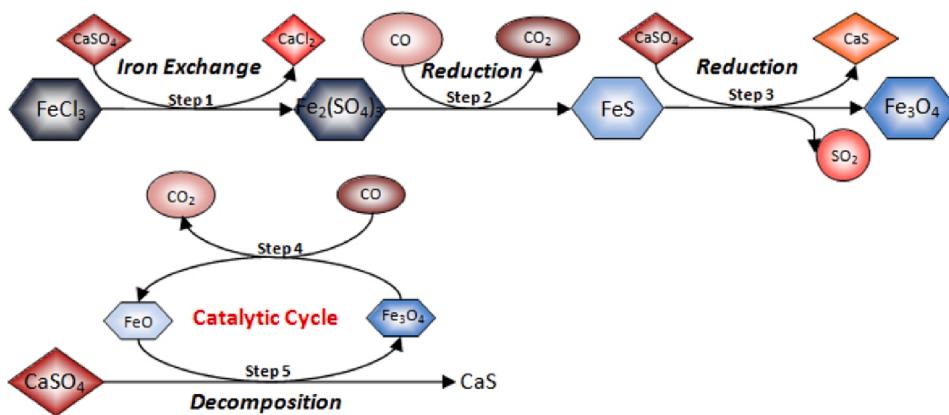
Fig. 26. Step 4: Reduction of Fe_3O_4 to FeO by CO.Fig. 27. Step 5: Reduction of CaSO_4 by FeO .

Fig. 28. Recycling system for PG's low-temperature catalytic decomposition.

decomposition were investigated. Under the action of reducing atmosphere and Fe-Ni-based catalyst, the decomposition product of PG was CaS at lower temperatures. Then, CaO could be obtained by oxidizing the CaS in air under the reaction temperature of 1000 °C. Therefore, high concentration of SO_2 and high purity of CaO could be prepared by adjusting the $\text{CaS}-\text{O}_2-\text{CO}$ in the reaction system. During this reaction, the

rate of conversion of PG reached 90.75 %, while the content of CaO in the final solid phase product was more than 70 % [171].

The kinetic equation for the reduction product (CaS) under the use of air as the oxidizing atmosphere is given by Equation (E4) [124]:

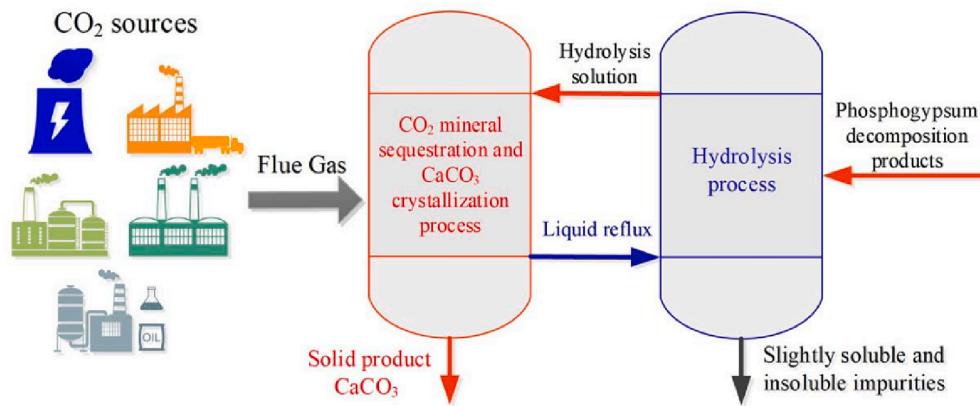


Fig. 29. Technology for mineralization of carbon dioxide by the solid product of PG's decomposition.

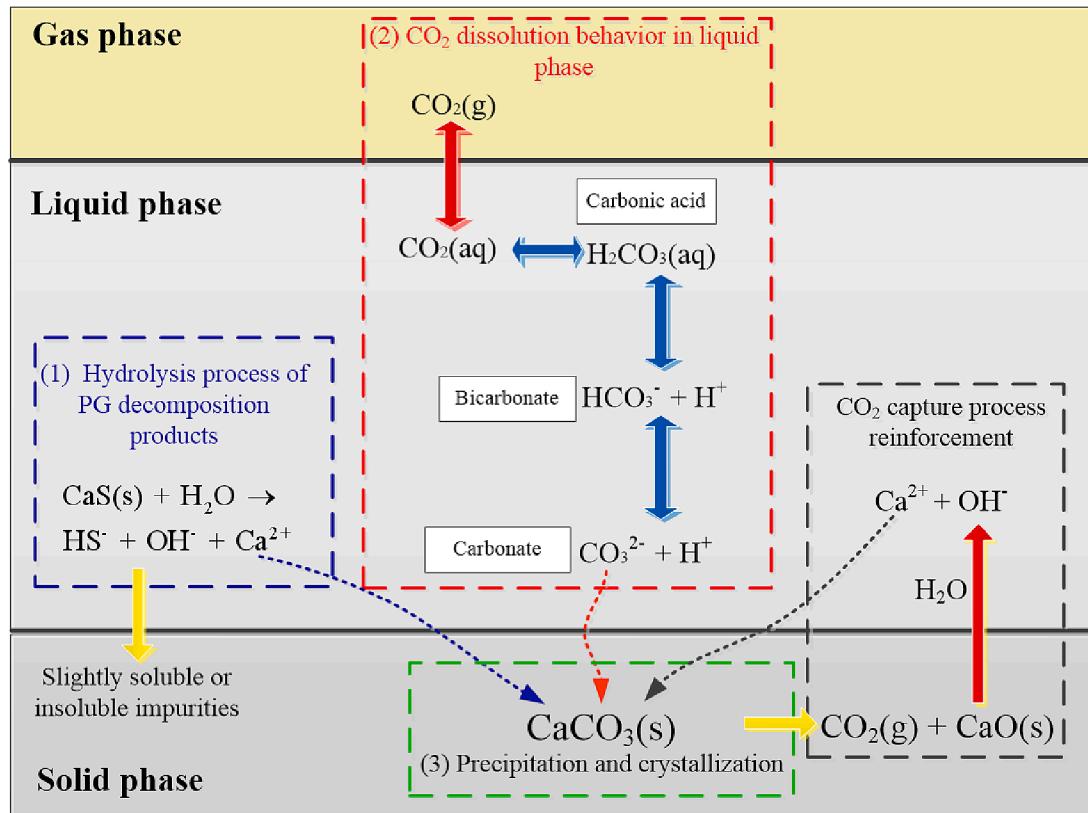


Fig. 30. Schematic of the mechanism of CO₂ capture [198].

$$\frac{d\alpha}{dt} = 1.04 \times 10^{11} \times \exp\left(-\frac{257.35 \times 10^3}{RT}\right) \times \frac{3}{2}(1-\alpha)^{2/3} \left[1 - (1-\alpha)^{1/3}\right]^{-1} \quad (E4)$$

where α (wt.%) is the rate of conversion of CaS, t (s) is the reaction time, R is the gas constant and T (K) is the reaction temperature.

By further revealing the reaction mechanism of PG in the cyclic reaction process of reduction and oxidation in different atmospheres, the distribution of the final products (CaS, CaSO₄ and CaO) and the role of Fe-based additives in different reaction stages were determined. The above studies elucidated the reduction-oxidation two-step decomposition control mechanism of the iron-based additive, and provided theoretical support for the two-step preparation of PG for cement clinker.

Two-step method and adding catalyst, the reduction temperature of phosphogypsum and the oxidation temperature of phosphogypsum

decomposition products decreased from 910 °C to 590 °C and from 1100 °C to 1000 °C, respectively. At present, the reaction mechanism of this process has been studied by means of phase diagrams and the establishment of reaction kinetics model. If the study of the reaction mechanism at molecular level is focused, the reaction mechanism of chemical reaction process can be quantitatively revealed.

4.2. Carbon dioxide capture by PG's decomposition slag for producing CaCO₃

For further efficient utilization of CaS (PG's decomposition slag), a new way for preparing CaCO₃ by capturing carbon dioxide from the hydrolyzed liquid phase of the decomposition solid product of PG has been put forward (Fig. 29) [94,119,198–200]. The hydrolysis of CaS could obtain an alkaline solution containing a large number of free

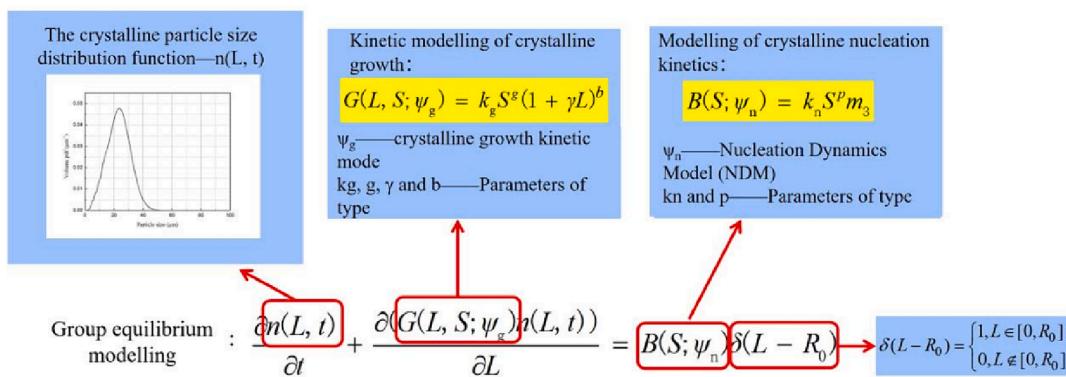


Fig. 31. Group equilibrium modelling [199].

calcium ions. The liquid–solid separation removed the insoluble impurities from the PG. Next, the alkaline-free calcium ion solution was used for capturing CO₂ and producing CaCO₃ through crystallization. The crystallization process of CaCO₃ also removed the soluble impurities from the solution. In this process, the H₂S was generated during the crystallization process [200], which could be used to reduce PG or to prepare thiourea.

Zhang et al. [198] studied the reaction mechanism of PG's decomposition slag to capture CO₂, as shown in Fig. 30. The research contents included the phase transition mechanism of insoluble impurities, soluble impurities and eutectic impurities during the crystallization of calcium carbonate. Moreover, the study also involved the impurity removal process and the interphase migration mechanism of sulfur, calcium and carbon ions. Carbon dioxide capture process consisted of gas-, liquid-, and solid-phase processes (crystalline particles, bubbles, particles agglomeration, fragmentation). During the process of CO₂ capture, the first step was to hydrolyze the PG's decomposition slag and break it down to various products, including calcium sulfide (through <2CaS(s) + 2H₂O → Ca(HS)₂(aq) + Ca(OH)₂(aq)> and other impurities. In the hydrolysis process, slightly soluble and insoluble impurities were separated through precipitation and filtration. In the second step, carbon dioxide diffused from the gas phase to the water phase. The concentration of CO₂-free water phase in hydrolytic solution obeyed Henry's law [201]. The third step was the crystallization of CaCO₃. The free calcium ion (Ca²⁺) reacted with the carbonate ion (CO₃²⁻) to form CaCO₃.

In addition, the population equilibrium model for the particle size distribution of calcium carbonate crystals was investigated [199]. The population balance model of the size distribution of crystals was established and solved. The corresponding changes in the crystals' particle sizes of calcium carbonate with time and its distribution characteristics were obtained, as shown in Fig. 31. These kinetic results can be applied for determining the kinetic parameters, process control, off-line estimation and the process design.

The decomposition slag of PG (CaS) was hydrolyzed and used to capture carbon dioxide through recrystallization method. 100 % CaCO₃ was obtained in the process. Mass transfer during the capture of CO₂ was also studied. Meanwhile, the corresponding changes and the distribution characteristics of calcium carbonate crystal size with time were obtained. Due to the presence of other impurities in phosphogypsum components (SiO₂, Fe₂O₃, and Al₂O₃), it is necessary to pay attention to the direction of impurities while transforming the main components of solid waste into treasure.

5. Conclusions and prospects

5.1. Conclusions

The process and the reaction mechanism of state-of-the-art

technology for using O and Ca present in PG were summarized. The main results are as follows.

- (1) In order to use O in PG, an innovative technology for lignite's CLG to produce syngas was put forward. PG was shown to be an excellent oxygen carrier due to its main component of CaSO₄. Analyzing the impurity in phosphogypsum shows that Si can improve the sintering resistance. It can provide CLG with four oxygens. Compared with PG used as an oxygen carrier, the PG containing transition metals (such as Ni, and Fe) to form compound oxygen carrier can reduce the reaction temperature to around 200 °C. It is of great significance for the development of clean energy from lignite and for the co-disposal and utilization of bulk industrial solid waste.
- (2) Aiming at the difficult problem of recycling Ca present in PG, the method of preparing high-purity CaCO₃ and CaO from PG was proposed. Compared with the traditional PG decomposition method, the reduction temperature of phosphogypsum and the oxidation temperature of phosphogypsum decomposition products decreased from 910 °C to 590 °C and from 1100 °C to 1000 °C, respectively by Two-step method and adding catalyst. Moreover, 100 % pure high-quality CaCO₃ can be obtained by recrystallization by mineralizing CO₂ using the PG's decomposition slag. The population balance model of crystal particle size distribution was established and solved. This provides guidance for the high-quality utilization of Ca present in PG.

5.2. Future prospects

This review summarized more than 20 years of work on novel uses of PG. The new ways to utilize O and Ca resources are summarized. The problem of the large-scale utilization of PG cannot be solved by a single technology and needs a variety of technologies to work together. At present, a large amount of research is focused on the utilization of a single solid waste. There are only a few studies focusing on the combined utilization of two or more solid wastes. PG can be combined with other solid wastes in cement, bricks, fillers, green adhesives, roadbed materials and other aspects of large-scale use. Comprehensive and multi-level integrated processing technology will become the main research focus of PG's consumption. When utilization of PG, migration and transformation of impurity in PG need attention. At present, the reaction mechanism of utilization of PG has been studied by means of phase diagrams and the establishment of reaction kinetics model. However, The reaction mechanism at molecular level should be focused, the reaction mechanism of chemical reaction process can be quantitatively revealed. Additionally, due to the lack of corresponding industrial standards and the low market recognition of PG's manufacturing products, the application of PG's secondary utilization products is limited and difficult to be promoted on a large scale. Therefore, the key to solving the problems

caused by PG is its large consumption, high value-added utilization and the introduction of policies providing incentives to this end.

CRediT authorship contribution statement

Jie Yang: Writing – original draft, Supervision, Funding acquisition, Formal analysis, Writing – review & editing. **Senlin Dong:** Visualization, Writing – review & editing. **Liping Ma:** Funding acquisition, Project administration. **Quxiu Dai:** Supervision, Validation. **Dalong Zheng:** Formal analysis, Validation, Visualization. **Bing Huang:** Investigation, Visualization. **Mingyi Sun:** Investigation, Visualization. **Bo Hu:** Formal analysis, Validation, Visualization. **Wang Du:** Investigation, Visualization. **Longgui Xie:** Investigation, Visualization. **Li Duan:** Visualization. **Xiang Yan:** Visualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgments

Financial support for this project was provided by the National High Technology Research and Development Program ("863"Program) (No. 2007AA06Z321 and No. 2011AA06A106), National Natural Science Foundation of China (NSFC) (No. 52300160, No. 21176108, No. 21666016 and No. 21868014), Sichuan Science and Technology Program (No. 2022 JDRC0101), Yunnan Fundamental Research Projects (No. 202401AU070150) and State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering (2021-K39), which is greatly acknowledged.

References

- [1] P.M. Rutherford, M.J. Dudas, R.A. Samek, Environmental impacts of phosphogypsum, *Sci. Total Environ.* 149 (1994) 1–38.
- [2] C. Papastefanou, S. Stoulos, A. Ioannidou, M. Manolopoulou, The application of phosphogypsum in agriculture and the radiological impact, *J. Environ. Radioact.* 89 (2006) 188–198.
- [3] J. Wang, F. Dong, Z. Wang, F. Yang, M. Du, K. Fu, Z. Wang, A novel method for purification of phosphogypsum, *Physicochem. Problems Mineral Process.* 56 (2020) 975–983.
- [4] S. Liu, L. Wang, B. Yu, Effect of modified phosphogypsum on the hydration properties of the phosphogypsum-based supersulfated cement, *Construct. Build. Mater.* 214 (2019) 9–16.
- [5] Global phosphoric acid markets, 2022-2027: opportunities in commercialization of chiral phosphoric acid as catalyst and increasing demand for phosphate fertilizers, *Focus on Catalysts*, 2023 (2023) 3.
- [6] X. Zhou, D. Xu, Z. Yan, Z. Zhang, X. Wang, Production of new fertilizers by combining distiller's grains waste and wet-process phosphoric acid: synthesis, characterization, mechanisms and application, *J. Clean. Prod.* 367 (2022) 133081.
- [7] S.C. Gad, Phosphoric acid, in: P. Wexler (Ed.), *Encyclopedia of toxicology (FOURTH EDITION)*, Academic Press, Oxford, 2024, pp. 605–610.
- [8] X. Liu, F. Wu, G. Qu, C. Jin, Y. Liu, L. Kuang, H. Li, X. Chen, Z. Wang, Y. Cheng, Application prospect of advanced oxidation technology in wet process phosphoric acid production, *J. Environ. Chem. Eng.* 10 (2022) 108868.
- [9] S. Fashu, V. Trabadelo, A critical review on development, performance and selection of stainless steels and nickel alloys for the wet phosphoric acid process, *Mater. Des.* 227 (2023) 111739.
- [10] T.F. Al-Fariss, H.O. Özbelge, H.S.H. El-Shall, Process technology for phosphoric acid production in Saudi Arabia, *J. King Saud Univ.-Eng. Sci.* 4 (1992) 239–254.
- [11] Z. Wang, X. Ma, H. Pan, X. Yang, X. Zhang, Y. Lyu, W. Liao, W. Shui, J. Wu, M. Xu, Y. Zhang, S. Zhang, Y. Xiao, H. Luo, Investigating effects of phosphogypsum disposal practices on the environmental performance of phosphate fertilizer production using energy analysis and carbon emission amounting: a case study from China, *J. Clean. Prod.* 409 (2023) 137248.
- [12] J. Yang, C. Han, L. Shao, R. Nie, S. Dong, H. Liu, L. Ma, Chemical looping gasification of lignite to syngas using phosphogypsum: overview and prospects, *J. Clean. Prod.* 445 (2024) 141329.
- [13] X. Qin, Y. Cao, H. Guan, Q. Hu, Z. Liu, J. Xu, B. Hu, Z. Zhang, R. Luo, Resource utilization and development of phosphogypsum-based materials in civil engineering, *J. Clean. Prod.* 387 (2023).
- [14] K.D. Weiksnar, K.A. Clavier, S.J. Laux, T.G. Townsend, Influence of trace chemical constituents in phosphogypsum for road base applications: a review, *Resour. Conserv. Recycl.* 199 (2023) 107237.
- [15] D.I.T. Fávaro, Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil, *J. Radioanal. Nucl. Chem.* 264 (2005) 445–448.
- [16] K. Fang, L. Xu, M. Yang, Q. Chen, One-step wet-process phosphoric acid by-product CaSO_4 and its purification, *Sep. Purif. Technol.* 309 (2023) 123048.
- [17] A.M. Rashad, Phosphogypsum as a construction material, *J. Clean. Prod.* 166 (2017) 732–743.
- [18] F. Li, W. Zhao, J. Li, H. Fan, M. Xu, G. Han, M. Guo, Z. Wang, J. Huang, Y. Fang, Investigation on influencing mechanisms of phosphogypsum (PG) on the ash fusion behaviors of coal, *Energy* 268 (2023) 126699.
- [19] M.-Z. Tang, Z.-Y. Wang, Y.-S. Wang, W.-J. Bao, G. Yang, Y. Sun, Characterization of the impurity phases in phosphogypsum by the EBSD-XPS method, *Spectrosc. Spectral Anal.* 42 (2022) 136–140.
- [20] S. Folek, B. Walawska, B. Wilczek, J. Miśkiewicz, Use of phosphogypsum in road construction, *Pol. J. Chem. Technol.* 13 (2011) 18–22.
- [21] M. Singh, M. Garg, C.L. Verma, S.K. Handa, R. Kumar, An improved process for the purification of phosphogypsum, *Construct. Build. Mater.* 10 (1996) 597–600.
- [22] M. Singh, Treating waste phosphogypsum for cement and plaster manufacture, *Cement and Conc. Res.* 32 (2002) 1033–1038.
- [23] M.M. Smadi, R.H. Haddad, A.M. Akour, Potential use of phosphogypsum in concrete, *Cem. Concr. Res.* 29 (1999) 1419–1425.
- [24] M. Pliaka, G. Gaidajis, Potential uses of phosphogypsum: a review, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ.* EN 57 (2022) 746–763.
- [25] F. Wu, Y. Ren, G. Qu, S. Liu, B. Chen, X. Liu, C. Zhao, J. Li, Utilization path of bulk industrial solid waste: a review on the multi-directional resource utilization path of phosphogypsum, *J. Environ. Manage.* 313 (2022) 114957.
- [26] R. El Zrelli, L. Rabaoui, H. Abda, N. Daghbouj, R. Pérez-López, S. Castet, T. Aigouy, N. Bejaoui, P. Courjault-Radé, Characterization of the role of phosphogypsum foam in the transport of metals and radionuclides in the southern Mediterranean Sea, *J. Hazard. Mater.* 363 (2019) 258–267.
- [27] L. Yang, Y. Yan, Z. Hu, Utilization of phosphogypsum for the preparation of non-autoclaved aerated concrete, *Construct. Build. Mater.* 44 (2013) 600–606.
- [28] X. Lv, L. Xiang, The generation process, impurity removal and high-value utilization of phosphogypsum material, *Nanomaterials* 12 (2022).
- [29] X. Lv, L. Xiang, Investigating the novel process for thorough removal of eutectic phosphate impurities from phosphogypsum, *J. Mater. Res. Technol.* 24 (2023) 5980–5990.
- [30] L. Ajam, A. Ben El Haj Hassen, N. Reguigui, Phosphogypsum utilization in fired bricks: radioactivity assessment and durability, *J. Build. Eng.* 26 (2019) 100928.
- [31] L.S. Alcordo, J.E. Rechegl, Phosphogypsum in agriculture: a review, *Adv. Agron.* 49 (1993) 55–118.
- [32] B. Bouargane, K. Laaboubi, M.G. Biyoune, B. Bakiz, A. Atbir, Effective and innovative procedures to use phosphogypsum waste in different application domains: review of the environmental, economic challenges and life cycle assessment, *J. Mater. Cycles Waste MANAGEM.*, (2023).
- [33] T.P. Mashifana, Chemical treatment of phosphogypsum and its potential application for building and construction, *Proc. Manuf.* 35 (2019) 641–648.
- [34] N.F. Fuleihan, Phosphogypsum disposal - the pros & cons of wet versus dry stacking, in: SYMPHOS 2011 - 1ST International Symposium on innovation and technology in the Phosphate Industry, 2012, pp. 195–205.
- [35] M. Renteria-Villalobos, I. Vioque, J. Mantero, G. Manjon, Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain, *J. Hazard. Mater.* 181 (2010) 193–203.
- [36] I. Fauziah, S. Zauyah, T. Jamal, Characterization and land application of red gypsum: a waste product from the titanium dioxide industry, *Sci. Total Environ.* 188 (1996) 243–251.
- [37] S. Wang, H. Jin, Y. Deng, Y. Xiao, Comprehensive utilization status of red mud in China: a critical review, *J. Clean. Prod.* 289 (2021) 125136.
- [38] J.E.I. Bureau, China's phosphogypsum resource utilization policy summary and interpretation strive to 2025 comprehensive utilization rate of 75%, in: J.E.I. Bureau (Ed.) https://mp.weixin.qq.com/s/?_biz=MzU3OTYzMzA5NA==&mid=2247521208&idx=7&sn=8680e4455402a0ae5df399b631ca52e7&chksm=fd61f911ca167007c8416ce94b91b523b18a7eddbe81f304be37f6ca569cc26f8a3289998590&scene=27.
- [39] Q. Wu, Z. Liu, Y. Chen, W. Teng, X. Liu, Y. Dai, Status and countermeasures of environmental Management of the Three Phosphorus'Industry in the Yangtze River Economic Belt, *Res. Environ. Sci.* 33 (2020) 1233–1240.
- [40] M. Ye, S.H. Peng, G.S. Yang, A study on nitrogen and phosphorus loads of the Yangtze Three Gorges reservoir, in: Proceedings of the ninth international symposium on river Sedimentation, VOLS 1-4, 2004, pp. 2201–2205.
- [41] H. Kamiya, H. Ohshiro, Y. Tabayashi, Y. Kano, K. Mishima, T. Godo, M. Yamamoto, O. Mitamura, Y. Ishitobi, Phosphorus release and sedimentation in three contiguous shallow brackish lakes, as estimated from changes in phosphorus stock and loading from catchment, *Landscape Ecol. Eng.* 7 (2011) 53–64.

- [42] H. Zhang, Q. Wang, J. Huang, China's policy for the marine engineering equipment industry and potential challenges: an appraisal of the new developments under the 14th five-year plans, *Front. Mar. Sci.* 9 (2022).
- [43] J. Yang, Y. Ren, S. Chen, J. Lu, Study on the mechanism and reaction characteristics of metal-supported phosphogypsum as oxygen carrier in a chemical looping gasification application, *J. Environ. Sci.* 138 (2024) 428–438.
- [44] C. Hepburn, Y. Qi, N. Stern, B. Ward, C. Xie, D. Zenghelis, Towards carbon neutrality and China's 14th five-Year plan: clean energy transition, sustainable urban development, and investment priorities, *Environ. Sci. Ecotechnol.* 8 (2021).
- [45] J. Gu, X. Liu, Z. Zhang, Road base materials prepared by multi-industrial solid wastes in China: a review, *Construct. Build. Mater.* 373 (2023).
- [46] B. Ren, Y. Zhao, H. Bai, S. Kang, T. Zhang, S. Song, Eco-friendly geopolymers prepared from solid wastes: a critical review, *Chemosphere* 267 (2021).
- [47] Y. Song, X. Xian, C. Zhang, F. Zhu, B. Yu, J. Liu, Residual municipal solid waste to energy under carbon neutrality: challenges and perspectives for China, *Resour. Conserv. Recycl.* 198 (2023).
- [48] Z. Jin, C. Cui, Z. Xu, W. Lu, Y. Su, X. He, S. Chen, W. Li, B. Wang, Recycling of waste gypsum from alpha-hemihydrate phosphogypsum: based on the atmospheric hydrothermal process, *Construct. Build. Mater.* 377 (2023).
- [49] N. Haneklaus, S. Barbosa, M.D. Basalote, M. Bertau, E. Bilal, E. Chajduk, Y. Chernysh, V. Chubur, J. Cruz, K. Dzarczykowski, P. Fröhlich, P. Grosseau, H. Mazouz, K. Kiegel, J.M. Nieto, S. Pavón, S. Pessanha, A. Pryzowicz, H. Roubík, C.R. Cánovas, H. Schmidt, R. Seeling, G. Zakrzewska-Kołtuniewicz, Closing the upcoming EU gypsum gap with phosphogypsum, *Resourc. Conserv. Recycl.* 182 (2022) 106328.
- [50] D. Xu, B. Zhong, X. Wang, X. Li, Y. Zhong, Z. Yan, J. Yang, X. Li, Y. Wang, X. Zhou, The development road of ammonium phosphate fertilizer in China, *Chin. J. Chem. Eng.* 41 (2022) 170–175.
- [51] N. Ahmad, M. Usman, H.R. Ahmad, M. Sabir, Z.U.R. Farooqi, M.T. Shehzad, Environmental implications of phosphate-based fertilizer industrial waste and its management practices, *Environ. Monit. Assess.* 195 (2023).
- [52] G. Huang, L. Wu, Y. Li, W. Zhang, Development situation and suggestions on phosphorus fertilizer industry in China, *Modern Chem. Ind.* 33 (2013) 1–4.
- [53] C. Rodrigues e Silva, F.M. de Oliveira, Natural radioactivity in mineral phosphate fertilizers and its impacts on human health: an overview, *Environ. Sci. Pollut. Res.* 30 (2023) 118149–118160.
- [54] I. Chouaybi, E.M. Moujahid, M. Bettach, From waste to clean water: effective removal of acid red 97 dye using green synthesized hydrocalumite from phosphogypsum and aluminum foils, *Inorg. Chem. Commun.* 158 (2023) 111653.
- [55] A. Ray, M. Kumar, A.A. Karim, K. Biswas, S. Mohanty, K.P. Shadangi, S. Kumar, B. Sarkar, Potassium-phosphorus-sulfur augmented biochar production from potentially toxic elements abated gypsum pond wastewater of phosphate fertilizer industry, *J. Environ. Chem. Eng.* 11 (2023) 110404.
- [56] F. Akfas, A. Elghali, A. Aboulaich, M. Munoz, M. Benzaazoua, J.-L. Bodinier, Exploring the potential reuse of phosphogypsum: a waste or a resource? *Sci. Total Environ.* 908 (2024).
- [57] Y. Cui, J. Bai, I.S. Chang, J. Wu, A systematic review of phosphogypsum recycling industry based on the survey data in China - applications, drivers, obstacles, and solutions, *Environ. Impact Assess. Rev.* 105 (2024).
- [58] Y. Ennaciri, M. Bettach, The chemical behavior of the different impurities present in phosphogypsum: a review, *Phosph. Sulfur Silicon Related Elements* 199 (2024) 129–148.
- [59] C. Nie, J. Zhong, H. Liu, X. Yang, G. Xie, J. Bi, C. Yang, Y. Shi, Y. Yi, Surface modification of anhydrous phosphogypsum and its application in isotactic polypropylene, *J. Thermoplast. Compos. Mater.* 36 (2023) 5078–5093.
- [60] R. Agrawal, S. Bhagia, A. Satlewal, A.J. Ragauskas, Urban mining from biomass, brine, sewage sludge, phosphogypsum and e-waste for reducing the environmental pollution: current status of availability, potential, and technologies with a focus on LCA and TEA, *Environ. Res.* 224 (2023).
- [61] G. Xie, Q. Guan, F. Zhou, W. Yu, Z. Yin, H. Tang, Z. Zhang, R.A. Chi, A critical review of the enhanced recovery of rare earth elements from phosphogypsum, *Molecules* 28 (2023).
- [62] L. Lu, T. Tian, R. Jin, Q. Ji, J. Zhou, Recovery of calcium and sulphur from phosphogypsum with zero by-product generation using a preparative vertical-flow electrophoresis system, *Sep. Purif. Technol.* 331 (2024).
- [63] M. Alla, M.L. El Hafiani, E.K. Gharibi, M. Ghilat, Thermodynamic study of the desulfurization process of phosphogypsum, in: MATERIALS TODAY-PROCEEDINGS, 2019, pp. 556–561.
- [64] L.F.O. Silva, M.L.S. Oliveira, T.J. Crissien, M. Santosh, J. Bolivar, L. Shao, G. L. Dotto, J. Gasparotto, M. Schindler, A review on the environmental impact of phosphogypsum and potential health impacts through the release of nanoparticles, *Chemosphere* 286 (2022).
- [65] P. Zheng, W. Li, Q. Ma, L. Xi, Mechanical properties of phosphogypsum-soil stabilized by lime activated ground granulated blast-furnace slag, *Construct. Build. Mater.* 402 (2023).
- [66] R. Fu, Y. Lu, L. Wang, H. An, S. Chen, D. Kong, The effects of admixtures on the durability properties of phosphogypsum-based cementitious materials, *Construct. Build. Mater.* 411 (2024).
- [67] S. Oubaha, A. El Machi, S. Mabroum, Y. Taha, M. Benzaazoua, R. Hakkou, Recycling of phosphogypsum and clay by-products from phosphate mines for sustainable alkali-activated construction materials, *Construct. Build. Mater.* 411 (2024).
- [68] G. Ouyang, T. Sun, Z. Yu, F. Xu, J. Bai, D. Xu, Investigation on macroscopic properties, leachability and microstructures of surface reinforced phosphogypsum-based cold-bonded aggregates, *J. Build. Eng.* 69 (2023).
- [69] Y. Liang, B. Guan, T. Cao, G. Liu, P. Tang, M. He, M.F. Cheira, A.M. Rashad, Study on the properties of an excess-sulphate phosphogypsum slag cement stabilized base-course mixture containing phosphogypsum-based artificial aggregate, *Construct. Build. Mater.* 409 (2023).
- [70] X. Meng, N. Ding, B. Lu, J. Yang, Integrated evaluation of the performance of phosphogypsum recycling technologies in China, *Waste Manag.* 171 (2023) 599–609.
- [71] E. Bilal, H. Bellefqih, V. Bourgier, H. Mazouz, D.-G. Dumitras, F. Bard, M. Laborde, J.P. Caspar, B. Guilhot, E.-L. Iatan, M. Bounakhlia, M.A. Iancu, Š. Marincea, M. Essakhraoui, B. Li, R.R. Diwa, J.D. Ramirez, Y. Chernysh, V. Chubur, H. Roubík, H. Schmidt, R. Beniazzza, C.R. Cánovas, J.M. Nieto, N. Haneklaus, Phosphogypsum circular economy considerations: a critical review from more than 65 storage sites worldwide, *Sci. Total Environ.* 414 (2023) 137561.
- [72] Z. Wei, Z. Deng, Research hotspots and trends of comprehensive utilization of phosphogypsum: bibliometric analysis, *J. Environ. Radioact.* 242 (2022) 106778.
- [73] G. Murali, M. Azab, Recent research in utilization of phosphogypsum as building materials: review, *J. Mater. Res. Technol.* 25 (2023) 960–987.
- [74] B. Corona, L. Shen, D. Reike, J. Rosales Carreón, E. Worrell, Towards sustainable development through the circular economy—A review and critical assessment on current circularity metrics, *Resourc. Conserv. Recycl.* 151 (2019) 104498.
- [75] B. Bouargane, A. Marrouche, S. El Issiouy, M.G. Biyoune, A. Mabrouk, A. Atbir, A. Bachar, R. Bellajrou, L. Boukbir, B. Bakiz, Recovery of Ca(OH)₂, CaCO₃, and Na₂SO₄ from moroccan phosphogypsum waste, *J. Mater. Cycles Waste Manage.* 21 (2019) 1563–1571.
- [76] B. Li, L. Li, X. Chen, Y. Ma, M. Zhou, Modification of phosphogypsum using circulating fluidized bed fly ash and carbide slag for use as cement retarder, *Construct. Build. Mater.* 338 (2022).
- [77] J. Yang, S. Dong, L. Xie, Q. Cen, D. Zheng, L. Ma, Q. Dai, Analysis of hydrogen-rich syngas generation in chemical looping gasification of lignite: application of carbide slag as the oxygen carrier, hydrogen carrier, and in-situ carbon capture agent, *Energy* 283 (2023) 128499.
- [78] J. Yang, L. Ma, H. Liu, Y. Wei, B. Keomounlath, Q. Dai, Thermodynamics and kinetics analysis of ca-looping for CO₂ capture: application of carbide slag, *Fuel* 242 (2019) 1–11.
- [79] Y.-C. Chen, Phosphorus and nitrogen removal from water using steel slag in soil-based low-impact development systems, *J. Water Process Eng.* 44 (2021).
- [80] J. Chen, Y. Xing, Y. Wang, W. Zhang, Z. Guo, W. Su, Application of iron and steel slags in mitigating greenhouse gas emissions: a review, *Sci. Total Environ.* 844 (2022) 157041.
- [81] W. Gao, W. Zhou, X. Iyu, X. Liu, H. Su, C. Li, H. Wang, Comprehensive utilization of steel slag: a review, *Powder Technol.* 422 (2023) 118449.
- [82] S.M. Pérez-Moreno, M.J. Gázquez, A.G. Barneto, J.P. Bolívar, Thermal characterization of new fire-insulating materials from industrial inorganic TiO₂ wastes, *Thermochim Acta* 552 (2013) 114–122.
- [83] S. Oubaha, Y. Taha, M. Loutou, M. Oualid Mghazli, M. Benzaazoua, R. Hakkou, Fired brick production using phosphogypsum and phosphate mining waste, *Construct. Build. Mater.* 403 (2023) 133149.
- [84] S.P. Raut, U.S. Patil, M.V. Madurwar, Utilization of phosphogypsum and rice husk to develop sustainable bricks, *Mater. Today-Proc.* 60 (2022) 595–601.
- [85] N. Degirmenci, The using of waste phosphogypsum and natural gypsum in adobe stabilization, *Construct.- Build.- Mater.* 22 (2008) 1220–1224.
- [86] Y. Zhou, Z. Liu, J. Shan, C. Wu, E. Lichtfouse, H. Liu, Efficient recovery of phosphate from urine using magnesite modified corn straw biochar and its potential application as fertilizer, *J. Environ. Chem. Eng.* 12 (2024) 111925.
- [87] L. Zeng, X. Bian, J. Weng, T. Zhang, Wetting-drying effect on the strength and microstructure of cement-phosphogypsum stabilized soils, *J. Rock Mech. Geotech. Eng.* (2023).
- [88] X. Wan, J. Ding, C. Mou, M. Gao, N. Jiao, Role of Bayer red mud and phosphogypsum in cement-stabilized dredged soil with different water and cement contents, *Construct. Build. Mater.* 418 (2024) 135396.
- [89] M.J. Gázquez, J.P. Bolívar, F. Vaca, R. García-Tenorio, A. Caparros, Evaluation of the use of TiO₂ industry red gypsum waste in cement production, *Cem. Concr. Compos.* 37 (2013) 76–81.
- [90] Z. Kazman, I. Shainberg, M. Gal, Effect of low levels of exchangeable sodium and applied phosphogypsum on the infiltration rate of various soils 1, *Soil Sci.* 135 (1983) 184–192.
- [91] L.-L. Zeng, X. Bian, L. Zhao, Y.-J. Wang, Z.-S. Hong, Effect of phosphogypsum on physiochemical and mechanical behaviour of cement stabilized dredged soil from Fuzhou, China, *Geomech. Energy Environ.* 25 (2021) 100195.
- [92] İ.A. Altun, Y. Sert, Utilization of weathered phosphogypsum as set retarder in Portland cement, *Cem. Concr. Res.* 34 (2004) 677–680.
- [93] J.H. Potgieter, S.S. Potgieter, R.I. McCrindle, C.A. Strydom, An investigation into the effect of various chemical and physical treatments of a south african phosphogypsum to render it suitable as a set retarder for cement, *Cement and Conc. Res.* 33 (2003) 1223–1227.
- [94] S. Zhao, L. Ma, J. Yang, D. Zheng, H. Liu, J. Yang, Mechanism of CO₂ capture technology based on the phosphogypsum reduction thermal decomposition process, *Energy Fuel* 31 (2017) 9824–9832.
- [95] S.I. Abu-Eishah, A.A. Bani-Kananeh, M.A. Allawzi, K₂SO₄ production via the double decomposition reaction of KCl and phosphogypsum, *Chem. Eng. J.* 76 (2000) 197–207.
- [96] R. Tokpayev, T. Khavaza, Z. Ibraimov, K. Kishibayev, A. Atchabarova, S. Abdumomyn, D. Abdulkhaytova, M. Nauryzbayev, Phosphogypsum conversion under conditions of SC-CO₂, *J. CO₂ Util.* 63 (2022) 102120.

- [97] J.D. Ramirez, R.R. Diwa, B.L. Palattao, N.H. Haneklaus, E.U. Tabora, A.T.B. Vii, R.Y. Reyes, Rare earths in Philippine phosphogypsum: use them or lose them, *Extractive Ind. Soc.* 10 (2022) 101082.
- [98] L. Xie, Y. Zhou, S. Xiao, X. Miao, A. Murzataev, D. Kong, L. Wang, Research on basalt fiber reinforced phosphogypsum-based composites based on single factor test and RSM test, *Construct. Build. Mater.* 316 (2022) 126084.
- [99] K.J. Mun, W.K. Hyoung, C.W. Lee, S.Y. So, Y.S. Soh, Basic properties of non-sintering cement using phosphogypsum and waste lime as activator, *Construct. Build. Mater.* 21 (2007) 1342–1350.
- [100] C. Ding, T. Sun, Z. Shui, Y. Xie, Z. Ye, Physical properties, strength, and impurities stability of phosphogypsum-based cold-bonded aggregates, *Construct. Build. Mater.* 331 (2022) 127307.
- [101] X. Li, Q. Zhang, Dehydration behaviour and impurity change of phosphogypsum during calcination, *Construct. Build. Mater.* 311 (2021) 125328.
- [102] J. Wang, Retraction notice to “utilization effects and environmental risks of phosphogypsum in agriculture: a review”, *J. Clean. Prod.* 330 (2022) 129604.
- [103] J. Hu, Z. Wang, G.D.Z. Williams, G.S. Dwyer, L. Gatiboni, O.W. Duckworth, A. Vengosh, Evidence for the accumulation of toxic metal(loid)s in agricultural soils impacted from long-term application of phosphate fertilizer, *Sci. Total Environ.* 907 (2024) 167863.
- [104] J. Li, J. Chang, T. Wang, T. Zeng, J. Li, J. Zhang, Effects of phosphogypsum on hydration properties and strength of calcium aluminate cement, *Construct. Build. Mater.* 347 (2022) 128398.
- [105] A.A. Tabikh, F.M. Miller, The nature of phosphogypsum impurities and their influence on cement hydration, *Cement and Conc. Res.* 1 (1971) 663–678.
- [106] J. Ma, J. Xu, C. Liu, Q. Yi, M. Zheng, L. Cheng, T. Song, Chemical looping combustion of sulfur paste to SO₂ by phosphogypsum oxygen carrier for sulfur acid production, *Fuel* 323 (2022) 124386.
- [107] S.P. Tayar, M.C. Palmieri, D. Bevilacqua, Sulfuric acid bioproduction and its application in rare earth extraction from phosphogypsum, *Miner. Eng.* 185 (2022) 107662.
- [108] Y. Ennacir, F.E. Mouahid, A. Bendriss, M. Bettach, Conversion of phosphogypsum to potassium sulfate and calcium carbonate in aqueous solution, in: REMCES XII - XIIIe Rencontre Marocaine SUR LA CHIMIE DE L'ETAT SOLIDE, 2013.
- [109] L. Reijnders, Phosphorus resources, their depletion and conservation, a review, *Resourc. Conserv. Recycl.* 93 (2014) 32–49.
- [110] E.P. Lokshin, O.A. Tareeva, I.R. Elizarova, Features of behavior of thorium at sulfuric acid processing of phosphogypsum, *Russ. J. Appl. Chem.* 87 (2014) 1254–1259.
- [111] E.P. Lokshin, O.A. Tareeva, I.R. Elizarova, Sorption of rare-earth elements from phosphogypsum sulfuric acid leaching solutions, *Theor. Found. Chem. Eng.* 49 (2015) 773–778.
- [112] E.P. Lokshin, O.A. Tareeva, Production of high-quality gypsum raw materials from phosphogypsum, *Russ. J. Appl. Chem.* 88 (2015) 567–573.
- [113] E.P. Lokshin, O.A. Tareeva, I.R. Elizarova, Ruling out accumulation of thorium in sulfuric acid solutions for leaching of phosphogypsum, *Russ. J. Appl. Chem.* 88 (2015) 719–723.
- [114] X. Peng, J. Zhu, T. Guo, X. Wu, H. Sun, Technology improvement of production of sulfuric acid integrated with cement from phosphogypsum, *ZKG Int.* 68 (2015) 66–71.
- [115] S. Wu, Y. Yao, X. Yao, C. Ren, J. Li, D. Xu, W. Wang, Co-preparation of calcium sulfoaluminate cement and sulfuric acid through mass utilization of industrial by-product gypsum, *J. Clean. Prod.* 265 (2020).
- [116] C. Yang, Y. Wei, F. Ye, Y. Ding, Y. Wu, Effect of additives on thermal decomposition of phosphogypsum, in: ADVANCED MATERIALS, PTS 1-3, 2012, pp. 735–+.
- [117] J. Li, S. Yu, L. Ma, Feasibility analysis for decomposition of phosphogypsum in cement precalciner, *Environ. Prog. Sustain. Energy* 30 (2011) 44–49.
- [118] H.M. Henrique, P.M. Parreira, Sulfur dioxide production from phosphogypsum: Thermodynamic analysis and experimental results, in: Advanced Powder Technology VII, 2010, pp. 253–258.
- [119] Y. Chen, L. Ma, R. Yang, H. Zhang, L. Xie, Q. Dai, The carbonic acid reaction of phosphogypsum decomposition slag in the three-phase fluidized bed, in: Advances In Chemical Engineering II, PTS 1-4, 2012, pp. 2921–2926.
- [120] W. Du, L. Ma, Q. Pan, Q. Dai, M. Zhang, X. Yin, X. Xiong, W. Zhang, Full-loop CFD simulation of lignite chemical looping gasification with phosphogypsum as oxygen carrier using a circulating fluidized bed, *Energy* 262 (2023) 125451.
- [121] J. Yang, S. Liu, L. Ma, H. Liu, J. Yang, Z. Guo, R. Ao, Q. Dai, Syngas preparation by NiO-CaSO₄-based oxygen carrier from chemical looping gasification technology, *J. Energy Inst.* 94 (2021) 191–198.
- [122] B. Yan, L. Ma, J. Ma, Z. Zi, X. Yan, Mechanism analysis of ca S Transformation in Phosphogypsum Decomposition with Fe Catalyst, *Ind. Eng. Chem. Res.* 53 (2014) 7648–7654.
- [123] B. Yan, L. Ma, L. Xie, J. Ma, Z. Zi, X. Yan, Reaction mechanism for iron catalyst in the process of phosphogypsum decomposition, *Ind. Eng. Chem. Res.* 52 (2013) 17383–17389.
- [124] X. Yan, L. Ma, B. Zhu, D. Zheng, Y. Lian, Reaction mechanism process analysis with phosphogypsum decomposition in multiatmosphere control, *Ind. Eng. Chem. Res.* 53 (2014) 19453–19459.
- [125] X. Lv, L. Xiang, The generation process, impurity removal and high-value utilization of phosphogypsum material, *Nanomaterials* 12 (2022) 3021.
- [126] S. Liu, F. Wu, G. Qu, L. Kuang, Y. Liu, Y. Ren, B. Chen, J. Li, Preparation of high-performance lightweight materials based on the phosphogypsum-inorganic material system, *Sustain. Chem. Pharmacy* 30 (2022) 100901.
- [127] R.P. Costa, M.H.G. de Medeiros, E.D. Rodriguez Martinez, V.A. Quarcioli, S. Suzuki, A.P. Kirchheim, Effect of soluble phosphate, fluoride, and pH in Brazilian phosphogypsum used as setting retarder on Portland cement hydration, *Case Stud. Constr. Mater.* 17 (2022) e01413.
- [128] K. Qamouche, A. Chetaine, A. Elyahyaoui, A. Moussaif, R. Touzani, A. Benkdad, H. Amsil, K. Laraki, H. Marah, Radiological characterization of phosphate rocks, phosphogypsum, phosphoric acid and phosphate fertilizers in Morocco: an assessment of the radiological hazard impact on the environment, *Mater. Today:* Proc. 27 (2020) 3234–3242.
- [129] S. Wu, X. Yao, C. Ren, Y. Yao, W. Wang, Recycling phosphogypsum as a sole calcium oxide source in calcium sulfoaluminate cement and its environmental effects, *J. Environ. Manage.* 271 (2020) 110986.
- [130] J. Yang, L. Ma, J. Tang, H. Liu, B. Zhu, Y. Lian, X. Cui, Chemical thermodynamics analysis for in-situ gasification chemical looping combustion of lignite with phosphogypsum for syngas, *Appl. Therm. Eng.* 112 (2017) 516–522.
- [131] L. Bing, J. Shu, M. Chen, X. Zeng, R. Liu, Y. Yong, A new basic burning raw material for simultaneous stabilization/solidification of PO43-P and F- in phosphogypsum, *Ecotoxicol. Environ. Safety* 252 (2023).
- [132] F. Wu, C. Jin, G. Qu, Y. Liu, C. Wang, B. Chen, S. Liu, J. Li, Enhancement of phosphogypsum mechanical block with the addition of iron and aluminum salts, *J. Build. Eng.* 52 (2022) 104397.
- [133] J. Li, X. Peng, J. Zheng, M. Mao, X. Sun, J. Wang, X. Li, X. Chai, Z. Lin, W. Liu, Simultaneous removal of phosphorus and organic contaminants from phosphogypsum using hydrothermal method for gypsum resource regeneration, *J. Environ. Chem. Eng.* 10 (2022) 108441.
- [134] W. Zhang, L. Zhao, M. Xue, X. Duan, C. Feng, J. Zhu, Efficient precipitation of soluble phosphorus impurities in the recycling of phosphogypsum to produce hemihydrate gypsum, *J. Clean. Prod.* 396 (2023) 136455.
- [135] Z. Zhou, Y. Lu, W. Zhan, L. Guo, Y. Du, T.C. Zhang, D. Du, Four stage precipitation for efficient recovery of N, P, and F elements from leachate of waste phosphogypsum, *Miner. Eng.* 178 (2022).
- [136] Y. Chernysh, 10 - recycling of radioactive phosphogypsum wastes, in: F. Pacheco-Torgal, J.O. Falkingham, J.A. Galaj (Eds.), *Advances in the Toxicity of Construction and Building Materials*, WOODHEAD PUBLISHING, 2022, pp. 225–240.
- [137] M. Wang, X. Yuan, W. Dong, Q. Fu, X. Ao, Q. Chen, Gradient removal of Si and P impurities from phosphogypsum and preparation of anhydrous calcium sulfate, *J. Environ. Chem. Eng.* 11 (2023) 110312.
- [138] C. Li, S. Wang, Y. Wang, X. An, G. Yang, Y. Sun, Study on synergistic leaching of potassium and phosphorus from potassium feldspar and solid waste phosphogypsum via coupling reactions, *Chin. J. Chem. Eng.* (2023).
- [139] J. Hou, X. He, X. Ni, Hydration mechanism and thermodynamic simulation of ecological ternary cements containing phosphogypsum, *Mater. Today Commun.* 33 (2022) 104621.
- [140] M. Statauskas, D. Vaiciukynienė, A. Grinys, R. Paul Borg, Mechanical properties and microstructure of ternary alkali activated system: red brick waste, metakaolin and phosphogypsum, *Construct. Build. Mater.* 387 (2023) 131648.
- [141] T. Ning, Efect of wet-process phosphoric acid technology on phosphogypsum quality, in: CHONGQING UNIVERSITY, 2011.
- [142] I. Sampón, F. García-Labiano, M.T. Izquierdo, L.F. de Diego, Understanding the structural changes on Fe₂O₃/Al₂O₃ oxygen carriers under chemical looping gasification conditions, *Fuel* 355 (2024) 129326.
- [143] Q. Hao, L. Zhu, Y. Wang, Y. He, X. Zeng, J. Zhu, Achieving near-zero emission and high-efficient combined cooling, heating and power based on biomass gasification coupled with SOFC hybrid system, *Fuel* 357 (2024) 129751.
- [144] H. Li, Z. Sun, Y. Cao, Particles attrition of binary mixtures in the coal-fueled chemical looping system based on fluidized bed, *Particuology* 86 (2024) 281–290.
- [145] Y. Niu, J. Xu, L. Chen, S. Guo, F. Guo, Y. Zhang, J. Wu, Cyclic catalytic Fe-N doped composite particle electrodes derived from gasification fine slag for non-selective mineralization of organic wastewater, *Fuel* 355 (2024) 129449.
- [146] R.-Y. Chein, W.-H. Hsu, Thermodynamic equilibrium analysis of H₂-rich syngas production via sorption-enhanced chemical looping biomass gasification, *Renew. Energy* 153 (2020) 117–129.
- [147] Z. Xia, X. Song, W. Wang, Reduction mechanism study on sorption enhanced chemical looping gasification of biomass waste rice husk for H₂ production over multi-functional Ni_xCa_{1-x}O particles, *Fuel Process. Technol.* 209 (2020) 106524.
- [148] W. Lulu, S. Laihong, J. Shouxie, S. Tao, Chemical looping gasification with potassium-catalyzed petroleum coke for enhanced production of H₂ and H₂S, *Chem. Eng. J.* 397 (2020) 124631.
- [149] Z. Sun, C.K. Russell, K.J. Whitty, E.G. Eddings, J. Dai, Y. Zhang, M. Fan, Z. Sun, Chemical looping-based energy transformation via lattice oxygen modulated selective oxidation, *Prog. Energy Combust. Sci.* 96 (2023).
- [150] G. Liu, G. Lisak, Cu-based oxygen carriers for chemical looping processes: opportunities and challenges, *Fuel* 342 (2023).
- [151] X. Zhang, R. Liu, T. Liu, C. Pei, J. Gong, Redox catalysts for chemical looping methane conversion, *Trend Chem.* 5 (2023) 512–525.
- [152] F. Tahir, M.A. Saeed, U. Ali, Biomass energy perspective in Pakistan based on chemical looping gasification for hydrogen production and power generation, *Int. J. Hydrogen Energy* 48 (2023) 18211–18232.
- [153] X. Zhang, A.C.K. Yip, S. Pang, Advances in the application of active metal-based sorbents and oxygen carriers in chemical looping biomass steam gasification for H₂ production, *Int. J. Hydrogen Energy* 48 (2023) 10394–10422.
- [154] R. Ramezani, L. Di Felice, F. Gallucci, A review of chemical looping reforming technologies for hydrogen production: recent advances and future challenges, *J. Physi.-Energy* 5 (2023).
- [155] S. Sunphorka, P. Kanokwannakorn, P. Kuchonthara, Chemical looping combustion of methane or coal by Fe₂O₃/CaSO₄ mixed oxygen carrier, *Arab. J. Sci. Eng.* 44 (2019) 5501–5512.

- [156] N. Ding, Y. Zheng, C. Luo, G. Bian, P. Fu, C. Zheng, Development of binder-supported CaSO_4 oxygen carriers for chemical looping combustion of methane, in: Cleaner Combustion And Sustainable World, 2012, pp. 851-857.
- [157] Y. Liu, M. Gao, X. Zhang, X. Hu, Q. Guo, Characteristics of a CaSO_4 composite oxygen carrier supported with an active material for in situ gasification chemical looping combustion of coal, *RSC Adv.* 8 (2018) 23372–23381.
- [158] Q. Guo, X. Hu, Y. Liu, W. Jia, M. Yang, M. Wu, H. Tian, H.-J. Ryu, Coal chemical-looping gasification of ca-based oxygen carriers decorated by CaO , *Powder Technol.* 275 (2015) 60–68.
- [159] Y. Guan, Y. Liu, B. Wang, Y. Feng, Q. Lyu, Reaction characteristics and lattice oxygen transformation mechanism of semi-coke chemical looping gasification with $\text{Fe}_2\text{O}_3/\text{CaSO}_4\text{-Al}_2\text{O}_3$ oxygen carrier, *J. Clean. Prod.* 369 (2022).
- [160] Q.I.N. Cui-juan, S. Lai-hong, Z. Min, X. Jun, Experimental study on the effect of gasification medium on chemical looping combustion of coal with CaSO_4 oxygen carrier, *Proc. Chin. Soc. Electr. Eng.* 29 (2009) 48–55.
- [161] Y. Liu, Q. Guo, Investigation into syngas generation from solid fuel using CaSO_4 -based chemical looping gasification process, *Chin. J. Chem. Eng.* 21 (2013) 127–134.
- [162] J. Yang, S. Liu, Z. Guo, R. Ao, Q. Dai, Y. Sun, Z. Deng, X. Tan, Y. Yang, L. Ma, Fluidization and reaction behavior in chemical looping gasification of lignite, *Sustain. Energy Fuels* 5 (2021) 3656–3665.
- [163] Y. Liu, Q. Guo, Y. Cheng, H.-J. Ryu, Reaction mechanism of coal chemical looping process for syngas production with CaSO_4 oxygen carrier in the CO_2 atmosphere, *Ind. Eng. Chem. Res.* 51 (2012) 10364–10373.
- [164] Y. Liu, W. Jia, Q. Guo, H. Ryu, Effect of gasifying medium on the coal chemical looping gasification with CaSO_4 as oxygen carrier, *Chin. J. Chem. Eng.* 22 (2014) 1208–1214.
- [165] J. Yang, L. Ma, S. Dong, H. Liu, S. Zhao, X. Cui, D. Zheng, J. Yang, Theoretical and experimental demonstration of lignite chemical looping gasification of phosphogypsum oxygen carrier for syngas generation, *Fuel* 194 (2017) 448–459.
- [166] J. Yang, L. Ma, D. Zheng, S. Zhao, Y. Peng, Reaction mechanism for syngas preparation by lignite chemical looping gasification using phosphogypsum oxygen carrier, *Energy Fuel* 32 (2018) 7857–7867.
- [167] J. Yang, Y. Wei, J. Yang, H. Xiang, L. Ma, W. Zhang, L. Wang, Y. Peng, H. Liu, Syngas production by chemical looping gasification using fe supported on phosphogypsum compound oxygen carrier, *Energy* 168 (2019) 126–135.
- [168] J. Yang, L. Ma, J. Yang, H. Xiang, H. Liu, Z. Guo, Mechanism of lignite-to-pure syngas low temperature chemical looping gasification synergistic in situ S capture, *Fuel* 222 (2018) 675–686.
- [169] J. Yang, L. Ma, J. Yang, H. Liu, S. Liu, Y. Yang, L. Mu, Y. Wei, R. Ao, Z. Guo, Q. Dai, H. Wang, Thermodynamic and kinetic analysis of CuO-CaSO_4 oxygen carrier in chemical looping gasification, *Energy* 188 (2019).
- [170] S. Zheng, P. Ning, L. Ma, X. Niu, W. Zhang, Y. Chen, Reductive decomposition of phosphogypsum with high-sulfur-concentration coal to SO_2 in an inert atmosphere, *Chem. Eng. Res. Des.* 89 (2011) 2736–2741.
- [171] X. Yan, Study on phosphogypsum fluidization for preparation of CaO , in, KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY, 2015.
- [172] D. Zheng, L. Ma, R. Wang, J. Yang, Q. Dai, Decomposing properties of phosphogypsum with iron addition under two-step cycle multi-atmosphere control in fluidised bed, *Waste Manag. Res.* 36 (2018) 183–193.
- [173] B. Yan, Mechanism analysis of phosphogypsum decomposition with catalyst in low temperature and Ca, S transformation, in, Kunming University of Science and Technology, 2014.
- [174] D. Zheng, The research on phosphogypsum's decomposition with Fe-based addition in multiple-atmosphere control, in, Kunming University of Science and Technology, 2018.
- [175] J. Yang, L. Ma, J. Yang, Y. Xiang, Research advances in chemical looping technology for preparation of syngas by phosphogypsum and lignite, *Modern Chem. Ind.* 38 (2018) 67–70.
- [176] R.F. Firmano, L.R.F. Alleoni, Properties of Fe-oxides and Fe fractionation in an Oxisol amended over long term with lime and phosphogypsum, *Appl. Geochem.* 135 (2021) 105116.
- [177] J. Yang, L. Ma, J. Yang, Z. Guo, H. Liu, W. Zhang, L. Wang, Gasification performance and mechanism of high-silicon phosphogypsum oxygen carrier in chemical looping gasification, *Energy Fuel* 33 (2019) 11768–11780.
- [178] T.M. Atanackovic, M. Janev, L. Oparnica, S. Pilipovic, D. Zorica, Space-time fractional Zener wave equation, *Proc. Roy. Soc. A-Math. Phys. Eng. Sci.* 471 (2015).
- [179] P.A. Manohar, M. Ferry, T. Chandra, Five decades of the zener equation, *ISIJ Int.* 38 (1998) 913–924.
- [180] Z. Li, Y. Liu, N. Cai, Understanding the effect of inert support on the reactivity stabilization for synthetic calcium based sorbents, *Chem. Eng. Sci.* 89 (2013) 235–243.
- [181] S.-J.L. Kang, Sintering: Densification, Grain Growth & Microstructure, *Int. J. Powder Metall.* (2005) 41.
- [182] J. Yang, Research on chemical looping gasification of lignite with Cu/Fe metal doped phosphogypsum composite oxygen carrier, in, Kunming University of Science and Technology, 2020.
- [183] J. Yang, L. Ma, H. Liu, Z. Guo, Q. Dai, W. Zhang, K. Bounkhong, Chemical behavior of fluorine and phosphorus in chemical looping gasification using phosphogypsum as an oxygen carrier, *Chemosphere* 248 (2020).
- [184] J. Yang, Analysis of the enhanced lignite gasification process by chemical looping gasification technology with transition metal/phosphogypsum oxygen carrier, in, Kunming University of Science and Technology, 2019.
- [185] J. Men, Y. Li, P. Cheng, Z. Zhang, Recycling phosphogypsum in road construction materials and associated environmental considerations: a review, *Heliyon* 8 (2022).
- [186] J. Yang, Y. Ren, J. Lu, H. Liu, Z. Zhang, H. Pang, K. Bounkhong, Chemical looping gasification with a CuFe_2O_4 -enhanced phosphogypsum oxygen carrier during reduction in a fluidized bed reactor, *Chem. Eng. J.* 426 (2021).
- [187] D. Ma, Q. Wang, Experimental study on preparation of calcium oxide by coal reduction of calcium sulfate in carbon dioxide atmosphere, *J. Chem. Technol. Biotechnol.* 98 (2023) 2192–2202.
- [188] Q. Chen, Q. Zhang, A. Fourie, C. Xin, Utilization of phosphogypsum and phosphate tailings for cemented paste backfill, *J. Environ. Manage.* 201 (2017) 19–27.
- [189] W. Jiang, C. Wu, C. Zhang, X. Wang, Y. Li, S. Wu, Y. Yao, J. Li, W. Wang, Effect of CaO sourced from CaCO_3 or CaSO_4 on phase formation and mineral composition of iron-rich calcium sulfoaluminate clinker, *Materials* 16 (2023).
- [190] R. Zhang, X. Wang, H. Yu, Research on modeling and optimization method of cement clinker calcination process based on EGPR model and steady state detection, *IEEE Access* 11 (2023) 39484–39495.
- [191] Y. Zhao, R. Wu, S. Zhang, H. Qu, X. Hao, Soft sensor modeling of cement clinker quality: a novel timing matching technique and data decoupling approach, *Meas. Sci. Technol.* 34 (2023).
- [192] L. Ma, P. Ning, S. Zheng, X. Niu, W. Zhang, Y. Du, Reaction mechanism and kinetic analysis of the decomposition of phosphogypsum via a solid-state reaction, *Ind. Eng. Chem. Res.* 49 (2010) 3597–3602.
- [193] L. Ma, P. Ning, Y. Zhang, X. Wang, Experimental and modeling of fixed-bed reactor for yellow phosphorous tail gas purification over impregnated activated carbon, *Chem. Eng. J.* 137 (2008) 471–479.
- [194] S. Meskini, I. Mechhnou, M. Benmansour, T. Remmal, A. Samdi, Environmental investigation on the use of a phosphogypsum-based road material: radiological and leaching assessment, *J. Environ. Manage.* 345 (2023) 118597.
- [195] D. Ma, Q. Wang, Copper slag assisted coke reduction of phosphogypsum for sulphur dioxide preparation, *Chin. J. Chem. Eng.* (2023).
- [196] D. Zheng, L. Ma, R. Wang, J. Yang, Q. Dai, Research on thermal decomposing properties of phosphogypsum with fe addition under multi-atmosphere control, *Thermochim Acta* 661 (2018) 59–66.
- [197] G.S. dos Reis, G.L. Dotto, J. Vieillard, M.L.S. Oliveira, S.F. Lütke, A. Grimm, L.F.O. Silva, É.C. Lima, M. Naushad, U. Lassi, Nickel-aluminium layered double hydroxide as an efficient adsorbent to selectively recover praseodymium and samarium from phosphogypsum leachate, *J. Alloys Comp.* 960 (2023) 170530.
- [198] W. Zhang, F. Zhang, L. Ma, J. Yang, Y. Wei, D. Kong, CO_2 capture and process reinforcement by hydrolysate of phosphogypsum decomposition products, *J. CO₂ Util.* 36 (2020) 253–262.
- [199] W. Zhang, F. Zhang, L. Ma, P. Ning, J. Yang, Y. Wei, An efficient methodology to use hydrolysate of phosphogypsum decomposition products for CO_2 mineral sequestration and calcium carbonate production, *J. Clean. Prod.* 259 (2020).
- [200] S. Zhao, L. Ma, D. Wang, J. Yang, Y. Peng, L. Wang, Sulfur-looping mechanism for the two-step cyclic process of fluidized-bed CO_2 capture and phosphogypsum thermal decomposition assisted by H_2S , *Energy Fuel* 31 (2017) 12582–12593.
- [201] C. Rosa, Evaluation of solubility data of the system $\text{CO}_2-\text{H}_2\text{O}$ from 273 K to the critical point of water, *J. Phys. Chem. Reference Data* 20 (1991) 575–589.