Research progress of CaO-based absorbents prepared from different calcium sources

Hongtao Zhao¹, Man Zhang²*

¹National Energy Investment Group Co., Ltd., Beijing 100011, China
²School of Environmental Engineering, North China Institute of Science and Technology, Langfang 065201, China

*Corresponding author’s e-mail: hous01@163.com

Abstract. CaO-based absorbent have been regarded as an ideal high-temperature CO₂ absorbent. However, as the number of cycles increases, the CO₂ absorption performance gradually decreases. In order to maintain high CO₂ removal efficiency, a large amount of fresh absorbent is required, resulting in a significant increase in economic costs and equipment load. Therefore, it is urgent to reduce the raw material cost of the CaO-based absorbent and maintain a high cycle absorption efficiency and stability by modification. Firstly, the decarburization principles of CaO-based absorbent and the reasons for absorption performance degradation were analyzed. Then, the main modification methods and the respective effects of CaO-based absorbents prepared using different calcium sources (natural minerals, chemical agents, bulk industrial solid waste) were summarized, from the aspects of enhancing absorption efficiency, improving cycling stability and reducing costs. The results show that the CaO-based absorbent prepared by industrial solid waste with high calcium content has good CO₂ absorption efficiency and cycle stability. A small amount of impurities in the solid waste may help to improve the corrosion resistance and wear resistance of CaO-based absorbent. In addition, the production cost of CaO-based absorbents can be minimized through the integration with industrial production.

1. Introduction

China is now facing tremendous pressure from carbon dioxide emissions[1]. Coal-fired power plants are the main CO₂ emitters; therefore, to alleviate CO₂ emission, the most effective way is to capture CO₂ directly from coal-fired flue gas[2,3]. However, due to the high temperature of the flue gas and the low partial pressure of CO₂, it is necessary to find an efficient, stable, and cheap absorbent to achieve efficient CO₂ capture under the actual temperature and pressure conditions[4]. High temperature CaO-based absorbents can cut off the cooling treatment before CO₂ separation, thereby reducing energy loss, saving energy, and reducing emission. They are also featured with various advantages such as a simple reaction mechanism, good absorption selectivity, large cyclic absorption capacity (theoretical maximum absorption is 0.786g CO₂/1g absorbent), a wide distribution of raw materials (limestone, dolomite, etc.), low price, no solvent loss, and convenient transportation, storage, and usage[5-8]. At the same time, the carbonation reaction of CaO-based absorbents is an exothermic reaction with high thermal grade, which can be almost directly integrated with the boiler power generation system, with minor changes to the existing system and equipment. Therefore, CaO-based absorbents have been regarded as an ideal high-temperature CO₂ absorbent[9,10].
However, as the number of cycles increases, the CO₂ capture performance of CaO-based absorbents, especially CaO-based absorbents prepared using natural mineral raw materials, tend to decline.[11] For example, the absorption efficiency of natural limestone CaO-based absorbents decreases from 80% to about 20% after ten times of collection.[12]. In order to maintain high carbon dioxide removal efficiency, it is necessary to supplement a large amount of fresh absorbent, which however, greatly increases the operating cost and equipment load. The cost of the CaO high-temperature circulating system for CO₂ capture depends largely on the cost of raw material of the absorbent, the cyclic absorption capacity and stability of the absorbent.[13,14]. Therefore, there is an urgent need to reduce the raw material cost of the CaO-based absorbent, and to maintain the high cycle absorption capacity and stability of the absorbent through modification.

This paper first analyzes the decarburization principles of CaO-based absorbents and the reasons for absorption performance degradation; then it summarizes the main modification methods and the respective effects of CaO-based absorbents prepared using different calcium sources (i.e. natural minerals (limestone, dolomite), chemical agents with low impurity content, and bulk industrial solid waste with high calcium content, from the aspects of enhancing absorption efficiency, improving cycling stability and reducing costs.

2. Analysis of decarburization principles and performance degradation of CaO-based absorbent

The decarburization principles of the CaO-based absorbents prepared using different calcium sources are basically the same, that is, the active component CaO in the calcium-based absorbent undergoes a carbonation/calcination reversible reaction (the cyclic reaction equations are shown in Reactions (1) and (2)). In Reaction (1), the reaction between CaO and CO₂ to generate CaCO₃ is a strong exothermic process, during which the heat released can be partially used in the calcination and regeneration process in Reaction (2). Figure 1 shows the cyclic capture process of CO₂ in coal-fired flue gas using CaO-based absorbent. The calcium-based absorbent circulates between the carbonation reactor and the calcination reactor. In the carbonation reactor, when the reaction temperature is 600–700°C, the CO₂ in the coal-fired flue gas with a volume fraction of 8–15% reacts with CaO in the absorbent to generate CaCO₃; in the calcination reactor, when the temperature is greater than 900°C, the generated CaCO₃ is thermally decomposed into CaO and CO₂. The compressed high-concentration CO₂ gas is stored or used while the calcined and regenerated CaO absorbent enters the next reaction cycle.

There are three reasons for the degradation of the CO₂ absorption performance of CaO-based absorbents: ① high temperature sintering; ② product layer coating; ③ micropore blocking by product layer. Among them, high temperature sintering, which leads to closed pore structure and reduced specific surface area, is the main reason for the decrease in absorbent activity.[15,16]. Analysis of sintering kinetics shows that the CaO sintering process is mainly controlled by lattice diffusion. The calcination temperature is generally greater than 900°C, leading to lower surface free energy of the absorbent crystal grains; as the crystal grains grows, they continue to bond and large grains grow up by engulfing small grains, which leads to the volume shrink of the entire CaO particle (Figure 2).[17]. From the SEM image of the pore structure of the CaO-based absorbent after multiple cycles, it can be seen that as the number of cycles increases, the number of small pores decreases while that of large pores increases, the absorbent particles continue to shrink, and the specific surface area and porosity decrease with the occurrence of sintering.[18]. Secondly, CaO at the outer layer of the calcium-based absorbent particles is converted into CaCO₃ in the carbonation reaction, and the generated CaCO₃ product layer covers the surface of the unreacted absorbent, preventing the CO₂ molecules from further diffusing into the interior of the CaO particles. In addition, the molar volume of CaCO₃ (36.9 cm³/mol) is much larger than that of CaO (16.9 cm³/mol)[19], so its particle volume rapidly increases during the absorption process, thereby reducing the gap between the particles and leading to micropore clogging, which further increases the CO₂ diffusion resistance and brings down its CaO absorption capacity. Therefore, in order to maintain the high activity of the CaO-based absorbent after multiple cycles, it is necessary not only to make calcium-based absorbent particles with a smaller size and a larger specific surface area, but also to maintain their stable microstructure after calcination for
multiple cycles. In addition, changing the conditions and bringing down the calcination temperature can also help to alleviate the sintering of CaO particles.[20]

\[
\begin{align*}
\text{CaO} (s) + \text{CO}_2 (g) & \rightarrow \text{CaCO}_3(s), \Delta H = -178 \text{ kJ/mol} \quad (1) \\
\text{CaCO}_3(s) & \rightarrow \text{CaO} (s) + \text{CO}_2 (g), \Delta H = +178 \text{ kJ/mol} \quad (2)
\end{align*}
\]

Figure 1. The cyclic capture process of CO₂ in coal-fired flue gas using CaO-based absorbent.

Figure 2. Schematic diagram of internal structure changes of calcium-based absorbent particles during cyclic calcination.[17]

Figure 3. The SEM image of the pore structure of the CaO-based absorbent after multiple cycles.[18]

3. Calcium-based CO₂ absorbents based on different calcium sources and their respective modification methods

3.1. Calcination and modification of natural minerals
Limestone and dolomite, among all the natural minerals, are important sources of calcium for preparing CaO-based absorbents due to their high calcium content, wide distribution, low price, and convenient availability\cite{21,22}. The preparation process of natural CaO-based absorbent is relatively simple: conduct calcination treatment at a high temperature above 900°C to decompose calcium carbonate and magnesium carbonate in natural minerals into calcium oxide and magnesium oxide. Table 1 shows the composition of limestone and dolomite. Because the content of MgO that can be used as a supporting framework in dolomite is higher than that in limestone, the CaO absorbent made using dolomite is better in terms of sintering resistance and cyclic stability. However, since the natural limestone/dolomite with a small specific surface area and small pore volume as well as complex components, the CO₂ cycle absorption efficiency of the limestone/dolomite absorbent without activation treatment attenuates significantly. To solve this, the current modification methods can be used are extraction and reconstruction, doping with inert component, and high-temperature pretreatment\cite{23-25}.

### Table 1. Chemical composition of limestone and dolomite determined by XRF\cite{21}

|          | CaO  | MgO  | Al₂O₃ | Fe₂O₃ | SiO₂  | Loss | Surplus |
|----------|------|------|-------|-------|-------|------|---------|
| Limestone| 54.70| 0.36 | 0.05  | 0.04  | 1.18  | 43.15| 0.52    |
| Dolomite | 30.11| 20.41| 0.44  | 0.20  | 2.01  | 46.43| 0.51    |

3.1.1 **Extraction and reconstruction**

Extracting the active component CaO and rebuilding a CaO-based absorbent with a high pore volume and specific surface area can make up for the shortcomings of the natural mineral. Adanez et al.\cite{12,26} used acetic acid solution and limestone to prepare calcium acetate, which was later used to prepare the absorbent; the absorption is conducted using the fixed bed reactor at 650°C and calcination is conducted at 920°C. The absorption performance evaluation shows that after 20 absorption/calcination cycles, the absorption efficiency is still as high as 50%, while that of the unmodified absorbent is only about 15% under the same conditions. When the calcination temperature increases from 920°C to 1100°C, the CO₂ absorption efficiency of the absorbent modified with acetic acid is still significantly higher than that of the unmodified one, thus indicating that the modified absorbent can deliver better anti-sintering performance.

3.1.2 **Doping with inert component**

Adding an inert medium high with a melting point can keep the absorbent in the shape of small grains; in this way, they can act as scaffolds that help to avoid the closure of internal pores, thereby improving the anti-sintering performance of the absorbent and ultimately enhancing the absorption efficiency and cyclic stability of CaO-based absorbent. Salvador et al.\cite{27} mechanically mixed sodium chloride and limestone, pointing out that the cyclic absorption efficiency of the absorbent was improved to a certain extent after the addition of the Na⁺ salt. Aihara et al.\cite{28} found that the addition of CaTiO₃ can effectively prevent the sintering of the absorbent particles, thereby improving the recycling and regeneration stability. Li et al.\cite{29} suggested that the Mn⁺ salt can greatly improve the cycle absorption efficiency and capacity. Ca₁₂Al₁₄O₃₃, as an inert, high-temperature resistant material that does not react with CO₂, can effectively prevent CaO from sintering during the cyclic calcination process. Li et al.\cite{9} proposed that CaO and calcium aluminate cement can generate Ca₁₂Al₁₄O₃₃ at high temperature, thereby ensuring that the CaO absorbent is of high cycle absorption efficiency and good abrasion resistance. When the mass ratio of Ca₁₂Al₁₄O₃₃ to CaO is 1:3, the CO₂ absorption efficiency of the absorbent still stands at 65% after 50 times of calcination cycles.

3.1.3 **High-temperature pretreatment**

High-temperature pretreatment of natural minerals such as limestone can help to form a CaO hard framework with a relatively stable pore structure. This framework structure can prevent the absorbent particles from collapsing during multiple cycles of calcination and maintain the stability of the CaO-
based absorbent structure. Manovic et al.\textsuperscript{30} found that after pre-treating limestone at 1000°C for 24 h, the phenomenon of "self-activation" will occur, that is, the CO\textsubscript{2} absorption capacity of the modified CaO-based absorbent was lower than that of unmodified in the first few cycles; as the number of cycles increased, the absorption efficiency of the modified sample increased to a certain extent, slightly higher than that of the unmodified one. After 30 calcination cycles, the CO\textsubscript{2} absorption efficiency of the absorbent could still reach about 50%. Ozcan et al.\textsuperscript{31} further pointed out that the smaller the size of the absorbent particles, the more significant the positive effect of high-temperature pretreatment on the cyclic stability. However, this method is not suitable for all CaO-based absorbents; for example, some high-purity lime stones tend to have lower absorption efficiency after pretreatment.

3.2. Chemical reagent synthesis and modification

Natural minerals such as limestone and dolomite have small specific surface area, small pore volume, and complex phase composition and mineral phase structure, resulting in limited space and means for the modification of natural CaO-based absorbents. In addition, higher modification cost will certainly weaken the economic advantage of natural CaO-base absorbent. Therefore, researchers have been trying to synthesize absorbent particles with better pore structure, larger specific surface area, and nanometer-sized absorbent particles with the chemical reagent precursor with lower impurity content and definite mineral phase composition. They also endeavored to enhance their sintering resistance and cyclic absorption performance by compounding specific functional elements.

3.2.1 Pore structure regulation using different precursors

The CO\textsubscript{2} absorption performances of CaO-based absorbents prepared using different precursors are different. Generally, organic metal is superior to inorganic metal as a precursor in this respect. What’s more, CO\textsubscript{2} absorption activity and anti-sintering ability of absorbents prepared using different organic precursors are also different. Commonly used organic precursors are calcium propionate, calcium acetylacetonate, calcium acetate, calcium oxalate, calcium gluconate, and calcium isooctanoate. Lu et al.\textsuperscript{32} found that the CaO-based absorbent made using calcium propionate and calcium acetate has bigger specific surface area and pore volume, therefore higher absorption capacity. Li et al.\textsuperscript{12} tested the absorbent made from calcium acetate, pointing out that after 100 cycles, its absorption efficiency remained at about 40%. In order to improve the anti-sintering ability of CaO absorbent, Huang et al.\textsuperscript{33} added ZrO\textsubscript{2} inert components with higher Tammann temperature to calcium acetate; after precipitation, alcohol washing and drying using ammonia water, the obtained zirconium-modified CaO-based absorbent showed a good mesoporous structure. When Zr:Ca is 1:40, the maximum absorption efficiency can reach 82.6%; after 10 cycles, it can still stand at 73.6%, showing good dispersibility without agglomeration.

The CaO-based absorbent prepared using inorganic metal precursors under certain conditions also have good absorption activity and anti-sintering ability. Karami et al.\textsuperscript{14} obtained CaO-based absorbent with higher specific surface area (16.5 m\textsuperscript{2}/g) and pore volume (0.35 cm\textsuperscript{3}/g) using the alkaline precipitant and inorganic calcium precursor solutions such as calcium nitrate and calcium chloride. The CO\textsubscript{2} absorption efficiency of this absorbent is as high as 98%, and it remains above 70% after 17 cycles. Applying precipitation method on Ca(OH)\textsubscript{2} precursor can generate light CaCO\textsubscript{3} with higher porosity and larger specific surface area. Surfactants can help to adjust the morphology of CaCO\textsubscript{3}, on which basis the CaO-based absorbent with more developed pore structure can be prepared after calcination. Gupta et al.\textsuperscript{15} injected CO\textsubscript{2} into the Ca(OH)\textsubscript{2} suspension liquid to obtain precipitated calcium carbonate with a high specific surface area, and then obtained mesoporous CaO absorbent after calcination. Yang et al.\textsuperscript{36} added a surfactant to the Ca(OH)\textsubscript{2} suspension when CO\textsubscript{2} was bubbled into it; the surfactant stabilized the presence of CO\textsubscript{2} bubbles and helped to complete the formation of CaCO\textsubscript{3}, thereby obtaining a CaO-based absorbent with a hollow structure. This absorbent is large in both the specific surface area and pore volume, exhibiting excellent absorption capacity and stability. After 50 cycles of absorption, the CO\textsubscript{2} absorption efficiency remains above 50%.
3.2.2 Preparation of nano calcium oxide and composite anti-sintering

CaO-based absorbents are mainly used in fluidized bed reactors. The gas-solid reaction time is short, and the reaction between calcium oxide and carbon dioxide mainly occurs in the reaction control stage[37]. Therefore, the smaller the grain size of the CaO absorbent, the higher the reactivity of carbonation reaction, and the higher the utilization. The long-term high-temperature calcination is the main reason for sintering and declining absorption performance. Calcination regeneration at a lower temperature is an effective way to avoid sintering. Li et al.[39] found that CaCO$_3$ with larger particle sizes needs more time for complete decomposition. Nano-CaCO$_3$ has a large specific surface area and a large pore volume; therefore, its regeneration temperature can be lower. The decomposition temperature of CaCO$_3$ with a particle size of 20 nm is about 200 °C lower than that of ordinary CaCO$_3$[38]. Therefore, nano calcium precursor can increase the absorbent activity, save energy, and reduce sintering. Barker et al.[39] pointed out that the CO$_2$ absorption efficiency of CaO-based absorbent obtained using the calcium carbonate precursor with a particle size of about 10 nm and a specific surface area of 200 m$^2$/g can reach 93%, and its performance remained unchanged after 30 cycles. Liu et al.[40] studied the CO$_2$ absorption capacity and stability of CaO-based absorbents prepared using different precursors such as nano-calcium carbonate, nano-calcium oxide, and nano-calcium hydroxide, pointing out that the nano-scale absorbent particles are significantly better in terms of stability and sintering resistance. Wu et al.[41] pointed out that the nano-CaCO$_3$/Al$_2$O$_3$ calcium-based absorbent has higher cycle absorption efficiency and lower calcination regeneration temperature than micro-CaCO$_3$/Al$_2$O$_3$ calcium-based absorbent; the absorption efficiency of the former one maintained at 68.3% after 50 cycles.

Nano-scale calcium-based absorbent particles are more likely to deliver high absorption efficiency, but too small particle size will cause excess surface energy and accelerate driving sintering. In order to improve the anti-sintering ability of nano-CaO absorbents, researchers have carried out studies on coating nano-particles and doping high-temperature inert components. Wei et al.[42] used the sol-gel method to coat active nano-CaO in a porous framework structure to prepare a mesoporous silica framework-coated nano-calcium absorbent. Through thermogravimetric analysis, it is found that this composite CaO-based absorbent still maintains high absorption efficiency after 15 cycles, which was about 41% higher than that of the untreated nano-calcium absorbent. Magnesium oxide has a wealth of sources and is low in price. Its melting point is as high as 2800°C and remains stable during the absorption/calcination cycle. It seldom combines with CaO or CaCO$_3$ to forms a new phase to reduce the content of CaO in the absorbent. Luo et al.[43] prepared a nano-composite CaO/MgO absorbent using sol-gel method with analytically pure Ca(NO$_3$)$_2$·4H$_2$O and Mg(NO$_3$)$_2$·6H$_2$O reagents and citric acid. The microstructure of this absorbent is fluffy, thereby effectively reducing the mass transfer resistance of CO$_2$. After 30 absorption/calcination cycles, its absorption efficiency can still reach 66%, which is much higher than that of the unmodified CaO absorbent.

3.3. Preparation of CaO-based absorbent using calcium-containing solid waste

The precursors used to prepare the CaO-based absorbent using the above-mentioned chemical synthesis method are generally analytically pure reagents. Pure raw materials lead to convenient adjustment of the pore size parameters, but also high cost of the absorbent preparation. At present, the major problem in the promotion of carbon capture and storage technology is still the high capture cost. In addition to high facilities and operating expenses, excessive absorbent cost is also an important factor that hinders the industrialization and commercialization of this technique. Therefore, reducing the raw material cost of CaO-based absorbents exerts an important positive effect on promoting the large-scale industrialization of carbon capture and storage techniques.

Calcium-containing solid waste is mainly the solid waste slag discharged during industrial production, such as steel slag, phosphogypsum, and calcium carbide slag, which are mainly treated in the form of storage. However, since it contains harmful impurities, its storage will not only takes up a large amount of land, but also pollute the soil and water. Preparing CaO-based absorbent using calcium-containing solid waste can not only help to alleviate the pollution caused by calcium-
containing solid waste, but also greatly reduce the raw material cost of CaO-based absorbent. Compared with natural ore, calcium-containing solid waste has a smaller particle size and higher reactivity. In addition, the sources of this waste are often close to CO$_2$ emission sources and reuse sites of failed calcium-based absorbents$^{[44]}$. In this respect, the production cost of CaO-based absorbents can be reduced if the process is integrated and optimized with industrial production.

3.3.1 Preparation of CaO-based absorbent using steel slag
Steel slag is an alkaline bulk industrial solid waste generated during the production of steel. About 150–250 kg steel slag is generated for producing each ton of crude steel. At present, the annual production of steel slag in China is nearly 100 million tons, with the utilization rate of only about 20% (most steel slag is stored in the open air)$^{[45]}$. As can be seen from Table 2, the composition of steel slag is complicated with the content of CaO reaching 46.3%. Ca(OH)$_2$ active calcium phase, which can capture and absorb CO$_2$, accounts for about 44% of the total calcium mass, and more than half of the calcium element exist in the inert form. Tian leached active calcium with acetic acid to prepare a CaO-based absorbent, and recovered iron-rich ore$^{[46]}$. The CO$_2$ absorption efficiency of this CaO-based absorbent was 79.5%. Under actual conditions of high-temperature calcium cycling, it is significantly more stable and its absorption efficiency was nearly twice that of commercial calcium oxide. The mechanism analysis shows that the small amount of Mg and Al contained in this CaO-based absorbent (Table 2) helps to improve its cyclic stability. Figure 4 shows the CO$_2$ capture process based on preparing the CaO-based absorbent using steel slag, recovery of iron, and utilization of waste heat. This process can be integrated through waste resource reuse, high-value by-product preparation, and waste heat utilization so as to maximize energy efficiency and reduce the cost of preparing CaO-based absorbent$^{[46]}$.

|                      | wt%  | CaO | Fe$_2$O$_3$ | MgO | Al$_2$O$_3$ | MnO | SiO$_2$ | Surplus |
|----------------------|------|-----|-------------|-----|-------------|-----|---------|---------|
| Steel slag           |      | 46.3| 18.1        | 4.6 | 11.6        | 1.3 | 14.5    | 3.6     |
| CaO-based absorbent  |      | 90.7| 1.4         | 4.9 | 0.2         | 1.2 | 0.4     | 1.2     |

Figure 4. Schematic diagram of CO$_2$ capture process based on preparing the CaO-based absorbent using steel slag, recovery of iron, and utilization of waste heat.

3.3.2 Preparation of CaO-based absorbent using phosphogypsum
Phosphogypsum (PG) is an industrial waste residue discharged during the production of wet phosphoric acid. Its main component is CaSO$_4$$\cdot$2H$_2$O, and the dry basis content is greater than 90%. About 4–5 tons of phosphogypsum will be generated for producing each ton of phosphoric acid$^{[47]}$. 

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Table 2. Chemical composition of steel slag and CaO-based absorbent prepared from steel slag$^{[46]}$

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Nowadays, the annual emission of phosphogypsum in China has exceeded 76 million tons with the stockpiles larger than 300 million tons. From Table 3, it can be seen that phosphogypsum contains many impurities, but the content of CaO reaches 33.6%, indicating its huge potential for fixing CO₂. Zhou et al. adjusted the reaction conditions to convert calcium sulfate dihydrate in phosphogypsum into nano-CaCO₃, which is then calcined for preparing nano-CaO absorbent, as shown in Figure 5. The results showed that the particle size of the obtained CaO absorbent was 73~260 nm. Further CO₂ absorption performance tests showed that the smaller the particle size, the higher the absorbent activity and the higher the cyclic stability. It can be seen from Figure 5 that this technique can not only be used to prepare nano-CaO absorbents, but also produce ammonium sulfate, an important sulfur-based compound fertilizer. The obtained income can offset part of the production cost of the absorbent. Therefore, it is a feasible way to get cheap CaO-based absorbents. In order to further enhance the cyclic stability of the absorbent, Lan et al. used the same preparation process to synthesize nano-CaCO₃, and then prepare nano-CaO/MgO composite absorbent by mixing magnesium sol with nano-CaCO₃ slurry. The results showed that the addition of MgO enlarges the specific surface area and pore diameter of the obtained nano-CaO/MgO composite absorbent were 15.25 m²/g and 21.3 nm, respectively. After 50 cycles, its CO₂ absorption efficiency still stood as 25.6%. There are many kinds of impurities in phosphogypsum, such as SiO₂ and Al₂O₃, which will react with CaO to form compounds, reducing the content of active calcium and slightly improving the absorbent stability, without affecting the absorption rate.

![Table 3. Chemical composition of phosphogypsum determined by XRF](image)

3.3.3 Preparation of CaO-based absorbents using other solid wastes

Other calcium-containing industrial wastes, including calcium carbide slag, red mud, white mud, can also be used as precursors of CaO-based absorbents. These solid wastes have developed pore structures; therefore they perform better than natural limestone in terms of CO₂ capturing. For example, the solid waste slag with Ca(OH)₂ as the main component is formed when calcium carbide is hydrolyzed to produce acetylene. Acetylene is the main raw material for the production of polyvinyl chloride (PVC). For producing each ton of polyvinyl chloride resin, about 1.9 tons of dry-based calcium carbide slag will be generated. In China, more than 25 million tons of dry-based calcium carbide slag is produced every year. Zhang et al. used calcium carbide slag instead of natural limestone for the preparation of CaO-based absorbent, showing that under the same process conditions, the CO₂ absorption performance of CaO-based absorbent prepared using calcium carbide slag was better than that of natural limestone and analytically pure CaCO₃ and Ca(OH)₂. In addition, Al₂O₃ contained in the calcium carbide slag can synchronize with calcium oxide to generate high-temperature inert mayenite (Ca₁₂Al₁₄O₃₃), thereby improving the anti-sintering and anti-wearing abilities of CaO-based absorbents.
4. Conclusion

(1) Natural CaO-based absorbents such as limestone and dolomite can deliver better CO₂ absorption performance to a certain extent by means of extraction and reconstruction, doping with inert components, and high-temperature pretreatment. However, the rising modification cost will weaken the economic advantages of natural CaO-based absorbents.

(2) When the chemical reagents with lower impurity content and definite phase composition are used as precursors, we can synthesize nano-sized CaO-based absorbent particles with better pore structure and larger specific surface area. By adding inert framework components, the anti-sintering can also be improved. However, the high price of the chemical reagents as raw materials restricts the industrialization and commercialization of this technique.

(3) Preparing CaO-based absorbents using bulk industrial solid waste with high calcium content can not only alleviate the stockpiling pollution of solid waste, but also greatly reduce the raw material cost. At the same time, the sources of calcium-containing solid waste are often close to CO₂ emission sources and re-use sites of failed calcium-based absorbents, so the production cost of CaO-based absorbents can be minimized through the integration with industrial production.

Acknowledgments

We acknowledge the financial support from the Fundamental Research Funds for the Central Universities (No.3142018011), and the National key research and development plan projects of China (No. 2017YFB0603300).

References

[1] Huang, C. Y., Guo, R. T., Pan, W. G., Tang, J. Y. (2018). Eu-doped TiO₂ nanoparticles with enhanced activity for CO₂ photocatalytic reduction. Journal of CO₂ Utilization, 26, 487-495.

[2] Hemmati, A., & Rashidi, H. (2019). Optimization of industrial intercooled post-combustion CO₂ absorber by applying rate-base model and response surface methodology (RSM). Process Safety and Environmental Protection, 121, 77-86.

[3] Sharifzadeh, M., & Shah, N. (2019). MEA-based CO₂ capture integrated with natural gas combined cycle or pulverized coal power plants: Operability and controllability through integrated design and control. Journal of cleaner production, 207, 271-283.

[4] Wang, M., Lawal, A., Stephenson, P., Sidders, J., & Ramshaw, C. (2011). Post-combustion CO₂ capture with chemical absorption: a state-of-the-art review. Chemical engineering research and design, 89(9), 1609-1624.

[5] Derevschikov, V. S., Lysikov, A. I., & Okunev, A. G. (2011). High temperature CaO/Y₂O₃ carbon dioxide absorbent with enhanced stability for sorption-enhanced reforming applications. Industrial & Engineering Chemistry Research, 50(22), 12741-12749.

[6] Wang, S., Yan, S., Ma, X., & Gong, J. (2011). Recent advances in capture of carbon dioxide using alkali-metal-based oxides. Energy & Environmental Science, 4(10), 3805-3819.

[7] Xie, M. S., Zhang, L., Yang, Z. Q. (2012). Research and Development Ca-based on Cyclic Sorption Characteristic of Sorbent for CO₂. Materials Review, 26(13):134-138.

[8] Kuang, W. J., Kao, H. T., Ren, B. (2012). Research progress of cyclic absorbing CO₂ technology with Ca-based sorbents. Chemical Industry and Engineering Progress, 30(6): 1356-1360.

[9] Li, Z. S., Fang, F., Cai, N. S. (2007). CaCO₃ Circulating Calcination Tests and its Simulation at a High Concentration of CO₂. Journal of Engineering for Thermal Energy and Power, 22 (6): 642-646.

[10] Wang, Q., Luo, J., Zhong, Z., & Borgna, A. (2011). CO₂ capture by solid adsorbents and their applications: current status and new trends. Energy & Environmental Science, 4(1), 42-55.
[11] Blamey, J., Anthony, E. J., Wang, J., & Fennell, P. S. (2010). The calcium looping cycle for large-scale CO$_2$ capture. Progress in Energy and Combustion Science, 36(2), 260-279.

[12] Li Y J, Zhao C S, Li Q Z. (2008). Cyclic Carbonation Characteristics of Calcium Acetate as a New CO$_2$ Sorbent[J]. Proceedings of the CSEE, 28(8): 65-70.

[13] Samanta, A., Zhao, A., Shimizu, G. K., Sarkar, P., & Gupta, R. (2011). Post-combustion CO$_2$ capture using solid sorbents: a review. Industrial & Engineering Chemistry Research, 51(4), 1438-1463.

[14] Albrecht, K. O., Wagenbach, K. S., Satrio, J. A., Shanks, B. H., & Wheelock, T. D. (2008). Development of a CaO-based CO$_2$ sorbent with improved cyclic stability. Industrial & Engineering Chemistry Research, 47(20), 7841-7848.

[15] Mohammadi, M., Lahijani, P., & Mohamed, A. R. (2014). Refractory dopant-incorporated CaO from waste eggshell as sustainable sorbent for CO$_2$ capture: experimental and kinetic studies. Chemical Engineering Journal, 243, 455-464.

[16] Donat, F., Florin, N. H., Anthony, E. J., & Fennell, P. S. (2012). Influence of high-temperature steam on the reactivity of CaO sorbent for CO$_2$ capture. Environmental science & technology, 46(2), 1262-1269.

[17] Liu, H. L. (2014). Sintering Phenomena of Cyclic Calcination/Carbonation CO$_2$ Capture and its Improve Measures. Energy Research and Management, 1(3): 59-62.

[18] Tang, S., Zhu, L., Fan, J. M. (2015). Research progress in modified Ca-based sorbents for cyclic CO$_2$ capture [J]. Modern Chemical Industry | Mod Chem Ind. (2): 44-48.

[19] KILIÇ, Ö. (2013). Impact of Physical Properties and Chemical Composition of Limestone on Decomposition Activation Energy. Asian Journal of Chemistry, 25(14).

[20] Shi, Y. Y., Lan, P. Q., Wang, Y. (2015). Modified Kinetics Model of Nano CaO Reactions with CO$_2$ in a CaO-Based Adsorbent. Journal of Chemical Engineering of Chinese Universities, 29(1): 96-101.

[21] Li, Y. J., Zhao, C. S. (2008). Carbonation Characteristics in Calcium-sorbents Cyclic Calcination/Carbonation Reaction Process. Proceedings of the CSEE, 28(2): 55-60.

[22] Chen, H. W., Zhao, Z. H., Huang, X. Z. (2012). Sequential SO$_2$/CO$_2$ capture using CaO-based sorbents reactivated by steam. Journal of Chemical Industry and Engineering (China), 63(8): 2566-2575.

[23] Yang, X., Zhao, L., Yang, S., & Xiao, Y. (2013). Investigation of natural CaO-MgO sorbent for CO$_2$ capture. Asia-Pacific Journal of Chemical Engineering, 8(6), 906-915.

[24] Donat, F., Florin, N. H., Anthony, E. J., & Fennell, P. S. (2012). Influence of high-temperature steam on the reactivity of CaO sorbent for CO$_2$ capture. Environmental science & technology, 46(2), 1262-1269.

[25] Yu, F. C., Phalak, N., Sun, Z., & Fan, L. S. (2011). Activation strategies for calcium-based sorbents for CO$_2$ capture: a perspective. Industrial & Engineering Chemistry Research, 51(4), 2133-2142.

[26] Adanez, J., De Diego, L. F., & Garcia-Labiano, F. (1999). Calcination of calcium acetate and calcium magnesium acetate: effect of the reacting atmosphere. Fuel, 78(5), 583-592.

[27] Salvador, C., Lu, D., Anthony, E. J., & Abanades, J. C. (2003). Enhancement of CaO for CO$_2$ capture in an FBC environment. Chemical Engineering Journal, 96(1-3), 187-195.

[28] Aihara, M., Nagai, T., Matsushita, J., Negishi, Y., & Ohya, H. (2001). Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/decarbonation reaction. Applied Energy, 69(3), 225-238.

[29] Li, Y., Zhao, C., Chen, H., Duan, L., & Chen, X. (2010). Cyclic CO$_2$ capture behavior of KMnO4-doped CaO-based sorbent. Fuel, 89(3), 642-649.

[30] Manovic, V., & Anthony, E. J. (2008). Thermal activation of CaO-based sorbent and self-reactivation during CO$_2$ capture looping cycles. Environmental science & technology, 42(11), 4170-4174.
[31] Ozcan, D. C., Shanks, B. H., & Wheelock, T. D. (2011). Improving the stability of a CaO-based sorbent for CO$_2$ by thermal pretreatment. Industrial & Engineering Chemistry Research, 50(11), 6933-6942.

[32] Lu, H., Khan, A., & Smirniotis, P. G. (2008). Relationship between structural properties and CO$_2$ capture performance of CaO-based sorbents obtained from different organometallic precursors. Industrial & Engineering Chemistry Research, 47(16), 6216-6220.

[33] Huang, S. L., Tong, H., Wang, J. G. (2011). Preparation and Property of Zr-doped Calcium Oxide for Carbon Dioxide Absorption at High Temperature. Environmental Science & Technology, 34(2): 85-90.

[34] Karami, D., & Mahinpey, N. (2012). Highly active CaO-based sorbents for CO$_2$ capture using the precipitation method: preparation and characterization of the sorbent powder. Industrial & Engineering Chemistry Research, 51(12), 4567-4572.

[35] Gupta, H., & Fan, L. S. (2002). Carbonation–calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. Industrial & engineering chemistry research, 41(16), 4035-4042.

[36] Yang, J. H., Shih, S. M., Wu, C. I., & Yi-Der Tai, C. (2010). Preparation of high surface area CaCO$_3$ for SO$_2$ removal by absorption of CO$_2$ in aqueous suspensions of Ca (OH) 2. Powder Technology, 202(1-3), 101-110.

[37] Zhang, T., Guo, Z. L., Cai, Z. H. (2012). Lattice Boltzmann method for simulating carbon dioxide capture with Ca-based sorbent. Journal of Chemical Industry and Engineering (China), 63(S1): 165-171.

[38] Liao, J., Duan, X., Li, Y., Zheng, C., Yang, Z., Zhou, A., & Zou, D. (2014). Synthesis and mechanism of tetracalcium phosphate from nanocrystalline precursor. Journal of Nanomaterials, 2014, 186.

[39] Barker, R. (1974). The reactivity of calcium oxide towards carbon dioxide and its use for energy storage. Journal of Applied Chemistry and Biotechnology, 24(4-5), 221-227.

[40] Liu, W., An, H., Qin, C., Yin, J., Wang, G., Feng, B., & Xu, M. (2012). Performance enhancement of calcium oxide sorbents for cyclic CO$_2$ capture A review. Energy & Fuels, 26(5), 2751-2767.

[41] Wu, S. F., Li, Q. H., Kim, J. N., & Yi, K. B. (2008). Properties of a nano CaO/Al$_2$O$_3$ CO$_2$ sorbent. Industrial & engineering chemistry research, 47(1), 180-184.

[42] Wei S Y, Han R, Su Y L. (2018). CO$_2$ Sorption Enhancement of Nano Calcium Carbonate Wrapped with the Mesoporous Skeleton. Journal of Combustion Science and Technology, 24(2): 132-138.

[43] Luo C, Zheng Y, Ding N. (2011). Synthesis and Performance of a Nano Synthetic Ca-based Sorbent for High Temperature CO$_2$ Capture. Proceedings of the CSEE, 31(8): 45-50.

[44] Tian, S. C., Jiang, J., Yan, F., Li, K., & Chen, X. (2015). Synthesis of highly efficient CaO-based, self-stabilizing CO$_2$ sorbents via structure-reforming of steel slag. Environmental science & technology, 49(12), 7464-7472.

[45] Tian, S. C., Jiang, J. G., Li, K. M., Yan, F., & Chen, X. J. (2014). Performance of steel slag in carbonation–calcination looping for CO$_2$ capture from industrial flue gas. RSC Advances, 4(14), 6858-6862.

[46] Tian, S. C. (2016). Synthesis of highly-efficient, Ca-based CO$_2$ sorbents from steel slag and application for carbon capture in the iron and steel industry. China, Tsinghua University.

[47] Zhao, H. T., Bao, W. J., Sun, Z. H. (2017). Study on the deep removal of impurities from phosphogypsum. Chemical Industry and Engineering Progress, 36(4):1240-1246.

[48] Ye, X. D. (2017). Present status, existing problems and suggestions of phosphogypsum utilization in China in 2016. Phosphate & Compound Fertilizer, 32(7).

[49] Zhou, J., Zou, H. T., Xing, Y. (2016). Optimization of preparation of nano CaO based sorbents from phosphogypsum.Inorganic Chemicals Industry, 48(10):73-76.
[50] Lan, P., & Wu, S. (2014). Synthesis of a Porous Nano-CaO/MgO-Based CO₂ Adsorbent. Chemical Engineering & Technology, 37(4), 580-586.

[51] Lan, P. Q. (2014). Studies on synthesis of nano CaCO₃ by reactive crystallization from phosphogypsum and its application for CO₂ capture. China, Zhejiang University.

[52] Sun, R., Li, Y., Zhao, J., Liu, C., & Lu, C. (2013). CO₂ capture using carbide slag modified by propionic acid in calcium looping process for hydrogen production. International Journal of Hydrogen Energy, 38(31), 13655-13663.

[53] Zhan, D. F., Bian, C., He, J. H. (2014). Research advance review over the activation methods for calcium oxide based sorbents for CO₂. Journal of Safety and Environment, 14(5): 222-227.