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Performance of steel slag in carbonation–calcination looping for CO_2 capture from industrial flue gas

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Abstract: We investigate the performance of steel slag during the carbonation–calcination looping as a potential CO_2 adsorbent. The existence of portlandite in the steel slag provided a maximum theoretical CO_2 capture capacity of 112.7 mg_{CO_2} g_{slag}^{-1}, and the maximum carbonation conversion of 39.8% was achieved in simulated flue gases with only 5-min duration of carbonation. Sintering of the steel slag particles during both the carbonation and calcination processes, especially the destruction of the 3-nm pores, is the main cause for the deactivation of steel slag. Carbonation–calcination looping of steel slag can significantly improve its total CO_2 capture capacity compared to the conventional technical route of direct carbonation sequestration, thus providing an alternative and more feasible option for the use of alkaline industrial wastes to capture CO_2 from industrial sources, such as the iron and steel production facilities.

Anthropogenic CO_2 emissions are generally acknowledged to be the most important driving force of global climate change, and contribute about two-thirds of the enhanced greenhouse effect.[1] At present, about 32 billion tons of CO_2 are emitted into the atmosphere annually,[2] and almost 40% of worldwide CO_2 emissions are directly

attributable to industrial activities,[3] such as iron and steel production, cement production, production of chemicals and petrochemicals, and the power generation sector due to electricity use in these industries.[4] Reducing CO_2 emissions from these industrial sources is an essential part of the global response to prevent dangerous climate change. As the first generation and also a classical post-combustion capture technology for CO_2, amine scrubbing has been widely investigated and recently demonstrated on a pilot-scale.[5,6] However, the problems of serious amine loss and the considerable energy consumption during the regeneration of absorbents, the weak vapor resistance in flue gas, and equipment corrosion, have significantly restricted the further development and application of this technology.[7,8] Therefore, the use of solid-state adsorptive materials, such as a CaO-based adsorbent[9,10], zeolite[11,12], metal organic frameworks (MOF)[13-15], and porous silica-supported amines hybrids[16-18], became the focus of the development of the second-generation carbon capture and storage (CCS) technologies, due to their superior heat and mass transfer[19], easier combination with existing industrialized facilities[20], and higher efficiency of energy utilization[21]. CaO-based adsorbents are one of the most promising of these solid adsorbents,[22] when considering the cost of adsorbent synthesis, the resistance of impurities in flue gas, and the temperature experienced under actual application conditions (the temperature of flue gas is generally higher than 373 K).

The mineral carbonation sequestration of CO_2, which is also based on the carbonation reaction between CO_2 and certain alkaline calcium- or magnesium-rich minerals,[23] is another promising technique.[24] Natural minerals, such as wollastonite, serpentine and olivine, were initially considered as potential CO_2 sequestration materials, due to their huge potential capacity to sequester all of the CO_2 that might be emitted from the combustion of all the coal present on Earth.[25] However, the problems of the slow CO_2 sequestration rate, severe reaction conditions, and mineral mining or flue gas transportation, makes the CO_2 capture cost of this route uneconomic.[26,27] Therefore, alkaline calcium-based industrial solid wastes, especially steel slag, have received more attention as alternative CO_2 sequestration materials,[28-30] because they have the advantages of being readily available within the same industrial processes

where CO_2 is produced and have a better reaction activity with CO_2.[31] Their use could reduce the cost of using industrial wastes for CO_2 sequestration by almost 30% compared to the use of natural minerals.[32] However, the total CO_2 sequestration capacity of alkaline calcium-based industrial wastes is very limited, with the amount of steel slag produced globally permitting theoretically 44-59 Mt CO_2 per year. Due to the amount of available industrial wastes being much lower than the amount of available natural minerals, and being far below the global demand for CO_2 capture from industrial sources, the development of this technology is restricted.

Therefore, to improve the total CO_2 capture capacity of industrial wastes such as steel slag, we investigated the performance of steel slag as a potential CO_2 adsorbent during carbonation–calcination looping. The characteristics of the reaction kinetics and the deactivation mechanism for CaO-based adsorbents during the carbonation–calcination looping process were also analyzed.

The weight range curves in Fig. 1 clearly show the influence of temperature and CO_2 concentrations on the carbonation–decarbonation of steel slag. The steel slag sample almost had no capture effect on CO_2 in all reaction gases below 300 ℃, but then begun to capture CO_2 with the sequestration rate accelerating gradually as the CO_2 concentration in the reaction atmosphere increased from 5% to 100%. The CO_2 sequestration rate remained at a high level as the temperature was continuously increased to 600 ℃. When the heating continued, the steel slag abruptly decarbonated, and the maximum decarbonation rate was achieved at higher temperatures for gases with the higher CO_2 concentrations in the reaction atmosphere. The range of temperatures for the maximum decarbonation rate could be as large as 150 ℃ from 700 ℃ in a 5% CO_2 atmosphere to 850 ℃ in a 100% CO_2 atmosphere. This indicates that a temperature higher than 800 ℃ is required for steel slag to achieve the acceptable level of desorption for pure CO_2 to be further compressed and transported for permanent storage, since a purge gas with a higher CO_2 concentration is needed for the desorption process.

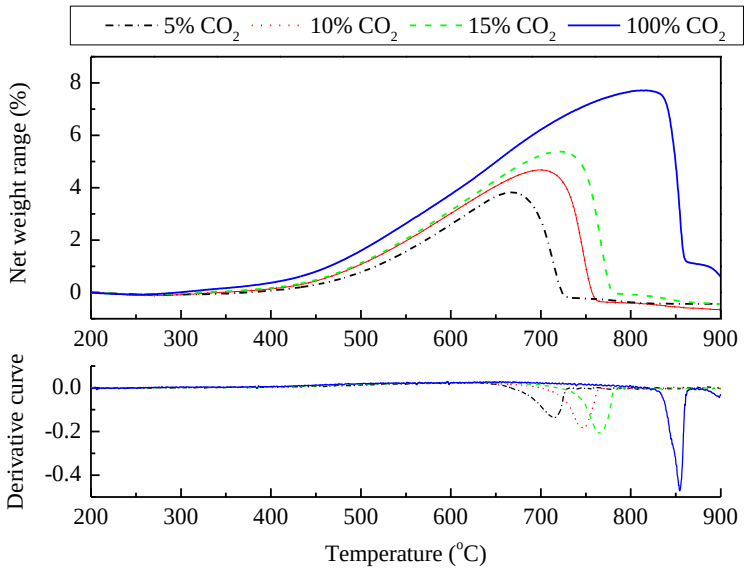

Fig. 1 Net CO_2 sequestration curve of steel slag at a heating rate of 10 °Cmin^{-1} in different CO_2 concentrations.

Fig. 2 shows that although the steel slag achieved the same uptake of CO_2 from different reaction gases (see Table S1 in Electronic supplementary information) during the first carbonation–calcination looping, the CO_2 capture capacity of steel slag in a pure CO_2 atmosphere was clearly higher than in a 5–15% CO_2 atmosphere (i.e., the typical CO_2 concentrations in actual flue gas) during all the other cycles, and the cyclic capture of CO_2 by steel slag was equally efficient at CO_2 concentrations of 5–15%. This indicates that although CO_2 concentrations can influence the uptake of CO_2 by steel slag, there is almost no variation over the range of typical flue gas CO_2 concentrations.

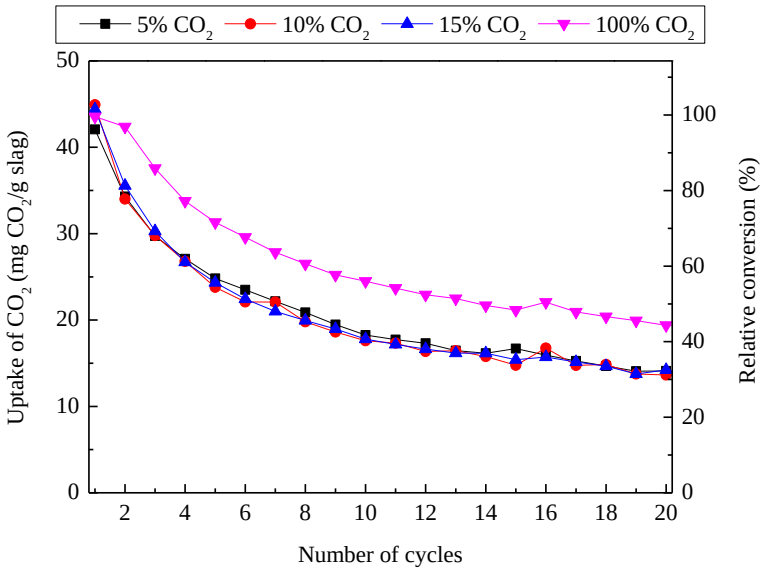

Fig. 2 CO_2 capture capacity of steel slag through 20 cycles in various CO_2 concentrations. The operating conditions were carbonation for 5 min at 600°C and calcination for 5 min at 800°C.

XRD patterns of the raw steel slag revealed the presence of $Ca(OH)_2$ in the sample, giving the steel slag a maximum theoretical CO_2 capture potential of 112.7 mg_{CO_2} g_{slag}^{-1} (see Fig. S1 and Table S3 in Electronic supplementary information). This value is not very high because almost 63.86% of the total calcium content in the slag sample determined from an XRF analysis (see Table S2 in Electronic supplementary information) existed in other phases than $Ca(OH)_2$, and was not available for the capture of CO_2. The maximum practical uptake of CO_2 by the steel slag used in this experiment all occurred in the first cycle, and was 43.5 mg_{CO_2} g_{slag}^{-1} in a 100% CO_2 atmosphere and 44.9 mg_{CO_2} g_{slag}^{-1} in a 10% CO_2 atmosphere. The uptake of CO_2 then decreased gradually as the looping continued. The CO_2 capture capacity of steel slag decayed sharply during the first five cycles, but maintained almost half of the initial level of CO_2 capture after 10 cycles. The steel slag sample then had a much better durability (cyclic stability) for CO_2 capture until the 20th cycle, with the variation of CO_2 capture capacity ranging by only about 20%. The uptake of CO_2 by steel slag from simulated flue gases (5%–15% CO_2) decreased to 13.6–14.2 mg_{CO_2} g_{slag}^{-1} at the end of 20 cycles, which was ~30–35% of its initial capacity. However, the total CO_2

capture capacity of the steel slag was improved by at least fivefold compared to the conventional technical route of direct carbonation sequestration, even if only 10 carbonation–calcination looping cycles were considered.

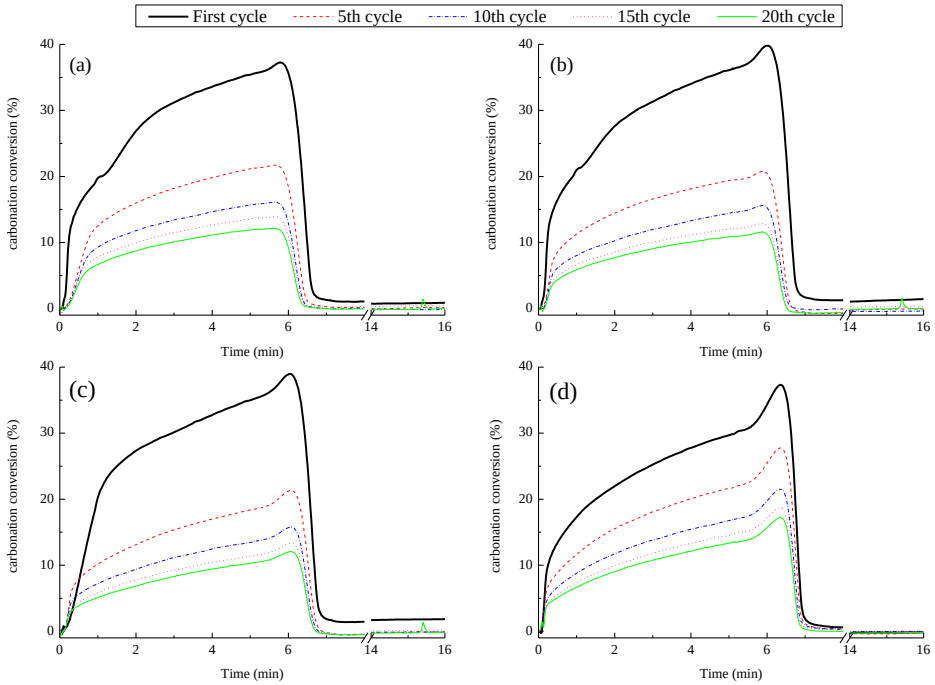

Fig. 3 Carbonation–decarbonation rates and the conversion of steel slag in simulated flue gases containing (a) 5% CO_2, (b) 10% CO_2, (c) 15% CO_2, and (d) 100% CO_2.

The CO_2 capture profiles of steel slag in the first, 5th, 10th, 15th, and 20th cycles (in Fig. 3) showed that in any individual looping cycle, the capture of CO_2 by steel slag occurred via a two-stage mechanism: a short but rapid stage, which was controlled by carbonation kinetics, followed by a long but slow stage, which was controlled by product layer diffusion. The carbonation rate of steel slag during the CO_2 adsorption process gradually reduced after multiple looping cycles in all reaction gases, and matched the decarbonation rate during the CO_2 desorption process. The carbonation of steel slag was still in the diffusion-controlled stage at the end of the CO_2 adsorption process, which was of 5-min duration, and the decarbonation rate was clearly faster than the carbonation rate in each looping cycle, with the adsorbed CO_2 abruptly released in a few tens of seconds. The carbonation conversion of the steel

slag used in this study ranged between 37.3% and 39.8% in the different simulated flue gases at the end of the initial looping cycle, which was slightly lower than that of the steel slag in other studies[33] and some other alkaline industrial wastes[34], which were used for the conventional carbonation sequestration of CO_2. This was a consequence of the much shorter reaction time (only 5-min duration for carbonation in this study) compared to direct carbonation sequestration. The carbonation conversion of the steel slag declined to about 16.1% after the 10th cycle, and finally 12.2% after the 20th cycle in the simulated flue gases.

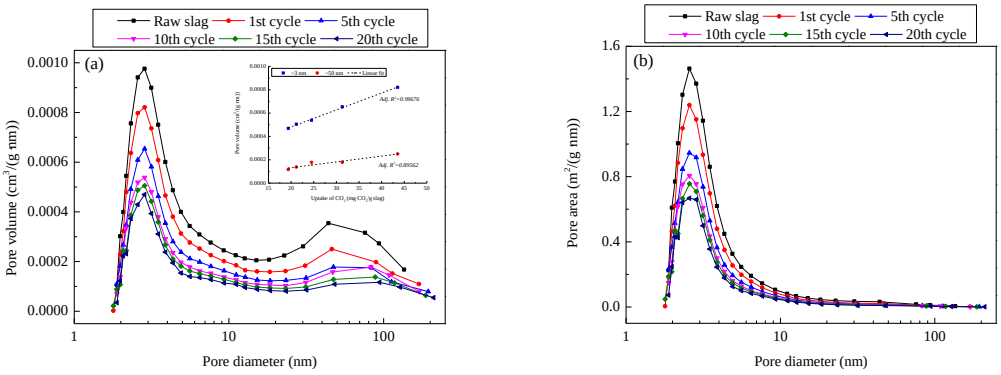

Fig. 4 Performance of the surface and pore properties of steel slag after multiple carbonation–calcination cycles in a pure CO_2 atmosphere: (a) Nitrogen physical adsorption of Barrett–Joyner–Halenda (BJH) dV/dD pore volume at 77 K, (b) Nitrogen physical adsorption of Barrett–Joyner–Halenda (BJH) dA/dD pore area at 77 K.

Surface and pore properties of the steel slag sample after multiple carbonation–calcination cycles in pure CO_2 are shown in Fig. 4. The Brunauer–Emmett–Teller (BET) surface area (see Fig. S3(a) in Electronic supplementary information) gradually decreased with the cyclic calcination in both air and a pure CO_2 atmosphere, and the steel slag that was calcined in a pure CO_2 atmosphere clearly had a lower BET surface area compared to the steel slag in air. This indicates that both the carbonation and calcination processes could cause a decay in the surface area of steel slag, which is typical for CaO-based CO_2 adsorbents. Furthermore, the carbonation process appeared to have a greater influence on the decay of the surface area than the

calcination process. The micro-pore area of the steel slag (see Fig. S3(b) in Electronic supplementary information) was not significantly influenced by the cyclic calcination in air after the 5th cycle, but decreased gradually in the presence of CO_2. This indicates that CO_2 could not only arrive at the meso-pores which largely existed in the steel slag sample, but also further diffuse into the micro-pores to react with the available Ca (CaO) in the steel slag particles. The formation of a bimodal pore-size distribution of the steel slag was observed after multiple carbonation–calcination cycles in Fig. 4(a), indicating that the smaller pores of ~3 nm and the larger pores of ~50 nm contributing most to the pore volume of the steel slag. Although pore volumes at both pore sizes had a significant decrease with the looping cycles, the 3-nm pores clearly had a stronger correlation with the CO_2 capture capacity of the steel slag than the 50-nm pores. This was probably because that the 3-nm pores could exactly provide the maximum surface area among all pore sizes of the steel slag (Fig. 4(b)), leaving relatively sufficient CaO active sites for the capture of CO_2. Therefore, sintering of the steel slag particles during both the carbonation and calcination processes, especially the destruction of the 3-nm pores, is the main cause for the decay of the CO_2 capture capacity of steel slag after multiple carbonation–calcination cycles. Besides sintering, an inadequate release of the adsorbed CO_2 during each carbonation–calcination looping cycle is another reason for the deactivation of steel slag, which can be clearly verified by the significant increase of the remaining $CaCO_3$ phase in the steel slag after multiple looping cycles (Fig. S4).

In summary, carbonation–calcination looping of steel slag for CO_2 capture from flue gas can significantly improve the CO_2 capture capacity of alkaline industrial wastes, such as steel slag, compared to the conventional route of direct carbonation sequestration, thus providing an alternative and more feasible option for the use of alkaline industrial wastes to *in situ* capture CO_2 from industrial sources. If the raw steel slag can be further restructured at the nano-micron scale to increase the content of the available CaO, it would become an ideal CO_2 adsorbent with the advantages of cost-savings, an abundant source and a high performance.

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