Highly efficient CO₂ capture with simultaneous iron and CaO recycling for the iron and steel industry†

Sicong Tian,a Jianguo Jiang,*a,b,c Feng Yan,a Kaimin Li,a Xuejing Chena and Vasilije Manovic*d

An efficient CO₂ capture process has been developed by integrating calcium looping (CaL) and waste recycling technologies into iron and steel production. A key advantage of such a process is that CO₂ capture is accomplished by simultaneous iron and CaO recycling from waste steel slag. High-purity CaO-based CO₂ sorbents, with CaO content as high as 90 wt%, were prepared easily via acid extraction of steel slag using acetic acid. The steel slag-derived CO₂ sorbents exhibited better CO₂ reactivity and slower (linear) deactivation than commercial CaO during calcium looping cycles. Importantly, the recycling efficiency of iron from steel slag with an acid extraction is improved significantly due to a simultaneous increase in the recovery of iron-rich materials and the iron content of the materials recovered. High-quality iron ore with iron content of 55.1–70.6% has been recovered from waste slag in this study. Although costing nearly six times as much as naturally derived CaO in the purchase of feedstock, the final cost of the steel slag-derived, CaO-based sorbent developed is compensated by the byproducts recovered, i.e., high-purity CaO, high-quality iron ore, and acetone. This could reduce the cost of the steel slag-derived CO₂ sorbent to 57.7 € t⁻¹, appreciably lower than that of the naturally derived CaO. The proposed integrated CO₂ capture process using steel slag-derived, CaO-based CO₂ sorbents developed appears to be cost-effective and promising for CO₂ abatement from the iron and steel industry.

1. Introduction

CO₂ emissions from industry are increasing, having reached 13.14 Gt in 2010 and making up 40% of the total anthropogenic CO₂ emissions worldwide.1,2 In addition, industrial energy consumption worldwide is expected to grow from 211 EJ in 2010 to 324 EJ in 2040 due to global industrialization, mainly in Asia, Africa, South America, and the Arab countries.3 This will result in an increase in total industrial CO₂ emissions of 74–91% by 2050 compared to 2007.4 However, to limit the increase in the global average temperature to 2 °C, direct CO₂ emissions from industry must be 24% lower by 2050 than those in 2007.4,5 Therefore, large energy-intensive industries manufacturing iron and steel, cement, and petrochemicals, which account for more than half of total industrial CO₂ emissions, should be the first targets to be completely decarbonized by 2050.

Implementation of CO₂ capture technologies in existing industrial sectors is urgently required, as carbon capture and storage (CCS) is the only current technology that would allow industrial sectors to realize a deep reduction in CO₂ emissions.6 The development of CCS in various industrial sectors is springing up worldwide, leaving much room for deploying applicable technologies for industrial CO₂ capture.7 As a promising alternative to conventional amine scrubbing and oxy-fuel combustion CO₂ capture technologies, calcium looping (CaL), which relies on CaO as a regenerable CO₂ sorbent upon cyclic carbonation and calcination reactions,8 has been widely investigated recently through bench- and pilot-scale demonstrations at sizes of 1 kWth–1.7 MWth.9–12 A recent techno-economic analysis of post-combustion CO₂ capture technologies found that CaL is more energy-efficient and cost-effective than other emerging CO₂ capture technologies, including chilled ammonia absorption, alkali–metal carbonate adsorption, and membrane separation;13 a further reduction in the CO₂ capture cost can be achieved by integrating CaL with thermal energy storage.14 However, the dramatic decay in the cyclic CO₂ capture performance of naturally occurring precursors-derived CaO, trig-
gered mainly by sintering of CaCO₃ during the CaL-based CO₂ capture process, remains as an obstacle for the development and implementation of this technology. To overcome this limitation, various strategies have been investigated to date. Several measures, including thermal activation, steam hydration, and recarbonation, have been demonstrated to be effective in stabilizing the CO₂ capture performance of naturally occurring sorbents. Another approach involves developing synthetic CaO-based CO₂ sorbents with thermally stable surface areas and pore volumes, thereby minimizing performance deterioration for CO₂ capture. This can be achieved by employing organic-carbon templates during sorbent preparation and introducing refractory supports into the CaO matrix. Broda and colleagues developed a highly effective MgO-stabilized, CaO-based CO₂ sorbent via recrystallization of calcium and magnesium acetates in organic solvents. The as-prepared material exhibited an excellent CO₂ uptake of 10.71 mmolCO₂/gsorbent after 10 harsh CaL cycles, with only 8 wt% of MgO required. However, the significantly increased cost for sorbent preparation due to the employment of organic acids should be considered before practical application.

The iron and steel industry is the largest energy-consuming manufacturing industry in the world. Currently, more than 2.5 Gt of CO₂ is emitted annually from the global iron and steel industry without implementation of any effective CO₂ reduction measures. In addition to an urgent demand for CO₂ abatement in the iron and steel industry, valorization of steel slag, a Ca-rich and Fe-containing industrial waste, is another challenge faced in iron and steel production. Global annual generation of steel slag is almost 200 Mt a⁻¹, half of which is contributed by China. However, only 20% of the steel slag produced annually in China is utilized, and the other 80% is stockpiled in the open air.

The CaL-based CO₂ capture process can be operated readily in a dual circulating fluidized bed system with regard to practical applications. Importantly, limestone is an essential feedstock for many energy-intensive manufacturing industries (e.g., the iron-and-steel and cement industries), making it feasible for integration into industrial processes for CO₂ abatement. The potential synergy among power generation, cement production, and CO₂ abatement in the cement industry has been investigated by integrating CaL into cement manufacturing processes, where spent CaO from the CaL cycle is reused directly as a “carbon-free” feedstock for cement production, resulting in almost zero sorbent cost and waste production for CO₂ capture from the cement industry. However, no research on the integration of CaL into the iron and steel industry for CO₂ abatement has been reported to date. Therefore, we have developed an efficient CO₂ capture process (Fig. 1) by integrating CaL and waste recycling technologies into iron and steel production to help realize simultaneous CO₂ abatement and steel slag minimization in the iron and steel industry. In this system, Ca and Fe in the steel slag are separated via leaching of steel slag using acetic acid solution, with Ca extracted into the leachate and Fe concentrated in the residues. The Fe-rich materials can be recycled directly into the blast furnace, substituting for iron ore as the feedstock for iron production after magnetic separation. The CaO-based sorbent, derived from the precipitation of ions in the Ca-rich leachate and a subsequent dry-distillation of the resulting precipitate, is delivered to the CaL unit for CO₂ capture. The spent sorbent can also be recycled into the blast furnace as a substitute for natural limestone to remove impurities in the iron ore during iron production. Such an integrated CO₂ capture process is demonstrated to be highly efficient and cost-effective in this study, which is promising for application to CO₂ abatement in the iron and steel industry.

2. Experimental section

2.1 Material preparation

Steel slag sample. The steel slag used in this study was obtained from the Beijing Shougang Steel Company in Qian’an, Hebei Province, China. The fresh slag, sampled after washing and crushing, was dried overnight at 105 °C and passed through a 0.1 mm sieve before use. The major elemental composition [expressed in the form of oxides] of the raw steel slag was 46.4 wt% CaO, 18.1 wt% Fe₂O₃, 14.5 wt% SiO₂, 11.6 wt% Al₂O₃, 4.7 wt% MgO, and 1.3 wt% MnO, as determined by X-ray fluorescence (XRF, XRF-1800 Analyzer, Shimadzu, Japan).

Preparation of CO₂ sorbents from steel slag. The CaO-based CO₂ sorbents were derived from steel slag using an acid extraction–precipitation approach (Scheme 1). In a typical synthesis, the steel slag sample was mixed with a 1 M solution of acetic acid at a solid/liquid ratio of 1 g to 10 mL. The mixture was stirred mechanically at room temperature for 0.5 h. Then, the steel-slag leachate was obtained by centrifugation of the slurry using a high-speed refrigerated centrifuge (himac CR22G, Hitachi, Japan), and the remaining steel-slag residues were gathered and dried for use in the iron recycling experiment described below. The obtained steel-slag leachate was directly dried overnight at 105 °C. Table 1 summarizes the parameter ranges investigated in this study. For brevity, the following...
Jackson Walker et al.

2.1 Recycling of CaO and iron from steel slag

The experiments for recycling iron from raw steel slag and the steel-slag residues remaining after acid extraction were performed in a centrifugal-magnetic separator (CMS, KMS-181E, KEEZO, China), with a magnetic stirrer placed near the bottom of the separating chamber. The stirrer can maintain rotation at a specific centrifugal speed when the magnetic flux density on the surface of the stirrer is fixed at a desired value. Thus, phases with magnetic force from the stirrer strong enough to balance the centrifugal force it bears are separated. During the experiment, approximately 5 g of each residue or slag was placed into the chamber and the magnetic separation process was performed under a magnetic flux density of 0.4 T at different centrifugal speeds (100, 300, and 500 rpm) for 3 min.

2.2 Material characterization

Concentrations of Ca, Mg, Fe, Mn, Al, and Si in the steel slag leachate were detected using an ICP-AES, iCAP7400, Thermo Scientific, USA. The iron content in the magnetically separated materials was determined using an X-ray Fluorescence (XRF) analyzer (Niton XL2, Thermo Scientific, USA). Powder X-ray diffraction (XRD) was performed to determine the phase composition of the materials synthesized using an X-ray diffractometer (Smartlab, Rigaku, Japan) with the operating parameters of Cu Kα radiation (λ = 1.5418 Å) and a 40 kV/150 mA power generator. An angular range of 10–90° 2θ was measured, with a step size of 0.02° and counting time of 2 s per step. The morphology of the materials synthesized was observed using a Merlin scanning electron microscope (SEM, Zeiss, Germany), all samples were sputter-coated with an approximately 5 nm-thick layer of platinum before observation.

3. Results and discussion

3.1 Recycling of CaO and iron from steel slag

Ca and Mg are the main elements extracted from steel slag; other major elements include Fe, Si, Mn and Al (Fig. 2). This is in line with the elemental composition of the freshly calcined CO₂ sorbents prepared from the steel slag leachate, determined by using XRF (Table S1, ESL†). It was also revealed from
Fig. 2 that the extraction time and solid/liquid ratio did not result in any significant change in the amount of elements extracted from the slag sample, yielding approximately 0.27 g of CO$_2$ sorbents per gram of steel slag used. This is encouraging, as a shorter extraction time and higher solid/liquid ratio are required for practical application. The amount of Ca and Mg extracted from slag increased gradually with an increasing mass ratio of acid to slag; however, this limited increase was at the cost of a higher dosage and lower conversion of acetic acid. In addition, the higher dosage (i.e., mass ratio of acid to slag) resulted in a significant increase in the amount of Fe, Si, and Al extracted, which in turn lowered the total mass fraction of CaO and MgO from 96.3% (1 M–2 h–1 : 10) to 74.0% (5 M–2 h–1 : 10) in the freshly calcined sorbents prepared. For the freshly calcined 1 M–0.5 h–1 : 10, 1 M–2 h–1 : 10, 2 M–0.5 h–1 : 5, and 2 M–2 h–1 : 5 materials with a low acid-to-slag mass ratio of 0.6 : 1, high CaO purities of ~90% could be achieved (Table S1†), indicative of a promising alternative for natural limestone as feedstock for iron production.

Fig. 3 plots the recycling efficiency of iron from the steel slag with an acid extraction, with raw steel slag included for comparison. It is shown in Fig. 3(a) that recovery of all magnetically-separated materials decreased with increasing centrifugal speed, regardless of whether raw slag or the slag with an acid extraction was employed. This is because a stronger magnetic force is required to separate phases at a higher centrifugal speed. However, there was a significant increase in the recovery of the magnetically-separated materials from the steel slag with an acid extraction compared with that from the raw slag. Increasing the dosage of acetic acid from 1 M to 3 M or 5 M during the acid extraction did not significantly increase the recovery of the magnetically-separated materials, probably because more iron was extracted into the leachate from the steel slag with higher concentrations of acetic acid as shown in Fig. 2. The iron content of the magnetically-separated materials from either the raw steel slag or the steel slag with an acid extraction increased with centrifugal speed (Fig. 3(b)); this is because the more magnetic phases could be separated at higher centrifugal speeds. Importantly, the iron content of all magnetically-separated materials from the steel slag with an acid extraction was appreciably higher than that from the raw slag, exceeding 55% at a centrifugal speed of 500 rpm. The magnetically separated materials corresponding to 2 M–0.5 h–1 : 5 and 5 M–2 h–1 : 10 exhibited iron contents as high as 70.0% and 70.6%, respectively. These values were close to the theoretical iron content of 72.4% in pure magnetite, indicating that the as-separated materials could be a high-quality alternative to iron ore available for iron production. Therefore, when acid extraction of the waste steel slag is used, not only is high-purity CaO obtained for use in CO$_2$ capture (to be discussed below) and subsequent iron production, but the recycling efficiency of iron is also improved significantly by increasing...
both the recovery of iron-rich materials and the iron content of the materials recovered.

The mechanism underlying the significant enhancement in the recycling efficiency of iron from steel slag was studied by characterizing the XRD patterns, as shown in Fig. 4. Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) (mayenite), Ca(OH)\(_2\) (portlandite), (Ca\(_{1.92}\)Fe\(_{1.08}\))Fe\(_2\)(SiO\(_4\))\(_3\) (andradite ferroan), Ca\(_2\)SiO\(_4\) (calcium silicate), and Mg\(_6\)Fe\(_2\)(OH)\(_{16}\)CO\(_3\)·4H\(_2\)O (sjogrenite) were the major mineral phases in the raw steel slag sample. After acid extraction, the phases (Ca\(_{1.92}\)Fe\(_{1.08}\))Fe\(_2\)(SiO\(_4\))\(_3\) and Mg\(_6\)Fe\(_2\)(OH)\(_{16}\)CO\(_3\)·4H\(_2\)O were no longer identified in the remaining steel slag residues, and a new phase, SiO\(_2\) (quartz), was present. This was likely associated with the reaction between acetic acid and these phases during the acid extraction process, where Ca and Mg were dissolved, leaving SiO\(_2\) in the residues. Upon a subsequent magnetic separation, Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) became the major phase in the final steel slag solids. Fe\(_3\)O\(_4\) (magnetite) and MgFe\(_2\)O\(_4\) (magnesioferrite) were identified as the dominant phases in the magnetically-separated materials (at a centrifugal speed of 500 rpm), indicating that the formed Fe\(_3\)O\(_4\) and MgFe\(_2\)O\(_4\), with a theoretical iron content of 72.4% and 56.0%, respectively, are the Fe-rich phases available for magnetic separation from the steel slag with an acid extraction. Therefore, depending on the ratio of Fe\(_3\)O\(_4\) to MgFe\(_2\)O\(_4\), the iron content of the magnetically-separated materials should be 56.0–72.4%, which is in line with the results from samples at 500 rpm (Fig. 3(b)).

### 3.2 CO\(_2\) capture performance of the CaO-based sorbents derived from steel slag

The results of N\(_2\) temperature-programmed decomposition (N\(_2\)-TPD) analysis of the 2 M–2 h–1 : 5 material are presented in Fig. 5(a). Three distinctive decomposition steps were revealed in the weight (change) curve, corresponding to temperature regions of 130–225 °C, 360–500 °C, and 630–750 °C, respectively. These decomposition steps were associated with the three main endothermic peaks located at 185 °C and 215 °C, 435 °C, and 745 °C, respectively, in the heatflow signal. The first decomposition step, in which two H\(_2\)O peaks occurred together in the MS signal, represented the dehydration of acetates in the material. During the second decomposition step, a strong acetone peak was associated with small H\(_2\)O and CO\(_2\) peaks in the MS signal. This is mainly due to the decomposition of anhydrous calcium acetate into CaCO\(_3\).\(^{39,40}\)

The third step, with a CO\(_2\) peak in the MS signal, represented the decomposition of CaCO\(_3\) into CaO. A comparison of the normalized weight change in all materials synthesized during N\(_2\)-TPD is shown in Fig. 5(b). Materials 1 M–0.5 h–1 : 10, 1 M–2 h–1 : 10, 2 M–0.5 h–1 : 5, and 2 M–2 h–1 : 5 were fairly close in their normalized weight changes, likely due to their similar elemental compositions as shown in Table S1.† The weight loss of these materials during N\(_2\)-TPD was ~5.1%, ~34.5%, and ~22.9%, respectively, for the three decomposition steps. Compared with the above-mentioned materials, 3 M–2 h–1 : 10
and 5 M–2 h–1:10 did not present a clear platform between the dehydration and acetate-decomposition steps in the normalized weight curve, and more H2O was generated during their dehydration (Fig. S1 in the ESI†). In addition, weight loss during the CaCO3-decomposition step was less normalized for 3 M–2 h–1:10 and 5 M–2 h–1:10 than for the other four materials, indicative of a lower CaO content in the material, as is in line with the results shown in Table S1.†

The change in morphology of the material 1 M–2 h–1:10 during N2-TPD was further characterized using scanning electron microscopy (Fig. 6). The freshly dried 1 M–2 h–1:10 had a coarse structure with a comparatively compact surface (Fig. 6(a)). When heated to 600 °C, acetone was released due to the decomposition of calcium acetate, resulting in a slice-shaped morphology in the material (Fig. 6(b)). With subsequent decarbonation of CaCO3 before heating to 900 °C, a well-defined, porous structure, mainly comprised of fine CaO grains, formed in the freshly calcined 1 M–2 h–1:10 (Fig. 6(c)).

XRD patterns of typical as-prepared CO2 sorbents in the freshly calcined state are shown in Fig. 7. The major phase, CaO, along with minor phases, MgO and CaS, were identified in 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5, the materials with the same (low) mass ratio of acetic acid to steel slag during acid extraction (Fig. S2 in the ESI†). With increasing doses of acetic acid, small quantities of Ca2Fe2O5 and (MgFe)2SiO4 were detected in the 3 M–2 h–1:10 and 5 M–2 h–1:10 materials synthesized.

CO2 capture performance as a function of reaction time was compared between commercial CaO and the various CaO-based CO2 sorbents synthesized in this study (Fig. 8). Commercial CaO presented a classical two-stage CO2 capture regime under the conditions studied here.41 In the first 5 min, the commercial CaO experienced a fast and kinetically-controlled reaction stage as pores with a diameter <100 nm were filled by newly formed CaCO3. This was followed by a substantially slower reaction stage controlled by the diffusion of CO2 through the CaCO3 product layer. Alvarez and Abanades42 concluded that the transition between the two reaction stages occurs at a critical product layer thickness of ~50 nm, which was better explained later by Li and colleagues43 through a rate equation theory they developed. The carbonation rate of the synthesized CaO-based CO2 sorbents was not as fast as that of the commercial CaO during the kinetically-controlled reaction stage. However, materials 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5 exhibited significantly faster carbonation rates than commercial CaO during the diffusion-controlled reaction stage, allowing their uptake of CO2 to surpass that of commercial CaO after a 20 min carbonation period. After 120 min, 1 M–2 h–1:10 achieved a CO2 uptake of 0.62 gCO2 g−1 sorbent, which was 1.5 times as high as that of the commercial CaO, indicative of an activation effect of acetic acid on the CaO-based CO2 sorbents.44
exhibited similar uptakes of CO₂, indicating that the extraction time and solid/liquid ratio had almost no effect on the elemental (Table S1†) and mineral (Fig. S2†) compositions of materials. However, the CO₂ uptake experienced a significant decrease with increasing acetic acid dosage, which was likely associated with the lower CaO content in freshly calcined 3 M–2 h–1:10 and 5 M–2 h–1:10, as discussed in Fig. 2 and Table S1†.

The multicyclic CO₂ capture performance of commercial CaO and the steel slag-derived, CaO-based CO₂ sorbents synthesized in this study under realistic CaL conditions are compared in Fig. 9. The commercial CaO presented a slightly higher CO₂ uptake of 0.27 gCO₂ g⁻¹sorbent compared with the steel slag-derived sorbents 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5 in the first cycle, whereas 3 M–2 h–1:10 and 5 M–2 h–1:10 had lower CO₂ uptakes of 0.16 gCO₂ g⁻¹sorbent and 0.14 gCO₂ g⁻¹sorbent, respectively. However, the CO₂ uptake of the commercial CaO experienced a drastic decrease within the first five cycles, and began to stabilize after falling to 0.07 gCO₂ g⁻¹sorbent by the tenth cycle. For the steel slag-derived, CaO-based CO₂ sorbents synthesized, two types of multicyclic CO₂ capture characteristics were revealed. 3 M–2 h–1:10 and 5 M–2 h–1:10, although bearing a limited CO₂ capture performance compared to commercial CaO, displayed similar CO₂ capture characteristic as the commercial CaO, i.e., the CO₂ uptake dropped drastically during the first several cycles, followed by a comparatively stable uptake afterwards. However, 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5, the materials with the same (low) mass ratio of acetic acid to steel slag during acid extraction, exhibited a different CO₂ capture characteristic. A drastic decay in CO₂ uptake occurred mainly between the first two cycles. Then, the CO₂ uptake experienced a slow, linear decay with increasing CaL cycles. Because of this, the CO₂ uptake of 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5 exceeded that of the commercial CaO from the third cycle onward, and 1 M–2 h–1:10 captured almost twice as much CO₂ as the commercial CaO by the end of the twentieth cycle. One would expect that the well-preserved porous structure of the cycled 1 M–2 h–1:10, compared to that of the commercial CaO, ensured its favorable CO₂ capture characteristics (Fig. 6(c–f)). Therefore, the better carbonation reactivity (Fig. 8) and cyclic stability (Fig. 9) of the steel slag-derived, CaO-based CO₂ sorbents 1 M–0.5 h–1:10, 1 M–2h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5, when compared to commercial CaO, suggest that they are promising alternatives for use in CaL.

### 3.3 Preliminary cost structure of the proposed integrated CO₂ capture process

One inherent advantage of CaL over any other current post-combustion CO₂ capture technologies, when employed for CO₂ abatement in the iron and steel industry, is that the spent CaO can be recycled directly as a flux into the blast furnace for iron production. This would result in an additional reduction in CO₂ emissions associated with the calcination of limestone during conventional iron and steel production processes. With regard to the practical application of CaL-based CO₂ capture technology, the cost structure can be affected by a variety of operating parameters. MacKenzie and colleagues performed a sensitivity analysis on eight potentially key variables influencing the cost of CaL-based CO₂ capture technology used in practical applications. They confirmed that the CO₂ capture cost of the CaL process is most affected by the cost of CaO-based sorbents and their deactivation rate when the internal solid circulation (molar ratio of CaO to CO₂) and the make-up flow of solids (purge percentage of fresh CaO in the calciner) have been determined. The superior CO₂ reactivity and favorable deactivation rate of the steel slag-derived, CaO-based materials 1 M–0.5 h–1:10, 1 M–2 h–1:10, 2 M–0.5 h–1:5, and 2 M–2 h–1:5, when compared to the commercial CaO, have been verified above. Now we attempt to compare the preliminary cost structure between limestone-derived CaO and typical steel slag-derived CO₂ sorbents developed in this study, mainly based on the material flow analysis, as shown in Table 2. Naturally occurring limestone is the main feedstock of conventional CaO-based CO₂ sorbent for CaL. For the steel slag-derived, CaO-based CO₂ sorbents developed in this study, given that steel slag is almost zero-cost industrial waste, acetic acid is the main consideration in the cost analysis. For materials 1 M–0.5 h–1:10 and 1 M–2 h–1:10, ~2.5 g of acetic acid was consumed to produce 1 g of CO₂ sorbent, which is near the theoretically lowest requirement of ~2.1 g acetic acid g⁻¹sorbent. Although bearing a higher expense for feedstock than naturally derived CaO, the final cost of the steel slag-derived, CaO-based sorbent was well compensated by the byproducts recovered, i.e., the high-purity CaO, high-quality iron ore, and acetone. The cost of materials 1 M–0.5 h–1:10 and 1 M–2 h–1:10 was

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**Fig. 9** Multicyclic CO₂ capture performance of the steel slag-derived, CaO-based sorbents synthesized, with commercial CaO included for comparison, under realistic CaL conditions.
sorbent/CO₂ ratios and material make-up flows. Material naturally derived CaO. However, it should be pointed out that make-up flows (f) of sorbent/CO₂ ratios and material make-up flows, while the increase in the maximum average CO₂ capture capacity of CaO-templated CO₂ sorbents for use in Cal; we adapted this approach to use different CaL operations, and proposed a useful approach to assess the availability of new CaO-based CaO sorbents under different CaL conditions, and proposed a useful approach to assess the availability of new CaO-based CaO sorbents for use in Cal; we adapted this approach to assess the acceptable cost of the as-prepared CO₂ sorbents is acceptable as long as it remains below an upper limit, which largely depends on the CO₂ capture capacity of the materials. Romeo and colleagues studied in detail the relationship between the increase in the maximum average CO₂ capture capacity of CaO-based sorbents and the maximum acceptable investment in sorbents under different CaL operations, and proposed a useful approach to assess the availability of new CaO-based CaO sorbents for use in Cal; we adapted this approach to assess the acceptable cost of the steel slag-derived CO₂ sorbents developed in this study (Table 3). As expected, a more cost-effective CaO-based CaO sorbent is required when Cal is performed under higher sorbent-to-CO₂ ratios (R) or material make-up flows (fₚ), as more fresh sorbents are consumed under these operating conditions. Materials 1 M–0.5 h–1 : 10 and 1 M–2 h–1 : 10 exhibited appreciable superiority over naturally derived CaO with regard to the cost of sorbents under all sorbent/CO₂ ratios and material make-up flows. Material 2 M–2 h–1 : 5 was comparable with naturally derived CaO under low sorbent/CO₂ ratios and material make-up flows, while the cost of material 2 M–0.5 h–1 : 5 was marginally higher than naturally derived CaO. However, it should be pointed out that the cost structure of the proposed integrated CO₂ capture process was assessed here mainly based on the material flow analysis. The capital costs and variable operating costs commonly considered in practical Cal projects have not been mentioned yet at this stage. Nevertheless, the proposed integrated CO₂ capture process using materials 1 M–0.5 h–1 : 10 and 1 M–2 h–1 : 10 appears to be cost-effective, which is promising for CO₂ abatement applications in the iron and steel industry.

### 4. Conclusions

We have proposed and experimentally demonstrated the feasibility of an integrated CO₂ capture process for CO₂ abatement in the iron and steel industry. In such a process, highly effective CaO-based CO₂ sorbents were easily prepared via acid extraction of waste steel slag using acetic acid. Encouragingly, the recycling efficiency of iron from the steel slag residues remaining after acid extraction increased significantly due to improvement in both the recovery of iron-rich materials and the iron content in the materials recovered, allowing for recycling of high-quality iron ore with iron content as high as 55.1–70.6%. The steel slag-derived, CaO-based CO₂ sorbents 1 M–0.5 h–1 : 10, 1 M–2 h–1 : 10, 2 M–0.5 h–1 : 5, and 2 M–2 h–1 : 5 could achieve CaO content as high as ~90 wt%. The well-defined, porous morphology ensured these materials superior CO₂ reactivity, and importantly, significantly slower linear deactivation with Cal cycles, compared to commercial

### Table 2 Comparison of sorbent costs based on material flow analysis

| Material         | Feedstock consumed [t sorbent⁻¹] | Byproduct recovered [t sorbent⁻¹] | Cost of sorbents [€ t⁻¹] |
|------------------|----------------------------------|----------------------------------|-------------------------|
|                  | Acetic acid                      | Limestone                        | CaO | Iron ore | Acetone |                          |
| 1 M–0.5 h–1 : 10 | 2.50                             | —                                | 0.91 | 0.05    | 0.94    | 57.7                       |
| 1 M–2 h–1 : 10   | 2.50                             | —                                | 0.90 | 0.06    | 0.93    | 62.2                       |
| 2 M–0.5 h–1 : 5  | 2.86                             | —                                | 0.90 | 0.06    | 0.93    | 145.7                      |
| 2 M–2 h–1 : 5    | 2.73                             | —                                | 0.89 | 0.07    | 0.92    | 120.0                      |
| Naturally derived CaO | —                              | 1.98                             | —   | —       | —       | 102.0                      |

Note: Prices of the components mentioned were determined according to the average price from the past 3 years in the Chinese market, i.e., 231.9 € t⁻¹, 51.5 € t⁻¹, 103.1 € t⁻¹, and 450.9 € t⁻¹ for acetic acid, limestone (~90 wt%), iron ore (~62 wt%), and acetone (~99.5 wt%), respectively. The component was not consumed or recovered.

### Table 3 Maximum acceptable cost of the steel slag-derived, CaO-based CO₂ sorbents developed under various Cal conditions

| Material         | Xᵣose increase [%] | Maximum acceptable cost of sorbents [€ t⁻¹] |
|------------------|--------------------|---------------------------------------------|
|                  |                    | R = 1.5                                      |
|                  |                    | fₚ = 1%                                      |
|                  |                    | R = 3                                        |
|                  |                    | fₚ = 1%                                      |
|                  |                    | R = 5                                        |
|                  |                    | fₚ = 1%                                      |
| 1 M–0.5 h–1 : 10 | 3.8                | 117.2                                       |
| 1 M–2 h–1 : 10   | 7.6                | 132.3                                       |
| 2 M–0.5 h–1 : 5  | 5.9                | 125.6                                       |
| 2 M–2 h–1 : 5    | 5.4                | 123.6                                       |

|                  | fₚ = 2.5%          | 119.2                                       |
|                  |                    | 112.6                                       |
|                  | fₚ = 2.5%          | 112.6                                       |
|                  |                    | 111.4                                       |
|                  | fₚ = 2.5%          | 111.4                                       |
|                  |                    | 108.9                                       |
|                  | fₚ = 2.5%          | 115.4                                       |
|                  |                    | 115.4                                       |
|                  | fₚ = 2.5%          | 115.4                                       |
|                  |                    | 115.4                                       |

* The subtraction of average carbonation conversion during 20 cycles between the steel slag-derived CO₂ sorbent and naturally derived CaO. The molar ratio of the CaO-based sorbent to CO₂ during the Cal process. The make-up flow (purge percentage) of fresh CaO-based sorbents in the calciner.

57.7 € t⁻¹ and 62.2 € t⁻¹, respectively, appreciably lower than that of the naturally derived CaO (102 € t⁻¹).

Given the enhanced CO₂ capture performance of the steel slag-derived sorbents compared to naturally derived CaO, an increase in the cost of the as-prepared CO₂ sorbents is acceptable as long as it remains below an upper limit, which largely depends on the CO₂ capture capacity of the materials. Romeo and colleagues studied in detail the relationship between the increase in the maximum average CO₂ capture capacity of CaO-based sorbents and the maximum acceptable investment in sorbents under different CaL operations, and proposed a useful approach to assess the availability of new CaO-based CO₂ sorbents for use in Cal; we adapted this approach to assess the acceptable cost of the steel slag-derived CO₂ sorbents developed in this study (Table 3). As expected, a more cost-effective CaO-based CO₂ sorbent is required when Cal is performed under higher sorbent-to-CO₂ ratios (R) or material make-up flows (fₚ), as more fresh sorbents are consumed under these operating conditions. Materials 1 M–0.5 h–1 : 10 and 1 M–2 h–1 : 10 exhibited appreciable superiority over naturally derived CaO with regard to the cost of sorbents under all sorbent/CO₂ ratios and material make-up flows. Material 2 M–2 h–1 : 5 was comparable with naturally derived CaO under low sorbent/CO₂ ratios and material make-up flows, while the cost of material 2 M–0.5 h–1 : 5 was marginally higher than naturally derived CaO. However, it should be pointed out that the cost structure of the proposed integrated CO₂ capture process was assessed here mainly based on the material flow analysis. The capital costs and variable operating costs commonly considered in practical Cal projects have not been mentioned yet at this stage. Nevertheless, the proposed integrated CO₂ capture process using materials 1 M–0.5 h–1 : 10 and 1 M–2 h–1 : 10 appears to be cost-effective, which is promising for CO₂ abatement applications in the iron and steel industry.

### 4. Conclusions

We have proposed and experimentally demonstrated the feasibility of an integrated CO₂ capture process for CO₂ abatement in the iron and steel industry. In such a process, highly effective CaO-based CO₂ sorbents were easily prepared via acid extraction of waste steel slag using acetic acid. Encouragingly, the recycling efficiency of iron from the steel slag residues remaining after acid extraction increased significantly due to improvement in both the recovery of iron-rich materials and the iron content in the materials recovered, allowing for recycling of high-quality iron ore with iron content as high as 55.1–70.6%. The steel slag-derived, CaO-based CO₂ sorbents 1 M–0.5 h–1 : 10, 1 M–2 h–1 : 10, 2 M–0.5 h–1 : 5, and 2 M–2 h–1 : 5 could achieve CaO content as high as ~90 wt%. The well-defined, porous morphology ensured these materials superior CO₂ reactivity, and importantly, significantly slower linear deactivation with Cal cycles, compared to commercial
CaO. Although costing more than naturally derived CaO in the purchase of feedstock, the final cost of the steel slag-derived, CaO-based CO₂ sorbent developed here was compensated by the byproducts recovered, i.e., the high-purity CaO, high-quality iron ore, and acetone. Materials 1 M–0.5 h–1:10 and 1 M–2 h–1:10 were much more cost-effective than naturally derived CaO, making the integrated CO₂ capture process proposed in this study potentially very attractive for CO₂ abatement in the iron and steel industry.

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References

1 IPCC, Industry, in Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2014.
2 T. A. Napp, A. Gambhir, T. P. Hills, N. Florin and P. S. Fennell, A review of the technologies, economics and policy instruments for decarbonising energy-intensive manufacturing industries, Renewable Sustainable Energy Rev., 2014, 30, 616–640.
3 U.S. Energy Information Administration (U.S. EIA), International Energy Outlook 2013: With Projections to 2040, Washington, DC 20585; 2013. To be found at: http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf.
4 International Energy Agency (IEA), Energy technology perspectives 2010: scenarios & strategies to 2050, OECD/IEA, Paris and 2010.
5 IPCC, Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Geneva, Switzerland, 2007.
6 International Energy Agency (IEA), Executive Summary for Energy Technology Perspectives 2012: Pathways to a Clean Energy System, OECD/IEA, Paris, 2012. To be found at: http://www.iea.org/textbase/npsum/ETP2012SUM.pdf.
7 International Energy Agency (IEA), Tracking Clean Energy Progress 2014, OECD/IEA, Paris, 2014. To be found at: http://www.iea.org/publications/freereports/publication/Tracking_clean_energy_progress_2014.pdf.
8 S. Tian, J. Jiang, F. Yan, K. Li and X. Chen, Synthesis of highly efficient CaO-based, self-stabilizing CO₂ sorbents via structure-reforming of steel slag, Environ. Sci. Technol., 2015, 49, 7464–7472.
9 D. P. Hanak, E. J. Anthony and V. Manovic, A review of developments in pilot-plant testing and modelling of calcium looping process for CO₂ capture from power generation systems, Energy Environ. Sci., 2015, 8, 2199–2249.
10 B. Arias, M. E. Diego, J. C. Abanades, M. Lorenzo, L. Diaz, D. Martinez, J. Alvarez and A. Sánchez-Bizem, Demonstration of steady state CO₂ capture in a 1.7 MWth calcium looping pilot, Int. J. Greenhouse Gas Control, 2013, 18, 237–245.
11 J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, The calcium looping cycle for large-scale CO₂ capture, Prog. Energy Combust. Sci., 2010, 36, 260–279.
12 M. Alonso, M. E. Diego, C. Perez, J. R. Chamberlain and J. C. Abanades, Biomass combustion with in situ CO₂ capture by CaO in a 300 kWth circulating fluidized bed facility, Int. J. Greenhouse Gas Control, 2014, 29, 142–152.
13 M. Zhao, A. I. Minett and A. T. Harris, A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO₂, Energy Environ. Sci., 2013, 6, 25–40.
14 D. P. Hanak, C. Bilyok and V. Manovic, Calcium looping with inherent energy storage for decarbonisation of coal-fired power plant, Energy Environ. Sci., 2016, 9, 971–983.
15 D. C. Ozcan, B. H. Shanks and T. D. Wheelock, Improving the stability of a CaO-based sorbent for CO₂ by thermal pretreatment, Ind. Eng. Chem. Res., 2011, 50, 6933–6942.
16 V. Manovic and E. J. Anthony, Thermal activation of CaO-based sorbent and self-activation during CO₂ capture looping cycles, Environ. Sci. Technol., 2008, 42, 4170–4174.
17 Z. Chen, H. S. Song, M. Portillo, C. J. Lim, J. R. Grace and E. J. Anthony, Long-term calcination/carbonation and thermal pretreatment for CO₂ capture by limestone and dolomite, Energy Fuels, 2009, 23, 1437–1444.
18 V. Manovic and E. J. Anthony, Steam reactivation of spent CaO-based sorbent for multiple capture cycles, Environ. Sci. Technol., 2007, 41, 1420–1425.
19 B. V. Materić, C. Sheppard and S. I. Smedley, Effect of repeated steam hydration reactivation on CaO-based sorbents for CO₂ capture, Environ. Sci. Technol., 2010, 44, 9496–9501.
20 F. Donat, N. H. Florin, E. J. Anthony and P. S. Fennell, Influence of high-temperature steam on the reactivity of CaO sorbent for CO₂ capture, Environ. Sci. Technol., 2012, 46, 1262–1269.
21 N. Phalak, N. Deshpande and L. S. Fan, Investigation of high-temperature steam hydration of naturally derived calcium oxide for improved carbon dioxide capture capacity over multiple cycles, Energy Fuels, 2012, 26, 3903–3909.
22 B. Arias, G. S. Grasa, M. Alonso and J. C. Abanades, Post-combustion calcium looping process with a highly stable sorbent activity by recarbonation, Energy Environ. Sci., 2012, 5, 7353–7359.
34 P. Renforth, C. L. Washbourne, J. Taylder and D. A. C. Manning, Silicate production and availability for mineral carbonation, Environ. Sci. Technol., 2011, 45, 2035–2041.

35 A. Telesca, D. Calabrese, M. Marroccoli, M. Tomasulo, G. L. Valenti, G. Duelli and F. Montagnaro, Spent limestone sorbent from calcium looping cycle as a raw material for the cement industry, Fuel, 2014, 118, 202–205.

36 C. C. Dean, D. Dugwell and P. S. Fennell, Investigation into potential synergy between power generation, cement manufacture and CO2 abatement using the calcium looping cycle, Energy Environ. Sci., 2011, 4, 2050–2053.

37 N. Rodríguez, R. Murillo and J. C. Abanades, CO2 capture from cement plants using oxyfired precalcination and/or calcium looping, Environ. Sci. Technol., 2012, 46, 2460–2466.

38 K. Atonios, P. Grammelis, S. K. Antiohos, N. Nikolopoulos and E. Kakaras, Integration of calcium looping technology in existing cement plant for CO2 capture: process modeling and technical considerations, Fuel, 2015, 153, 210–223.

39 Y. Li, C. Zhao, L. Duan, C. Liang, Q. Li, W. Zhou and H. Chen, Cyclic calcination/carbonation looping of dolomite modified with acetic acid for CO2 capture, Fuel Process. Technol., 2008, 89, 1461–1469.

40 Y. Li, C. Zhao, H. Chen, C. Liang, L. Duan and W. Zhou, Modified CaO-based sorbent looping cycle for CO2 mitigation, Fuel, 2009, 88, 697–704.

41 J. C. Abanades, E. J. Anthony, D. Y. Lu, C. Salvador and D. Alvarez, Capture of CO2 from combustion gases in a fluidized bed of CaO, AIChE J., 2004, 50, 1614–1622.

42 D. Alvarez and J. C. Abanades, Determination of the critical product layer thickness in the reaction of CaO with CO2, Ind. Eng. Chem. Res., 2005, 44, 5608–5615.

43 Z. Li, H. Sun and N. Cai, Rate equation theory for the carbonation reaction of CaO with CO2, Energy Fuels, 2012, 26, 4607–4616.

44 E. R. Sacija, S. Ramkumar, N. Phalak and L. S. Fan, Synthesis and regeneration of sustainable CaO sorbents from chicken eggshells for enhanced carbon dioxide capture, ACS Sustainable Chem. Eng., 2013, 1, 903–909.

45 A. MacKenzie, D. L. Granatstein, E. J. Anthony and J. C. Abanades, Economics of CO2 capture using the calcium cycle with a pressurized fluidized bed combustor, Energy Fuels, 2007, 21, 920–926.

46 L. M. Romeo, Y. Lara, P. Lisbona and A. Martínez, Economical assessment of competitive enhanced limestones for CO2 capture cycles in power plants, Fuel Process. Technol., 2009, 90, 803–811.