Development of robust CaO-based sorbents from blast furnace slag for calcium looping CO2 capture

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HIGHLIGHTS

- Blast furnace slag is a promising feedstock for preparation of CaO-based CO2 sorbents.
- Acidity of the extracting agent determines the leaching efficiency of BFS elements.
- The developed sorbent shows a well balance between the CO2 uptake and cyclic stability.
- An effective separation of Ca and Si during acid extraction improves sorbent performance.

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ABSTRACT

CaO-based calcium looping materials have received great interest for their use in thermochemical CO2 capture and energy storage, as well as CO2-related energy conversion processes. In this paper, the development of robust CaO-based CO2 sorbents using waste blast furnace slag (BFS) as a sustainable and environmentally benign feedstock is reported. Calcium and magnesium in the BFS can be facilely acquired through an acid extraction process, and appear in the form of CaO and MgO, which serve as a CO2 carrier and structural stabiliser, respectively, in the prepared CO2 sorbents. The BFS-derived sorbent prepared in this study exhibited a superior CO2 capture capacity of 0.37 g CO2/g sorbent with an average cyclic deactivation rate as low as 2.3%, representing a balanced performance between CO2 uptake and cyclic stability as compared to most other waste-derived, CaO-based CO2 sorbents. This study demonstrated that CaO-stabiliser interaction largely determines the CO2 capture performance of CaO-based sorbents, and the Ca/Si ratio in the BFS-derived sorbent should be effectively controlled to allow the material to capture CO2 at a high performance.

1. Introduction

Calcium looping (CaL), which relies on the reversible CaO carbonation-decarbonation reaction at high temperatures (Eq. (1)), is an emerging thermochemical solid-looping process for CO2 capture as well as CO2-related energy conversion and storage [1–3]. In addition to the advantage of being naturally occurring as limestone, CaO is generally acknowledged to be a promising CO2 sorbent [4] and heat carrier [5,6] due to its superior theoretical CO2 capture capacity of 0.78 g CO2 g CaO\textsuperscript{-1} and energy density of 4.4 GJ m\textsuperscript{-3}, respectively. Recent studies have demonstrated that CaL is more energy-efficient and cost-effective for industrial decarbonisation than other emerging CO2 capture technologies [7,8], and therefore, interest is increasing in the development and implementation of CaL technology in global carbon management engineering [5,9].

\[ \text{CaO(s)} + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s), \quad \Delta H_{298K} = -178.2 \text{kJ mol}^{-1} \] (1)

However, the rapid decline in the CO2 uptake of the naturally derived CaO over repeated CaL cycles, due to sintering of CaCO3, has been a main drawback limiting the practical application of CaL for CO2 capture, thermochemical energy storage, and related energy conversion processes. Hence, in the past one or two decades, most attention on CaL has been paid to the development of sintering-resistant CaO-based CO2 sorbents operated in the process, which included activation of the naturally occurring limestone [10–12] and synthesis of the stabilised CaO-based CO2 sorbents with controllable structures [13–15]. Development of Ca-rich solid wastes into CaO-based CO2 sorbents represents another alternative option, which not only helps save the natural
limestone and/or synthetic Ca-precursor resources, but also brings environmental benefits by utilising large amounts of industrial and biogenesis calcium wastes [16,17]. The industrial solid wastes investigated as a potential CaO-based sorbent for calcium-looping CO2 capture include steel slag [18], carboide slag [19,20], lime mud [21,22], air pollution control residues [23], construction and demolition waste [24], and waste marble powders [25], while the investigated biogenesis calcium wastes include eggshells, seafood shells, snails shells, and cuttlefish bones [17]. In order to increase the CO2 capture capacity of the investigated calcium wastes, researchers tried to activate these wastes by improving their porosity. For example, Sun et al. [26] used plastic/rubber wastes as a template to alter the porosity of carbide slag, allowing the CO2 uptake to increase by 27% as compared to the raw slag after 25 CaL cycles; Sacia et al. [27] pretreated eggshells with acetic acid, resulting in the generation of a mesoporous structure to provide a 38% improvement in CaO conversion over the untreated eggshells after 10 CaL cycles.

In addition to the direct utilisation of raw or activated calcium wastes for CaL CO2 capture, interest is increasing in the development of CaO-based CO2 sorbents using these wastes as a feedstock. Eggshells were used to prepare robust CO2 sorbents by introducing ZrO2 [28] and bauxite tailings [29] into the CaO matrix via a solid-phase method, which exhibited superior capacity for CO2 capture. Waste oyster shells have also been employed as a Ca precursor to prepare stabilised CaO-based CO2 sorbents [30,31]. Industrial calcium wastes attracted more interest as Ca precursors for CaO-based CO2 sorbents when compared to biogenesis calcium wastes because of the volume and regularity of their generation. Carbide slag was used to produce different sintering-resistant CaO-based CO2 sorbents by introducing organic templates, including microcrystalline cellulose and rice husk [32], byproducts of biodiesel [33], and glycerol [34], to modify the pore structure of materials. Recent studies by Ma et al. [35,36] have demonstrated that CO2 capture performance of the waste-derived, CaO-based sorbents could be effectively improved by tuning porosity of the material using bio-templates. Lime mud was employed as a Ca precursor to prepare a series of CaO-based sorbents, which exhibited superior cyclic CO2 capture performance when stabilised by bauxite tailings [37] or aluminum nitrate [38] as dopants. Sun et al. [39] developed a CaO-based sorbent through a novel joint processing route that integrates the disposal of phosphogypsum wastes with CO2 emission reduction in a cement plant. Tian et al. developed different types of CaO-based CaO-based sorbents using steel slag as a feedstock, including the conventional sorbent stabilised by Al2O3 [40] or MgO [41], as well as the novel iron-functionalized sorbent for auto-thermal CO2 capture [42,43]. Sun et al. [44] investigated and optimised the main synthesis parameters, i.e., extraction time, extraction temperature, acid concentration, and solid/liquid ratio, influencing the CO2 capture capacity and stability of the CaO-based sorbent synthesised via acidification treatment. Taking the iron and steel industry as an example, the techno-economic superiority of CaL CO2 capture has been demonstrated when applying the CaO-based sorbent derived from industrial calcium wastes instead of the naturally derived CaO [41].

This study investigated the technical feasibility to develop robust CaO-based CO2 sorbents using blast furnace slag (BFS), which is a Ca- and Si-rich industrial waste generated at a large intensity of 270–320 Mt per year in the ironmaking industry worldwide [45], as a new promising feedstock. The leaching behaviour of main elements in BFS under acidic extraction conditions was studied, CO2 capture performance of the BFS-derived CaO-based sorbents was assessed, and key factors influencing the CO2 capture capacity of the BFS-derived sorbents were explored.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe2O3</th>
<th>SiO2</th>
<th>CaO</th>
<th>MgO</th>
<th>Al2O3</th>
<th>MnO</th>
<th>TiO2</th>
<th>Others</th>
</tr>
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<tbody>
<tr>
<td>Content (%)</td>
<td>0.35</td>
<td>33.31</td>
<td>40.94</td>
<td>8.46</td>
<td>14.99</td>
<td>0.26</td>
<td>0.57</td>
<td>1.12</td>
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2. Materials and methods

2.1. CO2 sorbent preparation

The blast furnace slag (BFS) used in this study was sampled from an integrated iron and steel plant in China. The fresh BFS sample was mechanically ground to a particle size of 0.05–0.1 mm before use. The elemental composition of the raw slag, expressed in the form of oxides, was determined by using X-ray fluorescence spectroscopy (XRF) as shown in Table 1. An acid extraction followed by precipitation approach [41] was employed in this study to transform the BFS sample into CaO-based CO2 sorbents. Accordingly, the BFS sample was mixed with a solution of acetic acid or nitric acid at a solid-to-liquid ratio of 1 g to 10 mL. Then, the mixture was shaken mechanically at a speed of 10 rpm at room temperature for a desired duration. The resulting slurry was centrifuged to separate the BFS leachate from the residues at 4 °C. The BFS leachate was dried overnight in a vacuum oven at 110 °C, and then calcined at 800 °C for 30 min to obtain the required CO2 sorbents. In addition to the type of acid, other factors influencing the preparation of the BFS-derived, CaO-based CO2 sorbents included the concentration of acid and duration of shaking, which were investigated in the range of 1–5 mol/L and 30–150 min, respectively, in this study. For brevity, the nomenclature of A_x/N_y, where A and N denote the use of acetic acid and nitric acid, respectively; the subscript x denotes the concentration of acid, and y denotes the duration of shaking, was used to refer to the prepared sorbents.

2.2. Material characterisation

A microwave plasma-atomic emission spectrometer (MP-AES, 4100, Agilent Technologies) was used to determine the concentration of main elements in the BFS leachate. In the measurement, the characteristic atomic emission peaks of Ca, Si, Mg, and Al, located at 317.933, 251.611, 280.271, and 396.152 nm, respectively, were employed for elemental calibration and quantification. A powder X-ray diffractometer (XRD, XPert Pro MPD, PANalytical) was used to determine the composition of crystalline phases in the raw BFS sample, BFS residues after acidic extraction, and prepared CaO-based CO2 sorbents. The main operating parameters to acquire the XRD pattern included an anode with Cu Kα radiation (λ = 1.5418 Å) and a 2θ range of 5–90°. A scanning electron microscope (SEM, Phenom XL, ThermoFisher Scientific) was used to observe morphology of the BFS residues after acidic extraction and prepared CaO-based CO2 sorbents. The main operating parameters to acquire the XRD pattern included an anode with Cu Kα radiation (λ = 1.5418 Å) and a 2θ range of 5–90°. A scanning electron microscope (SEM, Phenom XL, ThermoFisher Scientific) was used to observe morphology of the BFS residues after acidic extraction and prepared CaO-based CO2 sorbents. The main operating parameters to acquire the XRD pattern included an anode with Cu Kα radiation (λ = 1.5418 Å) and a 2θ range of 5–90°. A scanning electron microscope (SEM, Phenom XL, ThermoFisher Scientific) was used to observe morphology of the BFS residues after acidic extraction and prepared CaO-based CO2 sorbents. The main operating parameters to acquire the XRD pattern included an anode with Cu Kα radiation (λ = 1.5418 Å) and a 2θ range of 5–90°. A scanning electron microscope (SEM, Phenom XL, ThermoFisher Scientific) was used to observe morphology of the BFS residues after acidic extraction and prepared CaO-based CO2 sorbents. The main operating parameters to acquire the XRD pattern included an anode with Cu Kα radiation (λ = 1.5418 Å) and a 2θ range of 5–90°.

2.3. Sorbent test

Temperature-programmed carbonation (TPC) of the BFS-derived, CaO-based CO2 sorbents was performed in a thermo-gravimetric analyser (TGA, TGA/DSC 1, Mettler Toledo). The sample (~4 mg) was placed in an alumina crucible and heated to 1000 °C at a rate of 10 °C/min under a gas flow of 50 mL/min containing 20% CO2 (balance in N2). Isothermal CO2 capture characteristics of the prepared CO2 sorbents were investigated in the TGA by carbonating the sample at 650 °C under a 20% CO2 flow of 50 mL/min for 120 min. During the experiment, weight change of the sample was continuously recorded for...
calculation of the CO₂ uptake, expressed in the form of \( \frac{f_{CO_2}/g_{sorbent}}{g_{sorbent}} \), of the BFS-derived, CaO-based sorbents.

In the experiment to investigate the cyclic CO₂ capture performance of the BFS-derived, CaO-based sorbents, approximately 4 mg of sample was placed in an alumina crucible in the TGA and heated to 650 °C at a rate of 20 °C/min under a N₂ flow of 50 mL/min. The temperature was then held for 10 min, during which a gas flow of 50 mL/min containing 20% CO₂ (balance in N₂) was introduced into the reaction chamber, instead of the N₂ flow, to carbonate the sample. Subsequently, the temperature was increased to 900 °C and held for 5 min to calcine the sample. After the temperature was decreased back to 650 °C under a N₂ flow of 50 mL/min, a new CaL cycle would begin by switching the reaction atmosphere to a 20% CO₂ flow of 50 mL/min. The carbonation–calcination cycle was repeated 20 times for each sorbent, and a blank run was performed to correct for the buoyancy effect due to the change in temperature and gas flow between the carbonation and calcination steps.

3. Results and discussion

3.1. Extraction characteristics of main elements in the BFS

Acid extraction, i.e., leaching out useful metals under acidic aqueous conditions, is an effective solution to activate the alkaline industrial solid wastes [41,44]. In order to investigate the influence of acidity on the extraction performance of BFS elements, the acidic leaching experiments were performed in both nitric acid and acetic acid, which represent the aqueous environment with a high and low strength of H⁺, respectively. The concentrations of the main elements, including Ca, Mg, Al, and Si, in the BFS leachate under different concentrations of acids as a function of the leaching time are shown in Fig. 1. Two observations are clear. First, nitric acid has a stronger ability to activate the BFS, and thus, extract the main BFS elements than acetic acid; second, the leaching concentration of different BFS elements generally increases with the increasing concentration of acids in the solution. Nonetheless, each BFS element showed a different leaching behaviour under the conditions investigated in this study.

Calcium is the most abundant element in the BFS sample, as shown in Table 1, owning to the fact that limestone is fed into the blast furnace as a flux to remove impurities from iron ore during the production of pig iron. No matter nitric acid or acetic acid was used as the extracting agent, the concentration of Ca in the BFS leachate presented a remarkable increase when the acid concentration was increased from 1 to 3 mol/L, while did not go on increasing as the concentration of acids increased (Fig. 1). This indicates that an excessive amount of H⁺ in the solution would not contribute to the extraction of Ca from BFS. Al—though Ca experienced a marginal change in the leaching concentration as the extraction time increased from 30 min to 150 min, the maximum leaching concentration of Ca in nitric acid reached 73.0 g/L, which was more than 1.6 times that of in acetic acid. It is encouraging that Ca^{2+} was the dominant ion species in the BFS leachate when compared to other BFS elements, considering that CaO is the main component responsible for CO₂ capture in the as-prepared BFS-derived sorbents.

Silicon, the main impurity in iron ore, is removed by limestone and enriched in the resulting BFS during pig iron production in the blast furnace. In Fig. 1, the concentration of Si gradually declined with the increase of the leaching time regardless of the acity (nitric or acetic acid) and acid concentration of the extracting environment. Among all BFS elements, Si ranged the most in the leaching concentration, which, for example, decreased from 19.2 g/L at 30 min to 4.5 g/L at 150 min in 2 mol/L of acetic acid, and from 40.1 g/L at 30 min to 7.1 g/L at 150 min in 2 mol/L of nitric acid, respectively. This indicates that the dissolution–precipitation equilibrium of Si is more sensitive to the leaching time, as compared to other BFS elements, under acidic extraction conditions, and is also more sensitive in nitric acid than in acetic acid. Considering that the content of silicon in the prepared CaO-based CO₂ sorbent is preferred to be at a limited level, a prolonged duration for acid extraction of the BFS would be an alternative choice. This is because elevated amount of silicon would form inert solid solutions with CaO, lowering the availability of the free CaO phase in the material for CO₂ capture [46]. In addition, Fig. 1 shows that extraction using acetic acid also aids retention of Si in the BFS residue instead of being extracted into the leachate, which is in line with the experimental observations from previous studies [47].

Magnesium and aluminium are minor elements in the raw BFS compared with calcium and silicon, while an appropriate content of MgO and/or Al₂O₃ would be beneficial to CaO-based CO₂ sorbents since they have been widely demonstrated to be effective thermostable stabilisers to prevent the CaO grains from being sintered during repeated high-temperature CaL cycles. As shown in Fig. 1, both Mg and Al did not exhibit a significant difference in the concentration with the increase of leaching time in 1–5 mol/L of acetic acid, and a similar observation was found when nitric acid was used as the extracting agent. When acetic acid was used as the extracting agent, the leaching concentrations of both Mg and Al increased with an increase of acid concentration, and the concentration of Mg was appreciably higher than that of Al. With regard to extraction using nitric acid, the concentrations of Mg and Al kept increasing as that of nitric acid increased from 1 to 3 mol/L, but were stabilised when the concentration of nitric acid was over 3 mol/L. It is worth noting that the leaching concentration of Al was lower than that of Mg when the concentration of nitric acid was below 3 mol/L, but exceeded that of Mg in 3–5 mol/L of nitric acid. One would conclude from this observation that, a low H⁺ intensity in the solution is in favour of extracting Mg from BFS, while a high H⁺ intensity benefits the extraction of Al. It is also clearly observed in Fig. 1 that the leaching concentrations of Mg and Al were closer to each other when using nitric acid than acetic acid.

Micron-scale morphology of the selected BFS residues after acid extraction under different conditions is compared in Fig. 2. It is observed that the morphology of the BFS residues after leaching in acetic acid (Fig. 2, (a)-(c)) was obviously different from that of residues leached in nitric acid (Fig. 2, (d)-(f)). The slag treated by acetic acid presented a microstructure with a compact surface and filled with agglomerates of different shapes. However, the slag treated by nitric acid presented a loose and eroded surface, indicating a better interaction between the slag and acid during the extraction process. This finding is supported by the comparison of elemental leaching behaviour in acetic and nitric acids in Fig. 1, where the significantly improved leaching performance of elements when the concentration of nitric acid was increased from 1 mol/L to 3 mol/L was associated with the appreciably eroded morphology in Fig. 2(e) as compared to Fig. 2(d), and the marginal difference in the leaching performance of elements from 30 min to 120 min in 3 mol/L of nitric acid explained the close morphology in Fig. 2(e) and (f).

Interaction of the BFS and acid during the elemental extraction process was further investigated by comparing mineral composition of the raw BFS and its residues after acid extraction under different conditions, as shown in Fig. 3. Åkermanite (Ca₂Mg(Si₃O₉)) was the dominant crystalline phase in the BFS sample used in this study, which is in line with the mineral composition of the slags reported in previous studies [48,49]. The BFS residue corresponding to the sorbent A₃-30 presented an XRD pattern similar to the raw BFS, and no new crystalline phases were identified in this residue. This indicates an inferior activation of BFS at low concentrations of acetic acid, which could be verified by the experimental observation in Fig. 1(a) that the leaching concentrations of all BFS elements were less than 20 g/L in 1 mol/L of acetic acid. In the BFS residues corresponding to sorbents N₁-30 and A₃-30, the crystalline phases cordierite/indialite (Mg₆Al₂Si₅O₁₈) and clathrasil (Si₅O₁₈) were identified. This is likely attributed to the destruction of the Åkermanite phase in the BFS by the acids, thus resulting in the leaching of Ca into the acidic solution while leaving the less extractive elements Mg, Al, and Si in the residue. The appreciably
higher concentration of Ca, as compared to other elements, during the extraction process in 3 mol/L of acetic acid and 1 mol/L of nitric acid in Fig. 1 was a convictive evidence of this conclusion. As the leaching time increased, new Si-containing crystalline phases, i.e., quartz (SiO₂) and ringwoodite (Mg₂SiO₄) appeared in the BFS residues corresponding to sorbents A₃-120 and N₃-120, which was probably a result of the precipitation of the extracted Si back into the residue as evidenced by the decreased concentration of Si with the increasing leaching time (Fig. 1).

3.2. CO₂ capture performance of the BFS-derived, CaO-based sorbent

XRD patterns of the sorbents A₃-30 and N₃-30, as compared with that of the raw BFS, are shown in Fig. 4. In addition to the diffraction peaks corresponding to the crystalline Akermanite phase, a broad

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**Fig. 1.** The leaching concentration of main BFS elements as a function of the extraction time under different concentrations of (a) acetic acid and (b) nitric acid as the extracting agent.
A diffraction band located at 25–35° was observed, indicating the existence of amorphous phases in the slag. Therefore, the raw BFS was a solid waste composed of both amorphous and crystalline phases. However, the BFS-derived A3-30 and N3-30 sorbents were highly crystallised, as there were no obvious diffraction bands appearing in their XRD patterns. CaO was the major crystalline phase identified in A3-30 and N3-30, and periclase (MgO) existed as the minor component in the sorbents. In the sorbent N3-30, there was also a portion of larnite (Ca2SiO4) identified, which has been demonstrated to be an effective polymorphic spacer to improve the sintering-resistance of calcium looping materials at high temperatures [50]. Hence, it has been revealed in Fig. 4 that the waste BFS could be utilised as a potential feedstock to develop stabilised CaO-based sorbents for CO2 capture.

Temperature and time dependence of the BFS-derived, CaO-based sorbents for CO2 capture was investigated by performing the temperature-programmed carbonation and isothermal carbonation experiments, respectively, in Fig. 5. As shown in Fig. 5(a), all sorbents began to capture CO2 via the CaO carbonation reaction at around 400 °C, and the reaction rate kept increasing with temperature. Sorbents prepared using the same type of acid had a similar temperature at which the maximum carbonation rate was achieved (Fig. S1, Supporting information). Also, it is clearly shown in the differential thermogravimetric (DTG) curves in Fig. S1 that the sorbents N3-30 and N3-120 achieved the maximum carbonation rate at a temperature of around 100 °C lower than that for A3-30 and A3-120, indicating that the BFS-derived sorbent prepared using nitric acid as the extracting agent had a better reactivity to CO2 than that using acetic acid. When the temperature was over 800 °C, the weight of sorbents began to decrease owing to the occurrence of the reverse carbonation reaction to release CO2. All sorbents achieved the maximum decarbonation rate at a close
temperature of around 850 °C, therefore, the conditions for preparation of the BFS-derived, CaO-based sorbents have a smaller influence on CO2 release than its capture.

The isothermal carbonation profiles in Fig. 5(b) revealed that the reaction between BFS-derived, CaO-based sorbents and CO2 follows a two-stage regime. A short reaction stage lasting for several tens of seconds, which occurred at a high rate during the initial minutes, is controlled by carbonation kinetics. As the capture of CO2 continued, the carbonation reaction turned into a long stage, at a significantly lowered reaction rate, which is controlled by diffusion of CO2 through the CaCO3 product layer [51]. The carbonation rates of different BFS-derived sorbents in the kinetics-controlled stage were compared by using the DTG curves in Fig. S2. As observed, DTG of N3-30 was appreciably higher than that of A3-30, so did N1-120 as compared to A3-120. This indicates that the BFS-derived, CaO-based sorbent prepared using nitric acid as the extracting agent has a higher carbonation rate than that derived, CaO-based sorbents developed in this study.

Fig. 1, where a significantly higher Si/Ca ratio was observed in the BFS leachate for preparation of N1-30 than that for N3-120. Despite that all sorbents experienced a decay in the uptake of CO2 over the following cycles, the cyclic CO2 capture stability of these materials could be easily distinguished by comparing the average deactivation rate, calculated as the average percentage of decay in the CO2 uptake of a sorbent as compared to its CO2 uptake in the first cycle, over the 20 cycles performed in this study. N3-120 and N3-30 exhibited a lower deactivation rate of 2.3% and 2.6% per cycle, respectively, while other sorbents had an inferior stability for cyclic CO2 capture due to their higher deactivation rates of more than 3.5% per cycle. Therefore, under the conditions investigated in this study, the BFS-derived, CaO-based sorbent N3-120 had the best CO2 capture capacity in consideration of both the CO2 capture and cyclic stability. A further study on the deactivation of N3-120 was investigated by comparing the CO2 uptake profiles in selected cycles (Fig. S3, Supporting information). It is clearly observed that the decline in the CO2 capture ability during the carbonation kinetics-controlled stage is the main cause for the decreased CO2 uptake of the sorbent over repeated carbonation–calcination cycles.

3.3. Key factors determining the CO2 capture capacity of the BFS-derived, CaO-based sorbents

It is generally acknowledged that the main factors determining the CO2 capture capacity of any CaO-based sorbents are porosity and the
ratio of free CaO to inert stabiliser, which can be investigated by examining the micron-scale morphology and elemental composition of materials, respectively. The change in the morphology of sorbents after repeated carbonation-calcination cycles was observed in Fig. 7, where the SEM images of the BFS-derived sorbents exhibiting the best (N3-120), medium (A3-120), and worst (N1-30) CO2 capture capacity were compared. The porous structure with well-defined particles of the fresh N3-120 (Fig. 7(a)) was well maintained after 20 cycles (Fig. 7(d)), which helped explain the superior CO2 capture performance of this material. Similarly, the worse CO2 capture capacity of A3-120, as compared to that of N3-120, was probably due to its less porous structure with large agglomerated particles in the fresh sorbent (Fig. 7(b)). As for the sorbent N1-30, in addition to its inferior porosity, the excess in the content of inert phases in the material would be another important reason for its weak CO2 capture performance. It is clearly observed in Fig. 8 that CO2 uptake of the BFS-derived sorbents presented a positive correlation with the content of MgO, however, a negative correlation with that of SiO2 in the material. This is attributed to the different mechanisms of interaction between the two stabilisers and the CaO phase. The MgO stabiliser appears independently in the sorbent matrix without the formation of solid solutions with CaO, while the SiO2 stabiliser will react with CaO, as discussed above, to form a Ca2SiO4 layer on the CaO-SiO2 interface. The formation of solid solutions between stabilisers and CaO has also been reported in the studies on the investigation of other stabilisers, including Al2O3 [52] and ZrO2 [53]. These solid solutions on the interface would prevent the CaO particles from agglomeration and sintering, but come at the expense of a portion of the free CaO which is supposed to be available for CO2 capture. Accordingly, the fact that N1-30 has the highest content of SiO2 explained its inferior CO2 capture capacity in this study. With regard to the development of CaO-based CO2 sorbents using the BFS waste as a feedstock, special attention should be paid to controlling the content of Si in the material in order to balance its uptake of CO2 and cyclic stability for CO2 capture.

4. Conclusions

The waste blast furnace slag (BFS), which is generated in large quantities in the iron and steel industry has been demonstrated in this study to be a promising feedstock to prepare robust CaO-based sorbents for CO2 capture in high-temperature calcium looping cycles. All elements required to compose the stabilised CaO-based CO2 sorbent can be effectively extracted from BFS via a facile activation of this waste with acids. The type and concentration of the extracting agent, as well as the leaching time during the acid extraction process influenced the elemental extraction efficiency, and thus, CO2 capture performance of the BFS-derived sorbents in different ways. A stronger acidity of the extracting agent and longer leaching time were favourable to acquire the BFS leachate ready for preparation of an efficient CaO-based CO2 sorbent, which exhibited a trade-off performance between the uptake of CO2 and cyclic stability as compared to most CaO-based sorbents prepared from other types of industrial wastes.

The use of nitric acid to prepare BFS-derived, CaO-based CO2 sorbents allows the material a better reactivity to CO2 and higher
carbonation rate than the use of acetic acid, thus, resulting in a better CO2 capture capacity in terms of both the CO2 uptake and cyclic stability. The interaction between CaO and the inert stabiliser plays an important role in balancing the CO2 uptake and cyclic stability of a CaO-based CO2 sorbent, dependent on whether a solid solution between CaO and the stabiliser would be formed on their interface. CO2 capture capacity of the BFS-derived sorbent developed in this study correlated positively with the content of MgO, but negatively with that of SiO2 in the material. This explains why nitric acid is a more effective extracting agent under the conditions investigated in this study, as it facilitates the extraction of Mg while inhibits the extraction of Si into the BFS-derived sorbents. Therefore, an effective separation of Ca and Si during the acid extraction process is of great significance to allow the preparation of highly efficient CaO-based CO2 sorbents from blast furnace slag.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data can be found at online https://doi.org/10.1016/j.cej.2020.124140.

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