Calcium Looping: On the Positive Influence of SO₂ and the Negative Influence of H₂O on CO₂ Capture by Metamorphosed Limestone-Derived Sorbents

Sally L. Homsy,* Joseba Moreno, Alla Dikhtiarenko, Jorge Gascon, and Robert W. Dibble

ABSTRACT: The CO₂ capture performance of sorbents derived from three distinct limestones, including a metamorphosed limestone, is studied under conditions relevant for calcium looping CO₂ capture from power plant flue gas. The combined and individual influence of flue gas H₂O and SO₂ content, the influence of textural changes caused by sequential calcination/carbonation cycles, and the impact of CaSO₄ accumulation on the sorbents' capture performance were examined using bubbling fluidized bed reactor systems. The metamorphosed limestone-derived sorbents exhibit atypical capture behavior: flue gas H₂O negatively influences CO₂ capture performance, while limited sulfation can positively influence CO₂ capture, with space time significantly impacting CO₂ and SO₂ co-capture performance. The morphological characteristics influencing sorbents' capture behavior were examined using imaging and material characterization tools, and a detailed discussion is presented. This insight into the morphology responsible for metamorphosed limestone-derived sorbent's anomalous capture behavior can guide future sorbent selection and design efforts.

1. INTRODUCTION

Calcium looping (CaL) is a promising postcombustion CO₂ capture technology that can potentially contribute to global decarbonization efforts. CaL is a high-temperature separation process that utilizes a dual fluidized bed system to continuously cycle solid CaO particles between carbonation conditions and calcination conditions, where carbonation conditions favor the forward and calcination conditions favor the reverse of the following reaction: CaO + CO₂ ⇌ CaCO₃.¹ During CaL, CO₂ is captured from industrial or power plant flue gas by exothermic carbonation in the first fluidized bed reactor, the carbonator. Carbonation is performed at 650 °C to limit equilibrium constraints on efficient CO₂ capture while maintaining a fast carbonation rate.² The resulting CaCO₃ is produced by endothermic calcination. The energy required for calcination is often supplied by in situ oxy-combustion, which leads to a high CO₂ partial pressure in the calciner and shifts the thermodynamic equilibrium discouraging calcination.³,⁴ Calcination temperatures >900 °C are therefore required for efficient and fast sorbent regeneration.⁵ Note that under CaL process conditions, CaO simultaneously irreversibly reacts with SO₂ allowing CO₂ and SO₂ co-capture from sulfated flue gases. The resulting gas stream leaving the calciner therefore mainly comprises CO₂ and H₂O. High purity CO₂, suitable for sequestration in appropriate geological formations, is obtained by simply dewatering the calciner effluent gas stream. CaL has been demonstrated at three pilot plants (≥1 MWₑ) achieving a technology readiness level of 6.⁶–⁸

The high-temperature nature of CaL allows high-grade heat recovery and auxiliary power generation downstream of the calciner and carbonator, which can improve the process energy efficiency relative to first generation capture technologies such as amine scrubbing.⁹–¹¹ The CaL process is most appealing when limestone-derived CaO is used as the sorbent. Limestone is a widely available natural CaCO₃ source used in cement production, steel manufacturing, and flue gas desulfurization. The opportunity for synergy with industrial processes, coupled with the low cost of limestone, contributes to the economic viability of CaL, with competitive capture costs estimated by multiple technoeconomic studies.¹²–¹⁴ While CaL with limestone-derived sorbents is an appealing approach to decarbonization, some technological concerns remain.

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Moreover, Pinheiro et al.\textsuperscript{27} correlated these observations with changes in the CaO surface area with calcination/carbonation cycles. Reduction in mean pore diameters and therefore an increase in real surface area means that metamorphosed limestone-derived sorbents experience a structural change primarily resulting in increased grain sizes.\textsuperscript{22} The CO\textsubscript{2} capture performance of metamorphosed limestone metamorphism primarily results in increased grain sizes.\textsuperscript{22} The CO\textsubscript{2} capture performance of metamorphosed limestone-derived sorbents is expected to differ from that of unmetamorphosed limestone-derived sorbents because limestone-derived sorbent activities and reactivities are determined by sorbent morphology, specifically, crystalline structure, porosity, and surface area.\textsuperscript{23−25}

The primary sintering mechanisms responsible for reducing unmetamorphosed limestone-derived sorbent activity with progressing calcination/carbonation cycles entail grain coarsening, or growth, by crystallite migration and coalescence, and particle shrinkage, or densification.\textsuperscript{25} These morphological changes result in an increase in the sorbent’s average pore diameter and a reduction in the surface area and porosity.\textsuperscript{25,26} A recent study by Pinheiro et al.\textsuperscript{27} demonstrated that metamorphosed limestone-derived sorbents experience a reduction in mean pore diameters and therefore an increase in the CaO surface area with calcination/carbonation cycles. Moreover, Pinheiro et al.\textsuperscript{27} correlated these observations with lower deactivation rates and improved CO\textsubscript{2} capture capacity relative to unmetamorphosed limestone-derived sorbents.

The underlying cause of the anomalous behavior reported by Pinheiro et al.\textsuperscript{22} merits further exploration. Deeper insights into this unexpected behavior can inform natural sorbent selection and synthetic sorbent design efforts. Moreover, flue gas H\textsubscript{2}O and SO\textsubscript{2} content impacts CO\textsubscript{2} capture by sorbents, but this impact has not been previously studied for metamorphosed limestone-derived sorbents. Examining capture in realistic chemical environments, by a sorbent that exhibits an atypical structure and capture behavior, can shed more light on the physiochemical characteristics and interactions that dominate CO\textsubscript{2} and SO\textsubscript{2} capture behavior.

In this manuscript, we address the underlying causes of the structural changes experienced by metamorphosed limestone due to cycling and we examine the influence of the CaO matrix and realistic chemical environments on capture. We use fluidized bed reactor systems to investigate the individual and combined influence of flue gas H\textsubscript{2}O and SO\textsubscript{2} content on metamorphosed limestone-derived sorbent CO\textsubscript{2} capture behavior. While H\textsubscript{2}O typically positively influences CO\textsubscript{2} capture and SO\textsubscript{2} negatively influences CO\textsubscript{2} capture in unmetamorphosed limestone-derived sorbents,\textsuperscript{16,28} we show that the metamorphosed limestone-derived sorbent unexpectedly demonstrates the opposite behavior. The roles of the chemical composition and structure are resolved by studying three limestones: a metamorphosed limestone, an unmetamorphosed limestone with a similar chemical composition, and a chemically distinct unmetamorphosed limestone. The influence of the particle structure is further explored by considering two distinct particle size distributions (PSDs) for each limestone. Furthermore, we examine the influence of multiple calcination/carbonation cycles and of CaSO\textsubscript{4} accumulation on limestone-derived sorbent textural evolution and capture behavior. We use imaging and material characterization tools to examine the limestones and their calcines at different instances in the process and devote a discussion to the underlying factors that control the morphological changes observed in metamorphosed limestone-derived sorbents.

2. EXPERIMENTAL SECTION

Metamorphosed Saabar limestone, from the Red Sea coastal plane, and unmetamorphosed Riyadh limestone, from the Arabian platform, were provided by United Mining Investments Co., Saudi Arabia. These limestones were milled by BHS-Sonthofen GmbH and sieved by Allgaier Process Technology GmbH to “fine” and “coarse” size fractions: 100−400 and 400−1000 \( \mu \)m, respectively. Unmetamorphosed German limestone, from the Central Uplands, was also obtained as fine and coarse size fractions. PSDs were measured using a Malvern Mastersizer 3000, equipped with an Aero S dry particle dispersion unit. The elemental composition of each limestone fraction was determined by X-ray fluorescence (XRF), performed using an XGT-7000 (Horiba). A Bruker D8 ADVANCE equipped with a Cu K\( \alpha \) radiation source (\( \lambda = 1.5418 \) Å) and operated at 40 mA was used to acquire powder X-ray diffraction (PXRD) patterns on 5−80° 2\( \theta \) range with 0.03°/step and 0.5 s/step. The crystalline phase identifications were carried out in Diffra.Eva software with the help of the PDF-4+ (2019) crystal database. The structural characteristics, unit cell parameters, estimated content, and degree of crystallinity were evaluated using Reflex from the Accelrys Material Studio software package. Elemental distribution within the limestone samples and limestone surface morphology were mapped and imaged using a Zeiss MERLIN field emission scanning electron microscope equipped with a Gemini II electron optical column and Oxford Instruments X-Max80 silicon drift detector for energy dispersive spectroscopy (EDS).

Two bubbling fluidized bed (BFB) reactor systems were used to study the individual and combined influence of flue gas H\textsubscript{2}O and SO\textsubscript{2} content on CO\textsubscript{2} capture by each of the limestone fractions. A 150 mm diameter, 3.5 m tall electrically heated 20 kW\textsubscript{th} BFB (BFB 1) was used to precalcine 5 kg samples of each limestone fraction. This BFB is equipped with a double cyclone system and a filter for separating entrained fines from the reactor effluent before sampling by a gas analyzer (ABB Advance Optima 2020) for continuous CO\textsubscript{2}, SO\textsubscript{2}, and O\textsubscript{2} monitoring. The limestones were calcined under N\textsubscript{2} for 20 min at 850 °C. The capture performance of...
the precalcined samples was examined using the second 70 mm diameter 7 kWth BFB (BFB 2), described in detail elsewhere,29 equipped with effluent line sampling for continuous CO2, SO2, and O2 gas analysis (X-STREAM Emerson Process Management GmbH & Co. OHG).

BFB 2 was preheated to 650 °C with an initial inert bed inventory composed of silica sand. Gas flow rates were set to achieve a fluidization velocity of 0.5 m/s, and depending on the experimental run, an influent gas composition of either (i) 12−14% CO2, (ii) 12−14% CO2, 10−14% H2O, (iii) 12−14% CO2, 2000 ppm SO2, or (iv) 12−14% CO2, 10−14% H2O, 2000 ppm SO2, with 3% O2 and the balance N2. Baseline gas concentrations were recorded. A sample of precalcined limestone was then dropped into BFB 2 and the semibatch carbonate/sulfation reaction was allowed to proceed for 30 min while gas concentrations were recorded. Four runs with variable initial space times were performed per gas atmosphere composition and per precalcined limestone fraction. The total BFB 2 bed inventory was held constant at 1 kg for all runs while the mass of precalcined limestone added into the reactor was varied to achieve different initial space times corresponding to 9.3, 4.7, 2.3, and 0.9 min. A number of random experimental repeats were performed with results used to calculate error bars.

The influence of limestone cycling and CaSO4 content on CO2 and SO2 co-recapture was studied using the same two BFB systems. Fine Riyadh and Saabar limestones were cycled between carbonation and calcination conditions in BFB 1. BFB 1 was electrically preheated to 400 °C, and a 10 kg limestone sample was added in an inert atmosphere of N2 with fluidization maintained at ~0.4 m/s. The temperature was then raised to calcination temperatures between 850 and 900 °C and held for 15 min. In addition to electrical heating, in situ methane combustion was employed to raise the reactor temperature from 750 to 900 °C. The resulting calcination atmosphere was ~30% CO2 and 13% H2O with the balance nitrogen. The calcined limestone was then collected by means of a valve at the bottom of BFB 1, the reactor was cooled to 650 °C, and carbonation conditions were set. The calcined limestone was then added back into BFB 1 and allowed to carbonate for 20 min. Afterward, the recarbonated sorbent was reheated to 750 °C in an inert atmosphere in BFB 1, and calcination and carbonation was repeated with multiple cycles performed per experimental run. Two runs were performed per limestone source with different carbonation gas atmospheres: (i) 12% CO2, 10% H2O and (ii) 12% CO2, 10% H2O, 2000 ppm SO2, with 0.5% O2 and the balance N2. Calcined and recarbonated samples were collected after each calcination and carbonation. Fines generated by particle attrition and fragmentation were collected from the cyclones and weighed after each calcination. The limestones were cycled until sorbent activity, Xp0, was reduced to 0.1 mol/mol. The co-capture performance of samples of the calcined limestones with Xp ≈ 0.6, 0.3, and 0.1 mol/mol was evaluated using BFB 2 and the experimental method previously described. A synthetic flue gas composed of 12% CO2, 10% H2O, 2000 ppm SO2, and 3% O2 with the balance N2 was used.

A custom simultaneous thermal analysis unit (Linseis GmbH) equipped with a gas mixing manifold was used to assess calcined limestone activity at different cycle numbers. Briefly, thermogravimetric analysis (TGA) was performed on 10 mg samples of calcined limestone by heating (200 °C/min) the sample to 650 °C in N2 and then isothermally carbonating the sample in a 12% CO2 atmosphere with the balance N2 for 30 min. The recorded changes in sample mass were used to calculate Xp. TGA was also used to support the capture trends observed in BFB 2 runs; the capture behavior of calcined limestone samples was examined with TGA carbonation atmospheres set to either (i) 12−14% CO2, (ii) 12−14% CO2, 10−14% H2O, (iii) 12−14% CO2, 2000 ppm SO2, or (iv) 12−14% CO2, 10−14% H2O, 2000 ppm SO2, with 3% O2 and the balance N2.

Imaging and characterization were performed on calcined and recarbonated limestone samples taken at different experimental stages. The effect of cycling on PSDs was monitored using the Mastersizer. Alterations to crystallinity and crystal composition were tracked using PXRD. Morphological changes were studied using scanning electron microscopy (SEM)−EDS. BFB 1 calcination and carbonation efficiencies and sorbent sulfur accumulation were monitored using XRF and a Flash 2000 CHNOS Organic elemental analyzer (Thermo Scientific) equipped with a thermal conductivity detector. Brunauer−Emmett−Teller (BET) theory was used to evaluate ASAP 2420 N2 adsorption data and determine the surface area of calcined limestones. Combined results from N2 adsorption and mercury intrusion porosimetry, performed using an Autopore IV 9510 (Micrometritics), were used to determine calcined limestone porosity and map pore size distribution.

3. RESULTS AND DISCUSSION

3.1. Experimental Approach Theory and Validation.

The capture performance of the calcined metamorphosed and unmetamorphosed limestones is compared using two key CaL system metrics that influence energy efficiency and thus financial viability: capture efficiency and capture capacity. Capture efficiency, Epc, is defined as the rate of pollutant (p) uptake by the sorbent, Fp, normalized to the rate of pollutants entering the carbonator, where p refers to either CO2 or SO2.

$$E_p = \frac{F_{p,c}}{x_{p,o} F_0}$$

(1)

Sorbent capture capacity, Xmax, is pragmatically defined as the maximum achievable CaO conversion to CaCO3 and CaSO4 while maintaining a fast CO2 capture rate.

$$X_{max} = \frac{1}{n_{CaO,a}} \int_{0}^{\tau_{max}} F_{CO2,c} + F_{SO2,c} dt$$

(2)

Note that carbonation is a two stage process, with an initial fast reaction stage followed by a slow product layer solid-state diffusion-controlled stage. The initial fast reaction stage is controlled by CO2 diffusion into sorbent pores, CO2 surface diffusion, and carbonation kinetics.30,31 In eq 2, tmax is the time at which the fast reaction stage ends. Sorbent capture efficiency and capture capacity are calculated using BFB 2 gas analyzer data and a mass balance across the gas phase.

$$F_{p,c} = x_{p,o} F_0 \left( \frac{x_{p,a} - x_p - \frac{dx_p}{dt}}{x_{p,a} - x_1 - \frac{dx_1}{dt}} \right)$$

(3)

where x1 refers to the combined mole fraction of inert in the gas phase.
Sorbent capture behavior is visualized by plotting capture efficiency versus CaO conversion, $X$. CaO conversion is calculated by solving eq 2 at discrete time intervals, $t$. Note that CaO conversion refers to the combined conversion of CaO to CaCO$_3$, $X_{CaCO_3}$, and CaSO$_4$, $X_{CaSO_4}$. The extent of CaO conversion in the carbonator, or carbonator conversion ($X_{carbon}$), is a key CaL system design parameter. System cost and energy requirements are minimized while sufficient capture efficiency is maintained by operating at an appropriate $X_{carbon}$. Therefore, monitoring changes to capture efficiency with respect to CaO conversion provides a valuable perspective.

The solid lines in Figure 1a show the CO$_2$ capture behavior of once-calcined fine metamorphosed Saabar and unmetamorphosed Riyadh and German limestones when exposed to a 14% CO$_2$ and 3% O$_2$ in N$_2$. The gray dashed line indicates $X_{max}$.

The assumption that capture behavior recorded in BFB 2 is correlated with the sorbent morphology is supported by solving for the apparent kinetic constant using gas analyzer data and eq 4 ($k_{s,Exp}$) and evaluating the results against the kinetic constant calculated from the BET surface area and porosity, $k_{s,Theo}$ such that

$$k_s = \frac{k_S}{1 - \varepsilon_o}$$

where $m$ is a semi-empirical exponent that varies from 2/3 under kinetic-controlled conditions to 4/3 under diffusion-controlled conditions. Bhatia and Perlmutter noted that in accordance with a spherical grain model, the kinetic constant, $k_s$, is a function of the surface reaction rate constant, $k_S$, the sorbent’s initial surface area, $S_0$, and porosity, $\varepsilon_o$, such that

$$k_s = k_S \frac{S_0}{1 - \varepsilon_o}$$

Table 1. Chemical Composition of Fine Limestones (wt %)

|        | CaO  | SiO$_2$ | MgO  | Al$_2$O$_3$ | Fe$_2$O$_3$ | SO$_3$ | Na$_2$O | K$_2$O | LOI$^{a}$ |
|--------|------|---------|------|-------------|-------------|--------|---------|--------|-----------|
| Saabar | 51.2 | 3.91    | 0.64 | 0.25        | 0.18        | 0.20   | 0.05    | 0.02   | 41.6      |
| Riyadh | 51.8 | 3.17    | 0.36 | 0.33        | 0.21        | 0.51   | 0.05    | 0.07   | 42.6      |
| German | 54.2 | 0.61    | 0.61 | 0.09        | 0.07        | 0.14   | 0.01    | 0.04   | 43.2      |

$^{a}$LOI: loss on ignition.
are introduced, the metamorphosed limestone-derived sorbent experiences reductions in both CO2 capture efficiency and capture capacity. This anomalous behavior is better understood by examining the individual and combined effects of H2O and SO2 on the capture behavior of metamorphosed and unmetamorphosed limestone-derived sorbents.

### 3.2. Influence of Gas Composition on CO2 and SO2 Capture Behavior

The reaction atmosphere composition on the CO2 capture performance of each of the once-calcined metamorphosed and unmetamorphosed limestone-derived sorbents is presented in Figure 3. Note that all limestones were calcined at 850 °C in N2. Although calcination at 850 °C in N2 is not practical for CaL systems, these conditions allow baseline comparison of our limestone-derived sorbents’ morphology and capture behavior with much of the published literature since a bulk of CaL sorbents has been studied under these conditions. The calcined limestone capture behavior was studied with BFB 2 in influent gas compositions in BFB 2 (see Figure 3a–d). Relative to baseline conditions (CO2 and O2 in N2), H2O addition positively influences the once-calcined unmetamorphosed limestone-derived sorbents’ capture efficiency and capacity. Conversely, SO2 addition reduces both capture efficiency and capacity. When both H2O and SO2 are added, the presence of H2O has a greater influence on the combined effect. These trends are observed for fine and coarse once-calcined Riyadh and German limestones, for all examined space times, and are in line with the results from previous studies.

The positive influence of H2O addition on CO2 capture efficiency and capacity is well documented. The phenomena has been attributed to the formation of a hydroxylated layer on the sorbent surface, which is reported to enhance surface diffusion and reactivity with carbon dioxide.
influence of H₂O on capture capacity, in an atmosphere containing both H₂O and SO₂, has also been previously reported. The hydroxylated layer formed on the sorbent surface in the presence of H₂O is polar and causes pore narrowing. Sorbent permeability to larger polar SO₂ molecules is therefore reduced in the presence of H₂O, while permeability to smaller nonpolar CO₂ molecules remains undisrupted.

The once-calcined metamorphosed Saabar limestone behaves unexpectedly when exposed to different influent gas compositions in BFB 2 (see Figure 3e,f). While H₂O addition initially enhances CO₂ capture efficiency, it ultimately has a negative effect on both CO₂ capture efficiency and CO₂ capture capacity. Once-calcined fine Saabar limestone experiences a shorter-lived positive effect due to H₂O addition and a significantly greater negative effect when compared to once-calcined coarse Saabar limestone. When SO₂ is added into the capture atmosphere, the impact on fine Saabar sorbent’s CO₂ capture efficiency varies from negative to positive, depending on the initial space time (see Figure 4). SO₂ addition may also positively influence the CO₂ capture capacity of fine Saabar sorbent; at τ₀ = 9.3 min, fine Saabar sorbent experiences enhanced conversion to CaCO₃ in the presence of SO₂. Note that CaL systems typically operate at relatively high space times to ensure a sustained high capture efficiency. Unlike the fine Saabar sorbent, once-calcined coarse Saabar limestone’s capture capacity and efficiency are not positively influenced by SO₂ addition; nonetheless, relative to the once-calcined Riyadh and German limestones, the coarse Saabar sorbent is less negatively impacted by SO₂ addition. Furthermore, for both fine and coarse Saabar sorbents, superior CO₂ capture capacity and capture efficiency are achieved in a capture atmosphere containing both H₂O and SO₂ when compared to a capture atmosphere with only H₂O added. Limited sulfation of once-calcined Saabar limestones enhances this sorbent’s CO₂ capture performance.

The influence of sorbent sulfation on carbonation performance is examined using data from the experimental sets in which BFB 2 influent gas composition is set to either: (i) 12–14% CO₂, 2000 ppm SO₂, or (ii) 12–14% CO₂, 2000 ppm SO₂, 10–14% H₂O, and 3% O₂ with the balance N₂. Note that the two once-calcined unmetamorphosed Riyadh and German limestones exhibit similar SO₂ capture performance, and therefore, once-calcined Riyadh limestone is selected as a representative example with its SO₂ capture performance discussed in more detail. Once-calcined German limestone’s SO₂ capture performance is presented in Figure S4.

Once-calcined unmetamorphosed Riyadh and metamorphosed Saabar limestones exhibit similar SO₂ capture efficiency under H₂O-free conditions (see Figure 5). Upon H₂O addition, once-calcined unmetamorphosed limestones exhibit enhanced SO₂ capture efficiency while the fine Saabar sorbent
In BFB 2 atmospheres that do not contain SO₂, the once-calcined Saabar, Riyadh, and German limestones achieve a slightly higher CO₂ capture capacity at higher space times; capture capacity is seen to increase by <0.1 mol/mol with a tenfold increase in space time (Figure S5). A similar effect was previously reported by Manovic and Anthony, and is caused by the slower carbonation rate allowing improved surface diffusion thereby reducing the probability of CaCO₃ forming in a manner that blocks unreacted CaO.

In BFB atmospheres that contain SO₂, experimental results indicate that the relative average concentration of SO₃ in the BFB (C_{SO₃}/C_{CO₂}) and the relative average SO₂ capture rate (F_{SO₂}/F_{CO₂}) decrease as the initial space time is increased (Figure S6). Consequently, the relative accumulation of CaSO₄ versus CaCO₃ diverges for different initial space times (see Figure 6). For both fine and coarse metamorphosed and unmetamorphosed sorbents, conversion to CaCO₃ is favored at higher initial space time. The slow accumulation of CaSO₄ observed at high initial space time, is correlated with enhanced carbonation efficiency and CO₂ capture capacity under H₂O-free conditions for the fine Saabar sorbent (as seen in Figure 4). The discrepancy in relative conversion (CaSO₄ vs CaCO₃) due to space time appears around X > 0.2 for the fine Saabar sorbent under H₂O-free conditions (Figure 6c), and the effects on CO₂ capture performance can be seen in Figure 4 at X > 0.2. Moreover, both size fractions of the once-calcined metamorphosed limestone are less susceptible to the influence of space time on relative conversion in the presence of H₂O.

For Saabar sorbents at all examined space times, H₂O addition reduces the once-calcined fine Saabar limestone’s carbonation efficiency, sulfation efficiency, and CO₂ capture capacity under H₂O-free conditions (Figure 6c), and the effects on CO₂ capture performance can be seen in Figure 4 at X > 0.2. Moreover, both size fractions of the once-calcined metamorphosed limestone are less susceptible to the influence of space time on relative conversion in the presence of H₂O. For Saabar sorbents at all examined space times, H₂O addition causes the sulfation reaction to slow before carbonation transitions to its slow solid-state diffusion-controlled stage (Figure S7). Consequently, the slow CaSO₄ accumulation has a dampened influence on CaCO₃ accumulation.

The TGA runs performed in parallel with the BFB runs support the observed positive influence of H₂O addition on once-calcined unmetamorphosed limestone capture capacity and the negative influence of H₂O addition on once-calcined metamorphosed limestone capture capacity (see Figure 7). Note that the TGA runs are executed with lower initial space times (<0.2 min) than the BFB runs and in line with our observations on the influence of space time: (i) once-calcined Riyadh limestone experiences a greater negative impact on CO₂ capture capacity due to SO₂ addition in TGA versus in the BFB, and (ii) once-calcined metamorphosed limestone experiences a negative impact on CO₂ capture capacity due to SO₂ addition in TGA.

Figure 5. SO₂ capture performance of once-calcined Saabar and Riyadh limestones (τᵢ ≈ 4.7 min): (a) fine and (b) coarse limestones.

Figure 6. Influence of space time on the relative conversion of the fine Riyadh sorbent in (a) H₂O-free, and (b) 10% H₂O atmospheres, and fine Saabar sorbent in (c) H₂O-free and (d) 10% H₂O atmospheres.
3.3. Role of the Sorbent Morphology on Capture Behavior. Pore size distributions for the once-calcined Saabar, Riyadh, and German limestones are presented in Figure 8, and the BET surface area and other relevant textural data are summarized in Table 2. Elemental analysis (Table S2) reveals that once-calcined fine Saabar limestone and both size fractions of the two unmetamorphosed limestone-derived sorbents exhibit similar purity, 85−90% CaO on a mass basis, but once-calcined coarse Saabar limestone is only 46% CaO. Since SEM−EDS imaging (Figure 9) reveals that the impurities are largely nonporous, porosimetry and surface area data are reported per gram of CaO allowing comparison.

Pore size distributions for the once-calcined Saabar, Riyadh, and German limestones are multimodal with an intense peak in the 50−200 nm range. The fine and coarse metamorphosed Saabar limestone-derived sorbents have smaller peak pore diameters relative to the unmetamorphosed Riyadh and German limestone-derived sorbents. Pinheiro et al.25 similarly found that metamorphosed limestone-derived sorbents exhibit peak pore diameters in the mesoporous range (2−50 nm), and unmetamorphosed limestones calcined once under similar conditions typically have peak pore diameters in the macroporous range (>50 nm).26 Moreover, once-calcined fine Saabar limestone has a high surface area and exhibits low porosity; these textural characteristics were also reported by Pinheiro et al.27 and appear to be typical of calcined fine metamorphosed limestones. While once-calcined fine Saabar limestone’s pore size distribution is narrow and uniform with macropores contributing very little to the pore volume, a significant fraction of once-calcined coarse Saabar limestone’s pore volume is due to macropores. These textural differences are likely responsible for the different capture behavior displayed by the fine and coarse Saabar sorbents.

Once-calcined metamorphosed limestone mesopores are susceptible to pore blockage during carbonation. Alvarez and Abanades demonstrated that while capture capacity is typically directly proportional to the surface area and coincides with the formation of a critical product layer, ∼50 nm in thickness,44 pore blockage is likely in “narrow pores”, defined as <150 nm in diameter.25 The pore blockage experienced by once-calcined fine Saabar limestone results in unreacted CaO, and therefore, this sorbent’s relatively high surface area does not equate to high capture capacity when carbonated in BFB 2 with an influent gas concentration of 14% CO2 and 3% O2 in N2 (Figure 1). Once-calcined fine Riyadh limestone also experiences some pore blockage during carbonation; although it has double the surface area of once-calcined fine German limestone, once-calcined fine Riyadh limestone does not exhibit a proportionally greater capture capacity. The wider pores exhibited by once-calcined German and coarse Riyadh limestones are less susceptible to pore blockage by carbonation. In the case of once-calcined coarse Saabar limestone, CO2 capture involves gas intrusion into the macropores followed by permeation into the mesopores. Consequently, once-calcined coarse Saabar limestone is initially exposed to lower concentrations of CO2 at mesopore openings. This shielding of the mesopores by the macropores reduces and postpones mesopore blockage, as seen in Figure 3f. While once-calcined coarse Saabar limestone’s baseline CO2 capture efficiency is relatively high at X<0.5, a steep drop in capture efficiency is observed at X≈0.5. We propose that this drop in capture efficiency coincides with the delayed mesopore blockage resulting from the macropore shielding effect.

The difference in CO2 capture performance between once-calcined fine and coarse Saabar limestones when H2O is added can also be attributed to the coarse Saabar sorbent’s macropores. In the case of once-calcined fine Saabar limestone, introducing a hydroxylated layer causes further mesopore narrowing and enhances CO2 reactivity. Since fast carbonation
rates further increase the probability of bottleneck formation.\textsuperscript{43} \( \text{H}_2\text{O} \) addition increases fine Saabar sorbent’s susceptibility to pore blockage. For once-calcined coarse Saabar limestone, initial \( \text{CO}_2 \) capture efficiency is controlled by gas intrusion into the sorbent’s macropores, and therefore, once-calcined coarse Saabar limestone initially displays a capture behavior similar to macroporous once-calcined unmetamorphosed limestones, with enhanced \( \text{CO}_2 \) capture efficiency observed due to \( \text{H}_2\text{O} \) addition. The subsequent restricted gas permeation into the once-calcined coarse Saabar limestone’s mesopores leads to a delayed and significantly reduced negative impact on the sorbent’s capture capacity relative to that experienced by once-calcined fine Saabar limestone. In Figure 3f, the drop in once-calcined coarse Saabar limestone’s capture efficiency due to \( \text{H}_2\text{O} \) addition is seen at \( X \approx 0.4 \). The once-calcined metamorphosed limestones’ susceptibility to sulfation deactivation; relative to once-calcined Riyadh and German limestones, the coarse Saabar sorbent experiences the least sulfation deactivation (Figure 3). While fine Saabar sorbent’s narrow pores influence this sorbent’s resistance to sulfation deactivation, the positive influence of \( \text{SO}_2 \) on fine Saabar sorbent carbonation is not explained by pore size distribution alone. SEM–EDS and PXRD are used to further examine the sorbents’ morphology and structural and compositional characteristics.

The mesoporous nature and low porosity of once-calcined fine metamorphosed limestones limit \( \text{SO}_2 \) intrusion into these sorbents’ pore network and contribute to these sorbents’ reduced susceptibility to sulfation deactivation. For once-calcined fine metamorphosed limestones, sulfation likely proceeds through the “unreacted core” mode,\textsuperscript{45} with a \( \text{CaSO}_4 \) shell forming on the external surface of the sorbent. Since direct sulfation occurs, the \( \text{CaSO}_4 \) shell that forms is porous.\textsuperscript{46} While the wider pores and higher porosity exhibited by once-calcined unmetamorphosed limestones are less susceptible to pore blockage by carbonation, they exhibit less diffusional resistance to \( \text{SO}_2 \) molecules, enhanced sulfation rates, and pore blockage by sulfation.\textsuperscript{47} In the case of once-calcined fine German limestone, this translates to the high sulfation deactivation seen in Figure 3c. Once-calcined coarse German limestone, which has a similar porosity and pore size distribution to the once-calcined fine German limestone in the <200 \( \mu \text{m} \) range, experiences less sulfation deactivation than once-calcined fine German limestone. This is due to the coarse German sorbent’s >200 \( \mu \text{m} \) diameter macropores that are less susceptible to pore blockage by \( \text{CaSO}_4 \) formation. Similarly, once-calcined coarse Saabar limestone’s high volume of macropores in the >200 \( \mu \text{m} \) range enhances this sorbent’s resistance to sulfation deactivation; relative to once-calcined Riyadh and German limestones, the coarse Saabar sorbent experiences the least sulfation deactivation (Figure 3). While fine Saabar sorbent’s narrow pores influence this sorbent’s resistance to sulfation deactivation, the positive influence of \( \text{SO}_2 \) on fine Saabar sorbent carbonation is not explained by pore size distribution alone. SEM–EDS and PXRD are used to further examine the sorbents’ morphology and structural and compositional characteristics.

Figure 9. SEM images of the (a) Saabar, (b) Riyadh, and (c) German limestones, and of the once-calcined fine (d) Saabar, (e) Riyadh, and (f) German limestones, and of the once-calcined coarse (g) Saabar, (h) Riyadh, and (i) German limestones. White arrows indicate impurities.

While fine Riyadh and Saabar limestones have a similar bulk chemical composition (Table 1), differences in the distribution of impurities and crystalline structure are likely responsible for
the distinctive textural features of once-calcined Riyadh and Saabar limestones. Figure 9a–c shows the textural quality resulting from Saabar limestone’s large CaCO₃ grains versus Riyadh and German limestones, which have more pronounced polycrystalline structures and exhibit lower crystallinity (Table S1). The structural refinements of the limestones suggest that their dominant phase is better described as calcium magnesium carbonate with a doping amount of magnesium (Table S1, Figure S8–S10). The large and active monomineralic grains of metamorphosed Saabar limestone have a composition of Ca₀.₉₁Mg₀.₀₉CO₃, while Riyadh and German limestones contain larger amounts of magnesium and reveal compositions of Ca₀.₈₈Mg₀.₁₅CO₃ and Ca₀.₃₄Mg₀.₆₆CO₃, respectively. The higher CaCO₃ purity of the metamorphosed limestone’s crystals may have resulted from metamorphic differentiation. The low incidence of structural defects in the metamorphosed limestone’s large, structured, highly crystalline, relatively pure CaCO₃ phase likely leads to the evolution of the once-calcined metamorphosed limestone’s uniform mesopores. Unmetamorphosed limestones’ more polycrystalline structure and lower crystallinity likely leads to the evolution of the larger macropores and wider pore size distributions seen for these once-calcined unmetamorphosed limestones.

The bulk of once-calcined fine metamorphosed limestones’ reactive surface area is only accessible after reactant diffusion through the mesopores. Therefore, once-calcined fine metamorphosed limestone’s initial carbonation rate is more diffusion-limited than that of unmetamorphosed limestone-derived sorbents. Moreover, the higher CaO purity of once-calcined metamorphosed limestones translates to higher surface reactivity and increased susceptibility to unreacted calcined metamorphosed limestone’s uniform mesopores. Unmetamorphosed limestones’ more polycrystalline structure and lower crystallinity likely leads to the evolution of the larger macropores and wider pore size distributions seen for these once-calcined unmetamorphosed limestones.

The introduction of a limited amount of impurities in the form of CaSO₄ pacifies sections of the highly reactive once-calcined Saabar limestone’s matrix and introduces some resistance to mesopore blockage due to fast carbonation. Sulfation may also have an effect analogous to the introduction of an inert support into the relatively pure recarbonated sorbent surface; note that CaSO₄ has a higher sintering or “Tamman” temperature (861 °C) than CaCO₃ (533 °C) and is therefore less susceptible to sintering under carbonation conditions. The larger molar volume of CaSO₄ relative to CaCO₃ may also lead to fractures, introducing defects in the Saabar sorbent’s uniform structure. These structural defects enhance reactant access to active (1, 1, 1) oriented surfaces and reactant permeation into the particle’s core. The introduction of fractures in the CaO matrix due to sulfation is discussed in greater detail in Section 3.4.

### 3.4. Influence of Sorbent Cycling on Morphology and Capture Behavior.

The influence of calcination/carbonation cycles, performed under practical conditions, on the textural evolution and co-capture behavior of metamorphosed and unmetamorphosed limestone-derived sorbents is examined. The fine Saabar sorbent, with its initial uniform mesoporous structure, is compared to the macroporous polycrystalline fine Riyadh sorbent. The sorbent cycled in a SO₂-free atmosphere is compared to the sorbent cycled with SO₂ in the carbonation atmosphere, and sorbents with activities $X_N \approx 0.1, 0.3,$ and 0.6 mol/mol are compared. We define $X_N$ as the baseline CO₂ capture capacity, when exposed to 12% CO₂ in N₂ for a sorbent calcined $N$ times. Note that once-calcined limestone activity $X_1 \approx 0.6$, and sorbent residual activity after innumerable cycles is typically $\approx 0.07$. Since sulfation, predictably, accelerates both metamorphosed and unmetamorphosed limestone-derived sorbent deactivation rates (Figure S14), sulfated and nonsulfated sorbents at different cycle numbers but equivalent activities are compared. This allows the comparison of textural changes experienced by sulfated and nonsulfated sorbents that result in similar activities but different co-capture behavior. Nonsulfated sorbents at $N = 13$ and sulfated sorbents at $N = 6$ have an activity, $X_N \approx 0.1$; nonsulfated sorbents at $N = 6$ and sulfated sorbents at $N = 3$ have an activity, $X_N \approx 0.3$.

Figure 10 shows the CO₂ and SO₂ capture behavior of fine Saabar and Riyadh sorbents at different cycle numbers and activities, when the sorbents are recarbonated in BFB 2 with an influent gas composition of 12% CO₂, 10% H₂O, 2000 ppm SO₂, and 3% O₂ in N₂ (hereafter referred to as “wet synthetic flue gas”). Similar trends are observed at all examined space times; results from $\tau = 4.7$ min are presented. For the unmetamorphosed Riyadh limestone-derived sorbents, the deactivation mechanism does not significantly impact CO₂ capture behavior from a gas atmosphere typical of coal or heavy fuel oil power plant flue gas; the nonsulfated and sulfated
Riyadh sorbents with similar activities exhibit similar CO₂ capture behavior (see Figure 10a). A slight reduction in fast stage \( (X < X_{\text{max}}) \) capture efficiency is observed for the sulfated Riyadh sorbent versus the nonsulfated Riyadh sorbent with similar activity, with the divergence in capture efficiency growing with CaSO₄ accumulation. A slight increase in slow stage \( (X > X_{\text{max}}) \) capture efficiency and conversion is also observed when the Riyadh sorbent is deactivated by sulfation. This is due to the introduction of CaSO₄ impurities, which increases lattice defects in the sorbent’s matrix and in turn enhances solid-state diffusion.⁵⁰ Unmetamorphosed Riyadh limestone-derived sorbent sulfation follows a similar trend to carbonation behavior as a result of the direct sulfation pathway (see Figure 10c).

Sulfated metamorphosed Saabar limestone-derived sorbents outperform nonsulfated Saabar sorbents with similar activity in terms of co-capture capacity, indicating that metamorphosed limestone sulfation significantly impacts the sorbent’s textural evolution (see Figure 10b). The superior slow stage capture efficiency and conversion exhibited by the sulfated Saabar sorbent is analogous to that observed for the sulfated Riyadh sorbent. The superior fast stage CO₂ capture efficiency exhibited by sulfated Saabar sorbents indicates that these sorbents’ capture rates are less diffusion-controlled in a carbonation environment containing H₂O than nonsulfated metamorphosed limestone-derived sorbents with similar activity. The superior co-capture capacity of the sulfated Saabar sorbent with \( X_N \approx 0.3 \) indicates that this sorbent is less susceptible to pore blockage in a carbonation environment containing H₂O than the nonsulfated Saabar sorbent with \( X_N \approx 0.3 \). Metamorphosed Saabar limestone-derived sorbent sulfation follows a similar trend to carbonation behavior as a result of the direct sulfation pathway (see Figure 10d).

Figure 11 presents the evolution of the pore size distributions of cycled fine Riyadh and Saabar sorbents, and BET surface area and other relevant textural data are provided in Table 2. Sintering, experienced with increasing calcination/carbonation cycles, causes surface area reduction and changes in pore size distribution and porosity.⁴⁰ Contrary to Pinheiro et al.’s observations,⁷ we find that the metamorphosed and unmetamorphosed limestone-derived sorbents experience a comparable decay in the activity (Figure S14) and surface area. Note that mild calcination conditions were employed in Pinheiro et al.’s study.⁷ While the high crystallinity associated with Saabar limestone is expected to reduce susceptibility to sintering,⁵¹ PXRD reveals that although the calcined Saabar’s CaO phase maintains a high crystallinity with cycling, its recarbonated CaCO₃ phase loses crystallinity with the cycle number (Table S3).

Porosity and pore size distributions for the sulfated and nonsulfated unmetamorphosed Riyadh limestone-derived sorbents with \( X_N \approx 0.3 \) are very similar. The sulfated Riyadh sorbent that has undergone the same number of calcination/carbonation cycles as the nonsulfated Riyadh sorbent, \( N = 6 \), is relatively more sintered; the sulfated \( N = 6 \) sorbent has larger peak pore diameters, a smaller surface area, and lower porosity than its counterpart. These textural changes are primarily due to enhanced sintering during calcination caused by the lower Tammann temperature of CaSO₄ (861 °C) versus CaO (1313 °C).⁴⁸ The enhanced sintering and CaSO₄ deactivation are responsible for sulfated Riyadh sorbent’s low activity at \( N = 6 \) \( (X_{\text{SO}_2/\text{SO}_2} \approx 0.1) \). The nonsulfated Riyadh sorbent with \( X_{13} \approx 0.1 \) has a similar surface area to its sulfated counterpart \( (X_{\text{SO}_2/\text{SO}_2} \approx 0.1) \) but lower porosity. Iskós et al. have previously reported on sulfation, especially direct sulfation, enhancing sorbent porosity.⁴⁶ While both the \( X_N \approx 0.1 \) sulfated and nonsulfated unmetamorphosed limestone-derived sorbent pore diameters peak at \( \sim 210 \) nm, the nonsulfated fraction has a secondary pore diameter peak emerging at \( \sim 90 \) nm (see Figure 11a).

The emergence of a population of small pores has been attributed to sorbent regeneration, which is experienced by sorbents subjected to an extended carbonation that surpasses the fast reaction stage and allows recarbonation of previously occluded CaO.⁵⁷ During sorbent cycling in BFB 1, the carbonator space time and residence time result in a carbonator conversion \( X_{\text{carb}} \approx 0.15 \). Since Riyadh sorbent \( X_{12} < 0.15 \), the carbonation reaction proceeds into the solid-state diffusion-controlled stage, leading to some sorbent reactivation postcalcination. The presence of occluded active CaO with cycling is corroborated by PXRD, which reveals that crystalline CaO remains available after \( N = 12 \) sorbent recarbonation (Table S4). While sulfation deactivation is mainly responsible for the worse co-capture performance of the sulfated Riyadh sorbent with \( X_{13} \approx 0.1 \) compared to the nonsulfated Riyadh sorbent with \( X_{13} \approx 0.1 \) (Figure 10a), enhanced diffusional resistance to SO₂ molecules due to the population of narrow pores emerging in nonsulfated Riyadh sorbent with \( N = 13 \), and this sorbent’s lower porosity may also play a role.

For the nonsulfated metamorphosed Saabar limestone-derived sorbent with \( X_{13} \approx 0.1 \), the bimodal pore size distribution is more developed, with a large population of \( \sim 50 \) nm pores and secondary populations of pores with diameters \( >250 \) nm (see Figure 11b). While \( X_{13} \) for the metamorphosed and unmetamorphosed limestone-derived sorbents is comparable, the enhanced regeneration experienced by the metamorphosed limestone-derived sorbent indicates that the nonsulfated Saabar sorbent retains its susceptibility to pore blockage in the presence of H₂O. This premature pore blockage lengthens the solid-state diffusion-controlled stage.
thereby amplifying the population of small pores that emerge postcalcination. Note that the metamorphosed limestone-derived sorbent mesopores disappear with initial cycling and larger pore diameters evolve, peaking at $\sim 110$ nm for the nonsulfated Saabar sorbent at $N = 6$. While nonsulfated Saabar sorbent’s pores are largely macroporous by $N = 6$, they remain $<150$ nm and are therefore susceptible to pore blockage. Additionally, nonsulfated Saabar sorbent’s negligible pore volume associated with pore diameters $>200$ nm indicates that negligible fractures or defects are present in the large dense metamorphosed limestone-derived sorbent’s monomineralic CaO structure, enhancing susceptibility to pore blockage. While once-calcined Riyadh and German limestones’ pore diameters also peak at $<150$ nm, these unmetamorphosed polycrystalline limestone-derived sorbents have pores with diameters $>200$ nm, have lower surface reactivity, and therefore do not experience pore blockage in the presence of H$_2$O.

While the sulfated metamorphosed Saabar limestone-derived sorbent with $X_{\text{H}_2\text{O}/\text{SO}_2} \approx 0.3$ has a similar pore size distribution and activity as the nonsulfated Saabar sorbent with $X_6 \approx 0.3$, the sulfated Saabar sorbent’s higher porosity and possibly its slightly lower purity lead to reduced susceptibility to pore blockage. This translates to the higher co-capture efficiency and capacity exhibited by the sulfated Saabar sorbent when exposed to wet synthetic flue gas in BFB 2 (Figure 10b). The sulfated Saabar sorbent with $X_{\text{H}_2\text{O}/\text{SO}_2} \approx 0.1$ retains a higher porosity and larger average pore diameter than the nonsulfated Saabar sorbent with $X_6 \approx 0.1$. The sulfated Saabar sorbent’s textural quality enhances pore diffusion, causing initial fast stage carbonation to be less diffusion-controlled relative to that experienced by the nonsulfated Saabar sorbent with $X_6 \approx 0.1$. This is responsible for the sulfated Saabar sorbent’s superior CO$_2$ capture efficiency when exposed to wet synthetic flue gas in BFB 2 (Figure 10b). Note that the sulfated and nonsulfated metamorphosed Saabar sorbents with $X_{\text{N}} \approx 0.1$ exhibit similar capture capacity when exposed to wet synthetic flue gas in BFB 2.

The sulfated metamorphosed Saabar limestone-derived sorbent at $N = 6$ also has a higher porosity than the nonsulfated Saabar sorbent at $N = 6$. The higher porosity of the sulfated fraction is partially due to the emergence of large pores, $>250$ nm, analogous to those seen for the nonsulfated Saabar sorbent at $N = 13$. SEM imaging reveals that sulfation significantly enhances metamorphosed limestone-derived sorbent grain coarsening, favoring this mechanism of sintering over densification, which is seen in nonsulfated metamorphosed limestone-derived sorbents (see Figure 12a,b). Lattice defects introduced by sulfation have been reported$^{52}$ to accelerate lattice diffusion, grain coarsening, and pore diameter widening. Grain boundary stresses due to the accelerated

Figure 12. SEM images of the cycled Saabar sorbent: (a) nonsulfated with $X_6 \approx 0.1$, (b) sulfated with $X_{\text{H}_2\text{O}/\text{SO}_2} \approx 0.1$, (c) recarbonated sulfated sorbent with $X_{\text{H}_2\text{O}/\text{SO}_2} \approx 0.1$. White arrows indicate impurities.

Figure 13. Illustration of the influence of reaction atmosphere gas composition and sorbent morphology and composition on capture behavior. The dashed lines illustrate the relative unreacted pore volume of the metamorphosed limestone-derived sorbent due to the different reaction environments.
textural changes caused by sulfation may lead to fractures by $N = 6$. In Figure 12c, a SEM image of the recarbonated sulfated metamorphosed limestone-derived sorbent is presented, and fractures are seen to propagate from phase boundaries with sorbent impurities. These large fractures play a similar role to the once-calcined coarse metamorphosed limestone-derived sorbent macropores, thereby enhancing co-capture from flue gas containing $\text{H}_2\text{O}$. Moreover, reactivation experienced by the sulfated metamorphosed Saabar limestone-derived sorbent leads to the emergence of a secondary pore population peaking at ~90 nm, similar to that seen for the Riyadh sorbent, versus ~50 nm for the nonsulfated Saabar sorbent. Sulfation alters the metamorphosed limestone-derived sorbent morphology leading it to more closely resemble unmetamorphosed limestone-derived sorbents. Sulfation also preserves the porosity of the metamorphosed limestone-derived sorbent, and for metamorphosed limestone-derived sorbents with initially low porosity, high surface reactivity, and relatively small pore sizes, the preservation of porosity reduces susceptibility to $\text{CO}_2$ diffusional resistance and pore blockage and leads to enhanced co-capture performance in an atmosphere containing $\text{H}_2\text{O}$.

The influence of different reaction atmospheres on unmetamorphosed limestone-derived sorbents’ capture behavior is relatively well understood. Unmetamorphosed limestone-derived sorbents in early calcination/carbonation cycle stages are typically polycrystalline and macroporous. These sorbents exhibit limited pore blockage due to carbonation, enhanced capture efficiency, and capture capacity in the presence of $\text{H}_2\text{O}$ and deactivation and pore blockage due to sulfation. In an atmosphere containing both $\text{H}_2\text{O}$ and $\text{SO}_2$, the positive influence of $\text{H}_2\text{O}$ counteracts the negative influence of $\text{SO}_2$ on capture capacity by limiting $\text{SO}_2$ intrusion into the sorbent pores. Calcined metamorphosed limestones’ high purity CaO arranged in large structured and dense monomineralic phases, with relatively low porosity and small pores, is likely responsible for the atypical capture behavior displayed by these sorbents in response to different gas atmospheres (see Figure 13). We propose that metamorphosed limestone-derived sorbents’ small pores are susceptible to pore blockage during carbonation. $\text{H}_2\text{O}$ addition further narrows the sorbents’ pores and increases reactivity with $\text{CO}_2$ enhancing pore blockage. Limited sulfation deactivates sections of the sorbents’ surface and introduces some resistance to pore blockage. In an atmosphere containing both $\text{H}_2\text{O}$ and $\text{SO}_2$, limited sulfation counteracts the enhanced reactivity caused by $\text{H}_2\text{O}$ addition and reduces its negative influence. The presence of relatively large macropores (>200 nm) in certain metamorphosed limestone-derived sorbents dampens the influence of the smaller pores on capture behavior. Furthermore, metamorphosed limestone-derived sorbent sulfation transforms the sorbent upon subsequent recalcination leading sulfated metamorphosed limestone-derived sorbents to behave more similarly to unmetamorphosed limestone-derived sorbents (see Figure 14).

The different textural evolutions experienced by the unmetamorphosed Riyadh limestone versus the metamorphosed Saabar limestone result in the nonsulfated Saabar sorbent underperforming in terms of co-capture efficiency from wet synthetic flue gas when compared to the nonsulfated Riyadh sorbent (see Figure 14a). While the nonsulfated Saabar sorbent retains a higher surface area with cycling, nonsulfated Saabar and Riyadh sorbents exhibit similar $\text{CO}_2$ capture capacities during co-capture from wet synthetic flue gas. The sulfated metamorphosed and unmetamorphosed limestone-derived sorbents perform similarly, with the Saabar sorbent exhibiting a slightly higher $\text{CO}_2$ capture capacity and efficiency with increasing cycle number (see Figure 14b). This indicates that while metamorphosed limestone-derived sorbent’s susceptibility to $\text{CO}_2$ diffusional resistance and pore blockage in the presence of $\text{H}_2\text{O}$ is carried through to sorbents with $X_N \approx 0.1$ when cycled in a $\text{SO}_2$-free environment, sorbent sulfation counteracts these propensities.

From a practical perspective, while metamorphosed limestone may not be preferred for $\text{CO}_2$ capture from prescrubbed flue gas sources, this limestone can be used in $\text{CO}_2$ and $\text{SO}_2$ co-capture CaL systems. Metamorphosed limestone attrition and fragmentation rates should be considered when assessing this sorbent’s promise. Preliminary analysis indicates that the Saabar sorbent may be more susceptible to both attrition and fragmentation. While little change to the PSDs within BFB 1 are observed for any of the cycled sorbent fractions, about 15–20% more fines were collected from the reactor cyclones when Saabar was cycled versus Riyadh. Furthermore, while gas analyzer data indicate that the metamorphosed and unmetamorphosed limestone-derived sorbents capture the same amount of $\text{SO}_2$ during cycling, elemental analysis reveals that the metamorphosed limestone-derived sorbent has a lower CaSO$_4$ content (see Table 2). The CaO purity of the Saabar sorbent also decreases with the cycle number (Table S2). This indicates that the Saabar sorbent is more prone to attrition than the unmetamorphosed limestone-derived sorbent, with the newly deposited surface CaSO$_4$ especially vulnerable to attrition. Saabar limestone’s slightly elevated attrition rate may therefore be favorable under co-capture conditions.

4. CONCLUSIONS

This manuscript reports on the $\text{CO}_2$ and $\text{SO}_2$ capture behavior of metamorphosed and unmetamorphosed limestone-derived sorbents. The individual and combined influence of flue gas
H₂O and SO₂ content on sorbent CO₂ and SO₂ capture performance is investigated. The influence of multiple calcination/carbonation cycles and of CaSO₄ accumulation on the limestone-derived sorbents’ textural evolution and capture behavior are also examined. While we find that the unmetamorphosed limestone-derived sorbents’ capture performance aligns well with previous work, the metamorphosed limestone-derived sorbent exhibits anomalous behavior. Our experimental results reveal the following:

1. Contrary to expectations, calcined metamorphosed limestone CO₂ capture performance is negatively influenced by flue gas H₂O content and positively influenced by flue gas SO₂ content.
2. The negative impact of flue gas H₂O content on metamorphosed limestone-derived sorbent CO₂ capture performance persists for sorbents with activities ranging from 0.6 to 0.1 mol/mol, when the sorbents have been cycled in a sulfur-free flue gas.
3. Metamorphosed limestone-derived sorbent that has been cycled in sulfurated flue gas exhibits similar capture behavior to unmetamorphosed limestone-derived sorbents.
4. Space time has a significant impact on SO₂ and CO₂ co-capture performance.

Analyzing the limestone-derived sorbents using material characterization and imaging tools, we conclude that the distribution of impurities in the metamorphosed limestone-derived sorbent matrix is ultimately responsible for the sorbent’s capture behavior. The metamorphosed limestone is primarily composed of large monomineralic phases separated by clear boundaries. The large, relatively pure, and highly crystalline monomineralic CaCO₃ grains in metamorphosed limestone are responsible for the evolution of relatively narrow uniform pores and high purity crystalline CaO with low overall porosity upon calcination. These morphological characteristics are likely responsible for the anomalous capture behavior of the metamorphosed limestone-derived sorbent. We postulate that the calcined metamorphosed limestone’s high CaO purity, narrow pores, and low porosity translate to higher surface reactivity and increased susceptibility to pore blockage during carbonation. As a result, flue gas H₂O content, known to enhance CaO reactivity with CO₂ and cause pore narrowing, exacerbates metamorphosed limestone-derived sorbent pore blockage. Furthermore, we propose that the introduction of a limited amount of impurities in the form of CaSO₄ may pacify sections of the metamorphosed limestone-derived sorbent’s highly reactive matrix and introduce some resistance to mesopore blockage due to fast surface carbonation. We also find that

1. Cycling metamorphosed limestone in an atmosphere containing SO₂ preserves the sorbent’s porosity and increases the sorbent’s grain and pore sizes, resulting in sulfated metamorphosed and unmetamorphosed limestone-derived sorbents exhibiting similar capture performance.
2. The influence of calcined metamorphosed limestones’ narrow pores on capture behavior is dampened in sorbents with a secondary population of large macro-pores (>200 nm).

Our findings indicate that the metamorphosed limestone may be more prone to attrition and fragmentation than the unmetamorphosed limestone. The mechanical stability of this sorbent requires further investigation. The influence of additional calcination/carbonation cycles and sulfation on the metamorphosed limestone-derived sorbent’s capture behavior also requires further investigation. The understanding gained regarding the underlying morphology that influences the anomalous capture behavior of the metamorphosed limestone-derived sorbent will help guide future sorbent selection and design efforts.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04157. Relevant PXRD patterns; crystallographic information; sorbent capture conditions and performance data; sorbent compositional data; and PXRD refinement plots (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Sally L. Homsy – Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0003-2767-0031; Email: sally.homsy@kaust.edu.sa

**Authors**

Joseba Moreno – Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Stuttgart 70569, Germany

Alla Dikhtiarzenko – KAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0002-3372-2435

Jorge Gascon – KAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0001-7558-7123

Robert W. Dibble – Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04157

**Notes**

The authors declare no competing financial interest.

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**NOTATION**

| Symbol | Description |
|--------|-------------|
| D      | diameter    |
| E      | capture efficiency [mol CO₂ or SO₂/mol CaO] |
| F      | molar flow rate [mol/s] |
| k      | kinetic constant [m³/mol·s] |
| k      | surface reaction rate constant [m⁴/mol·s] |
| n₀CaO  | initial moles of CaO [mol] |
| N      | calcination/carbonation cycle number |
| S      | surface area |

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