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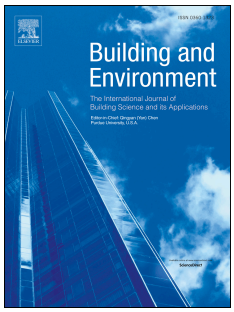

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Investigating CO_2 removal by Ca- and Mg-based sorbents with application to indoor air treatment

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Abstract

Indoor carbon dioxide (CO_2) levels serve as an indicator of ventilation sufficiency in relation to metabolic effluents. Recent evidence suggests that elevated CO_2 exposure (with or without other bioeffluents) may cause adverse cognitive effects. In shelter-in-place (SIP) facilities, indoor CO_2 levels may become particularly elevated. This study evaluates four low-cost alkaline earth metal oxides and hydroxides as CO_2 sorbents for potential use in indoor air cleaning applications. Sorbents studied were MgO, $Mg(OH)_2$, $Ca(OH)_2$ and commercially available soda lime. Uncarbonated sorbents characterized with nitrogen adsorption porosimetry showed BET surface areas in the 5.6-27 m^2/g range. Microstructural analyses, including X-ray diffraction, thermogravimetric analysis and scanning electron microscopy confirmed the carbonation mechanisms and extent of sorption under environmental conditions typical of indoor spaces. Ca-based sorbents demonstrated higher extent of carbonation than Mg-based sorbents. Laboratory parameterizations, including rate constants (k) and carbonation yields (y), were applied in material balance models to assess the CO_2 removal potential of Ca-based sorbents in three types of indoor environments. Soda lime (k = [2.2 - 3.6] × 10^{-3} m^3 mol CO_2^{-1} h^{-1}, y = 0.49-0.51) showed potential for effective use in SIP facilities. For example, CO_2 exposure in a modeled SIP facility could be reduced by 80% for an 8-h sheltering interval and to levels below 5000 ppm for an 8-h period with a practically sized air cleaner. Predicted effectiveness was more modest for bedrooms and classrooms.

Keywords: Ventilation, bioeffluents, air cleaning, indoor air pollution, sorption

1. Introduction

Excluding emissions from unvented combustion, carbon dioxide (CO_2) concentrations in occupied indoor spaces depend on three main factors: the CO_2 emission rate from human metabolism, the outdoor CO_2 concentration, and the outdoor air ventilation rate. Indoor CO_2 levels are primarily managed through the replacement of indoor air with outdoor air. However, providing outdoor air ventilation for buildings, while necessary to achieve indoor air quality objectives, can contribute substantially to building energy use [1]. Decreasing the outdoor air exchange rate is one strategy to reduce the energy demand of buildings, as mechanical ventilation requires energy input to fans and may contribute to heating, cooling, and dehumidification needs, depending on site- and time-specific environmental conditions. However, reducing outdoor air-exchange rates tends to increase the concentrations of indoor-generated air pollutants, including CO_2. Indoor CO_2 levels may also become elevated when building operation is altered temporarily (e.g. when air exchange is minimized to protect occupants from hazardous outdoor conditions) including events that precipitate the need for a shelter-in-place (SIP) response [2].

Carbon dioxide, a primary product of human metabolism, is often used as a proxy for indoor-emitted air pollutants [3,4]. It is generally not considered harmful at levels routinely encountered in buildings. Rather, high levels of indoor CO_2 imply that ventilation is insufficient to adequately dilute air pollutants emitted by occupants or other indoor sources. However, some emerging evidence suggests that exposure to elevated CO_2 at levels commonly encountered indoors may adversely affect human cognition [5–7]. The matter is not yet resolved; other recent studies imply that other bioeffluents or possibly some combination of CO_2 and other bioeffluents may be the causative agents [8–12].

The US Occupational Safety and Health Administration (OSHA) has set an 8 hour (h) permissible exposure limit (PEL) of 5,000 ppm for CO_2. Levels in SIP facilities might rise above this

55 threshold. One specific motivation for this study is that a household SIP facility is mandatory in
56 Singapore in all government constructed housing built after 1998 [13]. This requirement is
57 noteworthy as government housing in Singapore provides accommodation for approximately 85% of
58 the country's population [14]. A prior investigation of SIP habitability in the US context showed that
59 CO_2 levels could reach 16,000 ppm after 3 h of occupancy by five persons [15]. Exposure to such
60 levels could result in acute health consequences, as evidenced by studies investigating exposures in
61 spacecraft that show adverse effects including lethargy, malaise, and headache at CO_2
62 concentrations between 4,000 and 10,000 ppm [16]. Studies supporting the OSHA PEL showed
63 electrolyte imbalances, metabolic changes, and non-narcotic central nervous system effects for
64 short-term exposures to CO_2 in the range 10,000-30,000 ppm [16,17].

65 Given the common occurrence of elevated CO_2 concentrations in certain indoor spaces
66 combined with the possibility of acute health effects in SIP facilities and cognitive decrements in
67 other settings, this study investigates the possibility of controlling indoor CO_2 via active removal by
68 means of low-cost solid sorbents that could be integrated into a recirculating indoor air cleaner.
69 Capture of CO_2 with solid sorbents is an emerging area of research with promising potential for
70 future lower cost approaches for CO_2 control [18], including the application of sorbents that are
71 derived from waste materials [19]. Solid sorbents such as metal oxides and hydroxides are
72 considered promising candidates for removing CO_2 from flue gases through carbonation during
73 which oxides or hydroxides are converted into stable carbonates [20,21]. Sorbents under
74 development for use in carbon capture from fossil fuel combustion typically target operation at
75 higher temperatures (on the order of 400 °C or greater) and at elevated CO_2 levels (up to the order
76 of 10%), although approaches for room temperature operation at outdoor ambient CO_2 levels have
77 also been reported [22,23].

78 During the carbonation process, gaseous CO_2 dissolves in water, becoming carbonic acid,
79 which neutralizes the hydroxides (e.g. portlandite ($Ca(OH)_2$) or brucite ($Mg(OH)_2$)). Two main factors
80 control the rate and degree of carbonation of CaO and/or MgO and their derivatives: (i) sorbent

composition (chemical and physical properties of the solid components, water content and presence of additives) and (ii) environmental conditions (CO_2 concentration and pressure, relative humidity (RH), temperature and duration) [24–28]. The main factors influencing the carbonation of Ca- or Mg-based sorbents can be summarized as the transport of CO_2 to the sorbent surface and its reactivity with the sorbent. Transport is affected by environmental conditions (i.e. air pressure, CO_2 concentration, and abundance of water, etc.) and the pore structure of the sorbent, whereas the sorbent composition and material properties influence its reactivity. In the case of Mg-based sorbents, the hydration of MgO leads to the formation of magnesium hydroxide (brucite, $Mg(OH)_2$). In the presence of sufficient water, brucite reacts with CO_2, leading to the formation of hydrated magnesium carbonates such as nesquehonite ($MgCO_3{\cdot}3H_2O$), hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$), dypingite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$) and artinite ($Mg_2CO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$) [29–33]. Higher CO_2 concentrations increase the rate and degree of carbonation at initial stages [24]. The presence of water within the sorbent plays an important role in the degree of hydration and carbonation as the initial water content both facilitates the hydration and carbonation reactions and influences the rate of CO_2 diffusion through the sorbent system. In dry CO_2 scrubbing, low water content present in sorbent media and low RH in air surrounding the sorbent delay the carbonation reaction, whereas an increase in the water content of the media speeds the carbonation reaction but results in a decrease of CO_2 diffusion since the diffusivity of CO_2 is much slower in water than it is in air (i.e. the diffusion coefficient of CO_2 is 16 mm^2/s in air vs. 0.0016 mm^2/s in water [34]). Therefore, rapid sorption kinetics require sufficient water for hydration and subsequent carbonation but not so much water as to interfere with rapid diffusion of CO_2 through the sorbent system. Previous studies have shown that RH values in the approximate range 40-80% are preferable for increased carbonation of the Mg and Ca oxides [35–37]. The rates of diffusion of CO_2 into the sorbent matrix and its subsequent interaction with Ca and Mg are of interest in this study.

If solid sorbents can be integrated into stand-alone indoor air cleaners, they can be deployed to control CO_2 concentrations in locations such as SIP facilities and other indoor locations where CO_2

levels may be temporarily elevated. Apart from SIP environments, other potentially attractive locations are those where specific populations spend substantial proportions of their day in conditions that may not always be sufficiently ventilated, such as bedrooms overnight and classrooms during the day [38]. Several recent efforts further describe the potential and opportunity of CO_2 capture techniques specifically suited for built environments [39–41]. This study employs a range of experimental methods to characterize the physico-chemical properties and carbonation products, kinetics and yields of four alkaline earth metal oxides and their hydroxides. Also provided is an estimate of the efficacy of potentially promising sorbents when integrated into a standalone air cleaner under three hypothetical scenarios. Cases considered are those in which active CO_2 removal may be beneficial owing to one or more of these factors: high occupant density, small room volume, low air-exchange rate, and a susceptible population. Three specific cases are explored: (i) SIP facilities in residential environments, (ii) sleeping microenvironments, and (iii) school classrooms.

2. Materials and Methods

2.1 Sorbents

A commercial CO_2 solid sorbent, SodaSorb (Grace Chemical), consisting of a mixture of $Ca(OH)_2$, H_2O, NaOH and KOH, was purchased from Advanced Marine Pte Ltd, Singapore. The performance of this sorbent was compared to three other products: MgO (commercial name "calcined magnesite 92/200") obtained from Richard Baker Harrison Ltd (UK) and high purity (>95%) $Ca(OH)_2$ and $Mg(OH)_2$ purchased from Aik Moh Paints & Chemicals, Singapore.

Particle size distributions of three sorbents (MgO, $Ca(OH)_2$ and $Mg(OH)_2$), in the form received from the manufacturer, were measured with a particle size analyzer (Mastersizer 2000, Malvern). Particle size of the sorbents is reported as the d_{50}, or mass median particle size. The internal physical properties of the four sorbents were measured via nitrogen adsorption porosimetry conducted at 77 K (Quantachrome Quadrasorb). All four samples were ground to a fine powder in a mortar and pestle prior to analysis to facilitate outgassing of samples and equilibration with N_2

partial pressure during adsorption or desorption cycles. Note that this results in the reporting of a specific surface area, or the interior surface area normalized by mass. It is possible that transport limitations will reduce the 'effective' surface area below the specific surface areas reported if sorbents are implemented with larger grain size than the fine powders used in N_2 adsorption porosimetry. Samples of all four sorbents were outgassed at < 0.1 Torr and 125 °C for 8 hours before measuring nitrogen adsorption isotherms. Surface areas of the sorbents were determined by applying Quantachrome's BET theory; their cumulative pore volumes and average pore sizes were determined with Quantachrome's density functional theory.

2.2 Characterizing CO_2 uptake on sorbents

2.2.1 Carbonation of sorbents

The four sorbents were subjected to carbonation in a controlled laboratory apparatus as shown in Figure 1. Compressed laboratory air was first passed through a membrane dryer that included a 0.01 micron pre-filter (Laman MD-15LS and Laman SAM350-E, Air Parts Center Pte Ltd) to remove water vapor and particulate matter present in laboratory air. Dry air was then passed through an activated carbon packed bed (BPL 6 × 16, Calgon Carbon). The outlet flow was split to control the humidity level, with one stream passing through a washing column filled with deionized water. The flow rates through the dry and humidified air streams were regulated using mass flow controllers (Omega FMA5500, Omega Singapore). In parallel, a small flow supplied from a compressed gas cylinder of food-grade CO_2 (> 99% purity) was injected into the main flow to achieve the desired CO_2 concentration set-point. The two flow streams were combined and directed to a temperature controlled enclosure (KBE3.1, Binder GmBH). Inlet and outlet CO_2, temperature and RH (Teleaire 7001, Onset Computer Corporation) were measured upstream and downstream of a reaction chamber that was either a washing column loaded with a specific sorbent/water ratio or a packed bed reactor loaded with dry sorbent.

A calibration curve was developed between the two CO_2 monitors by collocating the monitors and recording responses at five CO_2 levels ranging between 0 and 2500 ppm. The resulting linear equation was applied to adjust the readings of the downstream CO_2 monitor.

Sorbents were tested in two sets of experiments. Longer term tests were conducted with sorbents in slurries with deionized water, at a loading rate of 0.1 g sorbent per gram of deionized water in a total volume of 100 cm^3 and maintained at a constant temperature of 25 °C. The RH in the inlet air stream was elevated to > 75% to limit the evaporation of water from the slurry. Tests were conducted for 7 days at a flow rate of 2.7 L/min with a constant CO_2 concentration of 2200 ppm to observe carbonation while minimizing limitations to CO_2 uptake that may result from the availability of H_2O. These experiments are subsequently referred to according to experimental conditions. For example, experiment 'MgO-0.1-2.7-2200' refers to the carbonation of the sorbent MgO at a loading rate of 0.1 g (sorbent)/g (H_2O), flow rate of 2.7 L/min, and inlet CO_2 concentration of 2200 ppm. Carbonated sorbent products were extracted from the column, centrifuged to separate the sorbent from residual water and dried for 48 hours under low RH in a temperature/RH controlled chamber (T = 20 °C, RH < 10%).

Sorbents that exhibited effective carbonation during the 7-day tests were selected for further analysis to characterize uptake kinetics and reaction yields. Sorbents were tested under dry and slurry conditions. Dry experiments were conducted with a loading of 5 g of media placed on a wire mesh under a constant inlet RH of 75%. Slurry experiments were conducted at a loading ratio of 0.03 g sorbent/g water in a total volume of 100 cm^3. Both dry and slurry experiments were conducted at two flow rates: 1.8 and 2.7 L/min. These flow rates correspond to contact times of 0.28 and 0.18 seconds, respectively, in dry experiments and 0.45 and 0.3 seconds, respectively, in slurry experiments. All experiments were conducted at 25 °C. Inlet and outlet temperature, RH and CO_2 levels were measured at five-minute intervals. Each experiment was conducted until the sample appeared to be fully carbonated under the set conditions, defined as when the 1-h running average inlet and outlet CO_2 concentrations were equal to within ±25 ppm.

Carbonation yields were determined from the time-integrated difference between inlet and outlet CO_2 monitors across the duration of an experiment to determine the total mass of CO_2 removed. This mass of CO_2 uptake was divided by the initial mass of sorbent and converted to moles to determine the molar yield, *y* (mol sorbed CO_2/mol sorbent initially present). For soda lime, the estimate of moles of sorbent was made from the mass of only $Ca(OH)_2$, as the KOH and NaOH served as catalysts and were not consumed in the carbonation reaction [42,43]. Measured masses of soda lime were multiplied by 0.85 to obtain the mass of $Ca(OH)_2$ used in subsequent interpretation of experimental results and modeling, according to the 85% $Ca(OH)_2$ content within soda lime as specified by the manufacturer. Reaction rate constants, *k* (m^3 (mol CO_2)$^{-1}$ h^{-1}), were determined using coupled equations describing the time-varying quantities of CO_2 and unreacted sorbent in the reactor. The model equations and procedures employed to estimate *k* and *y* are provided in the Supporting Information; Figure S1 illustrates results for a sample experimental run.

2.2.2 Microstructural analysis

Selected samples from the 7-day CO_2 uptake experiments were stored in acetone for at least 7 days to stop hydration, followed by vacuum drying for another 7 days in preparation for X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) analyses. The vacuum-dried samples were ground to a powder fine enough to pass through a 75 µm sieve before they were analyzed under XRD and TGA. The XRD measurements, aimed to determine the crystallinity of compounds and identify and distinguish between different phases within the samples, were made on a Philips PW 1800 spectrometer using Cu K_α radiation (40 kV, 30 mA) with a scanning rate of 0.04° 2θ/step from 5 to 55° 2θ. TGA was conducted on a Perkin Elmer TGA 4000 instrument using a temperature range from 50 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. The vacuum-dried samples were mounted onto aluminum stubs using double-sided adhesive carbon disks and coated with gold before SEM analysis. The SEM analysis was carried out with a Zeiss Evo 50 microscope to investigate the morphologies of the hydration and carbonation products within the prepared samples.

2.3 Modeling CO_2 removal in three indoor environments

Laboratory sorbent characterization results were used as inputs into material-balance models to conduct a scaling analysis of the efficacy of hypothetical deployments of stand-alone CO_2 scrubbers in three types of indoor environments where CO_2 concentrations are routinely elevated: shelter-in-place (SIP) facilities [15,44], bedrooms [14,45] and classrooms [46]. Model inputs describing indoor spaces and occupancy were selected to be generally representative of such environments in the Singapore context, as summarized in Table 1. Room volume and occupancy levels for the SIP facility (5 m^3 for 2 persons) were calculated considering measurements made in a typical Singaporean apartment and Singapore regulations that stipulate a minimum of 1.8 m^3 of shelter volume per occupant [47]. Note that regulations recommend greater SIP volume than the stipulated minimum for increased comfort during an emergency. Room volume for the bedroom was based on measurements of a recently constructed (< 5 y old) 3-bedroom apartment that is a typical Singapore residence; volume and occupancy levels of classrooms were taken from a study of six primary school classrooms in Singapore [46]. Emission rates of CO_2 were made following the procedure described by Persily et al. [48], with assumptions as described in Table 1 annotations.

Ventilation flow rates in the bedroom and SIP environments were determined from the average value of triplicate measurements of air exchange rates calculated from the decay of CO_2 that was injected into an unoccupied bedroom and household shelter. Ventilation flow rates in the classroom environment were taken as the average of CO_2 tracer decay measurement results made in six unoccupied, air-conditioned classrooms in primary schools in Singapore [46]. In bedrooms and classrooms, windows and doors were sealed during measurements to reflect a 'low flow' condition where the exchange of indoor and outdoor air is intentionally reduced to minimize intrusion of warm, humid outdoor air into the buildings. In the SIP facility, measurements were made in a typical household shelter and, per peacetime requirements dictated in the Singapore building code, the ventilation sleeve was opened to 25% of the total sleeve area [47]. During an emergency, the sleeve

would be fully closed, likely reducing the air exchange rate in the household shelter to a value lower than that reported here.

The efficacy of an air cleaner containing a CO_2-removing sorbent was evaluated for the three hypothetical indoor environments by solving coupled material balance equations written for (i) the concentration of CO_2 in the room, (ii) the concentration of CO_2 through a packed bed of sorbent and (iii) the quantity of the unreacted sorbent in the air cleaner. These equations are presented in the Supporting Information. Modeling of indoor environments was conducted for practically sized air cleaners considering the mass of media, volume of air cleaner, and resulting pressure drop across the packed media bed. Rates of carbonation were assumed to remain constant as total pressure varied across the modeled packed bed. Prior studies indicate that total pressure influences uptake but only for orders of magnitude higher changes in total pressure than are relevant in the present context [49]. Flow rates through a hypothetical air cleaner were selected to maintain air-media contact times for dry sorbents that matched those used in experiments described in §2.2.1. Scrubber dimensions were selected to allow the contact time to be held constant while providing a volumetric flow rate similar to commercial air cleaners appropriately sized for the indicated indoor microenvironment.

3. Results and Discussion

3.1 Physicochemical properties of sorbents

Physical and chemical properties of the four sorbents considered in this investigation are shown in Table 2. The MgO, $Mg(OH)_2$, and $Ca(OH)_2$ materials represent pure or nearly pure compounds that are commercially available, low-cost, and may be derived from waste streams [19]. A stream for reusing alkaline earth metal oxides or hydroxides that simultaneously addresses an indoor air quality concern could represent a valuable opportunity. The fourth sorbent considered, soda lime, is mainly $Ca(OH)_2$; however, it is specifically designed for CO_2 scrubbing by the addition of (a) two catalysts (KOH, NaOH) and (b) approximately 10% H_2O to accelerate the uptake of CO_2 and subsequent conversion of $Ca(OH)_2$ to $CaCO_3$. The physical properties summarized in Table 2 reveal

only modest variation in properties across the four sorbents. The measured mass median particle sizes (d_{50}) of the three powder samples (MgO, $Mg(OH)_2$, and $Ca(OH)_2$) ranged between 5 and 19 µm, whereas the grain size for the soda lime media was reported as 1 mm (by the manufacturer). Particle size distributions for the powder samples are provided in Figure S2 of the Supporting Information. Note that in the subsequent modeling of indoor spaces, granular media with a d_{50} of 1 mm is assumed for both soda lime and $Ca(OH)_2$; the implications of this assumption for the modeling of a hypothetical $Ca(OH)_2$ packed bed are discussed in §3.3. The specific surface areas of these materials are a few orders of magnitude lower than values for other engineered sorbents for CO_2 and gas-phase pollutants, such as metal organic frameworks [50,51]. Among the four sorbents considered, MgO has the highest internal surface area, 28 m^2/g, a factor of five higher than the value for pure $Mg(OH)_2$. Increasing specific surface area may present a useful pathway for enhancing the uptake of CO_2 to low-cost sorbents, as it is probable that the availability of CO_2 sorption and/or reaction sites is a factor that limits uptake of CO_2.

3.2 Characterizing CO_2 uptake by sorbents

3.2.1 X-ray diffraction

XRD patterns of Ca- and Mg-based sorbents subjected to a flow rate of 2.7 L/min under a constant CO_2 concentration of 2200 ppm for 7 days are shown in Figures 2 (a) and (b), respectively. Sorbents containing $Ca(OH)_2$ and soda lime indicate the formation of the carbonation product calcite, whose main peak is observed at 29.4° 2θ along with several secondary peaks. The absence of the major hydroxide phase portlandite ($Ca(OH)_2$) in the presented patterns is a clear indication that the prepared samples have fully carbonated during the 7 days of exposure. As these samples were subjected to accelerated carbonation conditions under an elevated CO_2 concentration and flow rate, the hydroxide phases within the soda lime and $Ca(OH)_2$ based sorbents have been transformed into calcite, as observed in the XRD patterns.

The crystalline phases forming after the carbonation of Mg-based sorbents are shown in Figure 2(b). In addition to magnesium carbonate, some of the common carbonation products

observed were hydrated magnesium carbonates (HMCs) such as dypingite and hydromagnesite. Dypingite (powder diffraction file (PDF) #029-0857) has its four highest intensity peaks at 15°, 30.4°, 13.7° and 21° 2θ followed by peaks at 12°, 20°, 27.9°, 41.3°, 45.5°, and 44.8° 2θ. Most of the strong peaks and many of the weaker ones can be seen in the XRD patterns presented, confirming the presence of dypingite. Hydromagnesite (PDF #025-0513) has its highest intensity peaks at 15.3°, 30.8° and 13.7° 2θ, which are similar to those of dypingite and hence are expected to overlap in the XRD spectra. Hydromagnesite (PDF #003-0093) also has sharp peaks in the high-angle region at 42° and 45.5° 2θ, where small peaks can be seen in the presented diffractograms. These peaks confirm the presence of hydromagnesite in the samples.

Other than the carbonation products, the presence of brucite is observed in both samples, where unhydrated MgO peaks can be seen in the MgO-based sorbent. The presence of the MgO peak at 42.9° 2θ indicates incomplete hydration, whereas the brucite peak at 38° 2θ is an indication of incomplete carbonation of both samples. These results clearly indicate that the carbonation conditions utilized in this study were not sufficient for the Mg-based samples to fully carbonate within the given exposure period. In principle, improved carbonation could be realized via (i) the use of a higher reactivity MgO with a larger specific surface area to increase the rate and degree of hydration and the subsequent carbonation process and (ii) optimization of the carbonation conditions to increase the rate and amount of CO_2 diffusion within the samples.

3.2.2 Thermogravimetric analysis

The TGA results for the Ca- and Mg-based sorbents are shown in Figure 3(a) and (b), respectively. As can be seen in Figure 3(a), the thermal decomposition of Ca-based sorbents followed a regular pattern, indicating the decomposition of the main carbonate phase, calcite. This decomposition occurred between temperatures of 650 and 830 °C as expected, resulting in a weight loss of about 44% in both samples. Corroborating the XRD results, this outcome shows that both samples have fully carbonated as the molar mass calculations of the carbonation reaction indicate that CO_2 (44 g/mol) represents 44% of the overall mass of calcite (100 g/mol). The similar

312 decarbonation behavior and weight loss of soda lime and $Ca(OH)_2$-based samples is a clear indication
313 that they demonstrated similar carbonation capabilities notwithstanding the additives (i.e. NaOH
314 and KOH) included in the commercial soda lime sorbent.

315 The thermal decomposition behavior of Mg-based samples, shown in Figure 3(b), is slightly
316 more complex as in addition to uncarbonated brucite, these samples contain several carbonate
317 phases with different decomposition patterns. According to the weight lost shown in the TGA curves,
318 the decomposition steps of Mg-based samples can be divided into 3 main stages, whose details are
319 listed in Table 3: (i) < 300 °C: loss of unbound water and water of crystallization of HMCs associated
320 with their dehydration; (ii) 300-500 °C: dehydroxylation of HMCs and decomposition of any
321 uncarbonated brucite; and (iii) > 500 °C: decarbonation process involving the decomposition of
322 HMCs into MgO.

323 The two endothermic peaks corresponding to the loss of unbound water and dehydration of
324 water bonded to HMCs were observed at ~120 and 250 °C, respectively. A strong endothermic peak
325 reflecting the decomposition of uncarbonated brucite accompanied by the dehydroxylation of HMCs
326 (hydromagnesite and dypingite) was observed at ~450 °C. This transformation was followed by a
327 broader peak corresponding to the decarbonation of HMCs at ~680 °C. The similar decomposition
328 patterns and final weights demonstrated by the MgO and $Mg(OH)_2$ samples clearly indicate their
329 comparable extents of carbonation. The presence of the large brucite peak within both samples is a
330 clear indication of incomplete carbonation, which was in agreement with the XRD patterns.

331 **3.2.3 Scanning electron microscopy**

332 Figure 4 shows the microstructures of the 4 samples analyzed by XRD and TGA. The SEM
333 images of the soda lime (Figure 4(a) and (b)) and $Ca(OH)_2$-based samples (Figure 4(c) and (d)) reveal
334 similar morphologies at both magnifications. The formation of tightly packed calcite crystals of
335 different sizes can be observed in both samples. Hexagonal calcite crystals are accompanied by
336 sparsely distributed crystals of acicular shape in the $Ca(OH)_2$ based sample, as shown in Figure 4(c).

In general, both samples indicate a dense formation of calcite, in agreement with the results of the TGA and XRD analyses.

As depicted in Figure 4(e)-(h), the microstructure of MgO and $Mg(OH)_2$ based samples are dominated with rosette-like formations of brucite, as was indicated by the TGA and XRD analyses. The main difference between the two samples is the size and density of brucite formations. The direct hydration of MgO results in the dense formation of brucite particles that are fused into large agglomerates. The direct inclusion of $Mg(OH)_2$ produces a porous distribution of brucite particles with smaller sizes. However, the morphology of these brucite formations did not influence their carbonation potential as both samples demonstrated similar carbonation behaviours and capacities. Minor formations of hydromagnesite and dypingite are observed around the brucite crystals, which is a clear indication of limited carbonation within these samples.

3.2.4 Kinetics and capacity of CO_2 uptake by Ca-based sorbents

This section describes the results of the uptake experiments for the Ca-containing sorbents. The Mg-containing sorbents did not sufficiently carbonate under the experimental conditions to justify characterizing their kinetic and yield parameters. Some combination of catalysis (as in the case of soda lime) or alteration of physical parameters (e.g., increasing the specific surface area) would be required to increase the kinetics and capacity such that MgO or $Mg(OH)_2$ based sorbents may be considered effective for CO_2 removal under conditions relevant to indoor environments.

Experimental conditions, rate constants and carbonation yields for soda lime and pure $Ca(OH)_2$ are reported in Table 4. Rate constants and yields are generally higher for soda lime than for $Ca(OH)_2$, which is as expected given the presence of two catalysts plus water in soda lime to facilitate the carbonation reaction. Under dry conditions (i.e., for solid sorbents with inlet airflow at 75% RH), low yields were determined for $Ca(OH)_2$. As will be further explored in §3.3, these limitations constrain the effectiveness of dry $Ca(OH)_2$ as a CO_2 sorbent under representative indoor conditions. However, when the experimental flow rate was increased from 1.8 to 2.8 L/min, the reaction rate of CO_2 with $Ca(OH)_2$ increased to nearly that of soda lime, albeit with substantially lower yield. This

increase in kinetics illustrates potential for subsequent optimization of air cleaners utilizing $Ca(OH)_2$ media in indoor air treatment applications.

We explored the role of water availability by conducting experiments in both slurry and packed dry-bed configurations. Under slurry conditions, the carbonation yield for $Ca(OH)_2$ is substantially higher than for dry-bed conditions, approaching that of soda lime. A slurry configuration is likely infeasible for indoor air cleaning applications owing to high pressure drops across a water column and the high-humidity effluent. However, future research could be worthwhile to pursue, investigating in more detail the role of water or water vapor influencing the uptake of CO_2 by Ca-containing sorbents with the goal of increasing CO_2 removal rates on low-cost sorbents.

3.3 Modeling indoor CO_2 removal

Modeled indoor CO_2 concentrations for the three hypothetical scenarios (SIP, bedroom, and classroom settings) are shown in Figure 5. In each case, a duration of 8 h is simulated, to approximate a single-event occupancy in each of the three types of spaces. In this section, results for CO_2 removal for 8-h model durations are described for each scenario, focusing on conditions that result in greater observed removal of CO_2 from the hypothetical indoor environments. A sensitivity analysis is then presented for the most efficacious scenario. Finally, implications of model results regarding feasibility of $Ca(OH)_2$ as a reagent for indoor CO_2 removal are discussed.

The application of active CO_2 control to the shelter-in-place (SIP) scenario shown in Figure 5 illustrates the most efficacious outcome among the scenarios considered. This favorable result is a consequence of the small volume and relatively low air exchange rate of the modeled SIP facility. For the SIP scenario with a soda lime containing air cleaner, the CO_2 level is maintained below 5000 ppm until 7-8.5 h after initial occupancy. After 10 h of operation, the soda lime packed bed is effectively spent (see Figures S4-S6 of the Supporting Information), and the SIP CO_2 concentration begins to increase, exceeding 10,000 ppm shortly after 10 h of occupancy (see Figure S4). These times contrast with the no air cleaning case, where the 5000 ppm CO_2 level is reached after only 1.1 h of sheltering

and 10,000 ppm is reached after only 1.9 h. Without air cleaning, concentrations of CO_2 in the SIP environment would reach values in excess of 25,000 ppm after 8 h of occupancy. These results imply that occupancy under the "no scrubber" condition shown in Figure 5 for more than a few hours may result in CO_2 exposures that can produce acute adverse health effects [17].

Bedrooms represent an important microenvironment contributing to daily exposures of CO_2, as shown in a recent study of personal exposures to CO_2 in Singapore [52]. As can be observed in Figure 5, in the absence of air cleaning, levels of CO_2 in the bedroom scenario exceed 1000 ppm after just 1 h of exposure. An air cleaner containing a soda lime packed bed, operating either at low or high flow rate, can maintain sub-1000 ppm CO_2 concentrations in the bedroom for the duration of the 8-h sleeping period. As with the SIP scenario, an air cleaner containing a pure $Ca(OH)_2$ dry sorbent appears to have more modest impacts on indoor CO_2 concentrations. However, worth noting is that the average CO_2 concentration during the 8-h sleeping period for the high flow rate $Ca(OH)_2$ treatment is approximately 950 ppm.

In the case of classrooms, due to the larger room volume and higher air exchange rate than the bedroom and SIP scenarios, the presence of the air-treatment unit has a relatively small impact on CO_2 concentrations. Levels of CO_2 in the classroom after 8 h of operation in absence of air cleaning would be approximately 1400 ppm, compared to a range 900-1050 ppm with a soda lime air cleaner. Since a classroom would not typically be occupied continuously for 8-h periods, the CO_2 concentrations presented in Figure 5 for the classroom case may be considered as an upper limit. Given the modest reductions in classroom CO_2 levels for a substantial mass of media and volume of air cleaner (see Table 1), the results indicate that the classroom scenario described here does not appear to present a good opportunity for active CO_2 removal given the present state of sorbent development.

Model runs for longer durations (16 h, 40 h, and 40 h, respectively, in the SIP, bedroom, and classroom) assuming continuous occupancy are shown in Figure S3 (Supporting Information) with pertinent results of the sensitivity analysis summarized in Table 5. Removal of CO_2 under the

conditions of the SIP facility occurs over a range of achievable pressure drops (150-435 Pa) when compared with commercially available air cleaners. Because of the small volume and low air exchange rate, impacts of air cleaning on CO_2 concentrations are substantial: the time to reach a 10,000 ppm threshold is extended by 4-12 hours, and cumulative 8-h exposures are reduced by 60-90%. However, the relatively small mass of media combined with the high CO_2 concentrations results in substantial media usage; in all cases the scrubber media is exhausted after 13 h of continuous operation.

In the bedroom scenario, the scrubber appears effective over the range of media masses considered, with pressure drops ranging from 120-290 Pa. Reductions in cumulative exposures are again substantial, in the range 50-66%, and at higher sorbent masses appear to exhibit cumulative run-times that are 40 h or greater. Note that these estimates are conservative, as an air-cleaner deployed to a bedroom would not operate continuously for 40 h, and would likely be utilized in sequential 8-h periods that begin with CO_2 concentration nearer to ambient levels.

Model results for a $Ca(OH)_2$ containing air cleaner across all three scenarios illustrate more modest removal of CO_2 from the indoor space than for soda lime. While the cost of $Ca(OH)_2$ itself is relatively low and the efficacy of the air cleaner could be increased by recirculating air at higher flow rates through the $Ca(OH)_2$ bed, effectively increasing the removal rate of CO_2 could become prohibitive with respect to energy use owing to the nonlinear relationship between flow rate and pressure drop. Also worth noting is that the estimates of k and y for $Ca(OH)_2$ are likely best-case values with respect to room-scale air cleaning. The $Ca(OH)_2$ used in laboratory parameterizations was purchased from a commercial supplier and was of a finer grain than the granular media that would typically be used in an air cleaner; transport limitations resulting from the geometry of a larger $Ca(OH)_2$ granule may reduce the effective yield, rate constant or both, possibly a result of the formation of a diffusion limiting carbonate shell [53]. Achieving the uptake reported from laboratory tests in the applied scenarios by use of a fine grain $Ca(OH)_2$ may, in practice, create prohibitively large pressure drops across the air cleaner. Testing granular $Ca(OH)_2$ with varying physical

441 properties, including size of particles as deployed in the packed bed, would more fully inform the
442 potential use of $Ca(OH)_2$ as a low cost sorbent for active indoor CO_2 control.

443 **4. Conclusions**

444 This study investigated the ability of Mg- and Ca-based sorbents to take up gaseous carbon
445 dioxide through the formation of solid carbonates. The work establish links between a range of
446 controlling parameters and the progress of carbonation through a sorbent matrix. Four alkaline
447 earth metal oxides or hydroxides were characterized for their potential as CO_2 sorbents in an active
448 indoor air cleaning application. A comparison between Mg- and Ca-based sorbents was provided in
449 terms of carbonation degree, microstructure and parameterizations of carbonation kinetics and
450 yields from laboratory experiments. These results were supported by XRD, TGA and SEM analyses,
451 which provided information on the hydration and carbonation phases, the progress and degree of
452 carbonation and the morphology of the sorbents.

453 Results indicate that extensive carbonation of sorbents occurred at conditions typical of
454 indoor spaces (25 °C and CO_2 levels of approximately 2200 ppm), although Mg-containing sorbents
455 carbonated slowly such that parameterization of kinetics and capacity were not pursued. Modeling
456 of hypothetical scenarios in which packed beds of sorbents were part of an active indoor air cleaner
457 show potential for the substantial removal of CO_2 from SIP facilities with the use of soda lime.
458 Reductions in integrated CO_2 exposures of over 80% are predicted and indoor CO_2 levels are
459 maintained below the OSHA PEL for an assumed 8-h period of occupancy. These reductions were
460 accomplished with reasonable masses of soda lime (1.7 kg) and at a pressure drop (approximately
461 300 Pa) achievable by fans similar to those present in a typical HEPA filter-containing portable air
462 cleaner. Modeling for low-ventilation bedrooms showed that meaningful reductions are also
463 possible in this setting, with reductions in CO_2 levels after 8 hours of occupancy from 2500 ppm (with
464 no air cleaner) to 550-750 ppm for a continuously operating soda-lime containing air cleaner.
465 However, regular occupancy in bedrooms would necessitate the weekly replacement of the sorbent
466 media as the model shows nearly full exhaustion of the media after 40 hours of operation. The

relatively large mass of sorbent needed in bedrooms could make the use of soda lime cost-prohibitive, a disadvantage that could potentially be removed by enhancing the kinetics and capacity of the lower cost sorbents ($Ca(OH)_2$, MgO and $Mg(OH)_2$).

The empirical kinetic and yield findings were supported by detailed microstructural and thermal analyses, which enabled a thorough comparison of the different media studied. Mg-based sorbents experienced low carbonation rates in the conditions utilized in this study. The carbonation of Mg-based sorbents could be further enhanced via the use of a higher reactivity MgO with a larger specific surface area to induce hydration and the subsequent carbonation process and optimization of the carbonation conditions to increase the rate and amount of CO_2 diffusion within the samples. Efforts to develop sorbents tailored for CO_2 removal in conditions typical of indoor spaces could enable practical utilization of new methods of removing CO_2 from indoor spaces, which appear especially promising in special circumstances where increasing air exchange is infeasible owing to adverse outdoor conditions, such as shelter-in-place facilities.

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643

Table 1. Summary of model inputs to three scenarios considered for active CO_2 removal [a]

Building and air cleaner parameters	Shelter-in-place	Bedroom	Classroom
Room volume, V (m^3)	5	50	150
Occupancy (# of persons)	2	2	40
CO_2 emission rate, E (mol CO_2/h)[a]	1.4	1.4	19
Outdoor air ventilation, Q (m^3/h) (Air exchange rate, (h^{-1}))	1 (0.2)	15 (0.3)	450 (3)
Air cleaner flow rate, low/high Q_f (m^3/h)	13/21	40/61	198/306
Packed bed diameter (m)	0.15	0.25	0.45
Packed bed length (m)	0.11	0.12	0.09
Media mass (kg)[b]	1.7	5	25

[a] Total emission rate of CO_2. For classrooms, the average age of occupant was taken to be 10 years, weight of 35 kg, height of 1.4 m, Dubois surface area of 1.1 m^2, activity level of 1.2 met, and respiratory quotient of 0.83. For bedroom and shelter-in-place, age was taken to be 35 years, weight of 60 kg, height of 1.65 m, Dubois surface area of 1.7, activity level of 1.2 met, and respiratory quotient of 0.83.

[b] Media packing density for both sorbents in the scrubber was taken to be 900 kg/m^3, as per soda lime manufacturer specifications.

Table 2. Summary of physical and chemical properties of tested sorbents

	Chemical composition (% by mass)	Physical characterization			
Sorbent		Specific surface area [m^2/g]	Total pore volume [cm^3/g]	Avg. pore diameter [nm]	Mass median particle size (d_{50}) (μm) [d]
MgO	>91.5% MgO, 4% LOI [b], 2% SiO_2, 1.6% CaO, 1% R_2O_3 [c]	27	7.2×10^{-2}	0.56	16
$Mg(OH)_2$	>99% $MgOH_2$	5.6	8.7×10^{-3}	0.24	5.4
$Ca(OH)_2$	>99% $Ca(OH)_2$	15	3.9×10^{-3}	0.18	19
Soda lime[a]	85% $Ca(OH)_2$, 10% H_2O, 3% KOH, 2% NaOH	7.1	1.6×10^{-2}	0.15	1000 [e]

[a] Chemical composition determined as described by Gall et al. [54]
[b] LOI is loss on ignition, a determination of the amount of volatile substances within the sorbent composition.
[c] R_2O_3 refers to the group of oxides generally consisting of Al_2O_3, Fe_2O_3, and B_2O_3, and are impurities in the sorbent composition.
[d] Median particle size of unground media reported from particle size analyzer
[e] Median size of soda lime granules as reported by manufacturer.

Table 3. Thermal decomposition of hydrate and carbonate phases within Mg-based sorbents

Phases	Decomposition reactions		
	50 – 300 °C	300 – 500 °C	500 – 900 °C
Brucite $Mg(OH)_2$	-	$Mg(OH)_2 \rightarrow MgO + H_2O$	-
Hydromagnesite $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O \rightarrow 4MgCO_3 \cdot Mg(OH)_2 + 4H_2O$	$4MgCO_3 \cdot Mg(OH)_2 \rightarrow 4MgCO_3 + MgO + H_2O$	$MgCO_3 \rightarrow MgO + CO_2$
Dypingite $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O \rightarrow 4MgCO_3 \cdot Mg(OH)_2 + 5H_2O$	$4MgCO_3 \cdot Mg(OH)_2 \rightarrow 4MgCO_3 + MgO + H_2O$	$MgCO_3 \rightarrow MgO + CO_2$

Table 4. Summary of experimental conditions, reaction rate constants, *k*, and yields, *y*, for CO_2 uptake experiments to soda lime and $Ca(OH)_2$.

Sorbent	Experimental condition	Temperature [°C]	*Q* [L/min]	Contact time [s]	Inlet $[CO_2]$ [ppm]	Reaction rate constant, *k* [m^3 mol CO_2^{-1} h^{-1}]	Yield, *y* [mol CO_2/mol sorbent]
Soda lime	Dry packed bed	26.1	1.8	0.28	1870	2.2	0.49
		25.2	2.8	0.18	1890	3.6	0.51
	Slurry	25.2	1.8	0.28	2100	1.9	0.74
		25.2	2.7	0.18	2110	1.6	0.79
$Ca(OH)_2$	Dry packed bed	25.2	1.8	0.28	2200	1.0	0.05
		24.8	2.8	0.18	2310	3.3	0.18
	Slurry	25.0	1.8	0.28	2200	1.6	0.65
		25.0	2.7	0.18	2200	2.4	0.65

Table 5. Summary of sensitivity analysis of model output of indoor CO_2 concentrations in three scenarios of active CO_2 removal from indoor spaces.

Shelter-in-place, Soda lime, Scrubber diameter = 0.12 m				
Mass of media (kg)	Contact time (s)[#]	Pressure drop (Pa)[$]	Time to 10,000 ppm (h)	∫ exposure, 0-8 h (ppm-h)
-	-	0	1.9	139000
0.9	0.09	157	6.5	46150
1.3	0.14	226	8.4	27080
1.7*	**0.18**	**296**	**10.1**	**26200**
2.1	0.22	365	12.1	17780
2.5	0.26	435	13.8	17080
Bedroom, Soda lime, Scrubber diameter = 0.25 m				
Mass of media (kg)	Contact time (s)	Pressure drop (Pa)	Time to 1,000 ppm (h)	∫ exposure, 0-8 h (ppm-h)
-	-	0	0.9	14730
3	0.11	122	13	5370
4	0.14	163	18	5000
5	**0.18**	**204**	**22**	**4820**
6	0.22	245	27	4730
7	0.25	285	29	4730
Classroom, Soda lime, Scrubber diameter = 0.45 m				
Mass of media (kg)	Contact time (s)	Pressure drop (Pa)	Time to 1,000 ppm (h)	∫ exposure, 0-8 h (ppm-h)
-	-	-	0.4	11100
15	0.11	170	4.0	7950
20	0.14	337	6.6	7630
25	**0.18**	**580**	**8.9**	**7460**
30	0.22	910	11	7360
35	0.25	1340	12	7340

[#] Values for *k* and *y* at indicated contact time were determined by linearly interpolating/extrapolating from experimentally determined values.
[$] Pressure drop was calculated using the Ergun equation [55] with an equivalent spherical particle diameter of 1 mm and a packed bed porosity of 0.55.
* Conditions in bold are the 'base-case' conditions.

Figures

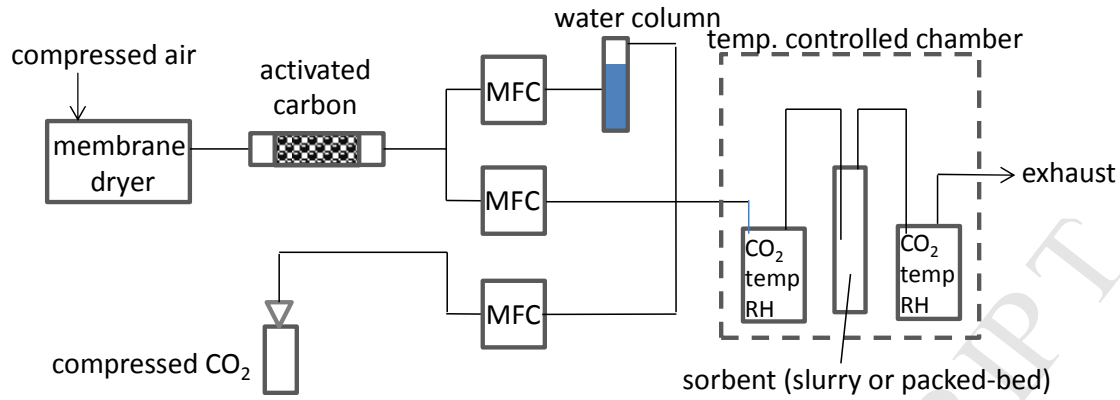
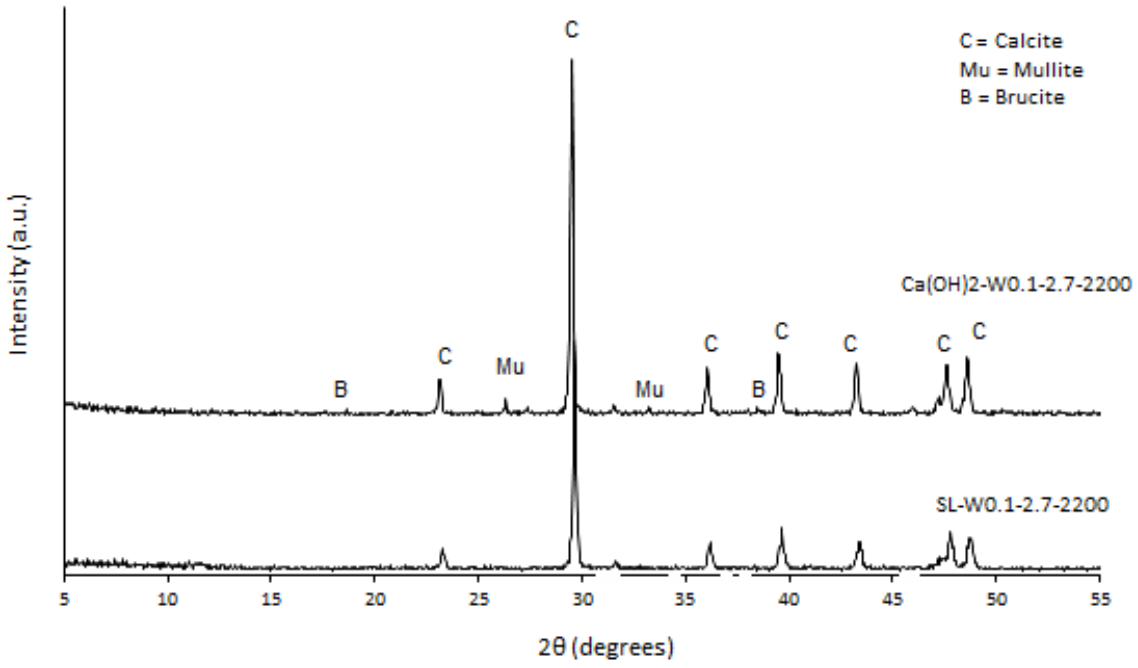
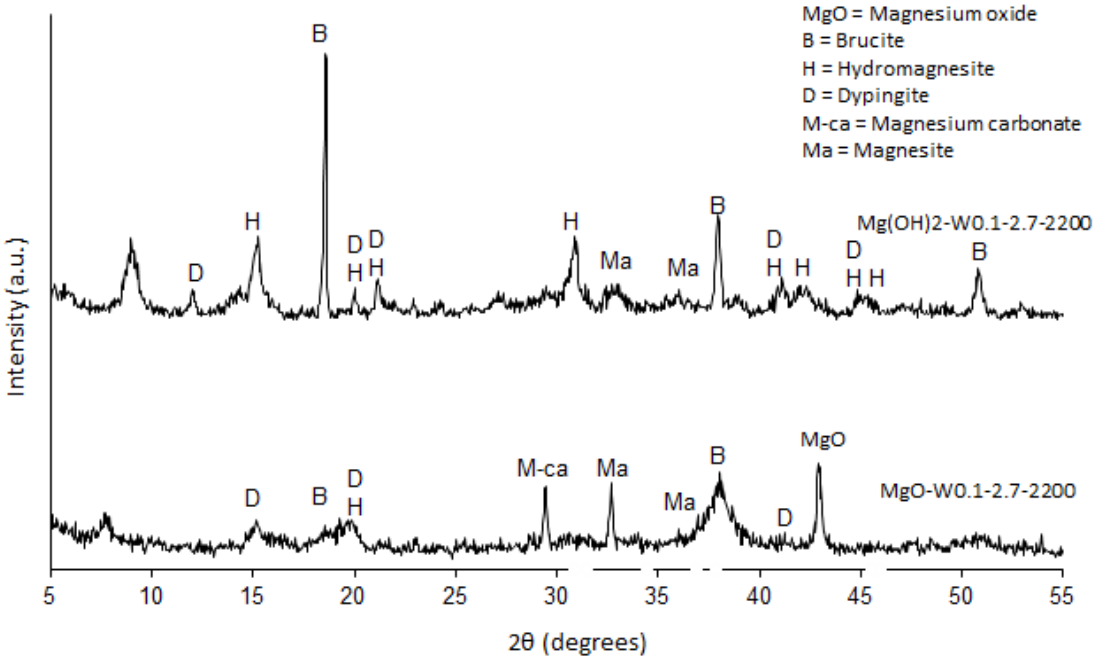


Figure 1. Schematic of laboratory apparatus used for carbonation experiments with controlled temperature, humidity and CO_2 levels. MFC = mass flow controller, temp. = temperature, RH = relative humidity.

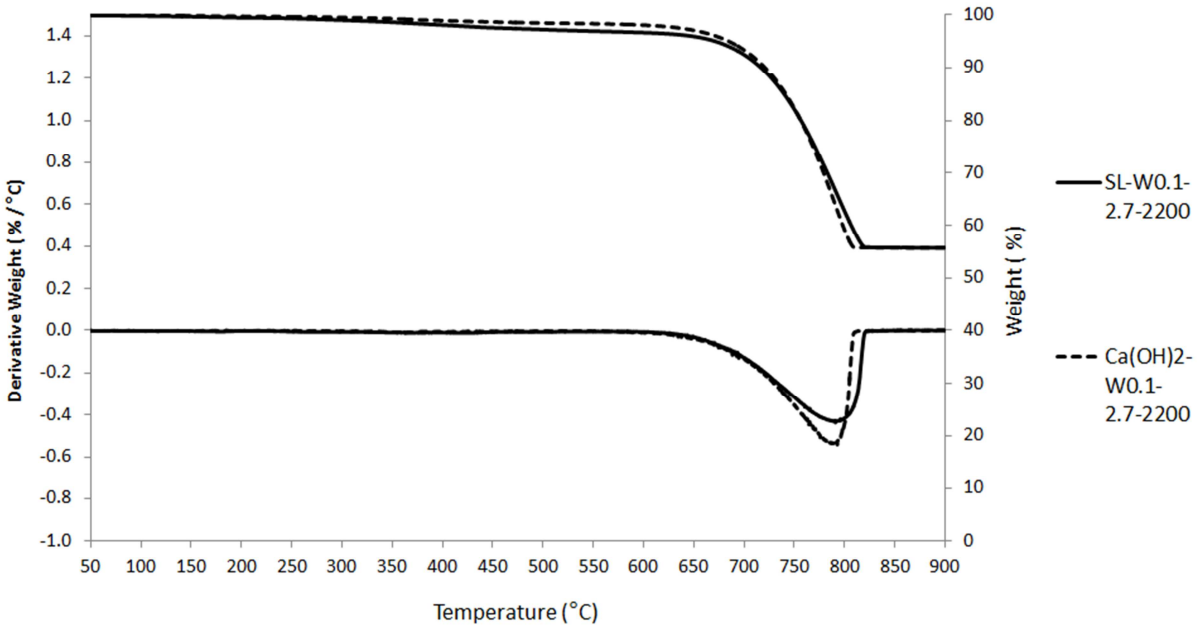


(a)

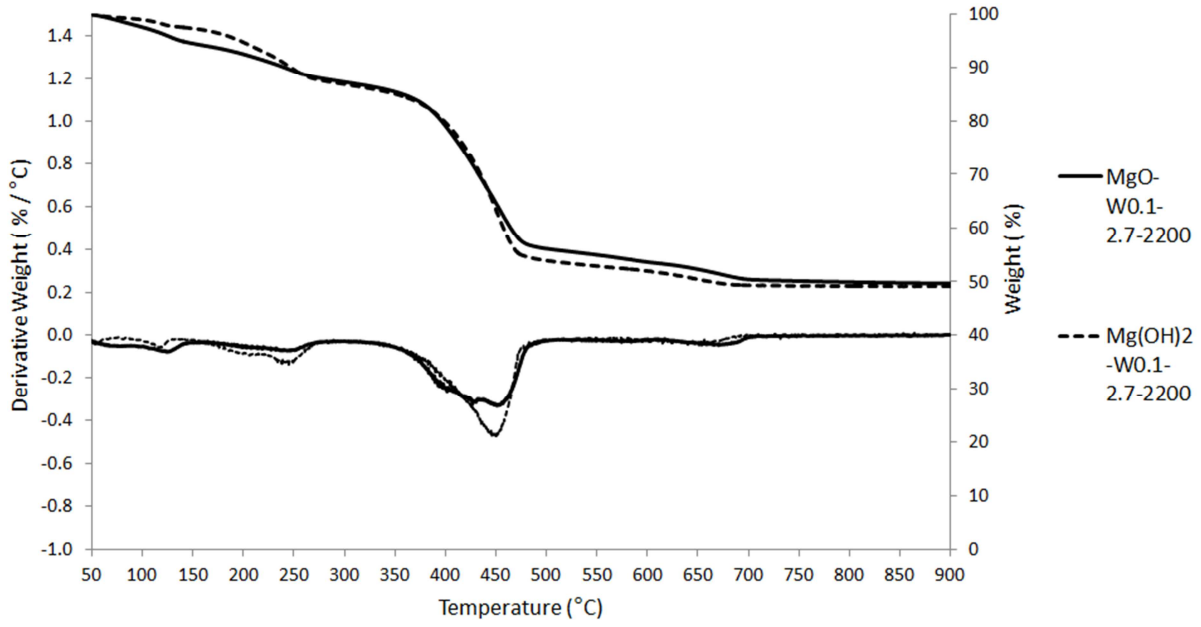


(b)

Figure 2. X-ray diffraction patterns of (a) Ca- and (b) Mg-based sorbents after exposure to CO_2.

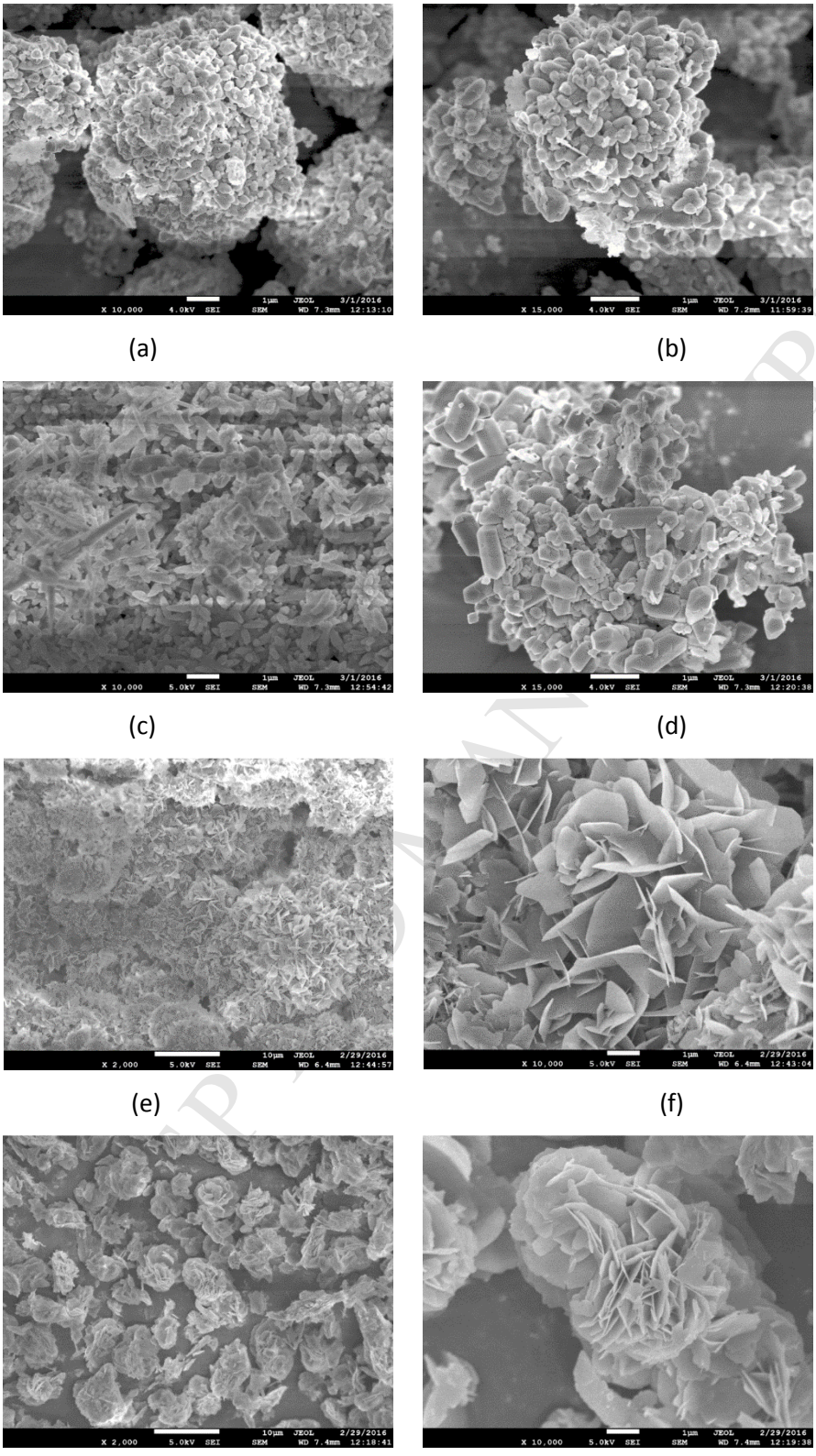


(a)



(b)

Figure 3. Thermogravimetric analysis graphs of (a) Ca- and (b) Mg-based sorbents (the primary *y*-axis (on the left) refers to the lower traces of derivative weight; the secondary *y*-axis (on the right) refers to the upper traces of percentage weight).



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 4. Scanning electron microscopy images of (a)-(b) SL-W0.1-2.7-2200, (c)-(d) $Ca(OH)_2$-W0.1-2.7-2200, (e)-(f) MgO-W0.1-2.7-2200 and (g)-(h) $Mg(OH)_2$-W0.1-2.7-2200. The white bar at the bottom of each photograph indicates the scale: 1 µm (a-d, f, h) or 10 µm (e, g). These images were acquired after exposure of the sorbents to CO_2.

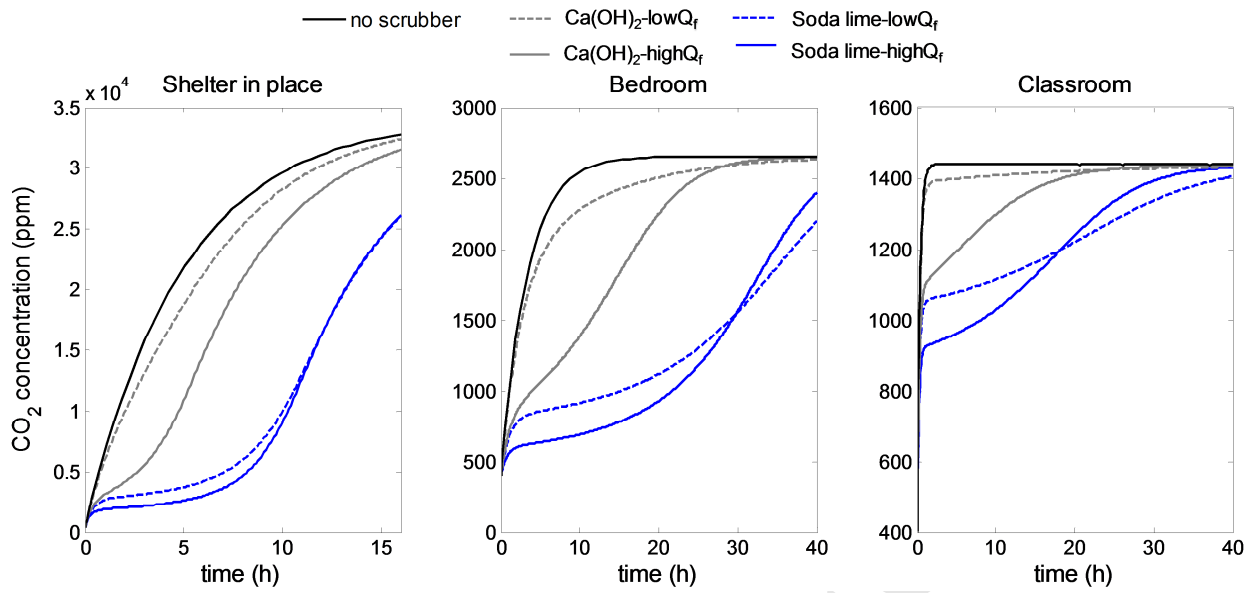


Figure 5. Modeled indoor CO_2 concentrations for three hypothetical indoor environments: a shelter-in-place facility, a bedroom and a classroom with and without the presence of an air cleaner that includes a CO_2 scrubbing bed. Relevant built environment and air cleaner parameters for each of the three indoor environments are provided in Table 1. '$LowQ_f$' refers to the low air cleaner flow rate condition, '$highQ_f$' refers to the high air cleaner flow rate condition.

Highlights:

- CO_2 can accumulate in indoor spaces with low air exchange, e.g. in shelter-in-place
- Various Ca- or Mg- based sorbents are investigated as potential air cleaner media
- Ca containing sorbents carbonated under conditions relevant to indoor spaces
- Active removal may substantially reduce CO_2 exposure in shelter-in-place facilities