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Influence of the Concentration of CO₂ and SO₂ on the Absorption of CO₂ by a Lithium Orthosilicate-Based Absorbent

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Ⓢ *Supporting Information*

ABSTRACT: A novel, high temperature solid absorbent based on lithium orthosilicate (Li_4SiO_4) has shown promise for postcombustion CO_2 capture. Previous studies utilizing a clean, synthetic flue gas have shown that the absorbent has a high CO_2 capacity, >25 wt %, along with high absorption rates, lower heat of absorption and lower regeneration temperature than other solids such as calcium oxide. The current effort was aimed at evaluating the Li_4SiO_4 based absorbent in the presence of contaminants found in typical flue gas, specifically SO_2, by cyclic exposure to gas mixtures containing CO_2, H_2O (up to 25 vol. %), and SO_2 (up to 0.95 vol. %). In the absence of SO_2, a stable CO_2 capacity of ∼25 wt % over 25 cycles at 550 °C was achieved. The presence of SO_2, even at concentrations as low as 0.002 vol. %, resulted in an irreversible reaction with the absorbent and a decrease in CO_2 capacity. Analysis of SO_2-exposed samples revealed that the absorbent reacted chemically and irreversibly with SO_2 at 550 °C forming Li_2SO_4. Thus, industrial application would require desulfurization of flue gas prior to contacting the absorbent. Reactivity with SO_2 is not unique to the lithium orthosilicate material, so similar steps would be required for other absorbents that chemically react with SO_2.
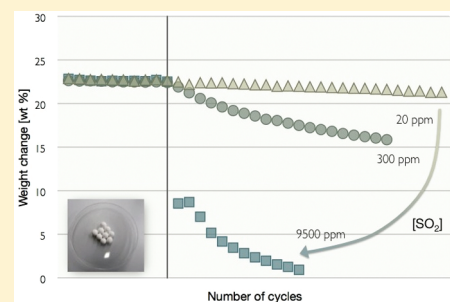
■ INTRODUCTION

For current combustion systems, the only commercially proven technology to separate CO_2 from flue gas relies on absorption with aqueous monoethanolamine (MEA). However, if a CO_2 capture and storage (CCS) system incorporating an amine-based process were applied to a conventional pulverized coal-fired power plant, it would suffer a parasitic energy penalty of up to 50% compared to a plant without CCS.[1−4] The CO_2 separation process alone accounts for up to 75% of the overall energy burden of the CCS system. As a result, a wide range of emerging technologies are being investigated as alternatives to the amine-based process.[5,6]

There is general agreement that if CO_2 capture from flue gas were required tomorrow, it would utilize an aqueous alkanolamine-based absorption process.[5] Aqueous alkanolamine solutions are exposed to flue gas at near-ambient temperatures, and CO_2 is captured by a chemical reaction with the amine. Regeneration is accomplished using a steam purge at elevated temperature (about 140 °C) and desorption of CO_2 requires a significant energy input, not only because of the high heat of adsorption for amines, but also because of the heat to raise the liquid temperature to that required for desorption. Additional limitations associated with alkanolamines are well documented and include O_2-based oxidation and irreversible reaction with SO_x. Furthermore, even though alkanolamines have relative low

vapor pressures, exposure to high flue gas flow may result in volatilization of amines. Additional amine losses may be incurred during the steam regeneration step. Without a downstream capture unit operation, vaporized amines can potentially escape to the atmosphere. As a result, a wide range of emerging technologies are being investigated as alternatives to the amine-based process[5,6] along with efforts to optimize the current MEA-based process and to develop alternative amines.[7]

A promising concept consists in using suitable metal oxides, either naturally occurring[8−11] or synthesized,[12−25] that reversibly react with CO_2 at elevated temperatures. In recent years, materials containing zirconates and silicates of lithium have gained increasing interest as potential absorbents for CO_2 at high temperature.[12,14−19] Nakagawa et al. have investigated the CO_2 absorption properties of lithium zirconate, Li_2ZrO_3, and lithium orthosilicate (Li_4SiO_4) pellets.[12,17−19] They concluded that Li_4SiO_4 could be a competitive absorbent in terms of both rate and extent of absorption. Furthermore, the absorbent requires less energy ($\Delta H_{r, 298}$ = +142.8 kJ/mol) and lower temperatures (T < 800 °C) for CO_2 desorption than other high-temperature absorbents such as CaO.[14]
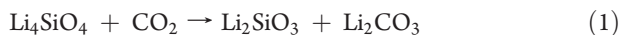
The absorption of CO_2 by Li_4SiO_4 proceeds by formation of lithium carbonate, Li_2CO_3, and lithium metasilicate, Li_2SiO_3, according to reaction 1.

$$Li_4SiO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \qquad (1)$$

The theoretical maximum amount of CO_2 absorbed is 1 mol for every mole of Li_4SiO_4, corresponding to a maximum capacity of CO_2 of 0.36 g CO_2/g absorbent. In practice, CO_2 capacities up to ~35 wt % have been reported[12,17−19] at a temperature of 700 °C in pure CO_2.

In a practical CO_2 capture process, the absorbent must be capable of performing over an extremely large number of absorption/desorption cycles. Studies of the cyclic and chemical stabilities of Li_4SiO_4 have been reported for experiments using a Thermo-gravimetric Analyzer (TGA). Exposure to gas containing 20% CO_2 in air at 1 atm and 600 °C followed by desorption at 820 °C resulted in a slight loss in capacity in the first 10 cycles from ~25 to ~23 wt %, but thereafter capacities were constant.[20]

An industrial process also requires an absorbent material that maintains a high CO_2 capacity in the presence of the numerous impurities found in coal-fired power plant flue gas. A typical gas composition is 10−15% CO_2, 3−4% O_2, 5−7% H_2O, 0.05−0.3 vol.% of SO_2, and 0.015−0.05 vol.% of NO_x, together with trace quantities of other compounds such as HCl, arsenic, mercury, and selenium.[21] Such species could have a significant impact on the reversible absorption of CO_2 leading to a decrease in capacity with time, as observed for high-temperature absorbents such as CaO.[26,27]

The capture technology proposed in this work utilizes a solid lithium orthosilicate (Li_4SiO_4)-based absorbent and addresses many of the limitations associated with amine-based technologies.[5] The solid sorbent is expected to be inert with respect to O_2 and NO_x. However, as for other CO_2-reactive materials, it could react with SO_2. The solid absorbent is inherently non-volatile and will not emit undesirable species to the atmosphere. Finally, the material offers a greater than 2-fold CO_2 capacity, 5.4 mmol CO_2/g sorbent, than a typical amine such as MEA, 1.5−2 CO_2 mmol/g sorbent (25 °C, 0.15 atm CO_2).[19]

The aim of the current work is to extend the aforementioned studies to more realistic conditions, by exposing the absorbent to gases containing CO_2, SO_2 and H_2O. Particularly, a range of [SO_2] was investigated to determine the maximum allowable SO_2 level that would have no effect on CO_2 absorption. This was investigated via the Integrated Microbalance System (IMS), developed by Air Products and Chemicals Inc. and the *Xarxa de Referència en Materials Avançats per a l'Energia* (XeRMAE, Barcelona, Spain). This instrument is based on a Magnetic Suspension Balance (Rubotherm Gmbh, Germany), that is, a high-resolution balance where the sample and balance electronics are physically separated so the electronics are always isolated from potentially reactive atmospheres at high pressures and/or temperatures. This is accomplished by using a magnetic suspension coupling which transmits the downward, gravitational force acting on the sample to the high resolution balance through the wall of a pressure and temperature resistant vessel.[28] In this way, highly accurate gravimetric measurements of the rate of absorption and adsorption and extent of reaction can be performed. Thus, the interaction of various absorbent materials with simulated flue gas or synthesis gas can be evaluated over a wide range of pressures and temperatures.

■ EXPERIMENTAL SECTION

All experiments were carried out using 5 mm spherical pellets of lithium orthosilicate-based absorbent provided by Toshiba, Ltd. Each pellet consists of lithium orthosilicate, Li_4SiO_4, with <10 mol. % K_2CO_3, and Li_2TiO_3 as binder. Details on their synthesis can be found elsewhere.[11] Three pellets were used in each gravimetric experiment. Pure CO_2 (99.995%), N_2 (99.9%) and mixtures of SO_2 in N_2 (2.0 vol. % SO_2 in N_2, 0.06 vol. % SO_2 in N_2) were all supplied by Carburos Metálicos S.A., Air Products Group (Spain).

The IMS located at MATGAS was used to carry out the tests — an illustration of the system is provided in Supporting Information (SI) Figure S1. It consists of the magnetic suspension balance, a multicomponent feed gas system, a downstream water condensation system, and an off-gas analysis system. The magnetic suspension balance is a high precision instrument capable of measuring minute weight changes of a sample with a stable resolution of 2 μg. The multicomponent gas system consists of eight calibrated mass flow controllers (Brooks Instruments), coupled with a steam line, that can generate a wide variety of gas compositions. Steam is produced in a $^1/_2$ in. stainless steel column filled with alumina beads operating at temperatures up to 650 °C; deionized water is fed to the steam generator by means of a HPLC pump. The desired gas mixture is fed to the sample cell by heat traced $^1/_4$ in. stainless steel tubing to avoid water condensation. The IMS is equipped with two interchangeable sample cells that can accommodate two ranges of pressure and temperature: mode A at low pressure (from 0 to 45 atm) and high temperature (25 to 950 °C) and mode B at high pressure (from 0 to 120 atm) and low temperature (from 5 to 500 °C). For this work, the IMS was used in mode A. The temperature inside the sample cell was measured with a K-type thermocouple. The pressure of the flowing gas in the sample cell was controlled by a needle valve (Kammer, Flowserve) placed at the outlet of the vessel. Gas exiting the needle valve was cooled to condense out the water in a knockout pot. The dry off-gas was either vented or fed to a quadrupole mass spectrometer (Ametek Proline) to analyze the off-gas composition. The whole IMS system was controlled by dedicated software specifically developed for this equipment (VTIPS, VTI Instruments). Metallic baskets made from Inconel 610 mesh were used as sample holders (SI Figure S1).

Prior to each experiment the balance was tared with an empty basket at room temperature and pressure and under stagnant conditions (no gas flowing). Then the sample cell was opened and three absorbent pellets were placed in the basket. A leak test was then performed and the experiment was started via the PC once the sample weight was stable.

Each experiment started with an activation/drying period in which the sample was heated to the working temperature in 1.5 L at STP of pure N_2 and held at these conditions for four hours. Steam was then added to the gas flow (25 vol. %) and fed to the reactor for 3 h. This steam presaturation step ensured that the change in weight experienced by the absorbent during H_2O/ CO_2/SO_2 exposure was due to reaction with CO_2 and/or SO_2 rather than steam.

Single cycle experiments were conducted by exposing the absorbent to 1.5 L at STP of mixed CO_2/N_2/H_2O (with and without SO_2), at a desired temperature and pressure and monitoring the change in mass indicated by the balance. After a prescribed amount of time (typically 1 h), the gas composition
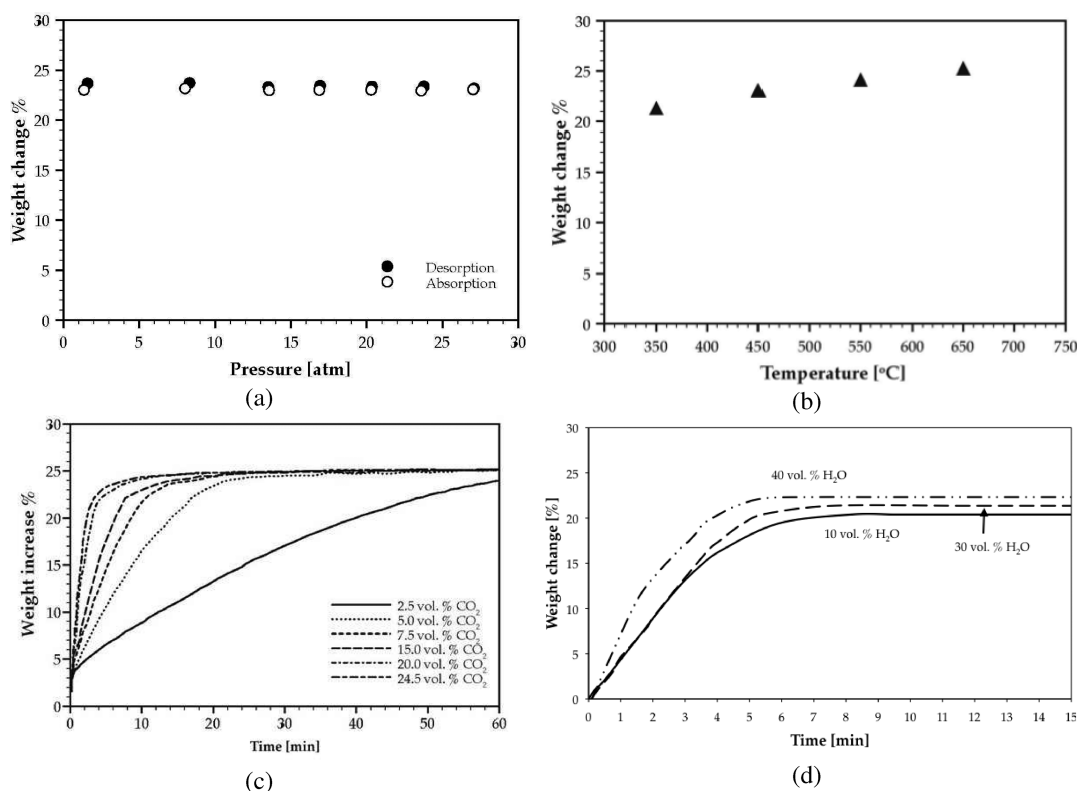
Figure 1. (a) Effect of the system pressure on CO_2 uptake at 550 °C. Absorption at 10 vol. % H_2O and 15 vol. % CO_2 in N_2; desorption in 25 vol. % H_2O in N_2. (b) Effect of temperature on CO_2 absorption. Absorption in 15 vol. % CO_2, 10 vol. % H_2O in N_2 at 2 atm; desorption in 25 vol. % H_2O in N_2. (c) Effect of $[CO_2]$ on CO_2 absorption capacity at 550 °C and 1 atm. Absorption is at the indicated $[CO_2]$ in 10 vol. % H_2O in N_2; desorption in 25 vol. % H_2O in N_2. (d) Effect of $[H_2O]$ on CO_2 capacity at 550 °C and 1 atm. Absorption in at the indicated $[H_2O]$ in 15 vol. % CO_2 in N_2; desorption in 25 vol. % H_2O in N_2.

was changed to a mixture of N_2/H_2O and desorption of CO_2 and SO_2 was tracked by the balance. The effects of buoyancy and gas flow on the balance reading were eliminated by running blank experiments at the same conditions mentioned above.

For cyclic experiments, a repetitive series of absorption/desorption steps were conducted at a fixed temperature. Pressure was maintained at atmospheric pressure for both the adsorption and desorption steps (mimicking the anticipated conditions of a flue gas application). 1.5 L at STP of the feed gas (typically 15 vol. % CO_2 and 10 vol. % H_2O in N_2) were passed to the sample for 1 h, followed by desorption with 25 vol. % H_2O in N_2 for 3 h. This cycle was repeated for 10—25 cycles. In cyclic experiments with SO_2, the absorbent sample was first exposed to 10 cycles of absorption and desorption as described above, followed by an additional 25 cycles with feed gas spiked with up to 1 vol. % SO_2.

After the absorbent samples were exposed to SO_2, they were analyzed by X-ray fluorescence spectroscopy (XRF) and X-ray diffraction analysis (XRD) to determine phase and elemental composition and energy dispersive X-ray spectroscopy (EDS) to evaluate the elemental composition throughout the absorbent pellets.

■ RESULTS AND DISCUSSION

Influence of the Operating Conditions on CO_2 Absorption in the Absence of SO_2. The uptake of CO_2 in the lithium orthosilicate beads was investigated over one cycle of absorption and desorption as a function of the system pressure, temperature, and $[CO_2]$ and $[H_2O]$ in the inlet gas.

The effect of the absorption step pressure was evaluated from 1 to 28 atm at 550 °C. The feed gas during absorption was 10 vol. % H_2O and 15 vol. % CO_2 in N_2, desorption gas consisted of 25 vol. % H_2O in N_2. The results, shown in Figure 1a, reveal that there was little effect of system pressure on CO_2 uptake.

The effect of temperature on the absorbent was evaluated between 350 and 650 °C at near-atmospheric pressure. The inlet gas consisted of 10 vol. % H_2O and 15 vol. % CO_2 in N_2 for absorption and 25 vol. % H_2O in N_2 for desorption. As shown in Figure 1b, the temperature greatly influences CO_2 absorption. In particular, the CO_2 capacity increased with increasing temperature to a maximum of 25 wt % at 650 °C. Further increasing the temperature had an adverse effect on the CO_2 capacity, as expected for an exothermic absorption reaction.

The effect of the composition of the inlet gas was investigated by varying the $[CO_2]$ and $[H_2O]$ between 2.5 and 24.5 vol. %, and between 10 and 40 vol. %, respectively, at 2 atm and 550 °C. Figure 1c and Figure 1d show the effect of $[CO_2]$ and $[H_2O]$, respectively. The final CO_2 absorption capacity was independent of the inlet $[CO_2]$ and was about ∼23.5 wt % (5.4 mmol CO_2/g absorbent, Figure 1c). As expected, the rate of CO_2 absorption increased with increasing $[CO_2]$ in the inlet gas. The effect of increasing $[H_2O]$ from 10 to 40 vol. % on both CO_2 capacities and absorption rates was relatively minor (Figure 1d).

Effect of Repeated Cycles of Absorption and Desorption in the Absence of SO_2. Cyclic experiments were carried out at 550 and 600 °C by exposing the absorbent to a feed gas
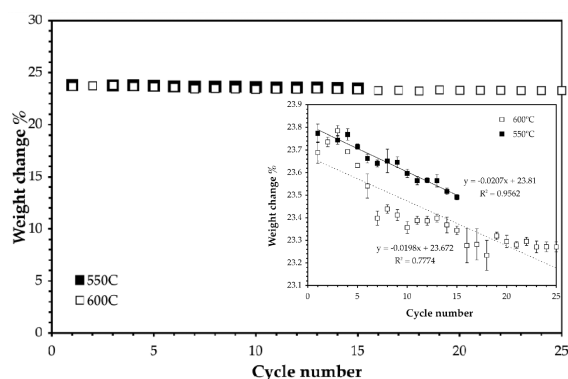
Figure 2. Absorbent weight change over 15 cycles at 550 °C (■) and 25 cycles at 600 °C (□) at 1 atm. Absorption in 15 vol. % CO_2, 10 vol. % H_2O in N_2; desorption in 25 vol. % H_2O in N_2. The error bars correspond to the standard deviation of each point.
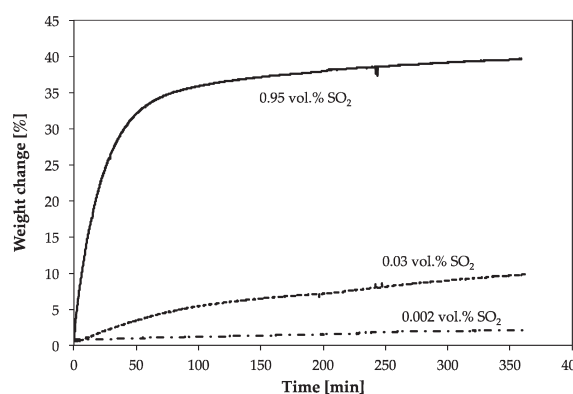

Figure 3. SO_2 uptake for various $[SO_2]$ at 550 °C and 1 atm. Absorption in 0.002 vol. % SO_2 (-··-), 0.03 vol. % SO_2 (----), or 0.95 vol. % SO_2 (—) in 10 vol. % H_2O, balance N_2.

consisting of 15 vol. % CO_2, 10 vol. % H_2O in N_2 followed by a desorption gas consisting of 25 vol. % H_2O in N_2. A total of 15 cycles were conducted at 550 °C, and 23 cycles at 600 °C. The results in Figure 2 show that the ultimate CO_2 capacity during the feed step remains essentially constant at 23.5 wt % (5.4 mmol CO_2/g) during the cycles.

A closer examination of the results reveals a slight capacity decline at both temperatures. If this decay were maintained over additional cycling, the absorbent would lose ~25% of its capacity over 300 cycles but, of course, further experiments would be necessary to confirm this estimate.

Effect of SO_2 on CO_2 Absorption. SO_2 reactivity in the absence of CO_2 was evaluated by exposing the absorbent for 6 h to a gas containing 0.002, 0.03, or 0.95 vol. % SO_2 in N_2 followed by purging with 10 vol. % H_2O in N_2. As shown in Figure 3, SO_2 exposure resulted in a weight increase, even at $[SO_2]$ as low as 0.002 vol. %.

Higher levels of SO_2 in the feed gas yielded faster rates of uptake and higher final weight changes — a total uptake of 40 wt % was obtained for six hours of exposure to 0.95 vol. % SO_2. Purging the SO_2-loaded absorbent samples with 15% H_2O/N_2 at 550 °C resulted in no desorption of SO_2. This indicates that SO_2 reacts irreversibly with the absorbent at these conditions.

Cycling in the Presence of SO_2. For experiments involving SO_2 exposure, the absorbent was first exposed to 10 cycles with 15 vol. % CO_2 and 10 vol.% H_2O in N_2 followed by 25 cycles with
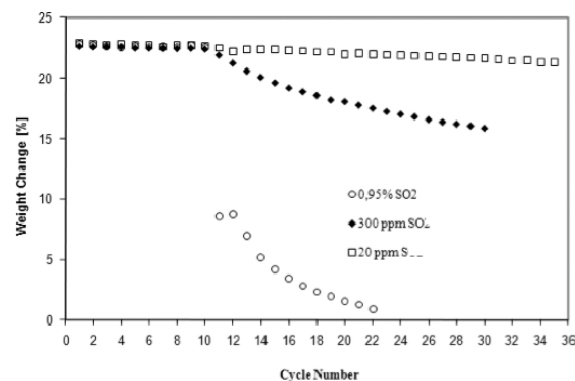

Figure 4. Absorbent weight change over cycles of absorption and desorption at 550 °C and 1 atm. Absorption in 15 vol.% CO_2 and 10 vol.% H_2O in N_2 (1−10 cycles) or in 15 vol.% CO_2, 10 vol.% H_2O and 0.002 vol.% SO_2 in N_2 (□), 0.03 vol.% SO_2 in N_2 (◆) and 0.95 vol.% SO_2 in N_2 (○); desorption in 25 vol.% H_2O in N_2. For the sake of clarity only absorption is shown here.

a gas containing 0.002 vol.%, 0.03 vol.%, or 0.95 vol.% of SO_2. Figure 4 shows the results obtained using 0.002 vol. % SO_2. In the first 10 cycles without SO_2 the absorption capacity remained nearly constant at around 22.7 wt %. In the next 25 cycles (with SO_2 addition) the weight change during absorption and desorption decreased from 22.8 wt % to 21.4 wt %. At higher $[SO_2]$, a more substantial decrease in weight change was observed. For 0.03 vol. % SO_2 exposure, the CO_2 capacity decreased to 16.2 wt % over 20 cycles (SI Figure S3). Similar results for 0.95 vol. % SO_2 exposure (SI Figure S4) — however in this case the weight change after 12 cycles was only 1.4 wt %.

In all these cases, especially those with higher $[SO_2]$, the weight change during the absorption step is higher than the weight change during the desorption step. This can be attributed to the absorption of both SO_2 and CO_2 during the absorption step, and only CO_2 desorption during the desorption step. Once again, SO_2 appears to be irreversibly absorbed by the solid, and its presence negatively impacts the CO_2 capacity. Results obtained using the three different $[SO_2]$ are summarized in Figure 4.

Absorbent Characterization and Mode of SO_2 Reactivity. The above experimental results clearly show that SO_2 reacts readily with the absorbent. It was initially thought that SO_2 reacted with Li_4SiO_4 via chemistry analogous to CO_2 with formation of lithium sulfite, Li_2SO_3, as in reaction 2.

$$Li_4SiO_4 + SO_2(g) = Li_2SO_3 + Li_2SiO_3 \qquad (2)$$

Analysis of the exposed absorbent samples was undertaken to establish elemental and phase composition of the products, and thereby shed light on the reaction chemistry. The results obtained from XRF and XRD are summarized in Table 1. XRD analysis shows that Li_2SO_4 rather than Li_2SO_3 is the SO_2 absorption reaction product. Even for exposure to the lowest $[SO_2]$ (0.002%), sulfur was found on the spent absorbent and the sulfur-containing phases $Li_2SO_4 \cdot H_2O$ and $KLiSO_4$ were identified by XRD.

Exposure to 0.95% SO_2 resulted in higher sulfur loadings and the sulfur containing phases Li_2SO_4, $KLiSO_4$, and K_2SO_4. The absence of Li_4SiO_4 implies that near quantitative reaction with SO_2 had occurred. However, the highest S loading of 12.1 wt % corresponds to 3.79 mmol SO_2/g, somewhat lower than the maximum CO_2 capacity of the absorbent, 5.4 mmol/g.

The CO_2 capacity of the Li_4SiO_4-based absorbent, ~5.4 mmol/g, requires near stoichiometric reaction with the quantity of Li_4SiO_4 present in the absorbent. This means that virtually all of the Li_4SiO_4 in an absorbent pellet is available for contacting with gaseous CO_2. It is therefore not surprising that EDS analysis shows that sulfur has been deposited throughout the absorbent pellets after exposure to SO_2-containing gas mixtures. EDS data for the SO_2 exposed pellets that had been cut to give cross sections is provided in Figure 5.

The expected elements were found (O, Si, K, Ti, S; Li is not detected by EDS). Although there were slight gradients from the outer edge to the center, sulfur was found throughout the pellets, even at the lowest S loading.
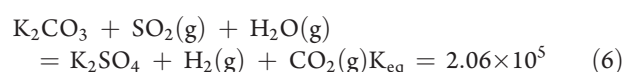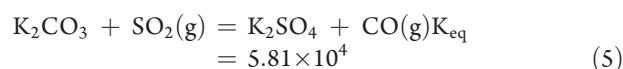
The presence of Li_2SO_4 rather than Li_2SO_3 in the SO_2-exposed absorbent was unexpected. It could perhaps be attributed to oxidation upon exposure to air after removal from the balance.

This was thought to be unlikely because oxidation is expected to be quite slow at room temperature. Alternatively, and more likely, CO_2 and/or H_2O may function as oxidizing agents at 550 °C, as in reactions 3 and 4:

$$Li_2SO_3 + CO_2(g) = Li_2SO_4 + CO(g) \tag{3}$$

$$Li_2SO_3 + H_2O(g) = Li_2SO_4 + H_2(g) \tag{4}$$

Similarly, K_2SO_4 in the spent absorbent following exposure to 0.95 vol. % SO_2 likely results from reaction with K_2CO_3 present in the fresh absorbent and subsequent oxidation via CO_2 and/or H_2O as in reactions 5 and 6. Both reactions are quite favorable at 550 °C based on calculated equilibrium constants (Thermodynamic calculations were performed using ref [29]).

$$K_2CO_3 + SO_2(g) = K_2SO_4 + CO(g) K_{eq} = 5.81 \times 10^4 \tag{5}$$

$$K_2CO_3 + SO_2(g) + H_2O(g) = K_2SO_4 + H_2(g) + CO_2(g) K_{eq} = 2.06 \times 10^5 \tag{6}$$

Since oxidation to Li_2SO_4 in the absence of O_2 apparently occurs in our experiments, its oxidation in the presence of actual flue gas containing ~3% O_2 seems fairly certain. The resulting formation of Li_2SO_4 precludes any reasonable process for regeneration of the SO_2 exposed absorbent. Such material will need to be replaced with fresh absorbent. In practice, the flue gas could be conditioned to reduce the $[SO_2]$ below at least 0.002 vol. % (based on our data) prior to contacting the absorbent. Removal of SO_2 to even lower levels may be necessary to minimize absorbent makeup rates. In this regard, the Li_4SiO_4-based absorbent is no different than any other material that chemically absorbs CO_2. All such materials will have a higher affinity for SO_2 than CO_2, and some desulfurization of flue gas

Table 1. Characterization of the Absorbent Exposed to Various $[SO_2]$

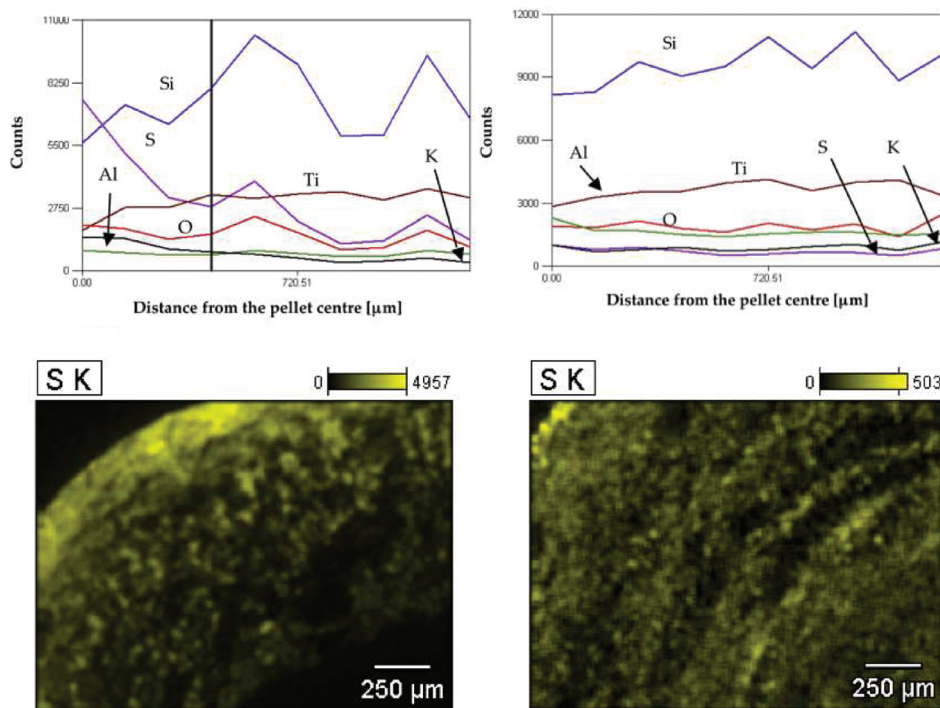| Feed SO_2	S, wt%	
conc.%	by XRF	XRD phases
0	0.0132	Li_4SiO_4, Li_2SiO_3, Li_2TiO_3,
0.002	1.43	Li_4SiO_4, Li_2SiO_3, Li_2TiO_3, K_2CO_3, $Li_2SO_4 \cdot H_2O$, $KLiSO_4$
0.03	4.84	Li_4SiO_4, Li_2SiO_3, Li_2TiO_3, K_2CO_3, $Li_2SO_4 \cdot H_2O$, $KLiSO_4$
0.95	12.15	$Li_2SO_4 \cdot H_2O$, Li_2SO_4, Li_2SiO_3, Li_2TiO_3, $KLiSO_4$, K_2SO_4

Figure 5. Cross-section of a pellet exposed to 0.95 vol.% SO_2 (left) and 0.002 vol.% SO_2 (right). Top: Signal intensity vs distance from outer edge to pellet center. Bottom: sulfur (yellow) map from pellet outer edge on upper left.

prior to contacting the absorbent will be required. This includes liquid based absorbents such as aqueous monoethanolamine, as well as other solid absorbents. For example, solid Na_2CO_3 is often mentioned as a potential absorbent for CO_2 capture from flue gas. However, the calculated $[SO_2]$ required to avoid Na_2SO_3 formation in a typical flue gas is 1.2×10^{-8} vol. % for absorption at 100 °C. If Na_2SO_4 were formed, still lower SO_2 concentrations would be required.

■ ASSOCIATED CONTENT

ⓢ Supporting Information.   Figures S1, S2, S3 and S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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