

A high temperature, lithium orthosilicate based solid absorbent for post combustion CO₂ capture

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ABSTRACT

A lithium orthosilicate (Li₄SiO₄) based solid absorbent supplied by Toshiba Corporation was found to be promising for post combustion CO₂ capture. The absorbent reacts chemically with CO₂ at elevated temperatures and very large capacities can be achieved. The presence of water vapor greatly enhanced CO₂ absorption rates without affecting capacity. Exposure to flue gas containing even low levels of SO₂ resulted in an irreversible reaction with the absorbent and a decrease in CO₂ capacity. Breakthrough experiments indicated capacities as high as 6.7 mmol CO₂/g. The absorbent will likely require a thermal swing process with absorption at 550°C and regeneration at 650°C.

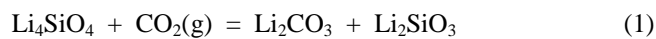
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1 INTRODUCTION

Capture of carbon dioxide from combustion processes presents a unique and challenging technical problem arising from low CO₂ partial pressures, high flow rates, and the presence of water vapor and reactive contaminants such as SO₂. In addition to these technical challenges, the scale of post combustion capture is daunting. A 500 MW coal fired power plant burns enormous quantities of coal, about 2 rail cars/h, and emits over 4 billion kg CO₂ in one year.[1] Based on the Department of Energy's target of 90% capture, 3.6 billion kg CO₂ must be separated each year. The current technology of choice, aqueous monoethanolamine (MEA), can effectively capture CO₂ but regeneration requires substantial heat input, 63-84 kJ/mol CO₂, resulting in plant inefficiencies and higher costs[1] even though recent efforts have achieved some cost and energy reductions.[2] Solid sorbents have been proposed as an alternative to aqueous MEA for post combustion CO₂ and numerous such materials have been evaluated.[3-5] We have identified a lithium orthosilicate (Li₄SiO₄) based absorbent supplied by Toshiba Corporation[6-10] as a promising candidate for post combustion capture.

2 RESULTS AND DISCUSSION

The Li₄SiO₄ based absorbent was provided by Toshiba Corporation as 2 and 5 mm diameter spheres and are referred to as LS 2 mm and LS 5 mm, respectively. X-ray diffraction (XRD) analysis indicated that both contained Li₄SiO₄ as the major phase along with Li₂SiO₃ and Li₂TiO₃. Elemental compositions as determined by x-ray fluorescence (XRF) are listed in Table 1 with the exception of lithium which is not detected by XRF. It is assumed that potassium was present as amorphous K₂CO₃ and, thus, not observed by XRD. Absorption of CO₂ occurs by formation of lithium carbonate and lithium metasilicate as in reaction 1[6-9] with K₂CO₃ functioning as a promoter.[10]



XRD analysis of the absorbent exposed to CO₂ confirmed the expected product, Li₂CO₃, along with Li₂SiO₃ and Li₂TiO₃. The absence of a Li₄SiO₄ phase implies near quantitative reaction with CO₂. Capacities at 650°C and 1 atm CO₂ were 5.51 mmol/g for LS 5 mm and 6.47 mmol/g for LS 2 mm. The heat of absorption for LS 2 mm was 82.0 kJ/mol CO₂ at 650°C as determined by differential scanning calorimetry.

Table 1. Elemental compositions as determined by XRF.

absorbent	concentration, weight %			
	Si	Ti	K	Na
LS 5 mm	33.66	14.28	3.15	-
LS 2 mm	33.77	12.92	4.38	0.491

Utilization of a solid absorbent for post combustion CO₂ capture requires knowledge of CO₂ uptake as a function of temperature. A high operating temperature is preferable so as to maximize absorption rates but lower temperatures favor absorption. An evaluation using a synthetic flue gas containing 15% CO₂ showed that the maximum absorption temperatures for 90% capture were 585°C for LS 5 mm and 571°C for LS 2 mm and 550°C was chosen as the absorption temperature. Thermogravimetric analysis (TGA) was used to determine absorption properties for a

feed gas containing approximately ~15% CO₂ in N₂ at 1 atm total pressure. Although CO₂ was absorbed to its equilibrium capacity, absorption was discouragingly slow at 550°C. Quite surprisingly, however, the use of humidified gas mixtures led to a substantial enhancement of absorption rates. Figure 1 compares CO₂ absorption as a function of time for LS 5 mm exposed to 14.7% CO₂ in N₂, either dry or containing ~2.6% water. The dramatic effect of water vapor is illustrated, for example, by comparing the quantity of CO₂ absorbed after 5 min at 550°C: dry gas, 1.05 mmol/g; humidified gas, 3.67 mmol/g. The enhanced absorption rate in the presence of water vapor does not result from water adsorption as shown by a 0.02 wt% increase upon exposure to humidified N₂ at 550°C.

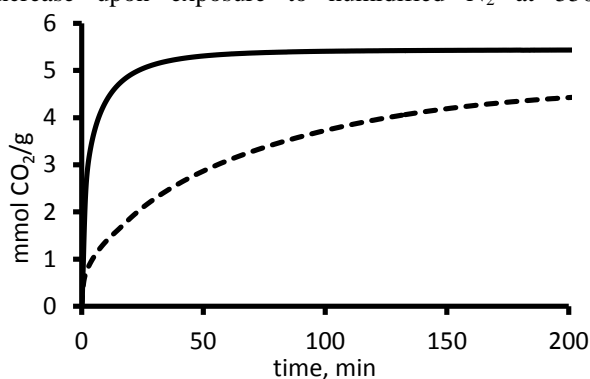


Figure 1. LS 5 mm CO₂ absorption rates at 550°C. Feed: 14.7% CO₂ in N₂, dry (dashed curve) or humidified to ~2.6% H₂O (solid curve).

The cyclic stability of the absorbent was demonstrated by a TGA experiment in which LS 5 mm was repeatedly exposed to humidified 14.7% CO₂ in N₂ for 10 min followed by a 30 min dry N₂ purge. The 1st cycle capacity of 4.12 mmol/g was lower than the equilibrium capacity due to the limited exposure time. A modest capacity decline to 3.81 mmol/g after 5 cycles was obtained but this was followed by a gradual *increase* in capacity and a final capacity of 4.31 mmol/g after 45 cycles. This is unusual compared to other high temperature solid sorbents that typically undergo a decreasing in capacity with cycling. Solid sorbents often undergo a decrease in crush strength with repeated cycling but this was not the case for the Li₄SiO₄-based absorbents. Also unusual was the higher crush strength of 45.1 lb after 50 cycles versus 16.2 lb before cycling.

A major concern for any post combustion sorbent is the effect of flue gas contaminants, particularly SO₂, on its performance.[11-13] The reactivity of SO₂ was investigated utilizing a Rubotherm magnetic suspension balance for which the sample was completely isolated from the instrument electronics permitting the use of reactive or corrosive gases to high pressures and temperatures.[13] Exposure of the LS 5 mm absorbent to 0.002, 0.03 or 0.95 vol.% SO₂ in N₂ for 6 hours at 550°C and 1 atm resulted in the weight changes shown in Figure 2. Exposure to SO₂ concentrations as low as 0.002% resulted in a weight

increase. Higher SO₂ concentrations resulted in faster absorption and a 40 wt% increase was obtained for a 0.95% SO₂ containing gas mixture. Purging the SO₂-loaded absorbent with 15% H₂O/N₂ resulted in no weight change consistent with an irreversible reaction.

The effects of SO₂ on CO₂ absorption were determined by cycling between an SO₂ containing feed gas and an inert purge gas (25% H₂O in N₂), both at 1 atm and 550°C. In each experiment, a baseline cyclic capacity was established using a SO₂-free feed for 10 cycles followed by repeated cycling using a SO₂-containing feed (Figure 3). Both SO₂ and CO₂ were absorbed during the feed step but only CO₂ desorbed under the inert purge. Absorption of SO₂ was irreversible. The weight changes in Figure 3 reflect those arising from CO₂ absorption alone. A feed containing 0.002% SO₂ led to a very modest decrease in the CO₂ capacity from 22.8 to 21.4 wt% over 25 cycles. Much more dramatic changes were observed for higher SO₂ concentrations: 0.03 vol.% SO₂, capacity 16.2 wt% after 20 cycles; 0.95 vol.% SO₂, capacity 1.4 wt% after 12 cycles.

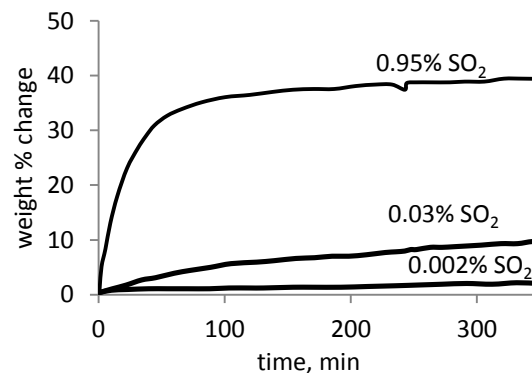


Figure 2. SO₂ uptake for various concentrations of SO₂ in N₂ at 550°C and 1 atm.

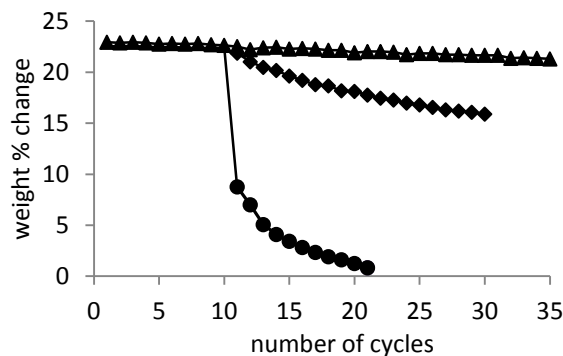


Figure 3. Weight change upon exposure to 15% CO₂, 10% H₂O in N₂, cycles 1-10, followed by 15% CO₂, 10% H₂O, in N₂ containing 0.002% SO₂ (▲), 0.03% SO₂ (◆), or 0.95% SO₂ (●).

XRF analysis of absorbent samples after SO₂ exposure confirmed the presence of sulfur with loadings of 1.43, 4.84, and 12.15 wt% S for the 0.002, 0.03, and 0.95% SO₂ containing feeds, respectively. XRD analysis showed that SO₂ absorption occurred by formation of a sulfate

containing product. For the sample exposed to 0.95% SO₂, Li₂SO₄, KLiSO₄, and K₂SO₄ phases were found along with the inert phases Li₂SiO₃ and Li₂TiO₃. The absence of Li₄SiO₄ implies that near quantitative reaction with SO₂ had occurred. Energy dispersive spectroscopy of the cross-sectioned SO₂ exposed pellets revealed the expected elements: O, Si, K, Ti, S (Li is not detected). Although there were slight gradients from the outer edge to the center, sulfur was found throughout the pellets, even at the lowest loading. This means that virtually all the Li₄SiO₄ was available for contacting with gaseous SO₂.

The formation of Li₂SO₄ as the major product requires the oxidation of SO₂. Excluding oxidation via exposure to air during sample handling, it is reasonable that CO₂ and/or H₂O function as oxidizing agents at 550°C. If oxidation to Li₂SO₄ occurs in the absence of O₂, it will very likely occur in the presence of an actual flue gas containing ~3% O₂. The resulting formation of Li₂SO₄ precludes any reasonable process for regeneration of the SO₂ exposed absorbent. In this regard, the Li₄SiO₄ based absorbent is no different than other materials that chemically absorb CO₂. All such absorbents, including aqueous MEA, will have higher affinities for SO₂ than CO₂ and desulfurization of flue gas prior to contacting the absorbent will be required or spent material will need to be replaced.

Breakthrough capacities were determined using a feed gas consisting of 14.7% CO₂ in N₂, either dry or containing water vapor, generally 10 vol%. Typical feed flows were 40-50 sccm with contact times generally near 4-6 sec. Because of the relatively small vessel diameter, the LS 5 mm spheres were crushed and sieved to 25-35 mesh prior to testing while LS 2 mm was used as intact 2 mm spheres. Figure 4 compares breakthrough curves at 550°C for LS 5 mm obtained with a dry gas feed and one containing 10% water vapor. Capacities at 100% breakthrough were about 4 times greater in the presence of water than in its absence, 4.18 mmol/g versus 0.90 mmol/g, respectively. The LS 2 mm absorbent exhibited larger breakthrough capacities with a similar enhancement of capacity in the presence of water vapor, 4.45 mmol/g for a dry feed and 6.77 mmol/g for a feed containing 10% water. The higher capacities in the presence of water vapor are a consequence of the enhanced CO₂ absorption rates as demonstrated by the TGA results described above. Breakthrough capacities as a function of temperature were evaluated between 350 and 650°C for LS 5 mm and a maximum capacity was achieved near 550°C.

Critical to the successful implementation of any sorbent for CO₂ capture is its regeneration properties. Two modes of regeneration can be considered. One is a pressure swing or, more accurately, a concentration swing process in which regeneration is carried out at the same temperature as sorption by purging with steam to reduce the CO₂ partial pressure above the sorbent. The CO₂ product is subsequently obtained by condensing liquid water. The concentration swing process has the advantage that no heating or cooling is required and cycle times can be short (<hours). The second approach is a temperature swing

process in which the sorbent is heated above the sorption temperature resulting in CO₂ desorption. This can be coupled with a steam purge. A temperature swing process has the disadvantage that the sorbent must be heated and cooled resulting in long cycle times (hours) and, thus, larger vessels and sorbent inventory are required. For both LS 2 mm and LS 5 mm, a temperature swing process with absorption at 550°C and regeneration at 650°C was sufficient to maintain capacity as demonstrated by largely constant capacities over three cycles. A concentration swing regeneration, however, in which the absorbents were purged with 45% H₂O in N₂ at 550°C for 2 h resulted in decreased capacities over three cycles. This implies that regeneration was incomplete and a temperature swing process will likely be required. As shown in Figure 5, desorption at 650°C was fast and much slower at 550°C.

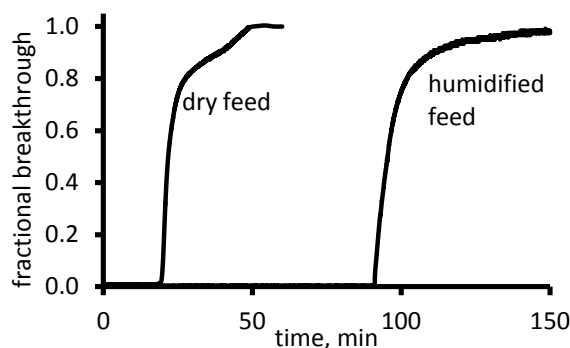


Figure 4. Breakthrough curves for LS 5mm at 500°C. Feed: 14.7% CO₂, dry or humidified to 10% H₂O as indicated.

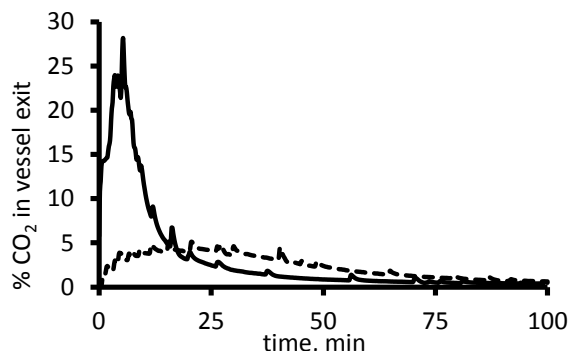


Figure 5. CO₂ concentration (dry basis) in reactor exit for regeneration of LS 2 mm at 550°C (dashed line) and 650°C (solid line); 700 sccm 45% H₂O/N₂ purge gas.

The scale of post combustion capture using the Li₄SiO₄ based absorbent in a fixed bed process was calculated based on the most optimistic assumptions. Considered was a 500 MW coal fired power plant with 90% CO₂ capture corresponding to about 419,000 kg CO₂/h.[1] It was assumed that the equilibrium breakthrough capacity could be achieved and this value was used to calculate the minimum quantity of absorbent required. A temperature swing process was used with a total cycle time of 8 h, 4 h each for absorption and regeneration. A 4.27 m diameter by 6.10 m high vessel was used (volume 87.2 m³) and the

number of vessels needed was taken to be twice that required for absorption. Based on this “best case” analysis, the scale of capture is immense; greater than 200 vessels and 5,600,000 kg of absorbent would be required.

It is clear that a fixed bed process using a sorbent that reacts chemically with CO₂ is unlikely to be practical for post combustion capture. This does not mean that solid sorbents cannot be applied to post combustion capture, rather an alternative to a conventional temperature swing fixed bed process is required. For example, if the Li₄SiO₄ based absorbent could be used with a cycle time of 30 min rather than 8 h, the number of vessels and quantity of absorbent become much more reasonable, 791,000 kg and 14 vessels, based on the same optimistic assumptions. A process that heats and cools vessels and contents rapidly could result in shorter cycle times, thus minimizing absorbent inventory and numbers of vessels. Briefly, three such alternatives are: (1) a “rapid thermal swing chemisorption” (RTSC) process that utilizes shell and tube type vessels to minimize heating and cooling times[14] (2) a moving bed process in which the sorbent is circulated between a sorption vessel and a regeneration vessel[15] and (3) an “adsorbent wheel” in which the sorbent is contained within a rotating wheel or disc that rotated through absorption and desorption zones.[16]

3 EXPERIMENTAL

The Li₄SiO₄ based absorbents were supplied by Toshiba Corporation as 5 mm or 2 mm diameter spheres. For use in breakthrough experiments, the 5 mm spheres were crushed and sieved into 25-35 mesh particles under an inert atmosphere.

Thermogravimetric analysis was performed using a TA Instruments TGA Q5000 instrument contained within a N₂ purge box to minimize exposure to atmospheric water or oxygen. Humidified gases were obtained by passage through a water bubbler at room temperature. Water concentrations were not measured and were assumed to be equal to the water vapor pressure at room temperature, 20 torr or 2.6% at ambient pressure. Heats of absorption were obtained using a TA Instrument 2960 SDT V3.0F. XRF and XRD analysis were performed as described elsewhere.[13] Sulfur dioxide experiments were performed using a Rubotherm magnetic suspension balance at 550°C and 1 atm. Details of the balance and its operation are described elsewhere.[13] In cyclic exposure experiments, the absorbent was first exposed to 10 cycles of absorption and regeneration using an SO₂-free feed gas (15% CO₂/10% H₂O/N₂) for 1 h followed by purging with 25 vol.% H₂O in N₂ for 3 hours. An additional 25 cycles using the above feed containing 0.002 to 0.95% SO₂ were then performed.

Breakthrough experiments were performed using a stainless steel tube measuring 0.37 in internal diameter and 7.25 in long. Following an initial purge with N₂, the absorbent was exposed to 14.7% CO₂ in N₂ generally humidified by passage through a water bubbler at 46°C.

Gases exiting the absorbent vessel were passed through a chilled trap to condense water vapor prior to analysis using a Horiba CO₂ analyzer. Breakthrough capacities were obtained by mass balance as the difference between the total quantity of CO₂ in the inlet and effluent gas. Regeneration was performed by purging with ~45% H₂O/55% N₂ stream.

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