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Development of sodium / lithium / fly ash sorbents for high temperature post-combustion CO₂ capture

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Abstract: CO₂ capture from combustion processes faces several challenges including high energy penalty, low CO₂ partial pressure, high flow rates and presence of water vapours. Absorption of CO₂ at high temperature is recently attracting increasingly attention. Alkali metal based sorbents present clear advantages compared to other high temperature sorbents, such as high CO₂ capture capacity, lower regeneration temperatures (< 750 °C) and excellent stability. In this work, Na/Li-silicates prepared by mixing Na/Li carbonates with fly ash (FA) in various molar ratios were evaluated for their capacity to chemisorb CO₂ at 500-700°C and in presence of H₂O (2-12vol%), diluted CO₂ (14vol%) and CO₂ sorption promoters.

The results indicate that the carbonate:silica ratio used in the sorbents synthesis significantly affects the CO₂ sorption capacity and regeneration temperature. The presence of steam enhances the diffusion of Li and Na ions resulting in higher CO₂ uptake. CO₂ chemisorption follows a double layer mechanism with formation of carbonate layer on the surface. The simultaneous presence of Li and Na (and K when used as additive) in the formed carbonate layer results in an eutectic melt between 600 and 700°C, which facilitates the diffusion of the ionic species. Li-Na-FA with molar ratio of 0.5:0.5:1 was the best prepared sorbent with a capacity of 2.54 molesCO₂/kg sorbent (12%H₂O, 14%CO₂ at 700°C). Absorption/desorption was completed in 15 minutes with reaction kinetics comparable to that of pure Li₄SiO₄ sorbents. The tested materials maintained their capacity and absorption/desorption rates after 10 cycles at 700°C. Overall, the Na/Li materials showed a CO₂ capture capacity, stability over time and sorption/desorption kinetics comparable to those of other high-temperature sorbents, such as Li-FA (Li₄SiO₄ prepared using fly ash), and higher stability than CaO and hydrotalcites.

Keywords: Absorption • fly ash • CO₂ sorbents• alkali metal silicates

1. Introduction

It is widely recognised that increasing anthropogenic CO₂ emissions are contributing to global warming and carbon dioxide capture and storage (CCS) technologies have been proposed as mitigation option [1]. Absorption processes have been developed to separate CO₂ from flue gas stream post combustion systems. However, using absorption is challenging for several reasons, such as solvent degradation, materials corrosion and large costs [1]. Solid sorbents have been proposed as alternative to the more developed liquid absorption systems. To be competitive to a large scale liquid amine process, solid sorbents should have high CO₂ capacity (≥ 2 mol CO₂/ kg sorbent) and selectivity, fast sorption/desorption kinetics, good mechanical properties, high stability and low costs of synthesis [2, 3]. So far, most of the work on the development of CO₂ sorbents has been focused on materials able to adsorb CO₂ at low temperature (up to 100°C). The materials tested include zeolites, MOFs, SBA-15, MCM-41, carbon based adsorbents, Na and K carbonates and amine doped materials [2-6]. The use of recyclable sorbents at high temperatures, which can be used in both pre- and post-combustion CO₂ capture systems are recently attracting increasing attention due to absence of
significant energy penalty associated to low temperature capture systems. With post-combustion capture, the flue gas is ideally available from the coal-fired boiler temperature (<1100°C) to that of the stack gas (about 50°C) and thus, a wide range of separation temperatures can be considered [7]. Also, industrial plants such as cement and steel works generate flue gas at temperatures higher than 900°C [8, 9]. Therefore, the development of efficient CO₂ sorbents able to work at high temperatures would help to reduce the associated CO₂ capture energy penalty, since CO₂ sorption thermodynamics and rapid sorption kinetics are favoured at high temperature [8,10]. Among solid sorbents, CaO-based sorbents are especially advantageous because of their high sorption capacity and rapid kinetics in the 400-800°C temperature range and have been tested in pilot scale (1.9MWth) [11]. However, despite the abundance and low cost of CaO, its performance is challenged by a rapid loss of activity during the capture cycles due to sintering, attrition and elutriation [12, 13]. Alkaline ceramics, mainly lithium containing compounds have recently been used as high temperature CO₂ sorbents [14-17]. These ceramics materials present the advantages of having high CO₂ capture capacity, high stability over time, adequate sorption-desorption kinetics and lower regeneration temperatures (<750 °C) compared to other high-temperature sorbents, such as CaO [18]. Typically, alkaline ceramics present a double-step sorption mechanism, with an initial chemical sorption of CO₂ over the ceramic surface, which forms a carbonate shell, followed by the CO₂ diffusing through the carbonate external layer to reach the surface and further react with the alkaline element [14]. Not many materials have been investigated so far at high temperatures, where the most notable are hydrotalcite-like materials, MgO precursors (dolomite, magnesite) and ceramics [9]. Amongst the materials tested, pure lithium silicate (Li₂SiO₄) has shown the largest CO₂ sorption capacity and the fastest CO₂ sorption rate over a wide range of temperatures and CO₂ concentrations [17-19]. The CO₂ sorption by Li₂SiO₄ has been associated to the reversible reaction of lithium oxide (Li₂O) in the Li₂SiO₄ crystal lattice with CO₂ leading to the formation of lithium carbonate (Li₂CO₃) and lithium metasilicate (Li₂SiO₃) [18]:

Li₂SiO₄(s) + CO₂(g) ↔ Li₂CO₃(s or l) + Li₂SiO₃(s) (1)

Additives such as K₂CO₃ can enhance the CO₂ uptake of activated carbons, zeolites and alumina based CO₂ sorbents reaching capacities of 51.9 mg/g sorbent [20]. It has also been reported that the presence of carbonates (e.g. K₂CO₃) and high temperatures affect the CO₂ sorption capacity for the pure Li-based sorbents [17,18, 21]. The use of waste materials such as fly ash as precursors of CO₂ sorbents is also a very promising area of research, since they are low-cost and widely available [17,22]. Olivares-
Marín and co-workers compared the CO$_2$ sorption capacity of pure lithium silicate and Li-silicate prepared from fly ash in presence of pure CO$_2$. Maximum sorption capacity after 1 hour for the pure Li$_4$SiO$_4$ was obtained at 600°C in presence of 10% and 20% K$_2$CO$_3$ with 244 and 272 mg CO$_2$/g sorbent, respectively [17]. For the fly-ash derived Li$_4$SiO$_4$, the CO$_2$ sorption capacity was of 107 mg CO$_2$/g sorbent in the presence of 40 mol% K$_2$CO$_3$ at 600°C, with the sorbents maintaining their original capacity over 10 cycles [17]. Diatomite has also been used as source of SiO$_2$ to prepare Li$_4$SiO$_4$ sorbents, which were tested at high temperature (700°C) in presence of 50% CO$_2$ gas [23]. However, the absorption capacity decreased with increasing cycle number [23].

Despite the very good performance of Li-silicates materials, it should be noted that the lithium carbonate used to produce the Li-silicate is expensive, toxic and rare [24]. Global production of lithium containing minerals was about 37,000 tonnes of contained lithium metal in 2012 [24]. Lithium silicate as such is not mined and is typically synthesised following the reactions presented below [25]:

\[ 2\text{Li}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Li}_4\text{SiO}_4 + \text{CO}_2 \]  
\[ \text{SiO}_2 + 4\text{LiOH} \rightarrow \text{Li}_4\text{SiO}_4 + 2\text{H}_2\text{O} \]

Lithium's geological resource data shows that there is insufficient lithium available on Earth to sustain current and future uses such as electric cars batteries [26]. The current high demand of Li and its low production results in very high costs of commercial Li$_2$CO$_3$ ($4000$-$5000$/t) [24]. Instead, sodium carbonate with a production of 51 Mt/y is much more abundant than lithium carbonate, presents a much lower cost ($150$-$200$/t) and very low toxicity [27]. Therefore, the production of binary Na-Li-sorbents would decrease associated costs.

Some studies have indicated that alkaline solid mixtures such as lithium-sodium zirconate, lithium-potassium zirconate and Li-Na ortho-silicate present better CO$_2$ sorption than pure lithium or sodium zirconate [28]. The latter work showed that the solubility limit of sodium into Li$_4$SiO$_4$ is 0.025% (Li$_3.9$Na$_{0.1}$SiO$_4$) and that addition of Na larger than 0.025% produces secondary silicate phase [28]. Therefore, the potential development of high temperature CO$_2$ sorbents from Li and Na solid solutions merits further investigation.

Moreover, thermodynamic calculations indicated that Li$_2$SiO$_3$, Li$_2$Si$_2$O$_5$ and Li$_2$Si$_2$O$_7$ require less free energy to reverse the CO$_2$ capture reactions and have lower regenerating temperatures, compared to the more studied Li$_2$O, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ [29]. Limited works on high temperature Li-Na silicate sorbents have been produced, where a high Li/Na:silica ratio (4:1) was used for the binary sorbents [28].
Accordingly, the aim of this work is to study the behaviour of high temperature mixed mineral phases Li/Na sorbents based on low cost and widely available fly ash as source of SiO₂ and Li/Na silicates in presence of diluted CO₂ in flue gas. Moreover, the effect of steam on high temperature Li-Na-FA sorption properties is also investigated. Finally, K₂CO₃ is evaluated as CO₂ sorption promoter.

2. Experimental Section

Fly ash (FA) has been used as SiO₂ source and collected from a cyclone filter. FA particles size distribution (obtained by a laser diffraction particle size analyser, Malvern Masterizer) was the following: D(0.5) 42 μm, D(0.8) 110 μm, D(0.98) 237 μm. XRF analysis were conducted using a PANalytical Axios-Advanced XRF spectrometer. Firstly, approximately 1 g of parent waste material was ground using agate mortar and pestle to fine powder. The fine powder was then ignited at 1100°C and the subsequent ignited powder was mixed with lithium metaborate and lithium tetraborate flux. The mixture was fused at the same temperature in the furnace which was then used in the XRF spectrometer to determine their quantitative elemental composition in the form of oxides. In this work, the CO₂ sorbents were prepared by solid state synthesis. Li/Na- silicates were prepared from a fly ash (FA) sample by mixing Li₂CO₃ and Na₂CO₃ (Acros Organics) at different molar ratio of Li₂CO₃:Na₂CO₃:SiO₂ by using an agate mortar and pestle. The mixed powder was calcined in ceramic crucibles in a muffle furnace at 800°C for 8 hours. Some of the sorbents were calcined at 600 or 900°C for 8 and 4 hr, respectively. This method was used because compared to other synthesis methods (e.g. spray drying and reflux) produces a single and highly crystalline orthosilicate phase, minimising the metasilicate phase (Li₂SiO₃) [25]. The nucleation of lithium orthosilicate occurs at temperature between 425 °C and 465 °C [25]. After calcination, the materials were homogenised using a Mortar Grinder (Pulverisette 2, Fritsch) for 1 minute to eliminate any potential agglomeration. Li₄SiO₄ was used as comparison with previous work [17]. K₂CO₃ (Acros Organics) was evaluated as additive. The resulting sorbents were grinded and characterized by different techniques, including Brunauer-Emmett-Teller (BET), powder X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and Fourier Transformed Infrared (FTIR). A Micromeritics Gemini (vii) was used to analyse the material surface and pore size distribution. A Bruker Nonius X8-Apex2 CCD diffractometer equipped with an Oxford Cryosystems Cryostream, typically operating at 100 K was used for the XRD analysis. To determine the volume fraction of the compounds
detected by XRD (Bruker AXS P4 4-circle), it was considered the integral intensity corresponding to the different identified mineral phases (in each sample) and assumed that this is proportional to the volume fraction in the sample. A PerkinElmer Frontier infrared spectrometer was used to gain additional information on the crystal structure of the synthetised sorbents before and after the CO₂ absorption experiments.

The CO₂ capture capacity of the resultant samples was measured by using a TGA (TA Q500) in a controlled gas flowing environment. About 20 mg of samples was loaded in the TGA pan for each experiment. Prior to CO₂ sorption testing, the samples were dried in N₂ flow (95 mL/min) at 25 °C/min for 30 or 60 min at the same temperature used for the CO₂ sorption (e.g. 500,600,700°C). The flowing gas was then changed to CO₂ (100% CO₂) to allow reaction and determine CO₂ absorption capacity. In addition, considering potential applications in which CO₂ is removed from coal power plants, the targeted diluted CO₂ concentrations in this test was also set to 14 vol% (balance with N₂). The weight increase due to CO₂ sorption (mg CO₂/g sorbent) was measured as a function of time at a constant temperature (500, 600, 645, 700 °C) and constant concentration of CO₂ or flue gas (95 mL/min) at atmospheric pressure. CO₂ uptake was calculated based on dry sorbents weight (after drying step). Also, the sorbents were evaluated in presence of humidified flue gas by passing pure CO₂ through a Dreschel bottle filled with distilled water placed on a hot stirrer plate (IKA C-MAG HS7) to control the temperature. The tube connecting the Dreschel bottle to the TGA was also heated at 20 or 50°C using a heating tape. Water concentration was calculated to be 2 vol% or 12 vol% (vapour pressure of H₂O at 20°C = 0.02 atm; 50°C = 0.12 atm). These values were chosen to represent humid flue gas from a coal power plant. To establish if water was absorbed by the silicate sorbent, the steam was delivered from the starting of the experiment during the initial desorption step, at the same temperature (of the following CO₂ uptake step) but in nitrogen atmosphere. K₂CO₃ (20 mol% or 30 mol%) (Acros Organics) was evaluated as CO₂ sorption promoter [17].

Triplicate measurements were conducted to estimate the % error in the experimental work. The differences in the measured values represent the repeatability error (random). A series of three absorption experiments were done on selected sorbents and repeating averages are reported. The measurements error (calculated as the SD of triplicates) resulted lower than 5%.
In order to quantify the rates of reaction at 600 and 700°C, the TGA isotherms were fitted with a double exponential model \( y = A \exp^{-k_1x} + B \exp^{-k_2x} + c \) \[17\]. Finally, ten regeneration cycles were used to ascertain the initial sorbents stability for selected sorbents.

3. Results and Discussion

3.1 XRF, BET and XRD analyses

Table 1 shows the FA chemical composition, where silica and alumina are the most abundant oxides.

Table 1. Loss on ignition (LOI) and chemical composition of starting fly ash.

<table>
<thead>
<tr>
<th></th>
<th>wt %</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.813</td>
<td>V₂O₅</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.957</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.051</td>
<td>SrO</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.128</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>MnO</td>
<td>0.124</td>
<td>BaO</td>
</tr>
<tr>
<td>MgO</td>
<td>2.138</td>
<td>NiO</td>
</tr>
<tr>
<td>CaO</td>
<td>4.897</td>
<td>CuO</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.842</td>
<td>ZnO</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.267</td>
<td>PbO</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.914</td>
<td>HfO₂</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.567</td>
<td>LOI</td>
</tr>
</tbody>
</table>

The BET surface area of Li-Na-FA was 0.83 m²/g, with median pore width (Horvath-Kawazoe equation) of 14.49 Å. Figure 1 and Table 2 show the XRD patterns of Li-Na silicates synthesised at 800°C for 8 hours using different molar ratio of Li₂CO₃, Na₂CO₃ and FA. Quartz, Na₂CO₃ and Li₂CO₃ patterns were not detected indicating that solid state reactions were completed. As expected, the synthesised sorbents present a mixture of numerous different crystalline silicate phases, with different distribution depending on the molar ratio used. All the synthesised sorbents present a mixture of silicate phases indicating that calcination at 800°C did not generate a pure ortho-silicate phase (Li₅Na₅Si₅O₁₄). Di-silicate (Si₂O₅), meta-silicate (SiO₃) and piro-silicate (Si₂O₇) phases were the most abundant for the Li-Na-FA 0.5:0.5:1 sorbent and their abundance decreased according to the increase of the Li/Na:FA molar ratio. At Li/Na:FA molar ratio of 1.5:1, the ortho-silicate species became predominant. The most abundant species were Na₂Si₂O₆ (19 %), (Na₂SiO₃) (18 %) and Na₄SiO₄ in presence of a 0.5:0.5:1 Li₂CO₃:Na₂CO₃:SiO₂ molar ratio.
Figure 1. XRD of Li/Na-FA sorbents. a) 1:1:1; b) 0.5:1:1; c) 0.5:0.5:1 Li$_2$CO$_3$:Na$_2$CO$_3$:SiO$_2$ molar ratios. 1-Li$_4$SiO$_4$, 2-Na$_2$Si$_2$O$_5$, 3-Li$_6$O$_2$(SiO$_4$); 4-Li$_2$Si$_2$O$_5$; 5-Na$_2$SiO$_3$; 6-Li$_3$NaSiO$_4$; 7-NaAlO$_2$; 8-Li$_6$Si$_2$O$_7$; 9-NaAlO$_2$, 10- Li/NaSiO$_4$; 11-NaAlSiO$_4$.

The sorbent prepared with a 0.5:1:1 molar ratio was particularly abundant in meta-silicate species (Na$_2$SiO$_3$, Li$_2$SiO$_3$). Also, alumina-silicates such as NaAlSiO$_4$ and aluminates...
(NaAlO$_2$ and Na$_7$Al$_3$O$_8$) were detected as expected from the fly ash composition (Table 1). Presence of Li$_2$Si$_2$O$_5$ phase can be attributed to the insufficient reaction between the lithium compound and silicon compound [30]. Presence of SiO$_3^{2-}$ and Si$_2$O$_5^{2-}$ can be an advantage for CO$_2$ sorption, since require less free energy to reverse the CO$_2$ capture reactions [29].

**Table 2.** XRD of Li-Na-FA CO$_2$ sorbents generated at 800°C.

<table>
<thead>
<tr>
<th>% intensity count</th>
<th>Li-Na-FA 0.5:0:5:1</th>
<th>Li-Na-FA 0.5:1:1</th>
<th>Li-Na-Fa 1:1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$Na$_2$Si$_2$O$_5$</td>
<td>17.4</td>
<td>11.7</td>
<td>33.4</td>
</tr>
<tr>
<td>Li$_2$Na$_2$Si$_2$O$_3$</td>
<td>6.9</td>
<td>23.5</td>
<td>19.9</td>
</tr>
<tr>
<td>Li$_2$Na$_3$Si$_2$O$_7$</td>
<td>6.0</td>
<td>8.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Li$_2$Na$_2$Si$_2$O$_4$</td>
<td>14.0</td>
<td>43.0</td>
<td>15.9</td>
</tr>
<tr>
<td>NaAlSiO$_4$</td>
<td>6.0</td>
<td>8.8</td>
<td>11.5</td>
</tr>
</tbody>
</table>

**3.2 FTIR analysis**

Information on the mineral phases formed during calcination was obtained by FTIR. Figure 2 shows the FTIR spectra of the synthesized Li-Na-FA sorbents. The bands observed at 1,038 and 965 cm$^{-1}$ are assigned to the Si-O-Si asymmetric stretching vibration. Also, the symmetric stretching vibration mode of Si-O-Si is observed at 749 cm$^{-1}$ [31]. The crystalline lithium ortho-silicate is built up of an isolated SiO$_4$ tetrahedron connected to LiO-polyhedra. The band in the range of 1,400–1,500 cm$^{-1}$ is linked to Li$_2$CO$_3$ and Na$_2$CO$_3$ present in the material [25]. The isolated SiO$_4$ tetrahedra presents a strong absorption band around 900 cm$^{-1}$ caused by the Si-O asymmetric stretching vibration, while the absorption band near 800 cm$^{-1}$ is due to the Si-O holo-symmetric one [32]. The vibration due to the SiO$_4$ structure is a triply degenerative splitting in three vibrations in the case of the Li$_4$SiO$_4$ structure [25]. Bands at 1,080, 740 and 847 cm$^{-1}$ are attributed to the SiO bond stretching in the silica tetrahedra, while the bands at 600 and 580 cm$^{-1}$ are related to the bending vibrations [25, 33].

The sorbent prepared with a Li$_2$CO$_3$:Na$_2$CO$_3$:SiO$_2$ ratio of 1:1:1 (b) and 0.5:1:1 (e) clearly present both Li$_4$SiO$_4$ and Na$_2$SiO$_3$ phases as the peak at 1,400 cm$^{-1}$ and peaks in the range 800-1,000 cm$^{-1}$ indicate. Instead, when the ratio Na$_2$CO$_3$:SiO$_2$ was 0.5 or lower, no free Na$_2$SiO$_3$ phase has been detected. This indicates that the Na has been incorporated in the Li$_4$SiO$_4$ lattice generating a Li$_3$Na$_8$SiO$_4$ material.

Previous work found that a maximum of 0.1 Na is soluble into solid Li$_4$SiO$_4$ ratio forming Li$_{3.9}$Na$_{0.1}$SiO$_4$ [28]. However, the absence of the peak at 1,427 cm$^{-1}$ and presence of Na-O peak at 897 cm$^{-1}$ in Figure 2 (b,d,e) suggests that a higher amount of Na can be incorporated.
into the lithium silicate by calcination at 800°C for 8 hours. Overall, FTIR analyses confirmed the XRD results indicating that a mixture of different silicate phases (meta-, pyro-
 etc) is produced by calcination at 800°C.

**Figure 2.** FTIR spectra of Li-Na-FA samples prepared by solid-state reactions at 800°C for 8 hr. a) Li$_4$SiO$_4$ (STD); b) Li-Na-FA (1:1:1); c) Li-Na-FA (0.5:0.12:1); d) Li-Na-FA (0.5:0.5:1); e) Li-Na-FA (0.5:1:1); f) Na$_2$SiO$_3$(STD).

### 3.3 CO$_2$ capture studies

A summary of the chemisorption experiments carried out using the synthetised sorbents is shown in Table 3. Temperature, Li-Na-FA molar ratio and additives were initially selected to compare the adsorbed CO$_2$ to the Li-FA materials studied by Marin et al [17]. As can be seen from Table 3, the Li-Na-FA CO$_2$ sorption capacity without additives in presence of 100% CO$_2$ at 600°C was higher compared to that of Li-FA used in previous work under the same conditions and in presence of 10% K$_2$CO$_3$ [17]. Li-Na-FA sorbent in presence of 14% CO$_2$ performed as Li-FA + 20% K$_2$CO$_3$ at 600°C in 100% CO$_2$. 
Table 3. CO₂ sorption experiments using Li/Na-FA sorbents in comparison to Li-FA sorbents previously developed [17]. Experiments carried out using 100% CO₂. * 14% CO₂ was used for this test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp., °C</th>
<th>Additive (mol%)</th>
<th>1 h</th>
<th>2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Li₂SiO₄ [17]</td>
<td>650</td>
<td>10% K₂CO₃</td>
<td>272</td>
<td>na</td>
</tr>
<tr>
<td>Li-FA 2:1 [17]</td>
<td>500</td>
<td>&lt;5</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Li-FA 2:1 [17]</td>
<td>600</td>
<td>10% K₂CO₃</td>
<td>26</td>
<td>na</td>
</tr>
<tr>
<td>Li-FA 2:1 [17]</td>
<td>600</td>
<td>20% K₂CO₃</td>
<td>56</td>
<td>na</td>
</tr>
<tr>
<td>Li-FA 2:1 [17]</td>
<td>600</td>
<td>40% K₂CO₃</td>
<td>107</td>
<td>na</td>
</tr>
<tr>
<td>Li-FA 2:1 [17]</td>
<td>650</td>
<td>10% K₂CO₃</td>
<td>21</td>
<td>na</td>
</tr>
<tr>
<td>Li-Na-FA 1:1:1 (this work)*</td>
<td>600</td>
<td>30% K₂CO₃</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>Li-Na-FA 1:1:1 (this work)</td>
<td>600</td>
<td>30% K₂CO₃</td>
<td>38</td>
<td>44</td>
</tr>
</tbody>
</table>

na: not available

The superior CO₂ capacities observed compared to previous work on the development of lithium based silicates from fly ash suggests that mixtures of Li and Na silicates could be applied to high temperature CO₂ capture processes. The experiments performed to establish the best conditions and mixtures to be used to maximise the CO₂ sorption capacity and absorption/desorption rate are discussed in detail in the following subsections.

3.3.1 Effect of molar ratio

Different Li/Na-FA sorbents have been evaluated for their capacity to chemisorb CO₂ at temperatures applicable to post-combustion technologies (e.g. industrial CO₂ emitters; coal power plants). The effect of the different Li-Na-FA molar ratios on CO₂ sorption and desorption at 700°C is presented in Figure 3. Li-Na-FA sorbent had its highest CO₂ uptake at molar ratio 0.5:1:1 (162 mg CO₂ / g sorbent or 16.2%). However, CO₂ desorption at this molar ratio rapidly decreased after desorbing about half of the adsorbed gas and then slowed down desorbing only 135 mg CO₂ after 1.6 hr.

Absorption/desorption was very fast when Li-Na-FA ratios of 0.5:0.5:1 and 1:1:1 were used, requiring about 10 minutes each. The maximum uptake was of 113 and 106.4 mg CO₂ / g sorbent for the Li-Na-FA sorbents with ratio 1:1:1 and 0.5:0.5:1, respectively. The higher CO₂ uptake for the Li-Na-based sorbents can be associated to alkali/Li carbonate eutectic melt formed during the CO₂ sorption [18,34]. The diffusion of CO₂ through the molten carbonate shell is much faster, compared to that through the solid Li/Na₂CO₃ shell in pure
Li$_4$SiO$_4$ or pure Na$_2$CO$_3$ [18]. Despite the fact that Li$_2$CO$_3$ and Na$_2$CO$_3$ have melting points higher than 700°C, the mix of the salts has melting point lower than 700°C [35].

**Figure 3.** Effect of different molar ratio on CO$_2$ sorption/desorption at 700°C. (a) Li-Na-FA 0.5:1:1; (b) Li-Na-FA 0.5:0.5:1; (c) Li-Na-FA 1:1:1.

Moreover, the higher performance in terms of CO$_2$ desorption of the Li/Na sorbents with low Na/Li:FA ratio (richer in species such as Li$_2$SiO$_3$ and Li$_2$SiO$_5$) compared to those with high Na/Li:FA ratio (richer in Li$_4$SiO$_4$) may also be related to the fact that the reverse reaction to release CO$_2$ from Li$_2$SiO$_3$ and Li$_2$SiO$_5$ requires less free energy than Li$_4$SiO$_4$ [29,36].

### 3.3.2 Effect of Temperature

CO$_2$ absorption isothermal experiments were carried out at 500, 600, 645 and 700°C (Figure 4) to evaluate the effect of temperature on CO$_2$ uptake and a summary is presented in Table 3. Sorption and desorption rates for Li/Na-FA were very fast requiring about 10 min for adsorbing 80% of the maximum CO$_2$ uptake and less than 10 min for the complete CO$_2$ desorption. In contrast, the Na-FA sorbents required longer reaction time under the same
temperatures. Another important feature observed in Figure 4 is that the rate of desorption drastically increases with temperature and that a temperature higher than 500°C must be used for CO₂ desorption to occur. Moderate and slow CO₂ sorption at 500 °C can be mainly attributed to alkali metals/CO₂ diffusion limitations, as discussed in the following section (3.3.3). Moreover, higher CO₂ capacity with increasing temperature can be explained by the thermal activation of the Na/Li diffusion in the bulk lattice [37]. Mejía-Trejo et al. investigated the chemisorption of CO₂ on pure Li₃₋ₓNaₓSiO₄ obtained by precipitation [28]. They found that a maximum uptake of CO₂ of 10.9 and 11.2 wt% on Li₃.83Na₀.15SiO₄ after 1 and 2 hr, respectively, and a much lower CO₂ uptake for the pure Li₄SiO₄ (3; 4.5 wt%) [28]. The CO₂ uptake increase at temperatures higher than 600°C can be related to a change in the mineral phases and formation of molten carbonates phase [7].

Figure 4. TGA profile of CO₂ sorption/desorption of Li-Na-FA 0.5:0.5:1 at different temperatures: (a) 700°C; (b) 645°C and (c) 500°C.

3.3.3 Effect of diluted CO₂ and moisture on sorption/desorption
Despite the fact that the performance of most sorbents decreases in the presence of water, previous work indicates that water vapour in the temperature range 30-60 °C improves CO₂ chemisorption for Na-silicate sorbents [33]. A moisture content of 80% was reported to result in 34 wt% CO₂ sorption after 2 hr at 50°C. However, CO₂ sorption drastically decreases to 2-3 wt% with relative humidity at 20% [33]. Therefore, a series of experiments with pure CO₂
and flue gas in the presence of different amount of water vapour (2 vol% and 12 vol%) were carried out to evaluate the effect of steam on high temperature post-combustion CO₂ sorption for the developed Li/Na-FA sorbents.

Figure 5 shows the CO₂ sorption-desorption profiles of Li-Na-FA 1:1:1 sorbents at 700°C under pure CO₂ in presence of 2% H₂O and 14% CO₂ balanced with N₂ with and without 12% water. The absence of weight increase in the initial desorption step in N₂ atmosphere and in presence of H₂O indicates that these materials do not absorb water under the studied conditions. CO₂ uptake was found to be the highest in presence of 100% CO₂ and 2% H₂O, with capacity values of 11.2 wt% (112 mg CO₂/g sorbent or 2.72 moles CO₂/kg sorbent). The CO₂ uptake did not change in presence of 2% H₂O compared to the test carried out in absence of water (Figures 3 and 5). Sorption was reduced to 7.9 wt% (1.81 mol CO₂/kg sorbent), which represents a reduction of 28%, in presence of 14%CO₂ gas stream. The addition of 12% moisture resulted in a similar CO₂ uptake with 7.7 wt% (1.75 mol CO₂/kg sorbent).

Previous works indicate that presence of more than 20% steam accelerates the sorption kinetics by increasing the mobility of Li⁺, Na⁺, which tend to segregate to the surface due to their low surface free energy [38]. Formation of hydroxyl species at the materials surface in presence of moisture also has been associated to enhanced CO₂ sorption, as illustrated in equation (4) [37]. However, this mechanism is unlikely at the employed temperatures, since dehydroxylation occurs at much lower temperature (250-450°C).

\[
\text{Li/Na}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow \text{Li/Na}_2\text{SiO}_3 \text{ superficially hydroxylated} \quad 2\text{CO}_2 \rightarrow \text{Li/NaHCO}_3 + \text{SiO}_2 \quad (4)
\]
The sorption capacities of the three materials were comparable to those reported using microporous carbon materials discrete chelating zinc species (2.4 mol/kg) in presence of 16% CO$_2$ [6]. This also indicates that 12% moisture fraction does not affect the Li-Na-FA 1:1:1 sorption properties. Both sorption and desorption were completed in less than 10 minutes under all the three conditions. The rapid sorption/desorption rates are desirable considering the large flue gas volumes emitted in industrial and power plants.

The decrease in CO$_2$ uptake in presence of 14 vol% CO$_2$ at 700 °C can be attributed to low CO$_2$ partial pressure [21]. To enhance the sorption capacity in the presence of flue gas and moisture, Li-Na-FA sorbents with molar ratio of 0.5:0.5:1 and addition of CO$_2$ sorption promoters were tested. Figure 6 shows the CO$_2$ sorption/desorption cycle of Li-Na-FA 0.5:0.5:1 under different conditions. Similarly to Li-Na-FA 1:1:1 (Figure 5), the Li-Na-FA 0.5:0.5:1 sorbents performed better in presence of pure CO$_2$ (2.43 mol CO$_2$/kg sorbent) than in presence of diluted CO$_2$ and 12% H$_2$O (1.36 mol CO$_2$/kg sorbent). Also, as for Li-Na-FA 1:1:1, the presence of 12% H$_2$O did not affect the CO$_2$ uptake capacity of Li-Na-FA 0.5:0.5:1. Therefore, a fraction of steam of 12% is not able to enhance the mobility of the alkali cations, which has been related to the enhanced CO$_2$ uptake in presence of large fraction of steam. This is in agreement with previous works, which indicate that improved CO$_2$ uptake take place only in presence of more than 20% steam [33,38].

The loading capacity was improved by adding CO$_2$ capture promoters to the silicate sorbent. The CO$_2$ sorption difference between Li/Na sorbent in presence of 100% and 14% CO$_2$ was completely eliminated by adding 20% K$_2$CO$_3$, which resulted in absorbing 2.54 mol CO$_2$/kg sorbent, compared to 1.36 mol CO$_2$/kg sorbent without K$_2$CO$_3$. The difference between the K$_2$CO$_3$ promoted and not promoted sorbent can be attributed to the eutectic carbonate mixture formed in presence of K$_2$CO$_3$, which further enhances CO$_2$ diffusion in the carbonated layer [39]. The slope of the CO$_2$ uptake profile presented in Figure 6 also indicates the sorption/desorption rates for the Li/Na-FA sorbents. Although complete sorption requires 2 hr in presence of pure CO$_2$, it should be noted that 85% of the total uptake can be completed within 30 minutes. Desorption is instead completed in 25 minutes under pure CO$_2$. Presence of 2% moisture shorten the time to reach the same CO$_2$ loading (88% of the total loading is obtained in 30 min), but complete CO$_2$ desorption requires 37 minutes.

In order to quantify the rates of reaction between 500 and 700°C and in presence of moisture (12%), diluted CO$_2$ (14%) and 20% K$_2$CO$_3$ additive, the CO$_2$ uptake profiles from TGA of the Li/Na-FA 0.5:0.5:0.5 sorbents were fitted to a double exponential model (y=A exp$^{-k_1x}$ + B exp$^{-k_2x}$ + c) widely used in sorption studies [17,21]. This model is used to describe a double
mechanism absorption process where a very fast chemisorption process \((k_1)\) is followed by a slow diffusion of reactants across the external carbonated shell \((k_2)\). Table 4 clearly indicates that the rate of absorption increased one order of magnitude when the temperature was raised from 500 to 700°C. This was also in agreement with the double mechanism process, where \(k_1\) is 2 orders of magnitude higher than \(k_2\) at 700°C. It is interesting to compare the kinetics with previous work that used pure \(Li_4SiO_4\) and Li-FA sorbents under the same conditions [17]. This work shows comparable kinetic constant values to those reported for pure lithium silicate, although the total \(CO_2\) uptake is about 50% lower.

![Figure 6. Effect of diluted \(CO_2\) on sorption/desorption at 700°C in presence of different additives and moisture concentrations. (a) Li-Na-FA 0.5:0.5:1, 12%H\(_2\)O, 14%\(CO_2\) and 20%\(K_2CO_3\); (b) Li-Na-FA 0.5:0.5:1, 2%H\(_2\)O and 100%\(CO_2\); (c) Li-Na-FA 0.5:0.5:1, 12%H\(_2\)O and 14%\(CO_2\).](image)

Table 4. Kinetic parameters of selected experiments. * Experiment carried out in presence of 14% \(CO_2\) and 12% H\(_2\)O.

<table>
<thead>
<tr>
<th>Sample Additives</th>
<th>(CO_2) uptake, (mg)(CO_2/g)sorbent</th>
<th>(k_1) (1/s)</th>
<th>(k_2) (1/s)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Na-FA 0.5:0.5:1, 500°C</td>
<td>21</td>
<td>1.10E-03</td>
<td>4.00E-04</td>
<td>0.9994</td>
</tr>
<tr>
<td>Li-Na-FA 0.5:0.5:1, 645°C</td>
<td>73</td>
<td>6.60E-03</td>
<td>5.00E-04</td>
<td>0.9794</td>
</tr>
<tr>
<td>Li-Na-FA 0.5:0.5:1, 700°C</td>
<td>107</td>
<td>1.05E-02</td>
<td>5.00E-04</td>
<td>0.9541</td>
</tr>
<tr>
<td>Li-Na-FA 0.5:0.5:1, 700°C * 20% (Li_2CO_3)</td>
<td>112</td>
<td>1.05E-02</td>
<td>4.00E-04</td>
<td>0.9412</td>
</tr>
</tbody>
</table>
Figure 7 shows the FTIR spectra of the Li-Na-FA 1:1:1 sorbent before (a) and after (b) one CO2 sorption/desorption cycle at 700°C and after (c) only the sorption step. Not significant changes are visible after one complete sorption/desorption cycle at 700°C. After the absorption step (c), the sorbent presents a clear carbonate peak at 1460 cm$^{-1}$ and also a SiO$_2$ associated peak at 1050 cm$^{-1}$, indicating that the reaction occurring is:

$$\text{Li/Na}_2\text{SiO}_3 + \text{CO}_2 \leftrightarrow \text{Li/Na}_2\text{CO}_3 + \text{SiO}_2.$$  (5)

This is in agreement with the above described two stage mechanism including formation of a Na/Li carbonate layer and silica layer and subsequent diffusion of Li/Na and O$_2^{2-}$ ions from the bulk silicate core to the surface to react with CO$_2$. Presence of steam and K$_2$CO$_3$ enhances the diffusion of alkaline species, as suggested by the faster reaction rate depicted in Table 4.

Moreover, at high temperature K and Li/Na carbonates form a eutectic mixture (molten liquid), which increases the CO$_2$ diffusion towards the inner solid unreacted layer of Na/Li-silicate between 600 and 700°C. The melt has negligible vapour pressure so that it is not lost by evaporation and since the eutectic liquid is a strong base, it has a high capacity for CO$_2$ [40,41].

Figure 7. FTIR spectra of (a) LiNaFA 1:1:1 sorbent, (b) LiNaFA 1:1:1 after 1 cycle (700°C), (c) LiNaFA 1:1:1 after CO$_2$ absorption (700°C).
### 3.3.4 Regenerability of developed sorbents

Figure 8 shows 21 and 10 absorption / desorption cycles for (a) Li/Na-FA 0.5:0.5:1 and (b) Li/Na-FA 1:1:1, respectively. All the three materials were able to maintain 100% CO₂ sorption capacity after each of the 21 or 10 desorption steps at 700°C. Compared to single cycle experiments (e.g. Figure 4), sorption and desorption were shortened from 2 hrs to 45 minutes each, since in an industrial application, the process can be designed to avoid the slow sorption/desorption rates; which corresponds to the formation of the carbonated shell in the sorbent particles by reducing the time of the CO₂ uptake to the faster rate (corresponding to the steep section on the curve).

**Figure 8.** Multiple cycles of CO₂ sorption and desorption at 700°C for (a) Li-Na-FA 0.5:0.5:1; (b) Li-Na-FA 1:1:1.
Sharp absorption/desorption of CO₂ in presence of Li/Na-FA sorbents were obtained under the employed process conditions. In this work, desorption was carried out by nitrogen purge at the same absorption temperature. Initially, a 10 cycles test was carried out for Li/Na-FA 0.5:0.5:1, but since a capacity gain with cyclic time was noticed, a prolonged test (21 cycles) was used to establish if the capacity was able to reach a plateau over more extended cycling. Both tested materials were stable over a number of cycles. In comparison, it has been reported that K-doped hydrotalcite sorbents lost capacity after just 3 cycles at 500°C [9]. Therefore, compared to other high temperature sorbents such as CaO, stability of Li/Na-FA is superior.

Moreover, the CO₂ uptake curves in Figure 8 show that the sorbent Li/Na-FA 0.5:0.5:1 increases its CO₂ uptake capacity after each of the first 6 cycles with about 10% CO₂ sorption increase between cycle 1 and 10 to stabilise its CO₂ uptake capacity in the remnant 15 cycles. It should be considered that the CO₂ uptake properties of the studies sorbents are not related to their “accessibility features” such as surface available (surface is lower than 1 m²/g). XRD analysis of the fresh synthesised sorbent and the same after 10 absorption/desorption cycles were performed to evaluate any potential phase change during the high temperatures desorption cycles. Figure 9 presents the XRD profiles of the Li-Na-FA 0.5:0.5:1 sorbent before and after the 10 cycles. The XRD patterns clearly indicate that a change in the mineral phases occurs in the sorbent after 10 cycles, with increase in abundance of bi-alkali species such as Na₃LiSiO₄/Si₂O₅/Si₃O₆, and in general, a reorganisation of the crystalline structure of the material, which is not achieved during the materials synthesis at 800°C. The structural reorganisation may be facilitated by the formation of a eutectic melt at 700°C. The formation of bi-alkali species during the first 6 cycles (Li/Na-FA 0.5:0.5:1) can explain the increase in the CO₂ uptake shown in Figure 8a. The contact of Li and Na species can be improved by their enhanced diffusion at 700°C. The increase of CO₂ uptake occurs only in the 1st cycle for Li/Na-FA 1:1:1 (Figure 8b). This is probably related to the larger abundance of Li and Na species that facilitates the formation of bi-alkali phases.

This work shows that the CO₂ sorption properties of the Li-Na-FA 0.5:0.5:1 sorbent are suitable to be used as high temperature sorbents. Also, the use of 0.5 moles of Li₂CO₃ for each mole of SiO₂ used to synthesise the sorbent could result in a large cost reduction compared to traditional Li₄SiO₄ sorbents, where 2 moles of Li₂CO₃ are required.
Figure 9. XRD of Li-NA-FA 0.5:0.5:1 before and after 10 CO₂ sorption and desorption cycles.

4. Conclusions

Na/Li-FA sorbent with different Na₂CO₃:Li₂CO₃:SiO₂ molar ratio obtained using fly ash as source of SiO₂ were synthesised and tested for CO₂ capture at high temperature, including in the presence of moisture (2-12%) and diluted flue gas (14%). XRD and FTIR analyses indicate that metastable phases were synthesised at 800°C and resulted to be more active in terms of CO₂ uptake and reaction rates. Na-Li-FA 0.5:0.5:1 and Na-Li-FA 1:1:1 were the best sorbents in terms of combined absorption /desorption rates, CO₂ uptake and regenerability. A maximum loading of 2.54 moles CO₂/kg sorbent at 700°C was achieved in presence of 12% H₂O, 14% CO₂ and when using 20% K₂CO₃ as promoter. Sorption/desorption can be completed within 15 minutes with reaction kinetics comparable to pure Li₄SiO₄ sorbents. The CO₂ sorption capacity of Li-Na-FA (0.5:0.5:1+20% K₂CO₃) were found to be higher than previously tested Li-FA (2:1 + 40% K₂CO₃) and sorbents and more stable than CaO and hydrotalcite sorbents. Sorption capacity was reduced by 33% in presence of 14% CO₂, while water (12%) did not affect the materials sorption capacity. The larger CO₂ uptake capacity at 700°C can be associated to enhanced diffusion of alkali ions through the carbonates layer, which forms a eutectic melt at that temperature.
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References


