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CO₂ capture at high temperature using fly ash-derived sodium silicates

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Abstract: Despite the fact that Na-silicates have been indicated as good sorbent at ambient temperature, their potential as HT CO₂ sorbent has not yet been examined. In this work, CO₂ sorption of fly ash derived sodium silicates was evaluated at 500, 600 and 700°C. The effect of 2-12vol% moisture, 12.5-100 vol% CO₂ and CO₂ sorption promoters on CO₂ sorption was also evaluated. The results indicate that the carbonate:silica ratio used in the sorbents synthesis significantly affects the CO₂ sorption capacity and regeneration temperature. Calcination at 800°C is preferred due to formation of metastable sodium silicate phases, which resulted in higher CO₂ uptake. Among the developed sorbents, Na-FA 0.5:1 was preferred because able to maintain CO₂ sorption/desorption capacity after 5 cycles (compared to 1:1 and 1.5:1). NA-FA 0.5:1 had good capacity at post-combustion conditions (12.5%CO₂, 12%H₂O, 700°C). The presence of 20% Li₂CO₃ additive enhanced the CO₂ sorption of 20%. Overall, the Na-FA 0.5:1 sorbent showed a CO₂ capture capacity and recyclability comparable to those of other high-temperature sorbents.

Keywords: CCS • CO₂ sorption • fly ash • sodium silicates

1. INTRODUCTION

CO₂ sorption on solid sorbents has been proposed as alternative to the more developed absorption systems in order to avoid significant regeneration energy requirements, high corrosion rates and high solvents costs [1,2]. High temperature (HT) sorbents can exploit the favourable thermodynamics of CO₂ sorption between 400 and 750°C and take advantage of the high temperature waste heat from power/industrial plants.

To be competitive to amine-based CO₂ capture processes, solid sorbents should have a CO₂ uptake capacity ≥ 8 wt% (2 mol CO₂/ kg sorbent), selectivity towards CO₂, suitable reaction kinetics, good mechanical properties, high thermal stability, low regeneration energy and low costs of synthesis [2]. Up to date, most of the developed CO₂ sorbents, such as activated carbons, zeolites, ceria based sorbents and amines doped materials are mainly designed for low temperature applications, while ceramics such as Li₄SiO₄ and Li₂ZrO₃ are designed for HT CO₂ sorption [2-9].

One of the most suitable processes for HT CO₂ sorption is the carbonate looping process, where porous alkaline earth and alkali oxides are used in a dual fluidized bed reactor in order to capture the CO₂ from the flue gases of coal fired power plants [1-2, 9]. CaO-based sorbents are particularly valuable because of their high sorption capacity and rapid kinetics in the 400-
800°C temperature range, but their performance is challenged by a rapid loss of activity during the capture cycles, high regeneration temperature (850°C) and poor mechanical strength [10-12]. CaO, Al-CaO, hydrotalcites, titanium silicates, MgO precursors (dolomite, magnesite) and ceramics are among the materials investigated for HT CO₂ sorption [2,8, 10,13]. Alkali-based ceramics such as Li₄SiO₄ are particular promising due to their high CO₂ uptake, sorption/desorption stability and rapid sorption-desorption kinetics [14-15].

The use of waste materials such as fly ash as precursors for CO₂ sorbents is receiving increasing interest due to their availability and low-cost [16]. Li₂SiO₄ sorbents synthesised from coal fly ash have shown a stable (10 cycles) CO₂ uptake of 10.7 wt% at 600°C (1 h) and in presence of 40% K₂CO₃ [15]. Despite the good performance of Li₂SiO₄, it should be noted that lithium is a rare and toxic element and recent assessments indicate that there is insufficient lithium available on earth to sustain current and future uses, such as electric cars batteries [17]. Its high demand results in a very high cost ($4,000-5,000/t), which limits large scale applications, such as for CO₂ capture [18]. Therefore, the development of efficient and stable HT sorbents based on more available and low-cost alkali metals, such as sodium silicates could favor the development of the HT CO₂ capture processes [19]. Compared to Li₂CO₃, Na₂CO₃ is an abundant nontoxic material with an annual production of 51 Mt and a cost of $150-200/t [19].

Despite presenting a CO₂ uptake similar to Li₂SiO₄ (36.7 wt%) , CO₂ capture using sodium silicates (e.g. Na₂SiO₃) has received little attention thus far [14, 20-23], where it has been shown that Na₂SiO₃ was able to capture very low quantities (<1.2 wt%) of CO₂ at low temperatures (80-120°C) under dry conditions [14]. The CO₂ sorption in presence of sodium meta-silicate is represented in the equations below:

\[ \text{Na}_2\text{SiO}_3 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2 \text{ (Theoretical CO}_2 \text{ uptake: 24\%)} \]
\[ \text{Na}_2\text{Si}_2\text{O}_5 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + 2\text{SiO}_2 \text{ (24\%)} \]
\[ \text{Na}_6\text{Si}_2\text{O}_7 + 3\text{CO}_2 \leftrightarrow 3\text{Na}_2\text{CO}_3 + 2\text{SiO}_2 \text{ (43\%)} \]
\[ \text{Na}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SiO}_3 \text{ (20.7\%)} \]
\[ \text{NaAlSiO}_4 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{NaAlCO}_3(\text{OH})_2 + \text{SiO}_2 \text{ (31\%)} \]

A kinetic analysis of the CO₂ sorption in presence of Na₂SiO₃ at 130°C showed that the sorption is limited by the sodium diffusion process and that sorption increases with decreasing particle size of Na₂SiO₃ indicating the influence of surface area on the sorption process [14, 20]. The aim of this work is, therefore, to understand the behavior of high
temperature Na-silicate sorbents (Na-FA) based on low cost and widely available fly ash (US$15-40/t) [24] as source of SiO₂ and sodium in presence of pure and diluted CO₂. Given that CO₂ sorption on Na₂SiO₃ has been reported to be favoured in presence of water at temperature between 30 and 60°C [23], as indicated in the equation below, the effect of steam on high temperature Na-FA sorption properties is also investigated here.

\[ \text{Na}_2\text{SiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{NaHCO}_3 + \text{SiO}_2 \] (6)

Since the material properties and CO₂ sorption can change according to the Na₂CO₃:SiO₂ ratio, a 1.5:1, 1:1 and 0.5:1 Na₂CO₃:SiO₂ molar ratios are investigated. Finally, different additives are evaluated as CO₂ sorption promoters, since previous work has indicated the beneficial effect of K/Na/Li addition on Li₂ZrO₃ due to eutectic mixtures formation at high temperature with consequent enhancement of Li ions diffusion from the unreacted core through the superficial molten carbonate layer [20- 22,25].

2. EXPERIMENTAL

2.1 Materials synthesis

In this work, sodium based silicates (Na-FA) were prepared from a fly ash (FA) by mixing Na₂CO₃ (Acros Organics) at different molar ratio of Na₂CO₃:SiO₂ (from fly ash) by using an agate mortar and pestle. The FA used here, as a source of silica, was collected from a cyclone filter in a UK coal power plant and had the following particle size distribution (obtained by a laser diffraction particle size analyser, Malvern Masterizer): D(0.5) 42 μm, D(0.8) 110 μm, D(0.98) 237 μm. The FA chemical composition, which was obtained by energy dispersive X-ray (Bruker Nonius X8-Apex2) was: SiO₂ 49.8%, Al₂O₃ 23%, Fe₂O₃ 7.1%, CaO 4.9%, K₂O 2.3%, MgO 2.2%, TiO₂ 1%, Na₂O 0.8%. The CO₂ sorbents were prepared by solid state synthesis. 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 hrs, respectively. After calcination, the materials were homogenised using a Mortar Grinder (Pulverisette 2, Fritsch) for 1 minute to eliminate any potential large agglomeration. K₂CO₃, Na₂CO₃ and Li₂CO₃ (all from Acros Organics) were evaluated as additives.

2.2. Materials characterization

The resulting sorbents were ground and characterized by different techniques, including powder X-ray diffraction (XRD), Fourier Transformed Infrared (FTIR), Brunauer-Emmett-
Teller (BET) and thermo-gravimetric analysis (TGA). The BET surface area and pore size distribution of the sorbents were obtained by N₂ physisorption using a Micromeritics Gemini VII. Na-FA 0.5:1, Na-FA 1:1 and Na-FA 1.5:1 BET areas were 1.58 m²/g, 1.28 m²/g and 0.82 m²/g, respectively, with median pores widths (Horváth-Kawazoe equation) of 15-16 Å. The small surface area is typical of solid state samples and in agreement with similar previous work, where Na₂SiO₃ had a BET surface of 1.35 m²/g [14]. A PerkinElmer Frontier FTIR spectrometer was used to gain additional information on the crystal structure of the synthetized sorbents before and after the CO₂ sorption experiments. Na₂SiO₃ (Acros Organics) was used as standard for metasilicate structure. (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, the integral relative intensity corresponding to the different identified mineral phases (in each sample) was assumed to be proportional to the volume fraction in the sample.

2.3 Experimental Procedures

The CO₂ uptake capacity of the resultant samples was measured by using a TGA (TA Instruments, Q 500) in a controlled gas flowing environment. Li₂CO₃ (5,10,20 mol%) and K₂CO₃ (10 mol%) were used also as additives to promote CO₂ sorption. Prior to CO₂ sorption testing, the samples were dried by flowing N₂ (100 mL/min) for 30 or 60 min at the same temperature used for the CO₂ uptake tests (see below). The heating rate used to achieve the final temperature was 25 °C/min. The flowing gas was then changed to CO₂ (100% CO₂ or 14%CO₂ balanced with N₂) to determine the CO₂ uptake capacity of the materials. The weight increase due to CO₂ sorption (wt%) 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. Also, the sorbents were evaluated in presence of humidified flue gas by passing pure CO₂ (or 14% CO₂ balanced with N₂) through a water bubbler at ambient temperature. Water concentration was calculated to be 2% or 12% (vapour pressure of H₂O at 20°C = 0.02 atm; 50°C = 0.12 atm). The % of CO₂ decreased to 12.5% in presence of H₂O was. These values were chosen to represent typical flue gas from a coal fired power plant (12-14%). Five regeneration cycles were used to give an indication of the sorbents stability for potential industrial application. After CO₂ uptakes, the CO₂ desorption was evaluated by switching the furnace atmosphere from CO₂ to N₂, at the same sorption
temperature for 1hr. In order to quantify the rates of the CO₂ sorption, the TGA isotherms were fitted to a double exponential model (y = A exp⁻ᵏ₁ᵗ + B exp⁻ᵏ²ᵗ + c), where y represents the CO₂ uptake, t is the time, K₁ and K₂ are the rate constants and A, B and C are the pre-exponential factors [14-15]. This model is typically used to describe simultaneous chemisorption (K₁) and diffusion (K₂) processes [14]. Temperature dependence of the reaction rates was used to calculate the activation energy (Ea) by plotting the log of the rate versus inverse absolute temperature to yield a straight line corresponding to –Eₐ/RT.

3. RESULTS AND DISCUSSION

3.1 XRD and SEM analyses

Figure 1 shows the XRD patterns of Na silicates synthetized at 800°C for 8 hours using different molar ratios of Na₂CO₃ and SiO₂ from FA. SiO₂, Na₂CO₃ patterns were not detected indicating that solid state reactions were completed. As expected, the synthetized sorbents present a mixture of numerous different crystalline silicate phases, due to heterogeneity of starting FA. The XRD patterns of the Na-FA sorbents prepared at different Na₂CO₃:SiO₂ molar ratios indicate formation of sodium di-silicate (Na₂SiO₅), sodium meta-silicate (Na₃SiO₃), sodium ortho-silicate (Na₄SiO₄), sodium piro-silicate (Na₆Si₂O₇) and sodium aluminium silicate (NaAlSiO₄) phases in all the prepared sorbents. Table 1 shows the semi-quantitative analysis of the synthetised sorbents. The meta-silicate phase was the most abundant among the different prepared sorbents. The di-silicate phase (Na₂SiO₅) and the piro-silicate phase (Na₆Si₂O₇) were mainly present in the sorbents with molar ratios 0.5:1 and 1:1. On the contrary, the ortho-silicate phases (Na₄SiO₄ and NaAlSiO₄) presented the opposite trend, being more abundant in the sorbent Na-FA 1.5:1 due to higher abundance of sodium. The formation of Na₆Si₂O₇ phase can be associated to heterogeneities in the sample with particles locally richer in sodium [14].

Table 1. XRD of sodium silicate materials.

<table>
<thead>
<tr>
<th>% intensity count</th>
<th>Na-FA 0.5:1</th>
<th>Na-FA 1:1</th>
<th>Na-FA 1.5:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SiO₅</td>
<td>13.3</td>
<td>12.9</td>
<td>6.5</td>
</tr>
<tr>
<td>Na₃SiO₃</td>
<td>43.3</td>
<td>44.1</td>
<td>43.2</td>
</tr>
<tr>
<td>Na₄SiO₄</td>
<td>11.7</td>
<td>7.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Na₆Si₂O₇</td>
<td>17.2</td>
<td>16.9</td>
<td>21.4</td>
</tr>
<tr>
<td>NaAlSiO₄</td>
<td>14.4</td>
<td>15.6</td>
<td>17</td>
</tr>
<tr>
<td>tot</td>
<td>99.9</td>
<td>96.9</td>
<td>93.2</td>
</tr>
</tbody>
</table>
Figure 1. Na-FA sorbents. a) 0.5:1; b) 1:1; c) 1.5:1 Na$_2$CO$_3$:SiO$_2$ molar ratios. Peaks labels: 1-Na$_2$SiO$_3$; 2-Na$_2$SiO$_5$; 3-NaAlSiO$_4$; 4-Na$_4$SiO$_4$, 5-Na$_6$Si$_2$O$_7$.

Figure 2 shows the morphology of the Na-FA materials obtained by solid state reactions obtained by SEM at different optical magnifications. The majority of the Na-FA particles were 5 to 10 μm in size when the Na$_2$CO$_3$:SiO$_2$ ratio was 0.5:1, whereas, larger particles were obtained where the ratio used was 1:1. These primary particles showed a tendency to form aggregates of different size with higher tendency to aggregation in presence of a 1:1 molar ratio.
Figure 2. SEM images of a) Na-FA 0.5:1 (1000x); b) Na-FA 1:1 (1000x); c) Na-FA 0.5:1 (5000x); d) Na-FA 1:1 (5000x).

3.2 FTIR analysis

Information on the mineral phases formed during calcination was obtained by FTIR. Figure 3 shows the FTIR spectra in the 2300-600 cm\(^{-1}\) region of the Na-FA sorbents at different ratios of Na\(_2\)CO\(_3\) to SiO\(_2\) and standard Na\(_2\)SiO\(_3\) as reference. The region 3400-2300 cm\(^{-1}\) is not shown since there was no absorption. Different structured crystalline solids can be observed between 1100/1200 and 750 cm\(^{-1}\) where species with a denser crystalline structure absorb at higher energies. Vibrations at 1200, 1050, 950 and 750 cm\(^{-1}\) correspond to SiO\(_2\), Si\(_2\)O\(_5\)\(^{2-}\), Si\(_2\)O\(_6\)\(^{4-}\), and Si\(_2\)O\(_7\)\(^{6-}\) or SiO\(^4-\) silicon centres, respectively. They appear to broadening and their frequencies decrease in intensity, as species depolymerise and the Si-O-Si bond angle decreases [26]. The peak at 1427 cm\(^{-1}\) can be attributed to CO\(_3^{2-}\) anion originating from the sodium carbonate. As can be seen, the standard Na\(_2\)SiO\(_3\) presents a prominent peak at 1427 cm\(^{-1}\) indicating presence of carbonate. The remnant peaks are characteristic of the ortho-meta- and piro- silicate structure. Based on previous studies, the infrared bands at ~890 and 1020 cm\(^{-1}\) could be assigned to Si-O stretching vibration involving the Si-O-Si entity [27]. Compared to the pure Na\(_2\)SiO\(_3\) (STD), Na-FA 0.5:1 and Na-FA 1:1 are clearly composed of a mixture of meta- ortho- and piro- silicates, while the Na-FA 1.5:1 peaks are less defined and difficult to interpret. The properties of sodium silicate solutions are determined by silica to alkali ratio and silicate concentration, where a solution with lower ratio of silica to alkali
should imply a higher pH value [27]. Therefore, metastable structures such as meta- di- and piro- silicates can be beneficial to CO₂ sorption of the materials surface.

![Figure 3. FTIR spectra of Na-FA samples prepared by solid-state reactions at 800°C for 8 hrs.](image)

### 3.3 CO₂ capture studies

A summary of the CO₂ sorption experiments carried out using the synthetized sorbents is shown in Table 2. Temperature, Na-FA molar ratio and additives were initially selected to compare the adsorbed CO₂ to the Li-FA materials studied by Marin et al [15]. As can be seen from Table 2, the Na-FA CO₂ sorption capacity at 600°C without additive was double that of Li-FA used in previous work under the same conditions [15].

The superior CO₂ capacities observed compared to previous work on the development of lithium based silicates from fly ash suggests that Na silicates can be used for 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.
Table 2. CO₂ sorption experiments carried out using 100% CO₂ at 600°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp., °C</th>
<th>Additive, mol%</th>
<th>CO₂ uptake, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-FA 2:1 [15]</td>
<td>500</td>
<td>10% K₂CO₃</td>
<td>0.5</td>
</tr>
<tr>
<td>Li-FA 2:1 [15]</td>
<td>600</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Li-FA 2:1 [15]</td>
<td>600</td>
<td>20% K₂CO₃</td>
<td>5.6</td>
</tr>
<tr>
<td>Li-FA 2:1 [15]</td>
<td>650</td>
<td>10% K₂CO₃</td>
<td>2.1</td>
</tr>
<tr>
<td>Na-FA 2:1 (this work)</td>
<td>600</td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>Na-FA 2:1 (this work)</td>
<td>600</td>
<td>10% K₂CO₃</td>
<td>4.0</td>
</tr>
</tbody>
</table>

3.3.1 Effect of molar ratio

Different Na-FA sorbents have been evaluated for their capacities to absorb CO₂ at temperatures representative of industrial CO₂ emitters (e.g. cement plants, steel works) and existing coal power plants.

Figure 4 shows the effect of the different Na₂CO₃:FA molar ratio on CO₂ sorption and desorption at 700°C. The Na-FA sorbent shows better performance at molar ratios 0.5:1 and 1:1 (8.2-8.6 wt%), while a Na-FA ratio of 1.5:1 was able to chemisorb only 4.2 wt% CO₂. Desorption was completed (in N₂ atmosphere) but required longer time for Na-FA 0.5:1 compared to Na-FA 1:1. The complete desorption requires about 1 h, under these conditions. Since high sorption/desorption rates are ideal to separate CO₂ from large volumes of flue gas, the CO₂ sorption/desorption cycle can be designed to match the point where the CO₂ uptake/release rate start to slow down (e.g. 20 min are required to adsorb 4.0 wt% CO₂ and 40 min to desorb it, using Na-FA 0.5:1). However, the above mentioned absorption and desorption time were found longer than using Li-FA sorbents under the same conditions, and are also too long for industrial applications [15, 22]. The XRD of the Na-FA obtained at 800°C (Section 2.1) confirmed the presence of transient sodium silicate phases, compared to sorbent richer in SiO₄⁻⁴ phase obtained at 950°C and not completed silicate formation calcining at 600°C. Figure 4 also indicates that Na-FA 0.5:1 and 1:1 present similar sorption capacity, which is higher compared to Na-FA 1.5:1. Table 1 shows that Na₂Si₂O₅ and Na₆Si₂O₇ abundancy decreases in the following order: Na-FA 0.5:1 > 1:1>1.5:1. The higher CO₂ uptake is therefore to be ascribed to the increase abundancy of these mineral phases. Also, although the surface available was low for all sorbents, the Na-FA sorbents BET surface decreases according to the sorbents uptake (0.5:1 > 1:1 > 1.5:1).
Figure 4. Effect of different Na-FA (Na$_2$CO$_3$: SiO$_2$) molar ratio on CO$_2$ sorption/desorption at 700$^\circ$C (30 min. sorption) using 100%CO$_2$.

3.3.2 Effect of temperature

Previous work suggests that when Na$_2$CO$_3$ is loaded on supports, CO$_2$ sorption at low temperatures (40-100$^\circ$C) is not significant. For example, a CO$_2$ uptake of 0.7 and 1.8 wt% was obtained in presence of Na$_2$CO$_3$/AC and Na$_2$CO$_3$/Al$_2$O$_3$, respectively [28]. A non-isothermal CO$_2$ absorption test (Figure 5) was conducted to evaluate the CO$_2$ sorption activation temperature and the temperature corresponding to the maximum CO$_2$ sorption capacity.

Figure 5. TGA curves with CO$_2$ sorption/desorption of (a) Na-FA 0.5:1 and (b) Li-Na-FA 1:1:1.
The Na-FA sorbent started absorbing CO$_2$ at 500°C, with a constant increase over temperature until a maximum CO$_2$ sorption occurs at 645°C, followed by the onset of CO$_2$ desorption. The observed increase near 645°C can be related to a change in the mineral phases and possibly the formation of a molten phase [7]. This behaviour was also observed for the isothermal CO$_2$ uptake experiments shown in Figure 6, where Na-FA 0.5:1 and Na-FA 1:1 sorbents were tested at three different temperatures. An insignificant CO$_2$ uptake was achieved at 500°C (~1 wt%), an intermediate uptake was obtained at 600°C (~4 wt%), while the higher CO$_2$ uptake occurred at 700°C (~8 wt%) after 30 minutes. This indicates that the CO$_2$ uptake occurs differently in the non-isothermal and isothermal experiments, with a shift of 50°C for the maximum sorption. This can be related to the different heating rate used in the iso- and non iso-thermal experiments. No significant differences in terms of CO$_2$ uptake were found between the 2 different materials, possibly due to their similar mineral phase composition (Table 1).

**Figure 6.** CO$_2$ sorption/desorption at different temperatures.
An important feature observed in Figure 6 is that the rate of desorption drastically increases with the temperature rise and that a temperature ≥ 600°C must be used for the CO₂ desorption to occur. A double exponential model was used to evaluate the CO₂ sorption mechanism, as in previous work [14-15]. This model describes the CO₂ chemisorption on the sorbent surface with formation of a carbonate product layer and following alkaline diffusion through this external layer. The model fits well with the experimental data as shown in Table 3. The calculated chemisorption (k₁) and diffusion (k₂) rates clearly indicate the carbonation is controlled by diffusion processes on the Na-FA sorbents; where the diffusion rate is an order of magnitude lower than corresponding chemisorption rates. These data are in agreement with previous work [15], but also indicate lower reaction rates of Na-FA sorbents compared to Li-FA materials [15]. K₁ values in Table 3 indicate that the sorption process was faster for the Na-FA 0.5:1 sorbent indicating that a ratio NaCO₃:SiO₂ of 0.5:1 favours the reaction kinetics. A further increase of the Na does not result in faster sorption rates and also lowers the CO₂ uptake, as shown in Figure 6. Instead, the k₂ values are almost identical. This can be explained with the formation of the dense double product layer (SiO₂ + Na₂CO₃), which obstable the diffusion of Na⁺, O²⁻ and CO₂ species [3]. To confirm presence of Na₂CO₃ and SiO₂, the XRD analysis (Figure 7-a) and FTIR (Figure 7-b) of the carbonated Na-FA (0.5:1) sorbent was carried out. Figure 7 indicates that Na₂CO₃ is the main carbonation product, together with SiO₂, as expected from equations 1 to 4. Moreover, the relative abundance of sodium aluminium silicate species indicates that the carbonation of aluminate species is not favoured at 700°C. Presence of Na₂SiO₃, may also indicate carbonation of Na₄SiO₄ (equation 4). Also, this indicates that the sodium excess physically modifies the particle surfaces due to the different structural packing of the Na-FA crystals [14]. This was confirmed by BET analysis, which shows that the surface area almost doubled from about 0.82 for Na-FA 1.5:1 to 1.58 g/m² for Na-FA 0.5:1.

Table 3. Kinetic parameters and R² values obtained for CO₂ sorption on Na-FA 0.5:1 and Na-Fa 1:1 at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>k₁ (1/s)</th>
<th>k₂ (1/s)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-FA 0.5:1, 500°C</td>
<td>6.5 x 10⁻³</td>
<td>6.2 x 10⁻⁴</td>
<td>0.9494</td>
</tr>
<tr>
<td>Na-FA 0.5:1, 600°C</td>
<td>8.2 x 10⁻³</td>
<td>4.0 x 10⁻⁴</td>
<td>0.9394</td>
</tr>
<tr>
<td>Na-FA 0.5:1, 700°C</td>
<td>9.1 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
<td>0.9441</td>
</tr>
<tr>
<td>Na-FA 1:1, 500°C</td>
<td>5.3 x 10⁻³</td>
<td>5.0 x 10⁻⁴</td>
<td>0.9494</td>
</tr>
<tr>
<td>Na-FA 1:1, 600°C</td>
<td>6.2 x 10⁻³</td>
<td>4.1 x 10⁻⁴</td>
<td>0.9694</td>
</tr>
<tr>
<td>Na-FA 1:1, 700°C</td>
<td>7.5 x 10⁻³</td>
<td>5.0 x 10⁻⁴</td>
<td>0.9241</td>
</tr>
</tbody>
</table>
Figure 7. (a) XRD and (b) FTIR of carbonated Na-FA 0.5:1 at 700° in presence of 100% CO₂.

Activation energies (Eₐ) for the chemisorption and diffusion processes were calculated for both Na-FA 0.5:1 and 1:1 by using the Arrhenius equation, plotting the natural log of k₁ and k₂ rate constants vs. 1/t. Linear trends (Figures S1 and S2 in supporting information) were observed, even if the diffusion process did not fit very well in the Arrhenius plot. Eₐ’s for the chemisorption (k₁) and diffusion (k₂) processes were found to be 8.6 and 29.7 kJ/mol for Na-FA 0.5:1 and 10.7 and 21.2 kJ/mol for the Na-FA 1:1 sorbents. This indicates that the diffusion of sodium through the formed carbonated layer on the surface is affected by temperature, while the initial chemisorption rates have lower temperature dependence. As expected, Eₐ for the CO₂ chemical sorption were lower compared to previous study carried out at 60-80°C (17.48 kJ/mol), while Na diffusion Eₐ were somehow comparable (23.97 kJ/mol) [14].

3.3.3 Effect of calcination

Na distribution in the calcination products can be tuned by increasing the calcination temperature, which can improve the diffusion of Na [27]. The CO₂ uptake profiles of Na-FA sorbents calcined at 600, 800 and 900°C are shown in Figure 8-a, which clearly indicates that these materials have a better CO₂ sorption capacity when calcined at 800°C. Calcination at 600 and 900°C were not beneficial toward CO₂ sorption. This point out that the diffusion of Na cations in the sample synthesized at 800°C was improved dramatically compared with that synthesized at 600°C. In a previous study, CO₂ sorption at 600°C on Li-FA sorbents where higher calcination temperature (900°C) was used, was found to be lower than in this
work [15]. FTIR spectra (Figure 8-b) indicate that a mixture of phases (di- meta- ortho- piro- silicates) was obtained by calcination at 800°C. The reason of the very low CO₂ uptake in presence of the material calcined at 600°C can be explained by the presence of large amounts of unreacted sodium carbonates and the absence of sodium silicate phase as indicated by the absence of the Si-O-Na stretching at 950-970 cm⁻¹ (Figure 8-b). Instead, the material calcined at 900°C does not present the typical vibration of carbonates (~1420-1430 cm⁻¹) and of Na₂SiO₃ phase and indicates complete conversion of the starting materials in more condensed (Na₄SiO₄) silicate phase.

**Figure 8.** a) Effect of calcination temperature on CO₂ sorption/desorption using Na-FA 2:1 at 700°C and in presence of 100% CO₂. b) FTIR of Na-FA (1:1) calcined at different temperatures.
The absence of the carbonate band calcining at 900°C represents the main difference compared to all the materials synthetised at 800°C and may be related to the absence of CO$_2$ sorption of this specific material. This also suggests a synergic effect of mixed species on the CO$_2$ sorption capacity.

It has been shown that Li$_4$SiO$_4$ and Li$_2$SiO$_3$ can coexist and retransform to each other, and so can Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$. The relative content of these mineral phases depends on the calcination temperature, time, and molar ratio of Li to Si [27]. Similarly, we found that the calcination temperature and sorption/desorption of CO$_2$ favours the re-arrangement of the sodium silicates structure. Na$_2$SiO$_3$ is the main mineral phase when the material is calcined in the range of 600–800 °C (see Figures 3 and 8-b). The contents of Na$_2$SiO$_3$ decreases with increasing the calcination temperature from 800 to 900°C. Moreover, the XRD of the Na-FA obtained at 800°C (Section 2.1) confirmed the presence of transient sodium silicate phases. Therefore, Na-FA sorbents richer in SiO$_3^{2-}$, Si$_2$O$_5^{2-}$ and Si$_2$O$_6^{4-}$ presented higher CO$_2$ uptake than those richer in SiO$_4^{4-}$ obtained when calcination took place at 900°C [15].

### 3.3.4 Effect of additives

The CO$_2$ sorption experiments suggest that Na-FA with molar ratios 0.5:1 and 1:1 have the capacity to absorb CO$_2$ at the temperature range studied of 600-700°C. Figure 9 compares the CO$_2$ sorption capacity of Na-FA 1:1 with and without additives at 700°C. The pure Na-FA 1:1 was able to capture 9.8 wt% CO$_2$. The CO$_2$ absorbed increased to 9.9 wt% and 11.4 wt% in presence of 10% K$_2$CO$_3$ and 10% Li$_2$CO$_3$, respectively. Similarly, the CO$_2$ uptake of Na-FA 0.5:1 was increased from 8.6 to 11.2 wt% by the addition of 20% Li$_2$CO$_3$. Therefore, the presence of Li$^+$ and K$^+$ carbonates promotes the CO$_2$ uptake, as shown in previous work [3,15]. In absence of additives, the formation of the double products layer (SiO$_2$ and Na$_2$CO$_3$) hinders the migration of Na$^+$ and O$^{2-}$ species in the formed external shell and the diffusion of CO$_2$ from the outside. Presence of K$_2$CO$_3$ and Li$_2$CO$_3$ form a molten carbonate region instead of a dense Na$_2$CO$_3$ shell that reduces the resistance of CO$_2$ molecular diffusion from the outside and Na$^+$ and O$^{2-}$ from the inside, resulting in higher CO$_2$ uptake as can be seen in Figure 9 [3].
Despite the fact that we did not observe molten carbonate phase in presence of K$_2$CO$_3$ additive, previous work indicated that ceramics with the composition similar to that developed in this work (Na$_{1.55}$K$_{0.45}$Si$_2$O$_5$) have eutectic decomposition temperature at 696 °C [27]. XRD data (Table 1) indicate that this phase (with comparable molar ratios) is present in the Na-FA sorbents, with K coming from the fly ash (see experimental section) or added as promoter (see Section 3.4.4). In addition, the system Na$_4$SiO$_4$–K$_2$SiO$_3$–Na$_2$SiO$_3$ with ratios similar to those used for Na-FA 0.5:1, presents a ternary eutectic point close to 700°C [26].

### 3.3.5 Effect of diluted CO$_2$ and moisture on sorption/desorption

The CO$_2$ uptake capacity of the Na-FA sorbents was studied in presence of diluted CO$_2$ (12.5%) and moisture (2-12%) to evaluate their effect on the CO$_2$ sorption capacity. Previous work has shown that the presence of water vapour in the temperature range 30-60°C improves CO$_2$ chemisorption of sodium meta-silicates [23], where a 80% relative humidity at 50°C resulted in 34wt% CO$_2$ uptake after 2 hrs. However, CO$_2$ sorption drastically decreased to 2-3wt% with relative humidity at 20% (50°C) [23]. However no data are available in open literature on the capacity of Na-silicates on CO$_2$ capture in presence of steam.

The sorption of Na-FA 0.5:1 in presence of 12.5% CO$_2$ (balanced with N$_2$) and 12% H$_2$O was 9.2 wt% (2.1 mol CO$_2$/kg sorbent), with this value being higher than using pure CO$_2$ (8.6
wt%). Addition of 2% H₂O to the CO₂/N₂ gas mixture also resulted in a CO₂ uptake of 11 wt% (2.5 mol CO₂/kg sorbent) sorption of CO₂. Therefore, Na-FA sorbents present an increased CO₂ uptake in presence of 2-12% H₂O at 700°C. This can be explained by the enhanced diffusion of sodium through the carbonate formed in surface in presence of moisture, which facilitates the further reaction with CO₂ [20]. This is supported by the faster sorption rate in presence of moisture as indicated by the increased slope (first minutes) in Figure 10. The sorption capacities can be further increased by the addition of CO₂ sorption promoters as shown in Section 3.3.4.

![Figure 10. Initial CO₂ uptake at 700°C with and without moisture.](image)

### 3.3.6 Regeneration of developed sorbents
Two important aspects to take into account in the selection of suitable high temperature sorbents are their cyclic behaviour and their capacity to be regenerated. Typical modes of regeneration for CO₂ sorption systems involve pressure, or temperature swing [7]. Figure 11 shows 5 CO₂ sorption/desorption cycles for the Na-FA sorbent with Na₂CO₃:SiO₂ molar ratios of 0.5:1, 1:1 and 1.5:1. Na-FA 1.5:1 and 1:1 were not able to maintain 100% CO₂ sorption capacity at 700°C, with 10% and 3% capacity lost, respectively after 5 cycles. On the contrary, Na-FA 0.5:1 CO₂ uptake increased cycle after cycle for a total of 5.5% increase after the 5th cycle. Therefore, the Na-FA 0.5:1 cyclic stability was comparable to other high temperature absorbents such as Li₂ZrO₃ [3].

Na-FA 1.5:1 and Na-FA 0.5:1 after 5 sorption/desorption cycles were studied by XRD to evaluate the potential re-arrangement of the mineral structure in relation to the increased CO₂
uptake capacity shown after 5 cycles. Table 4, which reports the semi-quantitative phases’ composition of the two materials, clearly indicates that sorption/desorption cycles, with formation of a carbonated layer on the surface of the materials and subsequent release of CO$_2$, affects the mineral composition of these materials. The main changes were an increase of Na$_4$SiO$_4$ phase in the Na-FA 1.5:1 sorbent, Na$_6$Si$_2$O$_7$ phase for Na-FA 0.5:1 and a decrease of the metasilicate phases in both materials after 5 cycles. Presence of more sodium (1.5:1) resulted in decreased CO$_2$ sorption capacity after 5 cycles, compared to scarcity of sodium (0.5:1/1:1). The reactions stoichiometry indicates that in theory, larger presence of Na should results in larger amount of CO$_2$ uptake. The experimental data are not in agreement since the formation of Na$_4$SiO$_4$ results in reduced CO$_2$ uptake compared to formation of Na$_6$Si$_2$O$_7$. Relative scarcity of Na species in Na-FA 0.5:1 and 1:1 compared to 1.5:1 may also increase the formation of eutectic phases in presence of the impurities (e.g. K$_2$O melting point is 740°C) from fly ash by enhancing the mobility and reaction of cations in the mineral lattice at prolonged repeated exposure at 700°C [27], which can enhance Na species diffusion.

![Figure 11](image-url). Multiple cycles of CO$_2$ sorption and desorption for the Na-FA sorbents at 700°C with 30 min. sorption and 60 min. desorption.
Table 4. XRD of Na-FA sorbents before and after 5 sorption/desorption cycles at 700°C in presence of 100% CO₂.

<table>
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<th>Na-FA 0.5:1</th>
<th>Na-FA 0.5:1, 5 cycl.</th>
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<th>Na-FA 1.5:1, 5 cycl.</th>
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<td>14.4</td>
<td>9.2</td>
<td>17</td>
<td>17</td>
</tr>
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</table>

4. CONCLUSIONS

Na-FA sorbents with different Na₂CO₃: SiO₂ molar ratio obtained using fly ash as source of SiO₂ were synthesised and tested as CO₂ sorbents at high temperature. Moisture enhances the diffusion of sodium through the carbonate formed on the surface enabling further CO₂ carbonation. As suggested by the XRD and FTIR analyses, metastable phases (meta- piro- di-silicates) developed at 800°C. These phases were more active in terms of CO₂ sorption and reaction rates, compared to ortho-silicate phase prevalently formed at 950°C. Although, NA-FA 1:1 was able to desorb CO₂ faster compared to Na-FA 0.5:1, its recyclability resulted not satisfactory. Instead, Na-FA 0.5:1 had a CO₂ uptake of 9.24 wt% at 700°C (in presence of 12.5%CO₂ and 12% H₂O) and was able to retain its sorption/desorption capacity for after 5 cycles. The CO₂ uptake resulted comparable to Li-FA and Li₂ZrO₃ ceramics previously tested. The better performance of the developed materials at 700°C can be attributed to the different mineral phases produced and to presence of a eutectic mix among Na and FA (K,Ca), which increases CO₂ uptake by enhancing sodium ions diffusion through eutectic melt. Therefore, NA-FA 0.5:1 resulted as the best CO₂ sorbent under the studied conditions. Its CO₂ sorption could be further increased to 11.2 wt% in presence of 20% Li₂CO₃, but the costs involved must be taken into consideration. Future work will be required to evaluate the sodium silicate materials in presence of contaminants (e.g. SO₂, NOₓ), at pre-combustion conditions (high pressure, presence of CO and H₂) and to establish if their sorption properties are maintained at larger scale.

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ASSOCIATED CONTENT
Supporting Information Available: Supporting material includes the Arrhenius equation plots for the for the Na-Fa 1:1 (Figure S1) and 0.5:1 (Figure S2) sorbents, where the natural log of $k_1$ and $k_2$ rate constants have been plotted vs. 1/t. This material is available free of charge via the Internet at http://pubs.acs.org.

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