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# Novel Na-silicates $CO_2$ sorbents from fly ash

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**Abstract**

Despite the very good $CO_2$ uptake of lithium based silicates at high temperature, this material is expensive and not very abundant. Therefore, there is the need to develop high temperature sorbents based on low-cost and widely available materials. In this work, Na-silicates prepared by mixing sodium carbonate with fly ash (FA) in the molar ratio of $Na_2CO_3$:$SiO_2$ of 1:1 and 4:1 were evaluated for their capacity to chemisorb $CO_2$ at 700°C. This temperature was chosen as it is compatible with post-combustion technologies. Pure Na-FA sorbent ($NaCO_3$:$SiO_2$ molar ratio of 1:1) was able to adsorb 1.8 mmol $CO_2$/g sorbent. The $CO_2$ uptake capacity increased to 2mmol $CO_2$/g sorbent in presence of 20% $Li_2CO_3$ as additive. Therefore, this work suggests that Na-silicate materials with acceptable $CO_2$ uptake can be developed as high temperature sorbents for post-combustion technologies.


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*Keywords:* $CO_2$ capture, Na-based sorbents, solid sorbents, carbonation/calcination cycles.

## 1. Introduction

Alkaline ceramics, mainly lithium and sodium containing compounds, have recently been used as $CO_2$ sorbents [1-5]. Typically, these ceramics present a double-step sorption mechanism, with an initial chemical sorption of $CO_2$ over the ceramic surface, which forms a carbonate shell, followed by the $CO_2$ diffusing through the carbonate external layer to reach the surface and further react with the alkaline element [1].

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At low temperature (100°C), Na sorbents have shown better $CO_2$ capture capacity compared to Li-based sorbents. For example, $Na_2ZrO_3$ absorbs twice more $CO_2$ than $Li_2ZrO_3$ (1.1 mmol$CO_2$/g sorbent vs 0.67 mmol $CO_2$/g sorbent), and its reaction rate is faster as well (100 min vs 200 min) [2]. $CO_2$ capture at high temperatures (450-700°C) based on regenerable sorbent materials produced from waste feedstocks has also received increasing attention [5]. Amongst the wide range of materials tested, lithium silicate ($Li_4SiO_4$) has shown the largest $CO_2$ sorption capacity and the fastest $CO_2$ sorption rate over a wide range of temperatures and $CO_2$ concentrations [5-7]. The authors have reported that the presence of carbonates (e.g. $K_2CO_3$) and high temperatures affect the $CO_2$ sorption capacity for the Li-based sorbents prepared from fly ashes [5], where at 600°C, both the $CO_2$ sorption capacity and the sorption rate increase significantly to a maximum $CO_2$ sorption capacity of 107 mg $CO_2$/g sorbent in the presence of 40 mol% $K_2CO_3$. It was also reported that $Li_4SiO_4$-based sorbents maintained their original capacity over 10 cycle processes [5].

Despite the very good performance of these materials, it should be noted that the lithium carbonate used to produce the Li-silicate is expensive and toxic, and not very abundant. Therefore, the aim of this work is to develop high temperature sorbents based on low-cost and widely available Na and mixtures of Na and Li silicates. $CO_2$ capture using sodium metasilicates ($Na_2SiO_3$) has not been studied at high temperature thus far, although it has been shown that $Na_2SiO_3$ was able to trap very low quantities of $CO_2$ at low temperatures (130°C) under dry conditions [1]. The $CO_2$ adsorption occurs as follows: $Na_2SiO_3 + 2CO_2 \rightarrow 2NaHCO_3 + SiO_2$. As expected, the presence of water vapour strongly favoured the $CO_2$ chemisorption on $Na_2SiO_3$ [6].

## 2. Methodology

In this work, Na -meta and -ortho silicates were prepared by mixing fly ash (FA) with $Na_2CO_3$ (Acros Organics) in the molar ratio of $Na_2CO_3$:$SiO_2$ of 1:1 and 4:1 by using an agate mortar and pestle. The mixed powder was then calcined in an alumina crucible in a muffle furnace at 800°C for 8 hours. The FA samples were collected from a coal-fired power plant in the UK.

The resulting sorbents were grinded and characterized by different techniques, including powder thermo-gravimetric analysis (TGA) and Fourier Transformed Infrared (FTIR). The $CO_2$ capture capacity of the resultant samples was measured by using a TGA (TA Q500) in a controlled gas flowing environment. $Li_2CO_3$ was used also as additives (20 mol%) to promote $CO_2$ sorption. Prior to $CO_2$ sorption testing, the samples were dried in flowing $N_2$ (100 mL/min) at 25 °C/min for 30 min. The flowing gas was then changed to 100% $CO_2$ to allow reaction and determine $CO_2$ adsorption capacity. The weight increase due to $CO_2$ sorption (mg $CO_2$/g sorbent) was measured as a function of time at a constant temperature (700 °C) and constant concentration of $CO_2$ (95 mL/min) at atmospheric pressure.

## 3. Results and Discussion

### *3.1FTIR study*

Information on the mineral phases formed during calcination was obtained by FTIR. Figure 1 presents the IR fingerprint of the Na-FA $CO_2$ sorbents between 2000 and 600 $cm^{-1}$ and those of standard silica and $Na_2CO_3$ for comparison. As can be seen in Figure 1, the peak representing $SiO_2$ is not present in the calcined Na-FA sorbents, indicating that the calcination process at 800°C mostly converted the $SiO_2$ from fly ash and the $Na_2CO_3$ into Na-silicates. The large peak at ~1427 $cm^{-1}$ in Figure 1 (c) suggests that unreacted sodium remains when a $Na_2CO_3$:$SiO_2$ ratio of 4:1 is used. Overall, major peaks shift to lower energy as the concentration of silica increases. [8]. Different forms of silicates from structured crystalline solids can be distinguished by the stretching energy between 1200 and 750 $cm^{-1}$ where species with higher connectivity values absorb at higher energies. Vibrations at 1200, 1050, 950 and 750 $cm^{-1}$ correspond to ($SiO_2$), ($Si_2O_5^{2-}$), ($Si_2O_6^{4-}$), and ($Si_2O_7^{6-}$ or $SiO_4^{-}$) silicon centres, respectively. They appear to broaden and their frequencies decrease in intensity as species depolymerise and the Si-O-Si bond angle decreases [9]. Key IR bands appear at near 800, 877, 952 and 1427 $cm^{-1}$. The peak at 1427 $cm^{-1}$ can be attributed to $CO_3^{2-}$ anion originating from the sodium carbonate, while the band with maximum at 963 $cm^{-1}$ is due to deformation

vibration of the atom in O-C-O bond of the same carbonate [10]. The remnant peaks are characteristic of meta-silicate structure. The IR spectra of sodium silicate present the most prominent bands between 1000 and 800 $cm^{-1}$ caused by un-dissociated Na-silicate species. Based on previous studies, the IR bands at ~890 and 1020 $cm^{-1}$ could be assigned to Si-O stretching vibration involving the Si-O-Si entity [9].

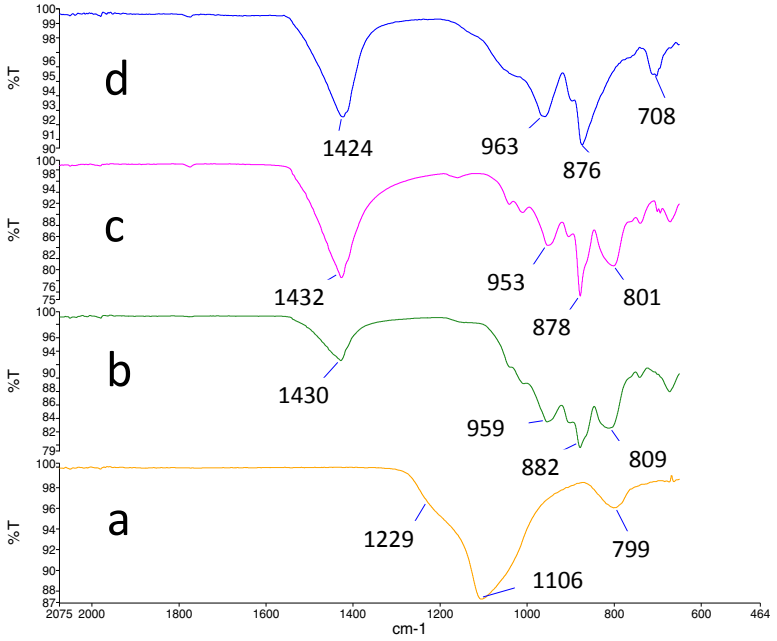


Figure 1. FTIR of $SiO_2$ standard (a); Na-FA 1:1 (b), Na-FA 4:1 (c) and $Na_2CO_3$ standard (d).

The band at around 959-950 $cm^{-1}$ represents silicate phase and the shifting to lower wavelength (953 $cm^{-1}$ for the Na-FA 4:1) is characteristic of high silica-silicates. Absence of asymmetric Si-O-Si band at 1100 $cm^{-1}$ in synthetized Na-FA sorbents (Figure 1b, 1c) indicates that the $SiO_2$ from FA has disappeared by the formation of Na-silicate. Some peaks seem somehow shifted to higher energies compared to typical $Na_2SiO_3$ peaks and may be associable to amorphous silicate phase (800 $cm^{-1}$).

Similarly, the peaks of the other synthesised sodium silicates present their main peaks at similar wavelength. Considering the two main factors determining the properties of sodium silicate solutions, namely silica to alkali ratio and silicate concentration, a solution with lower ratio of silica to alkali should imply a higher pH value [11]. This can be beneficial to $CO_2$ adsorption of the materials surface. Figure 2 shows the FTIR peaks of Na-FA 1:1 before (a) and after 1 adsorption/desorption cycle (b) at 700°C. The IR spectrum suggests that desorption of $CO_2$ was not completed and required more time. This can be deducted by the similarity of the band that represent the carbonates (1429 $cm^{-1}$) and those representing the silicate phase 1000-800 $cm^{-1}$ after the adsorption/desorption cycle.

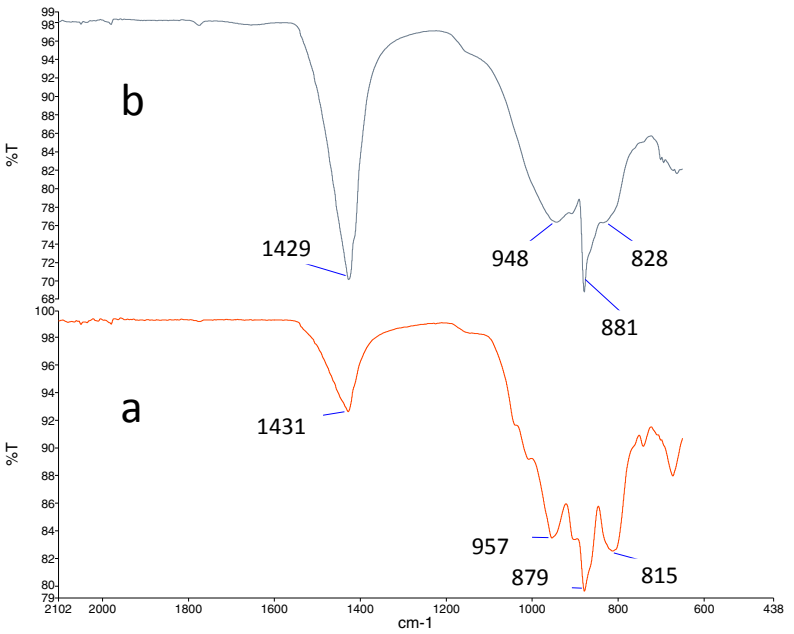


Figure2. FTIR of Na-FA samples obtained using a 1:1 before (a) and after 1 adsorption/desorption cycle (b) at 700°C.

### *3.2$CO_2$ uptake*

Different Na-FA sorbents have been evaluated for their capacity to chemisorb $CO_2$ at 700°C. This temperature was chosen as it is compatible with post-combustion technologies and industrial $CO_2$ emitters (e.g. cement plants steel works).

Figure 3 shows the effect of the different $Na_2CO_3$:FA molar ratio on $CO_2$ sorption and desorption at 700°C. Na-FA sorbent had its better performance at molar ratio 1:1 (a) with 1.8 mmol $CO_2$ / g sorbent, while a Na-FA ratio of 4:1 (b) was able to chemisorb only 0.45 mmol $CO_2$ / g sorbent. It is interesting to note that these materials can be regenerated by inert purge at the adsorption temperature. Both adsorption and desorption are rapid at the beginning of the process but then, the complete desorption requires about 1.6 h. For a commercial point of view, these long time may be a deterrent. However, 1.2 mmol/$CO_2$ / g sorbent can be adsorbed/desorbed in about 30 minutes.

Figure 4 compares the $CO_2$ sorption capacity of Na-FA 1:1 with and without additives at 700°C. Addition of lithium carbonate to the starting Na-silicate promoted $CO_2$ uptake and adsorption/desorption rate. The Na-FA 1:1 doped with 20% $Li_2CO_3$ was able to capture 2 mmol $CO_2$/g sorbent. Previous studies indicated that addition of up to 30 mol% K and Na carbonates promoted $CO_2$ sorption [12]. The addition of $Li_2CO_3$ to the Na-FA sorbent accelerated also the $CO_2$ adsorption and desorption steps, resulting in 1.4 mmol/$CO_2$ / g sorbent adsorbed/desorbed in about 25 minutes. Previous studies indicate that $Na_2SiO_3$ is not a good $CO_2$ sorbent at low temperature and under dry conditions, with a $CO_2$ uptake < 0.25 mmol $CO_2$/g sorbent [1]. Instead, this work suggests that Na-silicate materials may be developed as high temperature sorbents.

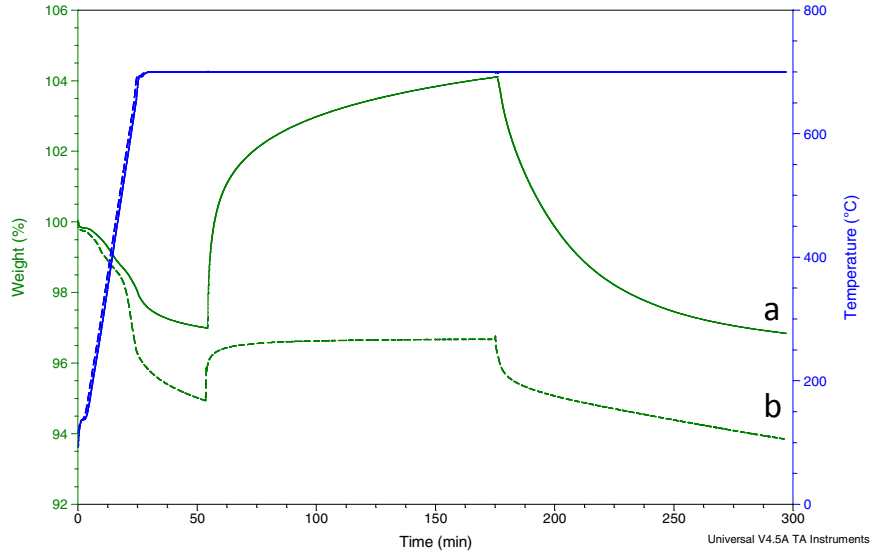


Figure 3. TGA of Na-FA 1:1 (a); Na-FA 4:1 (b).

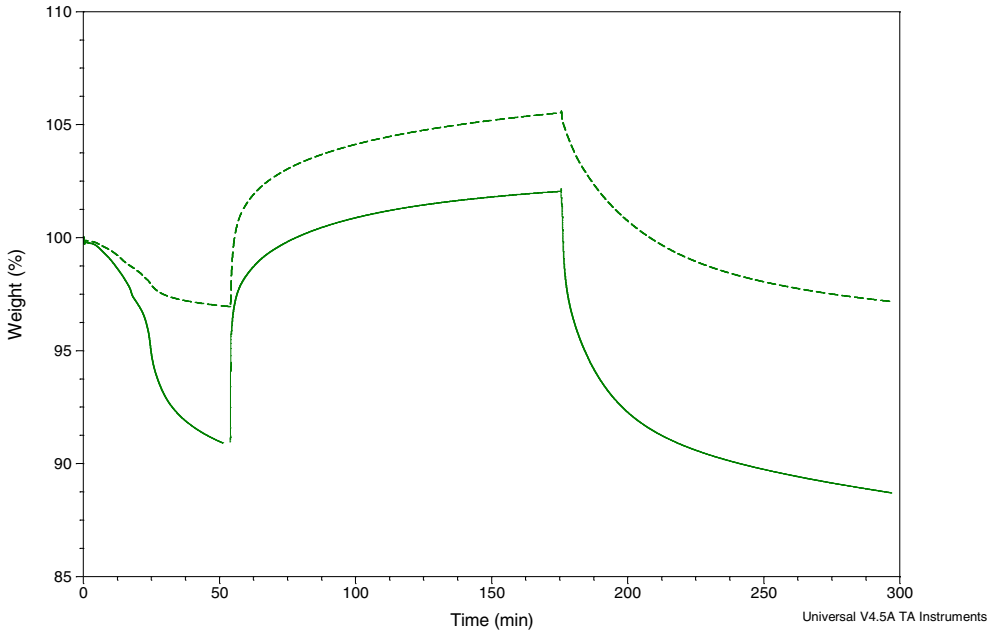


Figure 4. TGA of Na-FA 1:1 (a); Na-FA 1:1 20% $Li_2CO_3$ (b).

## 4. Conclusions

Na-FA sorbents with a $Na_2CO_3$:$SiO_2$ molar ration of 1:1 obtained using fly ash as source of $SiO_2$ were developed and tested as $CO_2$ sorbent at high temperature. Na-FA had its better performance on $CO_2$ sorption (1.8 mmol $CO_2$) and desorption at 700°C. Its performance was enhanced when the material was doped with 20% $Li_2CO_3$. In that case, it was able to capture 2 mmol $CO_2$/g. The $CO_2$ uptake at high temperature resulted much higher than found in previous experiments at temperature < 100°C (< 0.25 mmol $CO_2$/g sorbent) in dry conditions.

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