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## Preparation and Evaluation of CaO-based CO<sub>2</sub> Sorbents Deposited on Saffil Fibre Supports

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### Abstract

Calcium oxide-based sorbents were coated onto Saffil ceramic fibres by means of a wet impregnation method. The effect of synthesis parameters on the crystalline structure, morphology and texture of the CaO layer were investigated by X-ray diffraction, scanning electron microscopy and gas adsorption techniques. The analyses revealed that the optimised synthesis method produced a uniform coating composed of a network of CaO nanoflakes. The evaluation of the materials as CO<sub>2</sub> sorbents was performed under repeated carbonation-decarbonation cycles using thermogravimetric analysis (TGA). A nominal 25 wt. % loading of CaO gave a CO<sub>2</sub> uptake capacity of 0.118 mg CO<sub>2</sub>/mg of sorbent (carbonation at 650°C in 90% CO<sub>2</sub> and decarbonation at 850°C in N<sub>2</sub>). A 5 wt. % loading exhibited improved durability with a ~30% decay in carrying capacity after 30 TGA cycles, but at the expense of initial uptake capacity.

Keywords: CO<sub>2</sub> capture materials; CO<sub>2</sub> sorbents; CaO: thermogravimetric analysis; multicycle durability;

## 1. Introduction

Carbon capture and storage (CCS) has emerged as a promising approach for reducing anthropogenic CO<sub>2</sub> emissions into the atmosphere <sup>1,2</sup>. An estimation demonstrates that CCS technologies could be able to mitigate between 80-90% of the overall CO<sub>2</sub> emitted from combustion carried out in processes such as power plants <sup>1,3</sup>. There are three classes of capture technologies, namely pre-combustion, post-combustion and oxy-combustion <sup>4,5</sup>. In pre-combustion capture, the separation occurs in an exhaust stream derived from a gasification or reforming process prior to the combustion reaction <sup>6,7</sup>, allowing a decarbonised fuel stream to be combusted or oxidised downstream of the CO<sub>2</sub> capture stage. In post-combustion capture, CO<sub>2</sub> is removed from the combustion product stream, commonly composed of N<sub>2</sub>, CO<sub>2</sub> and O<sub>2</sub>. With respect to oxy-combustion, a special form of post-combustion capture, almost pure oxygen is introduced into the combustion environment rather than air, this results in combustion products devoid of N<sub>2</sub> which allows easy separation of the CO<sub>2</sub> by condensation of the steam co-product <sup>8</sup>. Although post-combustion capture technologies are considered more mature than pre-combustion systems, the costs can be higher for coal-fired plants <sup>6</sup>.

Sorption enhanced steam reforming (SESR) as a pre-combustion process is an attractive route to produce high purity H<sub>2</sub> through the separation of CO<sub>2</sub> from the gas phase at high temperature (>400°C). High conversions of methane (CH<sub>4</sub>) and CO with no requirement for a purification unit are advantages of the SESR approach. However, the optimisation of this process is intrinsically related to the appropriate selection of CO<sub>2</sub> sorbents, as these

materials must show an ability to withstand harsh operating conditions, with minimal degradation of CO<sub>2</sub> capture performance over multiple high temperature sorption-desorption cycles<sup>9</sup>. SESR applications are the motivation for the present study. Several criteria must be carefully considered in selecting an appropriate high-temperature CO<sub>2</sub> capture material, including their thermodynamic properties and capture capacity within the expected operating temperature and pressure ranges<sup>10, 11</sup>. Additionally, account must be taken of the kinetics of sorption and desorption and their dependence on textural properties (active surface area and pore volume). For applications at an industrial level, the production costs and the availability of the raw sorbent are also important factors to consider<sup>12, 13</sup>.

Inorganic sorbents such as CaO, MgO, hydrotalcites (HTC), Li<sub>2</sub>ZrO<sub>3</sub> and Li<sub>4</sub>SiO<sub>4</sub>, have shown promise as high temperature CO<sub>2</sub> capture materials. They have the ability to react chemically with dilute levels of CO<sub>2</sub> in gas streams at temperatures relevant to post combustion capture or SESR through a selective carbonation reaction, and can be regenerated by means of a calcination process<sup>10, 14, 15</sup>.

Sorbent	Carbonation temperature (°C)	Carbonation pressure (P <sub>CO<sub>2</sub></sub> -atm)	Calcination temperature (°C)	CO <sub>2</sub> sorption capacity (g CO <sub>2</sub> ·g <sup>-1</sup> sorbent)	References
Li <sub>2</sub> ZrO <sub>3</sub>	400-600	1	750-800	~0.28	16
Li <sub>4</sub> SiO <sub>4</sub>	450-700	1	>800	~0.36	17
Na <sub>2</sub> ZrO <sub>3</sub>	700	0.8	900	~0.17	18
CaO-Al <sub>2</sub> O <sub>3</sub>	~650	0.33	>800	~0.19	19
CaO/Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>	>650	0.2	>850	~0.56	20
CaO-MgO	>750	1	>750	~0.53	21
CaO-La <sub>2</sub> O <sub>3</sub>	>650	0.15	>950	~0.21	22
CaO-Cs <sub>2</sub> O	>600	0.29	-	~0.66	23
Hydrotalcite (HTC) promoted with K <sub>2</sub> CO <sub>3</sub>	400-550	0.38	400-550	~0.018	24

**Table 1.** CO<sub>2</sub> uptake capacity for leading metal-oxide sorbent materials tested under different operational conditions of temperature and pressure.

Natural sorbents such as limestone ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) have been extensively studied for  $\text{CO}_2$  removal using batch fluidized bed, fixed bed and dual fluidized bed reactors <sup>3, 25</sup>. However, sintering and performance degradation have been encountered. According to numerous publications, the loss of  $\text{CO}_2$  reactivity can reach around 80% in the course of carbonation-calcination cycles <sup>26, 27</sup>. The drastic decline in the performance of  $\text{CaO}$  is associated with textural changes such as changes in pore size distribution and reduction in specific surface area. The high temperatures ( $>800^\circ\text{C}$ ) required to regenerate the sorbent encourages a collapse of the pore network and sintering of the powder <sup>28, 29</sup>. In order to overcome the detrimental effects caused by sintering of limestone or dolomite derived sorbents, the preparation of synthetic sorbents has been proposed as a viable alternative to enhance and extend the thermal stability and lifetime <sup>30, 31</sup>. Their performance depends on the method of synthesis and this offers a means of optimising thermal stability and achieving levels of  $\text{CO}_2$  uptake close to the theoretical capacity <sup>32</sup>. Table 1 contains a list of some synthetic sorbents which have shown an ability to absorb  $\text{CO}_2$  at high temperature. Although they exhibit improved performance with regards to natural materials, there is scope for further improvements in high-temperature multicycle durability.

An extensive range of natural and synthetic solid materials for  $\text{CO}_2$  uptake at high temperature have been researched but  $\text{CaO}$  remains one of the most promising options because of its favourable  $\text{CO}_2$  carrying capacity, temperature range of operation, material availability and low production costs <sup>33, 34</sup>. Typical carbonation temperatures are between  $600\text{-}650^\circ\text{C}$ . However, as mentioned above, the main drawback from using  $\text{CaO}$  as a  $\text{CO}_2$  sorbent material is a loss of uptake capacity over repeated use due to densification and loss of porosity and surface area after multiple carbonation-decarbonation cycles due to

the effects of sintering. The rate of sorption slows down due to longer diffusion paths as a result of the sintered dense microstructure <sup>30, 35</sup>.

Studies reveal that incorporating CaO into a matrix of a refractory material can enhance multicycle stability. These blends are termed collectively as 'CaO-based sorbents' and include pre-prepared compounds such as  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ,  $\text{CaTiO}_3$ ,  $\text{CaZrO}_3$ , and CaO mixed with refractory powders such as MgO,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  <sup>36-38</sup>. These improve but do not eliminate loss of performance due to repeated carbonation-calcination cycles. Aluminium oxide powder is regarded as one of the most promising options to stabilise the CaO sorbent against sintering because of its thermal stability (high melting point  $>2050^\circ\text{C}$ ) and robust mechanical properties <sup>39, 40</sup>. In addition,  $\text{Al}_2\text{O}_3$  can be produced with high surface area and a mesoporous structure which is very relevant for a support material <sup>41, 42</sup>. The incorporation of CaO and with the  $\text{Al}_2\text{O}_3$  'spacer' powder is usually performed using wet chemical methods <sup>43</sup>.

In the present study, an alternative means of improving the thermal stability of CaO as a  $\text{CO}_2$  acceptor is proposed. A low-density fibrous mat of refractory Saffil with outstanding resistance to chemical attack and also to degradation in demanding conditions has been used as a support material on which to deposit CaO with the aim of inhibiting volumetric densification of the active sorbent layer. In addition to prolonging the cyclic reactivity of CaO, the incorporation of Saffil offers the potential to create a composite material which performs well in a fixed-bed reformer. Catalytic grade Saffil fibres are composed of 95-97%  $\text{Al}_2\text{O}_3$  and 5-3%  $\text{SiO}_2$ ; the median fibre diameter is 3-3.5 microns.

## **2. Materials and methodology**

Saffil fibres (catalytic grade) were supplied by Unifrax Limited (UK). The fibres were loaded with various amounts of CaO active phase (5, 15 and 25 wt. %) using a wet impregnation method. The fibrous mat (0.5 g) was added to an aqueous solution of calcium acetate monohydrate ( $C_4H_6CaO_4 \cdot H_2O$ , ACS reagent  $\geq 99.0\%$ , Sigma-Aldrich: CaAc) of appropriate concentration. This was heated to  $70^\circ\text{C}$  to promote evaporation of the solution over a  $\sim 4$  h period using a hotplate-stirrer. Comparisons of evaporation with or without stirring (500 rpm) were carried out. Afterwards, the fibrous mat of still moist fibres was removed and dried further in a tubular furnace at  $120^\circ\text{C}$  overnight. Then, in order to decompose the CaAc phase to CaO, the sample was heated in a tubular furnace at  $850^\circ\text{C}$ . Two different calcination times were used, 1 h and 4 h. The prepared sorbents were labelled as 'Ca-Sa-%-WI', where 'Sa' is the abbreviation for Saffil, '%' corresponds to the notional wt. % of CaO (based on proportions of starting reagents) and 'WI' refers to the wet impregnation method.

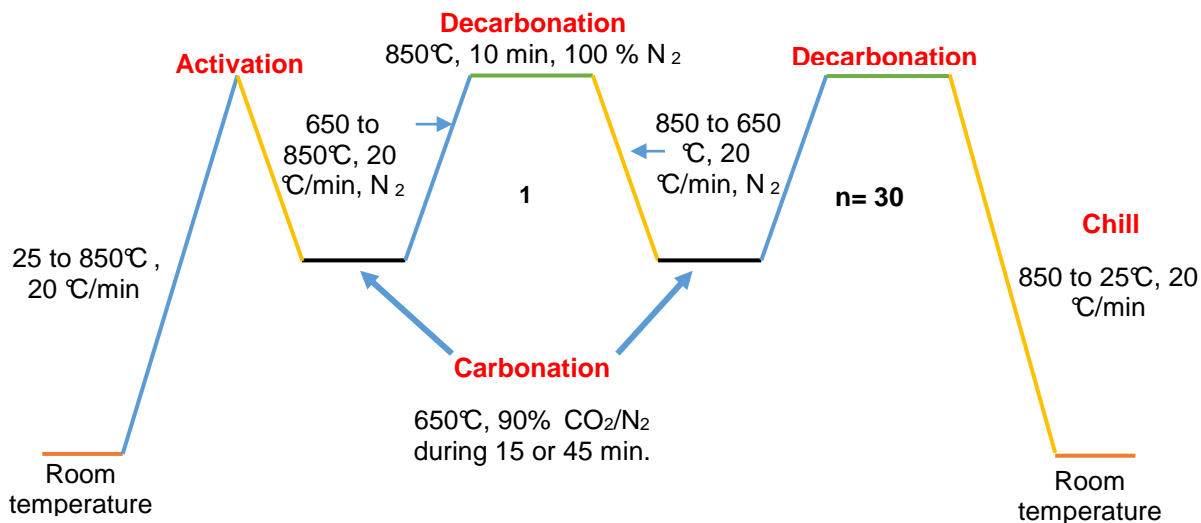
The morphology of the Saffil-CaO sorbents was examined using scanning electron microscopy (SEM; Hitachi SU8230). The distribution of the active phase over the fibrous support was investigated by energy-dispersive X-ray spectroscopy (Oxford Instruments Aztec Energy EDX system). The textural properties of the Ca-Sa-%-WI sorbents were investigated by gas adsorption. Surface areas were measured using the Brunauer-Emmett-Teller (BET) technique: pore size distributions were measured by means of a Nova 2002 Quantachrome Instrument. Before performing the analysis, the sorbents were degassed under reduced pressure for 3h at  $200^\circ\text{C}$ . The pore size distributions were calculated using the method proposed by Barrett-Joyner-Halenda (BJH).

The chemical composition of the as-prepared sorbents was determined through X-ray fluorescence spectroscopy (XRF: Rigaku ZSC Primus II). This enabled the CaO loadings

to be determined accurately. Because of the fibrous nature of the samples a fusion bead method was applied to prepare the XRF samples <sup>44</sup>. X-ray powder diffraction (XRD) was used for phase analysis (Bruker D8). In order to identify the crystalline phases, the peak positions and intensities were compared to reference patterns from the International Centre for Diffraction Data (ICDD) by means of X'Pert HighScore Plus software (version 4.5).

The CO<sub>2</sub> carrying capacity and multicycle durability of Ca-Sa-%-WI sorbents was assessed by thermogravimetry (Mettler Toledo TGA/DSC1). Initially an isothermal test was conducted for all three sorbent loadings over a 45 min time period ( $T_{\text{carbonation}} = 650^{\circ}\text{C}$ ). The first 'activation' step involved heating to 850°C at 20°C/min under an inert atmosphere (pure N<sub>2</sub>). Subsequently, the temperature was lowered to 650°C and then the gas flow was switched to 90% CO<sub>2</sub>/10% N<sub>2</sub>. After 45 min, the carbonated specimen was subjected to a higher temperature ( $T_{\text{decarbonation}} = 850^{\circ}\text{C}$  for 10 min) to decompose the carbonate phase and release the CO<sub>2</sub> previously captured (decarbonation). This process was conducted in flowing N<sub>2</sub>. The flow rate applied in the course of the activation, carbonation and decarbonation stages was 50 ml/min. Multicycle performance was evaluated over 30 continuous cycles of CO<sub>2</sub> sorption-desorption employing the TGA program illustrated in Figure 1.





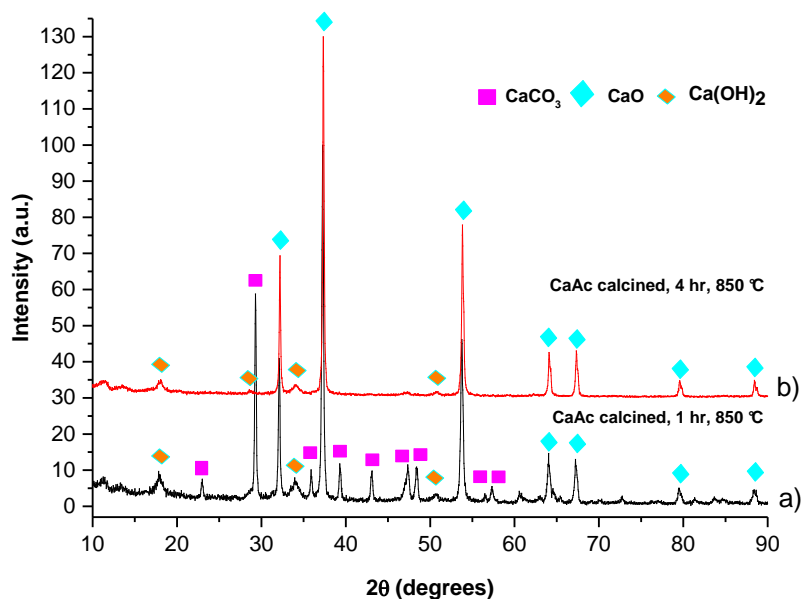
**Figure 1.** TGA program used for conducting uptake capacity and thermal stability (durability) in multicycle tests.

### 3. Results and Discussion

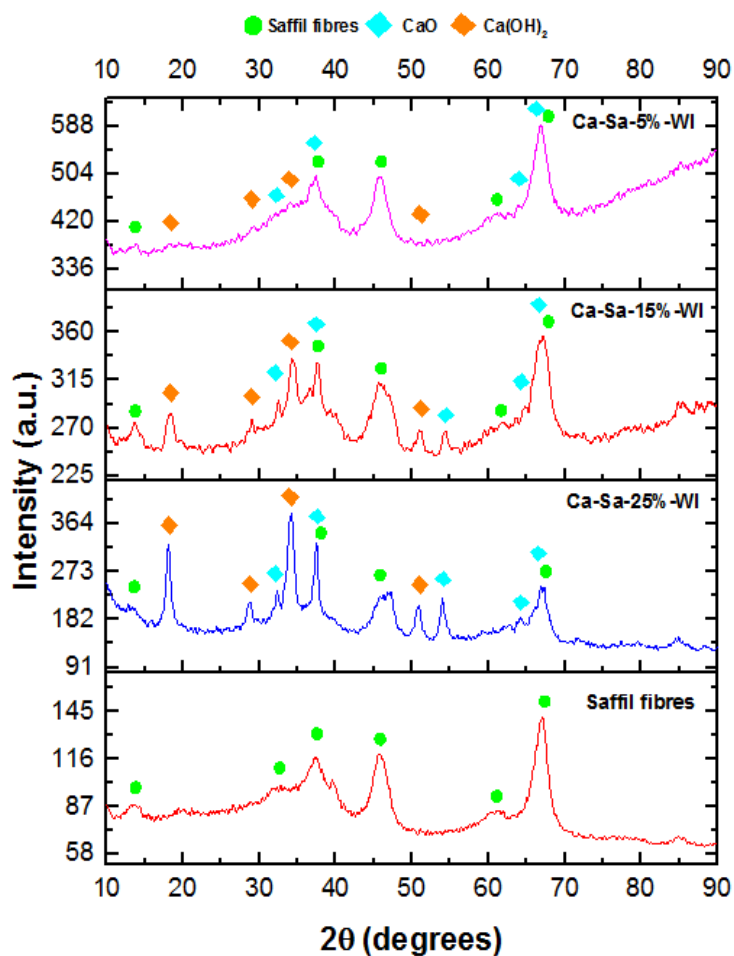
#### 3.1 Characterization of sorbents

XRD diffraction experiments were initially carried out to determine the optimal preparation conditions for CaO-Saffil sorbents. The patterns for decomposition of CaAc (without Saffil) performed at 850°C for 1 h gave a mixture of CaCO<sub>3</sub>, CaO and Ca(OH)<sub>2</sub>, Figure 2a. Rietveld refinement analysis confirmed that the mixture comprised only ~60% CaCO<sub>3</sub>. Increasing the calcination time to 4 h eliminated the CaCO<sub>3</sub> peaks, giving a mixture of CaO (~96%) and a minor amount of secondary phase (Ca(OH)<sub>2</sub>), Figure 2b. Hence, heat-treatment at 850 °C for 4 h was adopted as the standard calcination conditions for the next trial involving CaAc impregnation of Saffil: the resulting XRD patterns showed CaO and minor peaks owing to Ca(OH)<sub>2</sub> plus characteristic broad peaks of δ-Al<sub>2</sub>O<sub>3</sub> - the principal component of the Saffil fibres, Figure 3. The dominance of broad δ-Al<sub>2</sub>O<sub>3</sub> peaks

precluded any meaningful Rietveld analysis of the XRD data from impregnated samples. However, the proportion of sorbent was determined by chemical analysis, as described below. The  $\text{Ca(OH)}_2$  in the various samples probably forms due to interaction with moisture from air. This effect termed air-slaking was apparent because of the high reactivity of nanometric-sized  $\text{CaO}$  formed from decomposition of  $\text{CaAc}$ , as the surface area plays an important role in the air slaking process <sup>45</sup>.



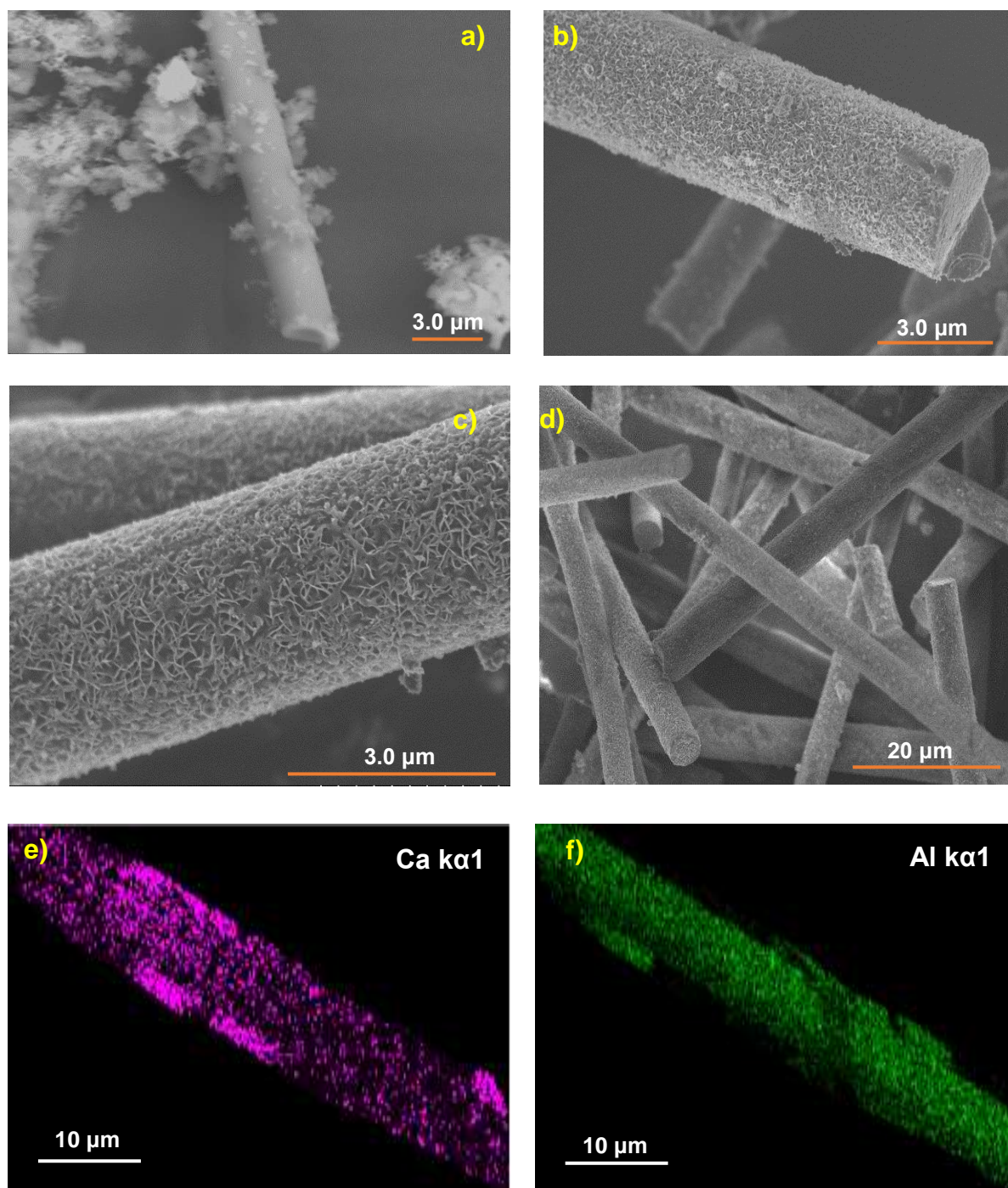
**Figure 2.** X-ray diffraction patterns collected from two  $\text{CaAc}$  samples which were subjected to thermal decomposition at  $850\text{ }^\circ\text{C}$  for (a) 1h and (b) 4h. Phase identification was performed by reference to ICDD  $\text{CaCO}_3$  01-080-9776,  $\text{CaO}$  01-070-5490 and  $\text{Ca(OH)}_2$  07-076-0570.



**Figure 3.** X-ray powder diffraction patterns of the CaO-based sorbents prepared by wet impregnation with different notional CaO contents, 5, 15, 25 wt. % and calcined at 850°C for 4 h. For comparison a Saffil fibre diffraction pattern is also shown.

The effect of solids loading and the effect of stirring during dehydration on the quality of the sorbent coating was examined using SEM, Figure 4. The vigorously stirred samples (~ 500 rpm), contained many agglomerated particles that were not attached to the support fibres, Figure 4a, whereas static conditions gave continuous coatings with fewer agglomerates, Figure 4b. Hence the static drying method was adopted throughout. The non-stirred 5 wt.% samples were of greatest uniformity-virtually all of the surface of the fibres was coated by CaO with no evidence of detached agglomerates, Figure 4c. High

magnification SEM micrographs revealed the coatings had a flake-like morphology with nanoscale dimensions. In non-stirred samples a predominantly heterogeneous nucleation process was implied by the uniformity of the sorbent coating on the Saffil substrate as evidenced from SEM-EDX mapping, Figure 4d-f.



**Figure 4.** SEM-EDX analysis performed for the Ca-Sa-%-WI sorbents prepared in different ways: a) Ca-Sa-25%-WI sorbents under vigorous stirring (500 rpm); b) Ca-Sa-25%-WI sorbents without stirring; c) Ca-Sa-5%-WI without stirring; d) lower magnification view of Ca-Sa-25%-WI coated fibres( non-stirred); e) and f) EDX chemical mapping indicating elemental distribution of calcium and aluminium performed for Ca-Sa-25%-WI .

Quantification of the total amount of sorbent deposited on the Saffil fibres was obtained using X-ray fluorescence spectroscopy (Table 2). The amount of CaO detected in all three sorbent loadings was in reasonable agreement with the notional values (5, 15 and 25 wt. %). For simplicity of presentation, the notional 5, 15, 25 wt. % terminology is retained throughout the manuscript, but reference to Table 2 provides the accurate loadings. The composition of the uncoated fibres was found to be within 1-2 % of the values specified by the supplier, confirming the accuracy of the analytical technique.

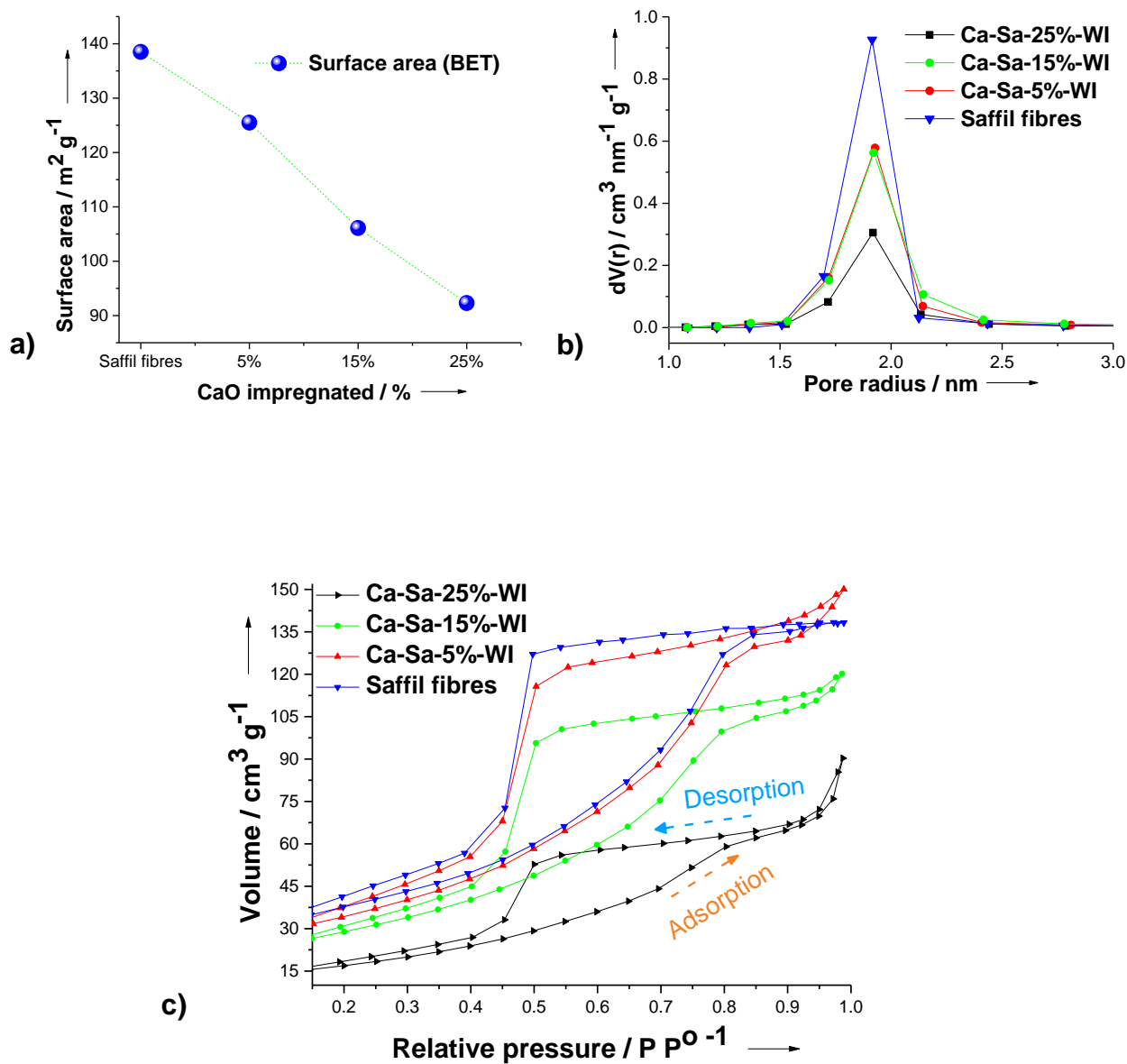
<b>CaO-based sorbents</b>	<b>CaO (%)</b>	<b>Al<sub>2</sub>O<sub>3</sub> (%)</b>	<b>SiO<sub>2</sub> (%)</b>
<b>Ca-Sa-25%-WI</b>	22.4	73.9	3.7
<b>Ca-Sa-15%-WI</b>	13.3	81.6	5.1
<b>Ca-Sa-5%-WI</b>	4.8	91.5	3.7
<b>Saffil fibres</b>	-	96.4	3.6

**Table 2.** Summary of the chemical composition in wt. % of Ca-Sa-%-WI sorbents prepared with different CaO loads (note, stated CaO content includes any CaOH<sub>2</sub> present).

An estimate of the thickness of the CaO coating for each of the three sample loadings was obtained from SEM observations of fibre terminations. This indicated an approximate thickness of 0.18  $\mu\text{m}$ , 0.229  $\mu\text{m}$  and 0.27  $\mu\text{m}$  for 5, 15 and 25 wt.% CaO loadings respectively.

In terms of textural properties, the specific surface area (SSA) of the CaO-Saffil sorbents was measured using the BET method. The BET surface areas declined as the CaO content increased, which indicates the CaO coating was lower in SSA than that of the Saffil substrate. For the uncoated Saffil, the SSA was measured at  $\sim 139 \text{ m}^2 \text{ g}^{-1}$ , this declined in a linear manner with increasing CaO loading, reaching  $\sim 92 \text{ m}^2 \text{ g}^{-1}$  for the Ca-Sa-25%-WI sample, Figure 5a. Pore size distributions and adsorption isotherms are

presented in Figure 5b and 5c respectively. Consistent with trends in the SSA data, the volume of mesopores (size range 1.5-2 nm) diminished relative to uncoated Saffil; the evolution of the type IV isotherms was consistent with the progressive coating off Saffil by the sorbent phase <sup>46, 47</sup>. The isotherms presented in Figure 5c each displayed hysteresis, with or without impregnation. However the degree of hysteresis (pore-volume width) decreased with increasing impregnation, notably for 15% and 25% CaO samples. The isotherms were of type IV with asymmetrical boundary hysteresis type H2. This type of isotherm is consistent with pore structures formed by a 3D network of cavities of different sizes connected mainly by constrictions <sup>46, 47</sup>. Cavitation processes will govern the evaporation of the physisorbed gas. The decreased width of hysteresis in the 25 wt.%, 15 wt.% and 5 wt.% with regards to uncoated Saffil fibres is associated with the filling of pores by CaO <sup>48, 49</sup>.

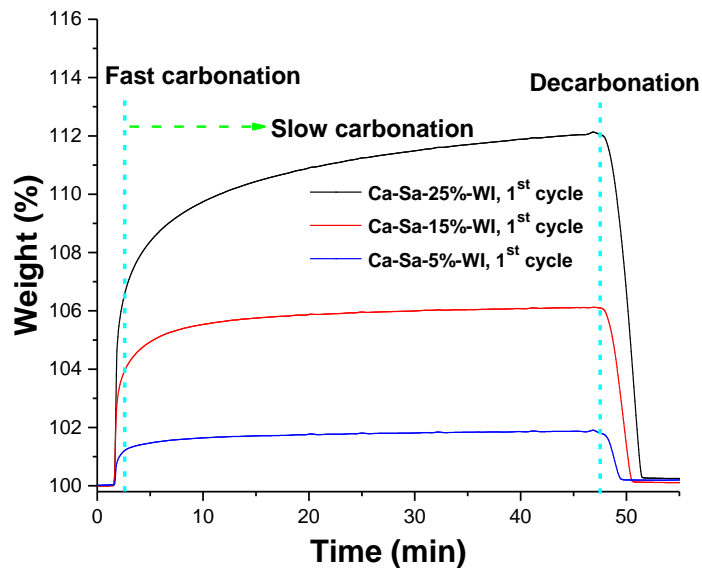


**Figure 5.** Textural properties evaluated for sorbents by  $\text{N}_2$  physisorption: a) Specific surface area as a function of CaO loading, b) pore size distribution curves and c) adsorption isotherm curves for 5, 10 and 15 wt.% CaO loadings, with data also shown for as-received Saffil fibres for comparison.



### 3.3 CO<sub>2</sub> carrying capacity

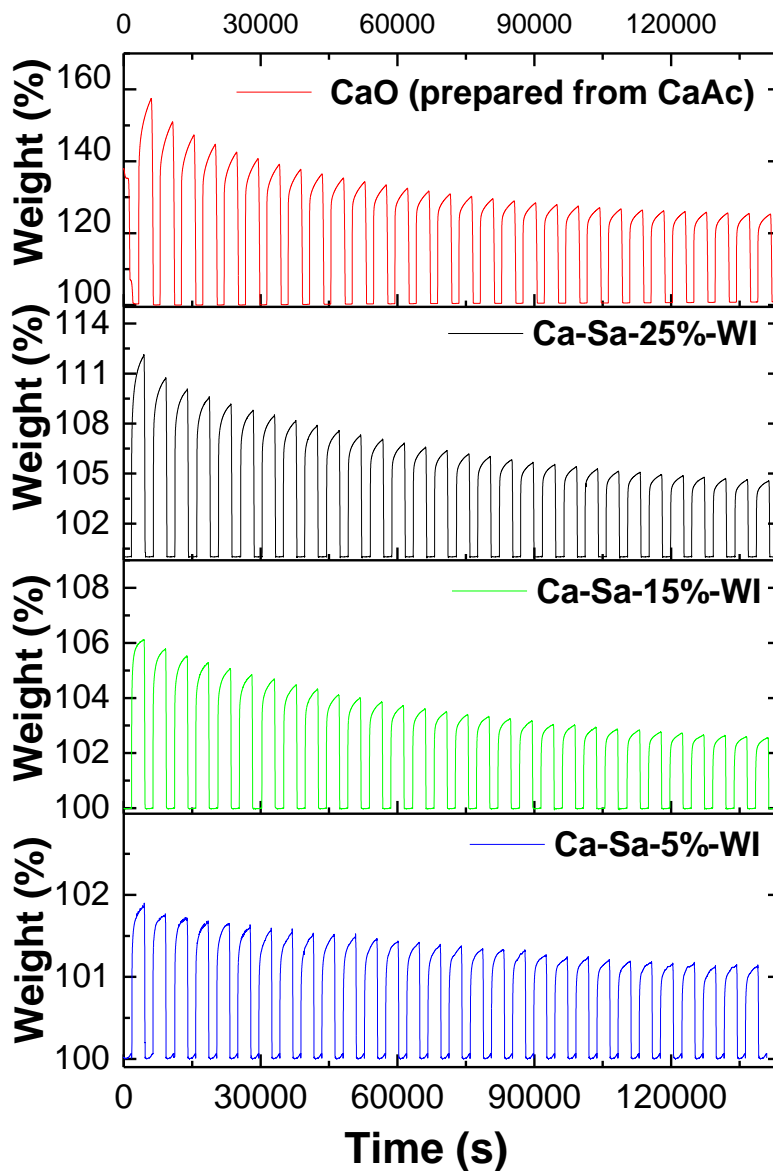
Initially, the CO<sub>2</sub> uptake was examined by isothermal TGA at 650°C for a 45 min period using a gaseous mixture composed of 90% CO<sub>2</sub>, balance N<sub>2</sub>. The results shown in Figure 6 indicate that the CO<sub>2</sub> capture process involves two stages; a fast carbonation reaction, with a ~65% mass increase in the first 2 min, followed by a slower diffusion-controlled regime<sup>50</sup>. The decarbonation reaction conducted at 850°C in presence of pure N<sub>2</sub> was rapid.



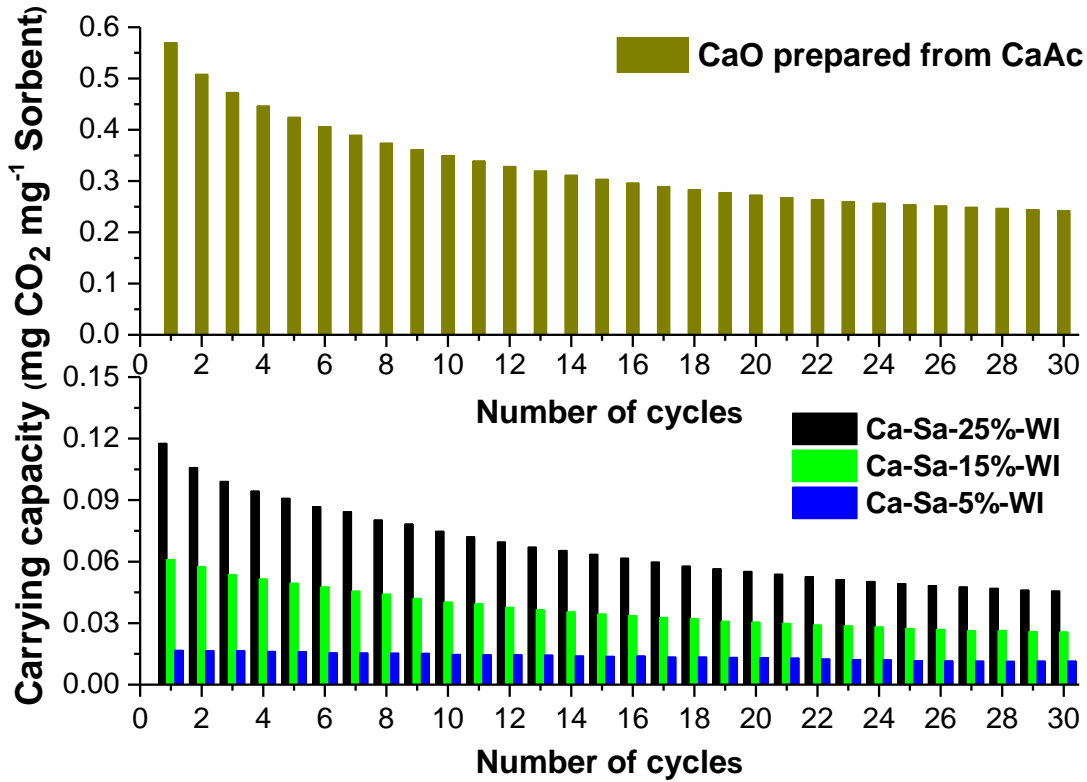
**Figure 6.** Isothermal carbonation profiles for the Ca-Sa-x%-WI sorbents tested by TGA (carbonation 650°C and decarbonation 850°C).

Multicycle carbonation-decarbonation TGA results are shown in Figure 7. The relative decay over 30 cycles was lowest in the Ca-Sa-5%-WI sample, albeit the carrying capacity was also lowest, as would be expected given the differing thicknesses of coatings and the additional particulate phase in the 15 and 25 wt.% samples. The carrying (CO<sub>2</sub> uptake) capacities in cycle 1 were 0.017 mg, 0.061 and 0.118 mg of CO<sub>2</sub>/mg of sorbent for 5, 15 and 25 wt.% samples, respectively.

and 25 wt.% samples respectively. Bar charts representing the changes in capacity are presented in Figure 8.



**Figure 7.** Carrying capacity evolution throughout 30 continuous carbonation-decarbonation cycles of Ca-Sa-%-WI sorbents impregnated with 25%, 15% and 5% of active phase and CaO prepared from CaAc. Carbonation (90 % CO<sub>2</sub>) at 650°C in presence of a gaseous mixture composed by 90% CO<sub>2</sub> with N<sub>2</sub> as balance, whilst the decarbonation stage was carried out in pure N<sub>2</sub> at 850°C. Note the difference in wt.% scales for different samples.



**Figure 8.** Carrying capacities over 30 TGA cycles of unsupported CaO (upper diagram) and Saffill supported CaO (lower diagram): (90% CO<sub>2</sub>). Note the different capacity scale on each diagram.

The uptake capacities were calculated on the basis of equation (1) presented below.

$$CC_N = \frac{(m_{f,N} - m_i)}{m_i} \quad (1)$$

Where the subscript  $N$  represent the cycle in progress,  $CC_N$  is the maximum carrying capacity of the sorbent at cycle  $N$ ,  $m_i$  is the mass of the sorbents post-activation and  $m_{f,N}$  is the mass of sorbent in the course of the cycle  $N$ .

By cycle 30 around 30% of carrying capacity was lost by the Ca-Sa-5%-WI sorbent whereas the higher loadings Ca-Sa-15%-WI and Ca-Sa-25%-WI exhibited a more substantial decline in reactivity of ~50% and ~60% respectively, Figure 8. As a benchmark, multicycle TGA and carrying capacity data for a sample of calcined CaAc, produced under comparable conditions but without Saffil, are also shown in Figure 8. This illustrates there is little difference in relative decaying performance of the unsupported sorbent and the two highest loadings studied, Ca-Sa-15%-WI and Ca-Sa-25%-WI. However the lowest loading 5 wt.% sample with the thinnest coating showed greatest durability. This is attributed to the mechanical clamping effect of the substrate and the tensile forces imparted throughout the coating (anticipated to arise due to different thermal expansion coefficients of Saffil and CaO) which prevent lateral shrinkage as is documented for thin films of other ceramic materials on planar substrates<sup>51</sup>. For the thicker coatings of the 15 and 25 wt.% samples, a smaller proportion of the depth of the coating is subject to the interfacial clamping by the Saffil substrate and so volumetric densification is more pronounced after repeat carbonation-decarbonation cycles. There would also be a contribution due to densification of the free-standing agglomerates identified by SEM in these higher loadings.

In the literature, several models have been proposed to predict sorbent degradation over a large number of thermal cycles. For instance, Abanades et al. and Lysikov et al. proposed equations to determine the CaO capacity decay in recarbonation-decomposition cycles. The conversion model proposed by Abanades et al. (equation (2)) arises from a series of adaptations performed to a second-order equation for a catalyst deactivated by sintering<sup>52</sup>. In equation (2),  $X_n$  is the conversion at cycle  $N^{\text{th}}$ ,  $k$  is the deactivation constant and  $X_r$  is the residual conversion. It must be mentioned that  $k$  is calculated by curve fitting. Moreover, Lysikov et al. rearranged the semi-empirical model suggested by Abanades et

al. and also introduced a sintering exponent  $n$  that is aimed to improve the correlation factor  $R^2$ . As can be noticed in equation (3), the authors changed the nomenclature but the same three fitting coefficients are involved ( $k$ ,  $n$  and  $a_\infty$ )<sup>53</sup>.

$$X_N = \frac{1}{\frac{1}{1-x_r} + kN} + x_r \quad (2)$$

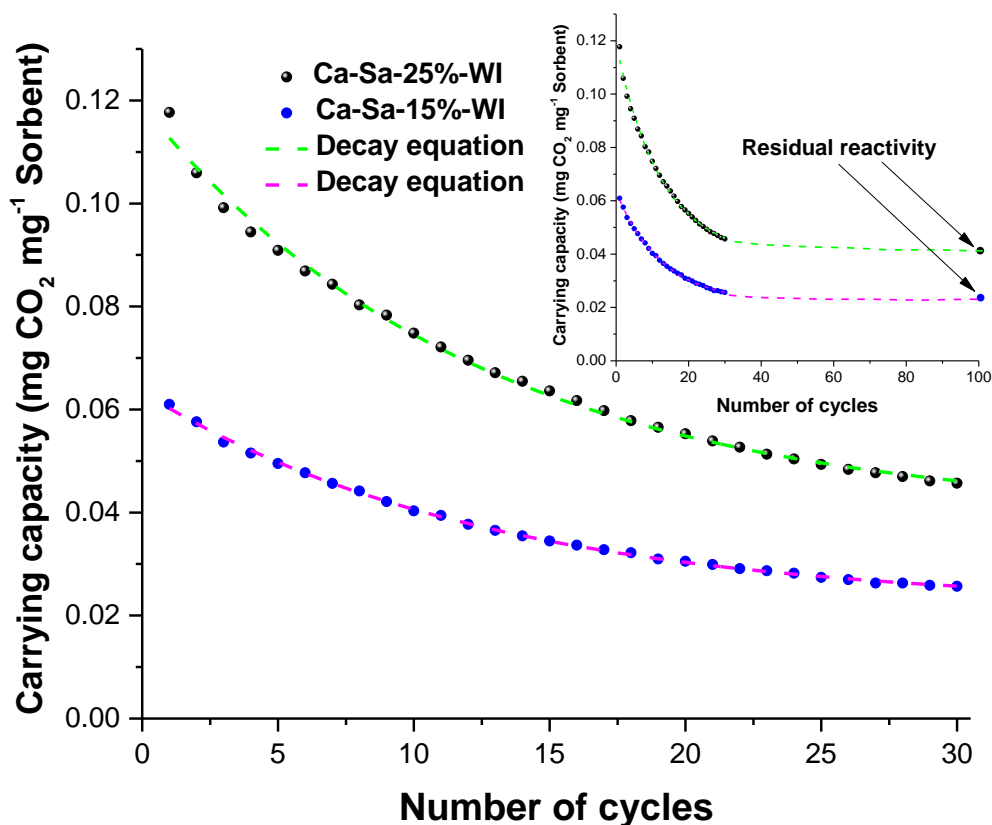
$$a_N = \frac{1 - a_\infty}{(1 + kN)^n} + a_\infty \quad (3)$$

In an attempt to determine the residual carrying capacities of both Ca-Sa-25%-WI and Ca-Sa-15%-WI sorbents, equations (2) and (3) were fitted with the experimental results showed in Figure 9. From the non-linear curve fitting analysis, the R-squared values were below 0.92. Accordingly, a simple exponential-decay model coming from a first-order deactivation equation was proposed and used to correlate the experimental data. In the equation (4) that best describes the recarbonation capacity ( $a_{cc,N}$ ) in the course of the carbonation-decarbonation cycles, the term  $K$  represent again the decay constant,  $a$  is pre-exponential factor,  $N$  is the cycle and  $a_r$  is the residual carrying capacity.

$$a_{cc,N} = a * e^{-kN} + a_r \quad (4)$$

In the curves displayed in Figure 9, dashed lines correspond to the non-linear fit performed to the experimental data. It can be discerned that there was a strong correlation between the exponential decay model and the experimental data. By using equation (4), it was possible to obtain R-squared values >0.995. According to the parameters evaluated, comparable decay constant values were obtained for the sorbents with 15 and 25 wt. %, namely, 0.0809 and 0.0816. The results apparently indicate that both sorbents exhibited very similar decay rates, as. Based on the fitting parameters, the residual carrying capacities calculated at  $a_N \cong a_r$  were 0.02191 and 0.03925 mg of CO<sub>2</sub>/mg of sorbent,

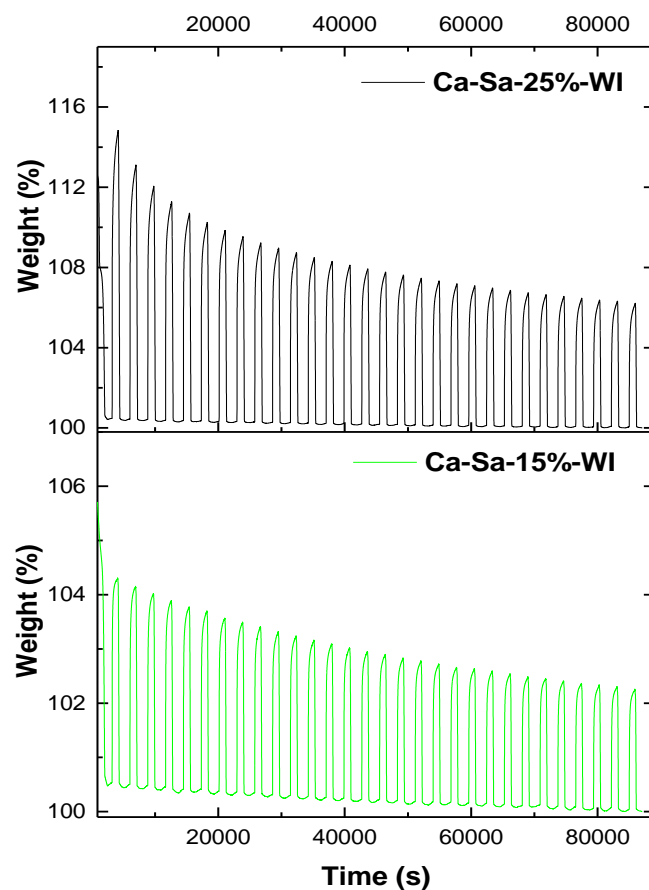
where the higher carbonation capacity belongs to the sorbent loaded with 25 wt.% of CaO. Residual reactivity in Ca-Sa-5%-WI was not modelled as the depletion trend was much less severe (Figure 8). The capture capacity was constant in 0.012 mg of CO<sub>2</sub>/mg of sorbent between cycles 25<sup>th</sup> to 30<sup>th</sup>, and so this value corresponds to its residual reactivity.



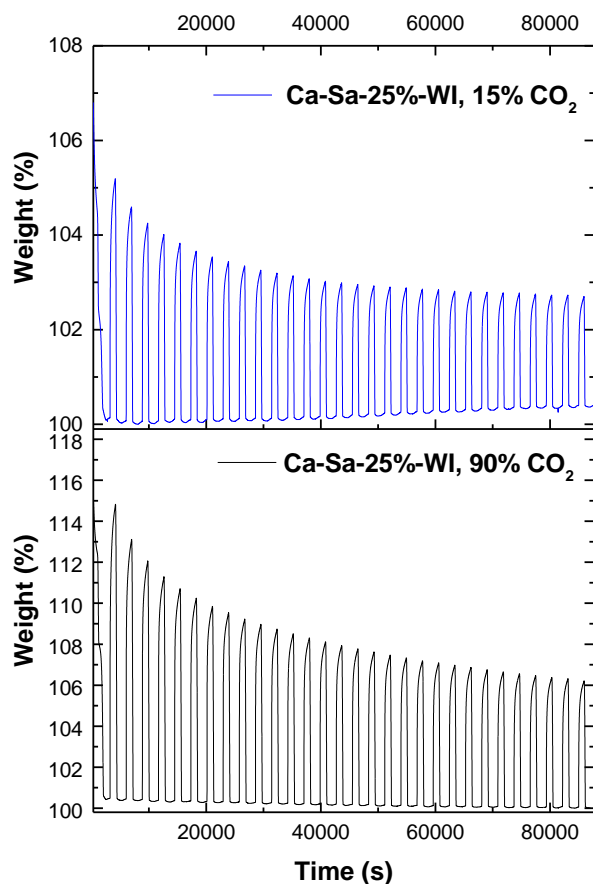
**Figure 9.** Residual reactivity predicted by fitting a decay model into carrying capacity curves. R-squared values >0.995 indicates that the exponential model (dashed lines) is in good agreement with experimental data.

Although CO<sub>2</sub> capture experiments performed with carbonation times of 45 min provided useful information on maximum CO<sub>2</sub> sorption capacity for Ca-Sa-%-WI sorbents, such a lengthy reaction is impractical for industrial applications. Consequently, sorbents with 15 wt % and 25 wt.% CaO were evaluated over shorter uptake periods, 15 min: the other carbonation-calcination conditions were the same as in the previous tests. Multicycle TGA

profiles presented in Figure 10 revealed capture capacities and performance losses for 30 cycles with 15 min carbonation periods similar to those observed in 45 min. This finding is consistent with the isothermal TGA data shown in Figure 6 indicating most of the uptake occurred within the first few minutes due to an initial fast carbonation associated with surface reactions. Furthermore, the sorption characteristics in 15 % CO<sub>2</sub> were compared to the results for 90 % CO<sub>2</sub> gas streams, for a 15 Figure 11. As expected, there was a decline in amount of CO<sub>2</sub> absorbed relative to 90 % CO<sub>2</sub> stream.



**Figure 10.** Multicycle CO<sub>2</sub> capture profiles for Ca-Sa-15%-WI and Ca-Sa-25%-WI (90% CO<sub>2</sub> carbonation). Carbonation-decarbonation reactions were conducted at 650°C and 850°C, respectively with a carbonation dwell time of 15 min .



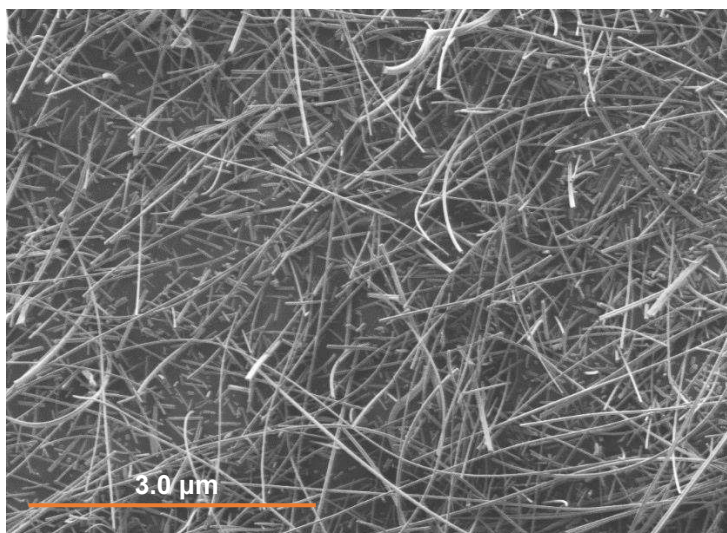
**Figure 11.** Comparison of 15 % CO<sub>2</sub> and 90 % CO<sub>2</sub> carbonation for Ca-Sa-25%-WI.

Carbonation and decarbonation reactions were conducted at 650°C and 85 0°C;  
carbonation dwell times of 15 min.

On the basis of the studies carried out by various authors, natural and synthetic unsupported CaO powders tend to present a marked capture capacity depletion in the course of the first 10 cycles (>60%). This sharp decay is occasioned by sintering as described earlier<sup>54, 55</sup>. However, the outcomes presented for the thinnest 5 wt.% CaO coating on Saffil revealed extended durability but at the cost of reduced initial capacity.



This sorbent retained 70% uptake capacity after 30 extended carbonation-decarbonation TGA cycles.



**Figure 12.** SEM micrograph of Ca-Sa-5%-WI sample revealing open structure of Saffil fibrous matt

The possibility of improved multicycle durability provided the motivation for selecting a fibrous low-density mat of Saffil as a sorbent support material. The concept being that the loosely entwined fibres present minimal contact between adjacent fibres onto which CaO was deposited. This open structure is illustrated in Figure 12. Thus any sintering should be restricted mainly to within an individual layer of sorbent coating. The experimental results indicate that if the coating is  $< 0.2 \mu\text{m}$  in thickness (Ca-Sa-5%-WI) there is indeed little change in carrying capacity over multiple cycles (Figure 8). The thicker layers present in the higher CaO loadings are more susceptible to sintering as substrate clamping is less effective in thicker coatings (separate agglomerates may also have an effect). The disordered network of cavities in low density assemblies of Saffil fibres may have other advantages as the structure may allow a much lower pressure drop in the fixed bed reforming unit compared to other types of sorbent.

In terms of durability, one of the best performing mixed powder sorbents reported in the literature is the nano CaO/Al<sub>2</sub>O<sub>3</sub> prepared through a complex solution synthesis procedure in which nano calcium carbonate, aluminium sol and hexametaphosphate are blended to form a powder composite <sup>19</sup>. This sorbent retained 68 % of its original capacity after 50 continuous cycles in which carbonation-calcination reactions took place at 650°C and 800°C, respectively. This durability associated with the formation of a Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> co-existing phase is comparable to that of Ca-Sa-5%-WI <sup>19</sup>. Synthetic CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (mayenite) sorbents evaluated during 25 carbonation-calcination cycles attained capture capacities of ~0.2 mg CO<sub>2</sub>/ mg sorbent. Their capture capacity remained stable after cycle 12: their much higher loadings of CaO (75% and 85%) allowed greater CO<sub>2</sub> carrying capacity than the 5-25 wt.% CaO/-Saffil sorbents in the present work <sup>56</sup>. Comparisons to a full range of alternative sorbents are available in references <sup>57, 58</sup>.

The simplicity of CaO/Saffil sorbent synthesis procedures, allied to the low thermal degradation of the sorbent and the possibility for future implementation as a CO<sub>2</sub> sorbent in SESR reactors with lower pressure drops suggest this type of fibrous substrate is worthy of further development.

## 4. Conclusions

Saffil fibres have been demonstrated as a new support material for CaO. The optimal synthesis parameters to load different contents of active phase (nominally 5, 15 and 25 wt.% CaO) by a wet impregnation method were determined. Microstructural analysis by scanning electron microscopy showed that CaO can be grown with a well-structured nanoflake morphology under appropriate synthesis conditions. The most favourable synthesis conditions in terms of multicycle durability were: wet infiltration of Saffil fibres without stirring; calcination at 850°C for 4h. The wt.% CaO loading produced the least degradation in multicycle TGA trials with only a ~30 % decline in CO<sub>2</sub> uptake capacity after 30 cycles. For 25 wt.% CaO samples the decay was ~ 60 %. The 25 wt.% sample had an initial uptake capacity of 0.118 mg CO<sub>2</sub>/mg CaO but this declined to 0.017 mg and 0.061 mg CO<sub>2</sub>/mg CaO for the 15 wt.% and 5 wt.% samples respectively. The improved consistency in sorbent performance of the 5 wt.% sample is attributed to the increased effects of substrate clamping and inhibition of the densification.

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