

# 1 Potassium based sorbents from fly ash for high temperature CO<sub>2</sub> capture

2

3 Aimaro Sanna<sup>1\*</sup>, M. Mercedes Maroto-Valer<sup>1</sup>

4

5 <sup>1</sup> Centre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences,  
6 Heriot-Watt University, Edinburgh EH14 4AS, UK.7 \* Corresponding author: Aimaro Sanna, 3.04 Nasmyth Building, School of Engineering and Physical Sciences,  
8 Heriot-Watt University, Edinburgh, EH14 4AS. E-mail: [A.Sanna@hw.ac.uk](mailto:A.Sanna@hw.ac.uk)

9

## 10 Abstract

11 Potassium-fly ash (K-FA) sorbents were investigated for high temperature CO<sub>2</sub> sorption. K-  
12 FAs were synthesised using coal fly ash as source of silica and aluminium. The synthesised  
13 materials were also mixed with Li<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> to evaluate their effect on CO<sub>2</sub> capture.  
14 Temperature strongly affected the performance of the K-FA sorbents, resulting in a CO<sub>2</sub>  
15 uptake of 1.45 mmol CO<sub>2</sub>/g sorbent for K-FA 1:1 at 700°C. The CO<sub>2</sub> sorption was enhanced  
16 by the presence of Li<sub>2</sub>CO<sub>3</sub> (10 wt%), with the K-FA 1:1 capturing 2.38 mmol CO<sub>2</sub>/g sorbent  
17 at 700°C in 5 min. This sorption was found to be similar to previously developed Li-Na-FA  
18 (2.54 mmol/g) and Li-FA (2.4 mmol/g) sorbents. The presence of 10% Li<sub>2</sub>CO<sub>3</sub> also  
19 accelerated sorption and desorption. The results suggest that the increased uptake of CO<sub>2</sub> and  
20 faster reaction rates in presence of K-FA can be ascribed to the formation of K-Li eutectic  
21 phase, which favours the diffusion of potassium and CO<sub>2</sub> in the material matrix. The cyclic  
22 experiments showed that the K-FA materials maintained stable CO<sub>2</sub> uptake and reaction rates  
23 over 10 cycles.

24

25 **Keywords:** Absorption, CO<sub>2</sub> sorbents, Fly ash, Potassium, CCS

26

## 27 Introduction

28 The requirement for mitigating climate change is supporting the development of CO<sub>2</sub> capture  
29 technologies. At the state of the art, CO<sub>2</sub> absorption by liquid organic amines is the most  
30 advanced technology (Leung et al., 2014). However, amine degradation in both absorption  
31 and stripping steps and the potential emission of harmful compounds need to be addressed for  
32 a widespread commercialisation of this technology (Manzoor et al., 2014; Vega et al., 2015).  
33 The incorporation of amines into porous support has been proposed as alternative approach,  
34 but the low amine utilization ratio and the loss of amine compounds in the regeneration step  
35 required the development of new sorbents (Zhao et al., 2014).

36 A suitable sorbent for CO<sub>2</sub> capture from flue gas should satisfy several important criteria to  
37 compete with the present technologies, including high sorption capacity, adequate  
38 sorption/desorption kinetics and stability, mechanical strength etc. (Sabouni et al., 2014). A

39 large number of physical adsorbent materials have been considered for low temperature (<  
40 150°C) CO<sub>2</sub> capture such as activated carbon, zeolites and metal organic frameworks (MOFs)  
41 (Samanta et al., 2012).

42 CO<sub>2</sub> capture at high temperatures (> 400°C) using solid sorbents with high selectivity and  
43 regenerability has also been proposed as an alternative to low-temperature CO<sub>2</sub> capture due to  
44 reduced efficiency penalties (Olivares-Marín et al., 2010). Due to their high decomposition  
45 temperature (T > 800°C), alkaline ceramics, mainly lithium containing compounds have been  
46 tested as CO<sub>2</sub> sorbents at high temperature (Rodríguez and Pfeiffer, 2008; Olivares-Marín et  
47 al., 2010). The CO<sub>2</sub> sorption on ceramics starts with the carbonation of the sorbents surface  
48 and continues with the diffusion of CO<sub>2</sub> through the carbonate external layer to react with the  
49 alkaline core (Rodríguez and Pfeiffer, 2008). So far, potassium has been mainly investigated  
50 as CO<sub>2</sub> sorption promoter associated to other ceramics such as Li- or Na- based sorbents,  
51 zeolites and alumina based CO<sub>2</sub> sorbents (Seggiani et al., 2013; Zhao et al., 2014; Olivares-  
52 Marín et al., 2010; Sanna et al., 2014; Sanna et al., 2015).

53 Amongst the wide range of materials tested, lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>) and aluminate  
54 (Li<sub>5</sub>AlO<sub>4</sub>) have shown the largest CO<sub>2</sub> sorption capacity and the fastest CO<sub>2</sub> sorption rate  
55 over a wide range of temperatures and CO<sub>2</sub> concentrations (Olivares-Marín et al., 2010; Kato  
56 et al., 2005, Flores-Martínez and Pfeiffer, 2015). It has been reported that the presence of 40  
57 mol% K<sub>2</sub>CO<sub>3</sub> at 600°C affects the CO<sub>2</sub> sorption capacity for Li-based sorbents (Li-FA)  
58 prepared from fly ashes (FA), with a sorption capacity of 2.43 mmol CO<sub>2</sub>/g sorbent  
59 (Olivares-Marín et al., 2010). Recently, sodium-fly ash (Na-FA) sorbents have also been  
60 proposed as high temperature CO<sub>2</sub> sorbents. Maximum CO<sub>2</sub> uptake of Na-FA sorbent was  
61 found to be 2 mmol CO<sub>2</sub>/g sorbent in presence of 20% Li<sub>2</sub>CO<sub>3</sub> additive (Sanna et al., 2014;  
62 Sanna et al., 2015). Even if lithium based materials present very good CO<sub>2</sub> uptake  
63 performance, it should be noted that lithium is considered a rare element in comparison to  
64 sodium and potassium. It has been assessed that demand for lithium is growing at a fast rate  
65 and that this rate exceeds projected availability by 25% (The Financialist, 2014). Therefore,  
66 K-based sorbents can be considered not rare compared to lithium based materials.

67 The use of potassium carbonate, in addition to other alkali-metal materials was firstly studied  
68 by NASA for space applications (Onischak et al, 1978). Also, potassium has been previously  
69 identified as a good candidate for low temperature CO<sub>2</sub> sorption while utilizing an activated  
70 carbon as support (Hayashi et al., 1998). In addition, silver carbonate in combination with

71 alkali metal silicate (including potassium), alkali metal carbonate (potassium and/or sodium)  
72 have been evaluated as CO<sub>2</sub> sorbent (Nalette et al., 1992).

73 Thermodynamic analysis including enthalpy and free energy changes have been calculated  
74 for both K-silicate sorption and regeneration reactions (Hoffman and Pennline, 2001). Results  
75 for alkali-based sorbents are generally favourable in that the forward (CO<sub>2</sub> absorption)  
76 reaction rate is typically much larger than the reverse reaction. Potassium carbonate was  
77 found to be suitable for CO<sub>2</sub> capture at low absorption temperatures (less than 145°C), while  
78 calcium oxide is more suitable for high absorption temperatures (less than 860°C) (Hoffman  
79 and Pennline, 2001). For this reason, potassium-based sorbents have been proposed as  
80 effective ambient temperature CO<sub>2</sub> sorbent in confined spaces (Zhao et al., 2014). The CO<sub>2</sub>  
81 sorption capacities were calculated as 0.87, 1.18, 0.34, 0.53, and 0.15 mmol CO<sub>2</sub>/g for  
82 K<sub>2</sub>CO<sub>3</sub>/Activate carbon, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>/zeolite-5A and K<sub>2</sub>CO<sub>3</sub>/13X-zeolite,  
83 respectively.

84 Despite the fact that potassium carbonate has been widely tested as CO<sub>2</sub> capture promoter  
85 (Olivares-Marín et al., 2010; Seggiani et al, 2011; Flores-Martínez and Pfeiffer, 2015; Sanna  
86 et al, 2015), there is a lack of works on the potential use of K-silicates derived from fly ash as  
87 high temperature CO<sub>2</sub> sorbents and their behaviour when used in presence of CO<sub>2</sub> sorption  
88 promoters. Moreover, previous studies have only examined the CO<sub>2</sub> capture behaviours of  
89 alkali metal-based sorbents under conditions of 50–100°C, 5–20% CO<sub>2</sub> and 5–20% H<sub>2</sub>O  
90 (Zhao et al, 2011; Zhao et al, 2013; Zhao et al, 2014). It is unclear whether CO<sub>2</sub> sorption  
91 capacity changes at higher temperatures. The aim of the present work was to produce pure  
92 and Li-doped aluminosilicates from fly ash and assess their CO<sub>2</sub> sorption capacity under  
93 different conditions.

94

## 95 **Experimental**

96 Fly ashes (FA) have been used as SiO<sub>2</sub> source and collected from a cyclone filter. The parent  
97 sample was characterised by particles size distribution and XRF in previous work (A. Sanna  
98 et al, 2015). The potassium based CO<sub>2</sub> sorbents were synthesised by mixing the FA with  
99 K<sub>2</sub>CO<sub>3</sub> (Acros Organics) at different K<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> (from FA) molar ratios (2:1 and 1:1) by  
100 using an agate mortar and pestle. The mixed powders were calcined in a muffle furnace at  
101 800°C for 8 hours. The sorbent synthesis is described as follow:



103

104 After calcination, the materials were homogenised using a Mortar Grinder (Pulverisette  
105 2, Fritsch) for 60 seconds to eliminate any potential agglomeration.  $\text{Ca}(\text{OH})_2$  and  $\text{Li}_2\text{CO}_3$   
106 were also used as  $\text{CO}_2$  sorption promoters (10 mol%) by addition after the calcination step.

107 The resulting sorbents were grinded and characterized by different techniques, including  
108 powder X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and Fourier  
109 Transformed Infrared (FTIR). A Bruker Nonius X8-Apex2 CCD diffractometer equipped  
110 with an Oxford Cryosystems Cryostream, typically operating at 100 K was used for the XRD  
111 analysis. A PerkinElmer Frontier infrared spectrometer was used to gain additional  
112 information on the crystal structure of the synthesised sorbents before and after the  $\text{CO}_2$   
113 absorption experiments.

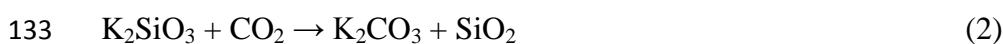
114 The  $\text{CO}_2$  capture capacity of the resultant samples was measured by using a TGA (TA Q500).  
115 About 15 mg of sample was loaded in the TGA pan for each experiment. Prior to  $\text{CO}_2$   
116 sorption testing, the samples were dried in  $\text{N}_2$  flow (95 mL/min) for 1 hr at the same  
117 temperature used for the  $\text{CO}_2$  sorption (600,700 °C). The heating rate used to rise the  
118 temperature to 600 or 700°C (before holding it for 1hr) was 25 °C/min. Then, the  $\text{CO}_2$   
119 absorption tests were performed by flowing 100%  $\text{CO}_2$  gas at the desired temperature. The  
120 weight increase due to  $\text{CO}_2$  sorption (mmol  $\text{CO}_2$ /g sorbent) was measured as a function of  
121 time at a constant temperature (600, 700 °C) and constant concentration of  $\text{CO}_2$  or flue gas  
122 (95 mL/min) at atmospheric pressure.  $\text{CO}_2$  uptake was calculated based on dry sorbents  
123 weight (after drying step). Triplicate measurements were conducted to estimate the % error in  
124 the experimental work. The measurements error (calculated as the standard deviation of  
125 triplicates) resulted lower than 5%. The  $\text{CO}_2$  desorption step was carried out at the same  
126 sorption temperature by switching the furnace atmosphere from  $\text{CO}_2$  to  $\text{N}_2$  for 1hr. Finally,  
127 ten (five for the sorbent with 10%  $\text{Li}_2\text{CO}_3$  additive) regeneration cycles were used to  
128 ascertain the stability for selected sorbents.

129

## 130 **Results & Discussion**

### 131 **Sorbents characterisation**

132 The  $\text{CO}_2$  capture reaction in presence of potassium silicate is described by the equation:



134

135 The reaction thermodynamics (Table 1) indicate that the capture reaction is overall  
 136 spontaneous ( $\Delta G < 0$ ), and at temperatures  $< 100^\circ\text{C}$   $\Delta S$  and  $\Delta H$  are negative, indicating  
 137 exothermic reaction. However, similarly to other alkali silicates, this experimental work  
 138 clearly indicates that  $\text{CO}_2$  capture is favoured at high temperature (Sanna et al., 2014).

139

140 **Table 1.** Thermodynamics of  $\text{CO}_2$  capture by K-FA in gas phase at different temperatures.

T, °C	deltaH, kJ	deltaS, J/°K	deltaG, kJ	K	Log(K)
0	-1409.8	-165.2	-1364.7	1.E+261	261.0
100	-1397.1	-125.7	-1350.2	1.E+189	189.0
200	-1382.4	-90.9	-1339.4	8.E+147	147.9
300	-1365.9	-59.4	-1331.9	2.E+121	121.4
400	-1347.6	-30.0	-1327.4	1.E+103	103.0
500	-1327.3	-1.7	-1326.0	4.E+89	89.6
600	-1307.9	21.9	-1327.0	2.E+79	79.4
700	-1289.2	42.2	-1330.2	3.E+71	71.4
800	-1269.8	61.1	-1335.4	1.E+65	65.0
900	-1220.1	104.5	-1342.6	6.E+59	59.8
1000	-1198.0	122.5	-1353.9	4.E+55	55.6

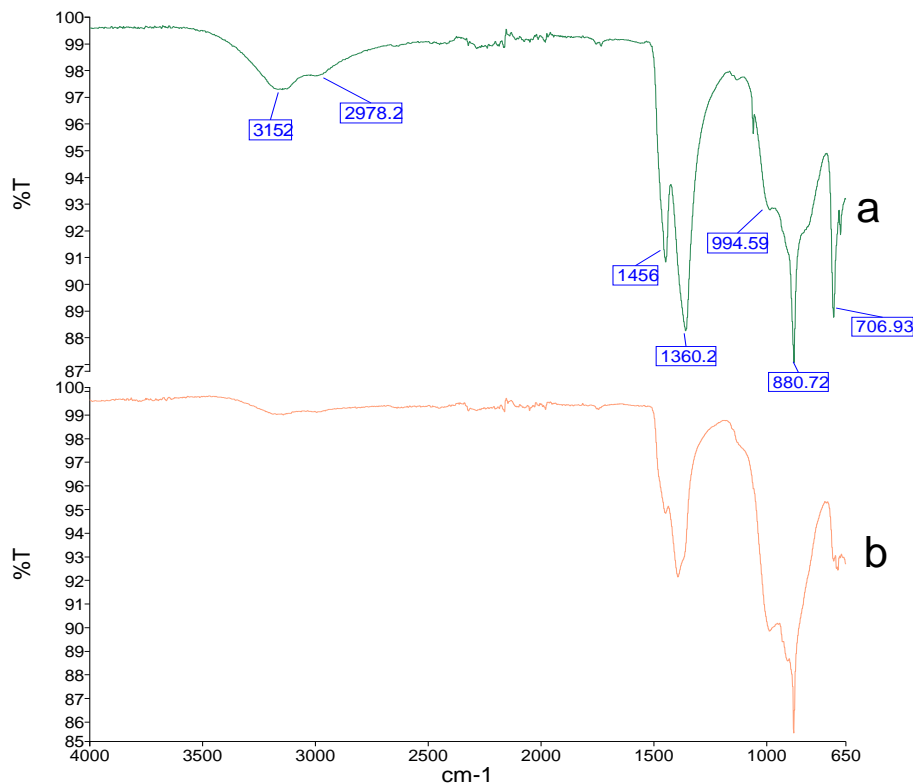
141

142

143 The major chemical bonds present in the synthesised alkali metals silicate were identified by  
 144 FTIR spectra, as shown in Fig. 1. The characteristic absorption band from deformation of  
 145  $\text{M}^+\text{OH}$  become  $\text{Si-O-M}^+$  are shown at  $880$  and  $994\text{ cm}^{-1}$  (Hindryawati et al, 2014), while the  
 146 predominant absorbance peak at  $1360\text{ cm}^{-1}$  is due to siloxane bonds ( $\text{Si-O-Si}$ ) (Thuadaij et al,  
 147 2008). The peak at  $1427\text{ cm}^{-1}$  can be attributed to  $\text{CO}_3^{2-}$  anion originating from the potassium  
 148 carbonate. As reported in previous work, the broadband between  $2800$  and  $3500\text{ cm}^{-1}$  is  
 149 attributed to silanol OH groups and adsorbed water (Kalapathy et al, 2000). The FTIR spectra  
 150 show formation of silicate structure.

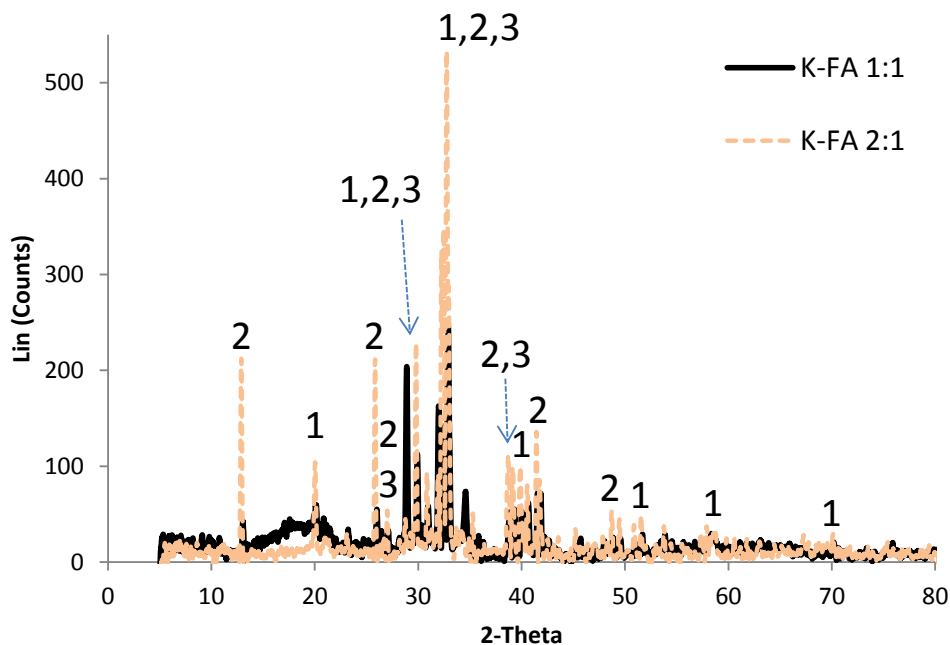
151 Figure 2 shows the XRD patterns of the synthesised K-FA. It was found that the X-ray  
 152 diffraction patterns of the two materials contain identical peaks but with different intensities.  
 153 The major peaks were identified and compared to potassium metasilicate ( $\text{K}_2\text{SiO}_3$ ), potassium  
 154 aluminium silicate ( $\text{K}_{1.25}\text{Al}_{1.25}\text{Si}_{0.75}\text{O}_4$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) using XRD  
 155 database and previous publication (N. Hindryawati et al, 2014). It was found that K-FA 1:1  
 156 structure presented a less defined crystal structure (see theta region between 15 and 25) and  
 157 with the increase of  $\text{K}_2\text{CO}_3$  used in the  $\text{K}_2\text{CO}_3$ :FA mixture (2:1), the materials structure  
 158 become more crystalline. The intense diffraction sharp peaks from 12 to 43 are associated to  
 159 potassium metasilicate and potassium aluminium metasilicate, while the sharp diffraction  
 160 peaks at 12 and 26 are solely attributed to  $\text{K}_2\text{SiO}_3$ . As can be seen in Figure 1, K-FA 2:1

161 presents more intense peaks ( $1456\text{ cm}^{-1}$ ) related to  $\text{K}_2\text{CO}_3$ . This indicates a not complete  
 162 reaction during synthesis, probably due to poor contacts between  $\text{K}_2\text{CO}_3$  and  $\text{SiO}_2$  from FA.



163  
 164 **Figure 1.** FTIR of (a) K-FA 2:1 (b) K-FA 1:1.

165



166  
 167 **Figure 2.** XRD patterns of K-FA 1:1 and K-FA 2:1. Mineral phases identified: 1 Potassium aluminium silicate;  
 168 2 Potassium carbonate; 3 Potassium metasilicate.

169

170

171 **CO<sub>2</sub> capture studies**

172 CO<sub>2</sub> capture experiments were carried out using the synthesized K-sorbents shown in Table 2.  
 173 The K-FA sorbents capacity was compared to those of Li-based and Li/Na-based fly ash  
 174 sorbents previously developed by our group (Olivares-Marin et al, 2010; Sanna et al, 2015).  
 175 The sorption experiment at 500°C was used to compare the K-FA sorbent prepared here to  
 176 the Li-FA sorbent, while the sorption at 600°C was used to evaluate the differences with the  
 177 Li-Na-FA sorbents. Table 2 shows that the K-Fa 1:1 CO<sub>2</sub> sorption capacity was three times  
 178 higher than that of Li-FA under the same conditions, while K-FA 2:1 possesses a CO<sub>2</sub>  
 179 sorption capacity double than that of Li-FA. The K-FA materials had however a lower  
 180 capacity compared to the Li-Na-FA sorbent at both 500 and 600°C.

181 Table 2 also shows a clear difference in the CO<sub>2</sub> sorption capacity when different K<sub>2</sub>CO<sub>3</sub>:FA  
 182 molar ratio were used. The K-FA sorbent shows better performance at molar ratios 1:1 (0.32,  
 183 0.36 and 1.45 mmol CO<sub>2</sub> / g sorbent at 500, 600 and 700°C, respectively), while a K-FA ratio  
 184 of 2:1 was able to chemisorb only 0.23, 0.36, 0.82 mmol CO<sub>2</sub> / g sorbent at the same  
 185 temperatures. This can be related to the different distribution of mineral phases formed during  
 186 the sorbent synthesis (see Figure 2), and a large presence of unreacted K<sub>2</sub>CO<sub>3</sub> is present in the  
 187 K-FA 2:1 (see Figure 1).

188

189 **Table 2.** Summary of the CO<sub>2</sub> capture experiments in presence of 100% CO<sub>2</sub>. 1:1 represents the K<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub>  
 190 (FA) molar ratio.

Sample	Temp., °C	Additive (mol%)	CO <sub>2</sub> sorption capacity mmol CO <sub>2</sub> / g sorbent	
			1 h	2h
<b>Olivares-Marín et al., 2010</b>				
FA-Li <sub>4</sub> SiO <sub>4</sub> (1 SiO <sub>2</sub> : 2 Li <sub>2</sub> CO <sub>3</sub> )	500		< 0.11	na
FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)	600	10% K <sub>2</sub> CO <sub>3</sub>	0.59	na
FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)	600	20% K <sub>2</sub> CO <sub>3</sub>	1.27	na
FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)	650	10% K <sub>2</sub> CO <sub>3</sub>	0.48	na
<b>Sanna et al., 2015</b>				
Li/Na-FA (0.5:0.5:1)	500		0.48	
Li/Na-FA (1:1:1)	600		0.86	1
<b>This work</b>				
K-FA 1:1	500		0.32	0.34
K-FA 1:1	600		0.36	0.39
K-FA 2:1	500		0.23	0.27
K-FA 2:1	600		0.36	0.45
K-FA 2:1	700		0.82	0.86
K-FA 1:1	700		1.45	1.50

191

## 192 **Effect of temperature and CO<sub>2</sub> promoters**

193 Figures 3 and 4 show the effect of temperature on the CO<sub>2</sub> capacity. The initial weight  
194 decrease was obtained in presence of N<sub>2</sub> flow, and represents desorption of absorbed water.  
195 The CO<sub>2</sub> sorption experiments indicate that K-FA 1:1 and 2:1 increase their CO<sub>2</sub> sorption  
196 capacity with temperature, with maximum sorption taking place at 700°C. This trend did not  
197 differ from that previously found in presence of Li- and Li-Na- silicate sorbents (Sanna et al,  
198 2015). As shown in Table 2, the K-Fa 2:1 CO<sub>2</sub> uptake (0.82 mmol CO<sub>2</sub>/g sorbent after 1 hour  
199 at 700°C) is about half compared to the CO<sub>2</sub> absorbed by using K-FA 1:1 at the same  
200 temperature (1.45 mmol CO<sub>2</sub>/g sorbent). Not only the CO<sub>2</sub> sorption capacity was higher at  
201 700°C, but also the sorption rate was faster as indicated by the slope of the sorption profiles  
202 in Figures 3 and 4. However, full desorption was not achieved under the studied conditions,  
203 as CO<sub>2</sub> desorption did not occur with both K-FA 1:1 and 2:1 and even in presence of K-FA  
204 doped with Ca(OH)<sub>2</sub>. Also, sorption took longer to achieve maximum capacity compared to  
205 using Li-FA sorbents under the same conditions, which results too long for industrial  
206 applications (Sanna et al, 2015; Olivares-Marín et al, 2010).

207 Since the pure K-FA silicates failed to desorb the CO<sub>2</sub>, a series of experiments were carried  
208 out to establish if the desorption could be improved by the presence of additives. Since  
209 previous works indicated that Li<sup>+</sup> provides the highest CO<sub>2</sub> capture capacity among all the  
210 univalent cations, if provided in the same amount in the ceramic (Walton et al, 2006; Ridha  
211 et al, 2009), was selected Li<sub>2</sub>CO<sub>3</sub> as sorbent promoter and Na<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> for  
212 comparison.

213 Figure 3 compares the CO<sub>2</sub> working capacity of K-FA 2:1 with and without Ca(OH)<sub>2</sub> at  
214 700°C. The pure K-FA 2:1 sample captured 0.82 mmol CO<sub>2</sub>/g. The CO<sub>2</sub> captured increased  
215 to 1.04 mmol/g in presence of 10% Ca(OH)<sub>2</sub>. Despite this, the Ca-additive was not able to  
216 promote CO<sub>2</sub> desorption, indicating the formation of a products layer (carbonates and  
217 oxides), which prevents CO<sub>2</sub> desorption. The addition of 10% Li<sub>2</sub>CO<sub>3</sub> to K-FA 2:1, further  
218 increased the CO<sub>2</sub> sorption to 2.25 mmol CO<sub>2</sub>/g as can be seen in Figure 6-a. Therefore, the  
219 presence of Li<sub>2</sub>CO<sub>3</sub> promoted the CO<sub>2</sub> uptake and also the CO<sub>2</sub> sorption rate, as can be seen  
220 comparing the slopes in the sorption profiles in Figures 3 and 6-a.

221 Different additives were tested in the weight ratio of 10% using the K-FA 1:1 sorbent at  
222 700°C, as presented in Figure 5. Figure 5-c indicates that the initial desorption of absorbed  
223 water in N<sub>2</sub> required longer time, so that the real CO<sub>2</sub> working capacity is larger than shown  
224 in Figure 6-b. Both Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> were successful in desorbing all the CO<sub>2</sub> previously



225 absorbed. The CO<sub>2</sub> loading capacity was also enhanced to 2.39 mmol CO<sub>2</sub>/g sorbent form  
226 1.45 mmol/g in presence of Li<sub>2</sub>CO<sub>3</sub>. Moreover, fast sorption and desorption in presence of  
227 10% Li<sub>2</sub>CO<sub>3</sub> were achieved, requiring only minutes to fully uptake the CO<sub>2</sub> and about 20  
228 minutes to desorbing it. The synergic effect of adding 10% Li<sub>2</sub>CO<sub>3</sub> can be explained with full  
229 activation of the Li-K eutectic melt at around 700°C, which increased CO<sub>2</sub> capacity and  
230 sorption rate (Sanna et al, 2015; Flores-Martínez and Pfeiffer, 2015). The CO<sub>2</sub> sorption  
231 capacities in presence of K-FA 1:1 and 2:1 were comparable to those shown by Li-FA  
232 sorbents (0.48 mmol CO<sub>2</sub>/g sorbent) in presence of 10% K<sub>2</sub>CO<sub>3</sub> additive at 650°C (Olivares-  
233 Marín et al, 2010). In the same study, 40% K<sub>2</sub>CO<sub>3</sub> was required (at 600°C) to absorb 2.43  
234 mmol CO<sub>2</sub>/g sorbent.

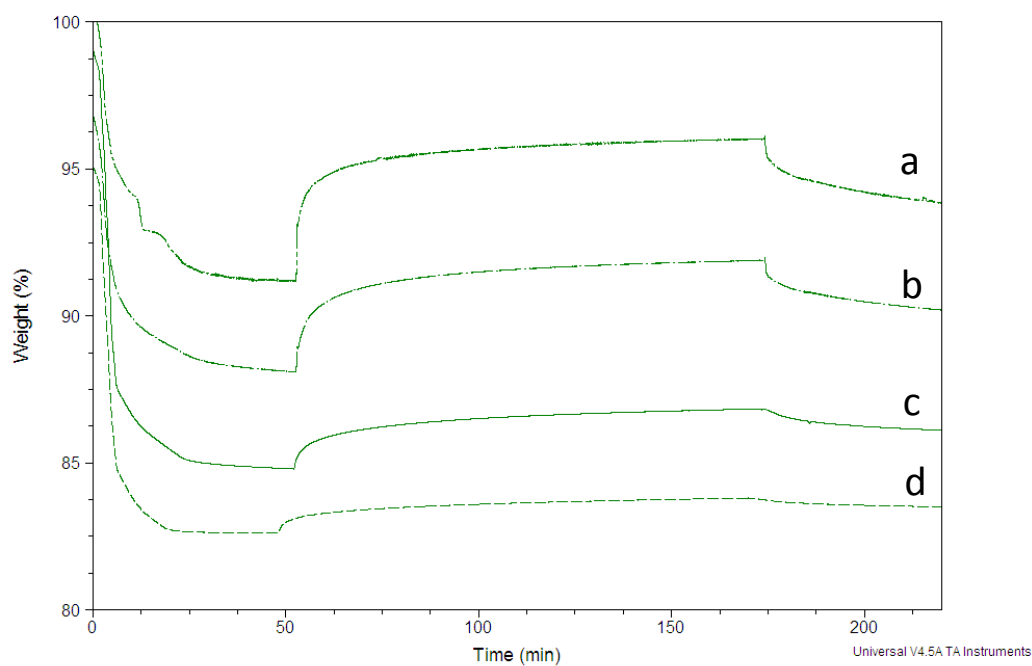
235 Based on our observations and previous works (Ortiz-Landeros et al, 2012; Sanna et al, 2015;  
236 Flores-Martínez and Pfeiffer, 2015), the different CO<sub>2</sub> sorption capacities and rates observed  
237 at 500, 600 and 700°C can be explained by surface chemisorption limited by the formation of  
238 external shell containing an KAlO<sub>2</sub> secondary phase and Li<sub>2</sub>CO<sub>3</sub> product at temperatures up  
239 to 500°C. Between 500 and 600°C, partial molten generated by eutectic phases starts to  
240 promote diffusion processes and then, at about 700°C, the CO<sub>2</sub> chemisorption is kinetically  
241 controlled by diffusion processes (Flores-Martínez and Pfeiffer, 2015; Sanna et al, 2015).

242 Moreover, it has been indicated that the binary compound K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub> (KAlO<sub>2</sub>) shows that at  
243 ambient pressure, KAlO<sub>2</sub> consists of tetragonal crystals between 1350 and 600°C (γ-KAlO<sub>2</sub>)  
244 and orthorhombic crystals below 600°C (β-KAlO<sub>2</sub>), with the structural re-arrangement  
245 comparable with that of NaAlO<sub>2</sub> and LiAlO<sub>2</sub> (de Kroon et al, 2001). Even if isolated silicates  
246 present melting points well above 700°C, compounds with the composition Na<sub>1.55</sub>K<sub>0.45</sub>Si<sub>2</sub>O<sub>5</sub>  
247 have eutectic decomposition temperature at 696°C (Yazhenskikh et al, 2008). The Li cations  
248 can decrease the melting point of the sorbent enhancing the diffusion of the species on the  
249 sorbent surface, which results in enhanced CO<sub>2</sub> sorption capacity and CO<sub>2</sub>  
250 sorption/desorption rates. Moreover, the formed eutectic phases in presence of Li<sub>2</sub>CO<sub>3</sub> clearly  
251 increase the carbonate decomposition processes by enhancing the diffusion of cations and  
252 CO<sub>2</sub>, enabling the recyclability of the material, as shown in Figure 5 (Flores-Martínez and  
253 Pfeiffer, 2015).

254

255

256

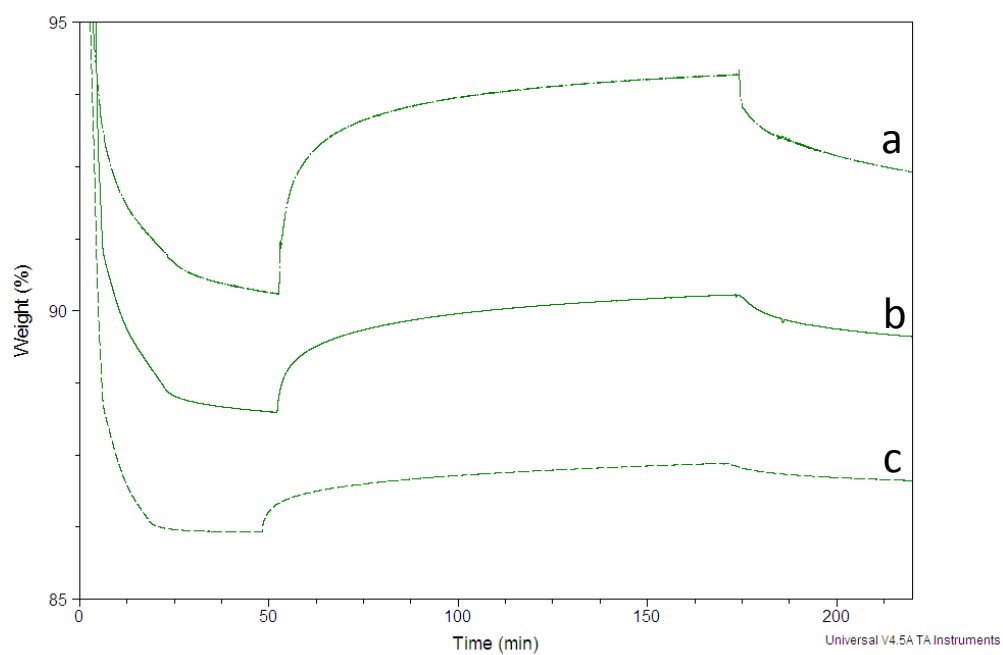


258

259 **Figure 3.** TGA of (a) K-FA 2:1 700°C+10% Ca(OH)<sub>2</sub>; (b) K-FA 2:1700°C; (c) K-FA 2:1 600°C; (d) K-FA 2:1

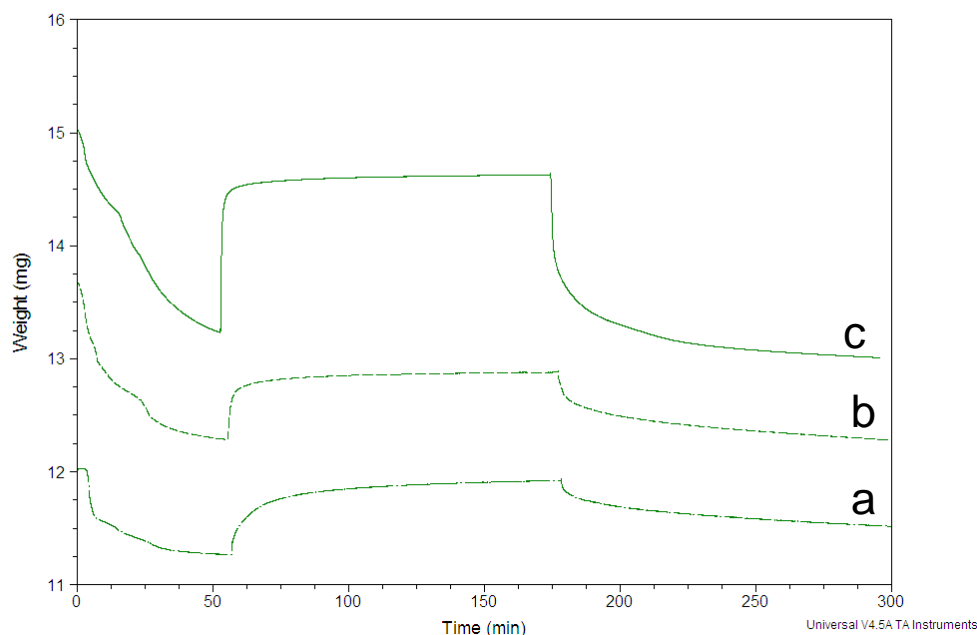
260

261



262

263 **Figure 4.** TGA of (a) K-FA 1:1 700°C; (b) K-FA 1:1 600°C; (c) K-FA 1:1 500°C.



264

265 **Figure 5.** TGA of (a) K-FA 1:1; (b) K-FA 1:1+10% Na<sub>2</sub>CO<sub>3</sub>; (c) K-FA 1:1+10% Li<sub>2</sub>CO<sub>3</sub>.

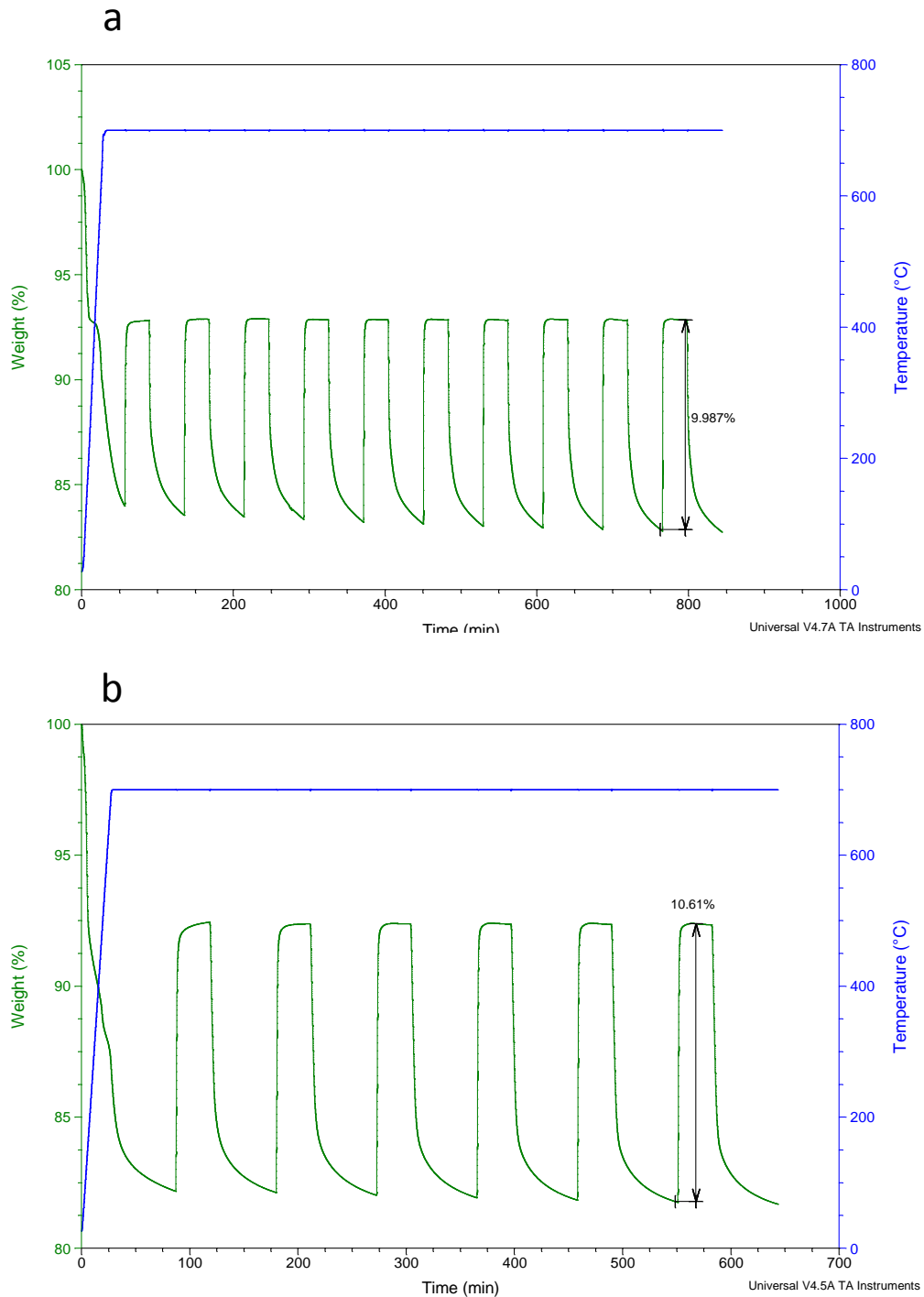
266

### 267 **Sorbents regeneration**

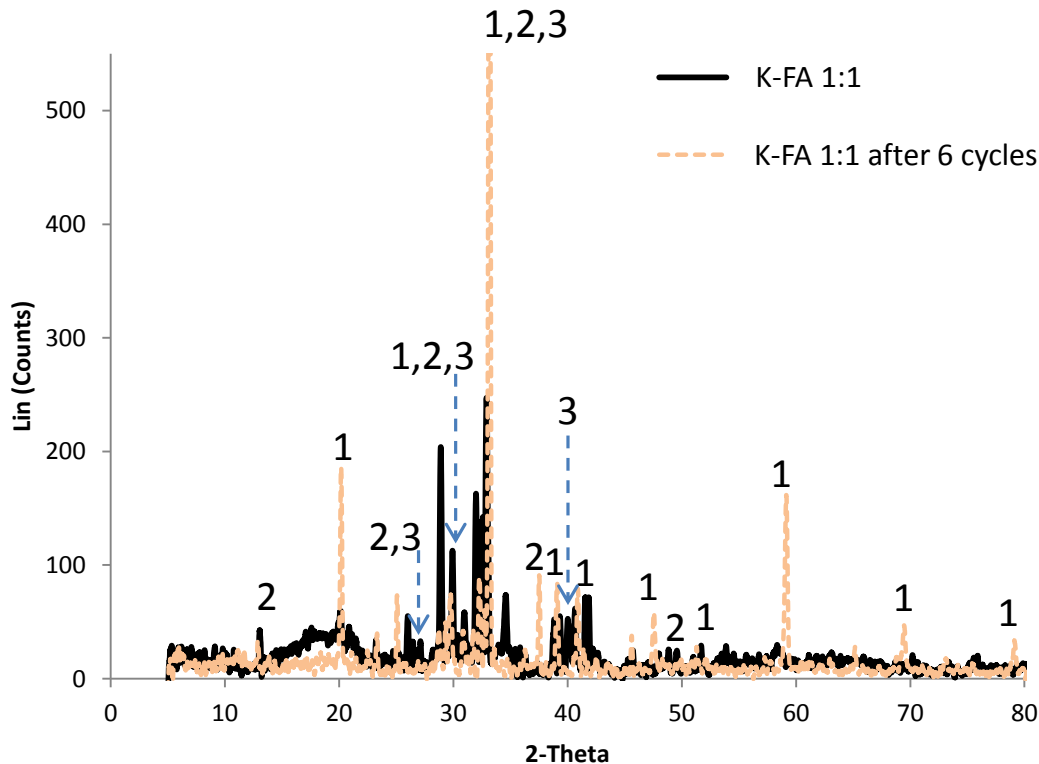
268 Figure 6 shows 10 and 6 CO<sub>2</sub> sorption/desorption cycles for the Na-FA sorbent with  
 269 K<sub>2</sub>CO<sub>2</sub>:SiO<sub>2</sub> molar ratios of 2:1 and 1:1 in presence of 10% Li<sub>2</sub>CO<sub>3</sub>. Both K-FA 2:1 and 1:1  
 270 were able to maintain 100% CO<sub>2</sub> sorption capacity at 700°C, respectively after 10 and 6  
 271 cycles. K-FA 1:1 showed a slightly increase of the CO<sub>2</sub> sorption cycle after cycle, which  
 272 could be ascribed to the not completed initial desorption under N<sub>2</sub> atmosphere before the  
 273 cyclic CO<sub>2</sub> sorption/desorption. K-FA presented superior cyclic stability compared to other  
 274 high temperature absorbents, such as hydrotalcites, where the capacity of the latter decrease  
 275 after a number of cycles (Maroño et al, 2014).

276 K-Fa 1:1 with 10% Li<sub>2</sub>CO<sub>3</sub> after 6 sorption/desorption cycles was analyzed by XRD to  
 277 establish any structural change in relation to the increased CO<sub>2</sub> uptake capacity shown after 6  
 278 cycles. The XRD patterns of the starting K-FA 1:1 and the K-FA after 6 cycles are shown in  
 279 Figure 7, which indicates that, the sorption/desorption cycles affects the mineral composition  
 280 of these materials. In fact, there was an increase of sodium aluminium silicate phase and a  
 281 decrease of the abundance of metasilicate phases. This behavior was already observed in our  
 282 previous work using Li-Na-FA silicates (Sanna et al, 2015). Both TGA and XRD data  
 283 suggest that the crystals structure modification improves the CO<sub>2</sub> sorption, which may be

284 related to enhanced K species diffusion due phase change (from solid to liquid-like) of  
285 eutectic Na-meta-silicates phases in presence of impurities such as K, Ca and Mg oxides  
286 (from fly ash) as indicated in previous work (Sanna et al, 2015; Flores-Martínez and Pfeiffer,  
287 2015).



288  
289 **Figure 6.** Cyclic stability at 700°C of a) K-FA 2:1 and b) K-FA 1:1 under 100%CO<sub>2</sub> atmosphere and in  
290 presence of 10% Li<sub>2</sub>CO<sub>3</sub>. Temperature profile shown in y2-axes.



291  
 292 **Figure 7.** XRD pattern of raw K-FA and K-FA after 6 absorption/desorption cycles. 1 Potassium aluminium  
 293 silicate ( $K_{1.25}Al_{1.25}Si_{0.75}O_4$ ); 2 Potassium carbonate; 3 Potassium metasilicate.

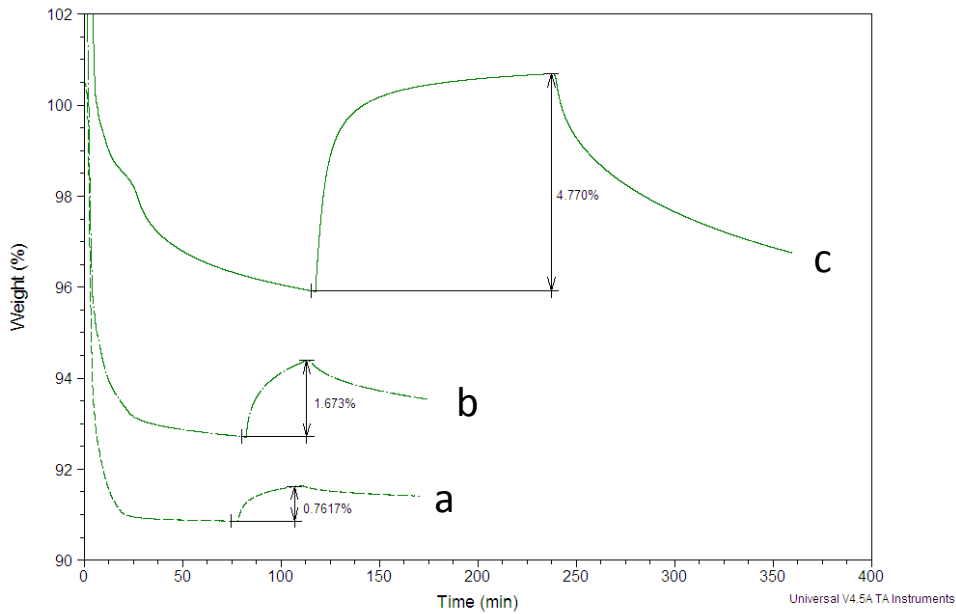
294  
 295 **Presence of diluted CO<sub>2</sub> and potential scale up**

296 The use of solid sorbents for CO<sub>2</sub> capture implies that the selected materials present rapid  
 297 CO<sub>2</sub> sorption/desorption rates and high CO<sub>2</sub> sorption capacity. This is required due to the  
 298 diluted CO<sub>2</sub> in flue gas, which results in large volumes to be treated.

299 The effectiveness of the K-FA sorbents in capturing CO<sub>2</sub> from a diluted stream was  
 300 investigated. Figures 8 and 9 show the variation of the CO<sub>2</sub> working capacity for the K-FA  
 301 2:1 and K-FA 1:1 in presence or absence of 10% Li<sub>2</sub>CO<sub>3</sub>. The CO<sub>2</sub> uptake with diluted CO<sub>2</sub>  
 302 (14%) were lower than those obtained in presence of pure CO<sub>2</sub> at 500°C, similar at 600°C and  
 303 somehow higher at 700°C (1.08 mmol CO<sub>2</sub> / g sorbent vs 0.82 for K-FA 2:1 and 1.50 vs 1.45  
 304 for K-FA 1:1) indicating that the eutectic melt favours CO<sub>2</sub> diffusion in/out from the sorbent  
 305 surface. However, the slopes of the sorption and desorption profiles suggest lower reaction  
 306 rates compared with those in presence of pure CO<sub>2</sub> stream and also, desorption was not  
 307 completed in reasonable times. Diluted CO<sub>2</sub> resulted in a lower CO<sub>2</sub> sorption when the K-FA  
 308 1:1 was tested in presence of 10% Li<sub>2</sub>CO<sub>3</sub> (1.84 mmol CO<sub>2</sub> / g sorbent vs 2.39), but reactions

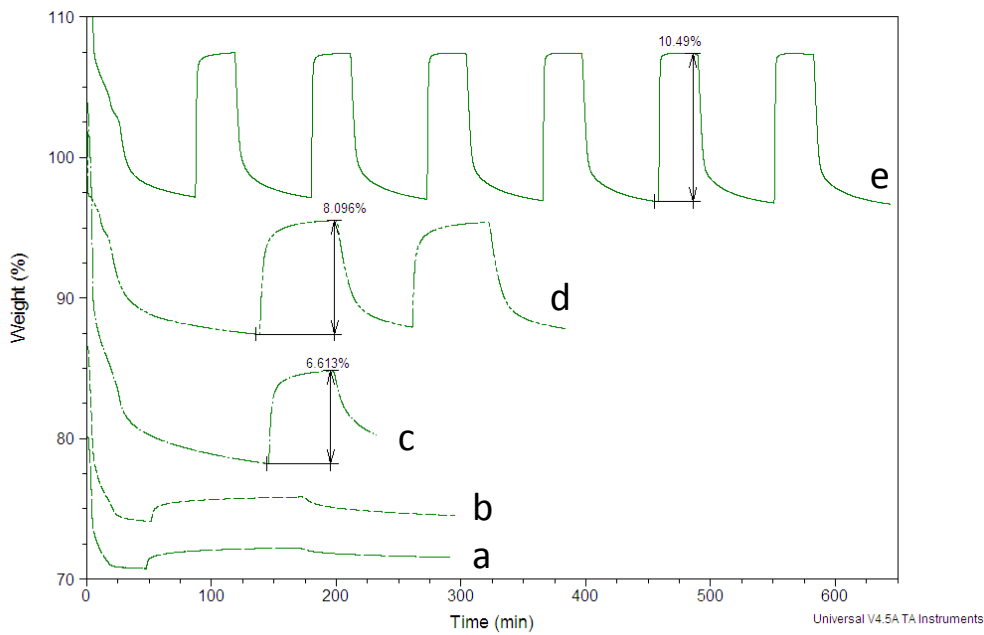
309 occurred faster and desorption was completed, compared to the tests carried out in absence of  
310 additive.

311 A 500 MW coal-fired power plant with 90% CO<sub>2</sub> capture (~419,000 kg CO<sub>2</sub>/h) was  
312 considered to evaluate the potential industrial scale application of the developed sorbent.



313

314 **Figure 8.** K-FA 2:1 CO<sub>2</sub> sorption at a) 500°C, b) 600°C and c) 700°C in presence of 14%CO<sub>2</sub>.



315

316 **Figure 9.** CO<sub>2</sub> sorption of K-FA 1:1. a) 100%CO<sub>2</sub> at 500°C; b) 100%CO<sub>2</sub> at 600°C; c) 100%CO<sub>2</sub> at 700°C; d)  
 317 14%CO<sub>2</sub> at 700°C in presence of 10% Li<sub>2</sub>CO<sub>3</sub>; e) 100%CO<sub>2</sub> at 700°C in presence of 10% Li<sub>2</sub>CO<sub>3</sub>.

318

319 The capture plant was sized considering fix bed units able to load a total of 28000 kg of  
 320 sorbent, as in previous work, to evaluate the feasibility of the developed sorbents (Quinn et  
 321 al, 2012).

322 K-FA 1:1 - 10% Li<sub>2</sub>CO<sub>3</sub> was selected for the calculations due to its high total CO<sub>2</sub> capacity of  
 323 2.4 mmol CO<sub>2</sub>/g sorbent after 1 hour at 700°C, as can be seen in Table 3. Also, a flue gas  
 324 containing 14%CO<sub>2</sub> (balanced with N<sub>2</sub>) was considered.

325 Four hypothetical cases were considered with adsorption taking place in 60, 30, 15 and 5  
 326 minutes to show how uptake time affects the hypothetical plant footprint. The number of  
 327 reactors required to capture 90% of the CO<sub>2</sub> emitted in a 500 MW coal power plant is  
 328 summarised in Table 3. Since the calculated number of vessels based on 60 minutes were  
 329 very large (3.9 mmol CO<sub>2</sub>/g sorbent for a total of 140 vessels), they were not reported in the  
 330 table. However, taking advantage of the rapid sorption and desorption rates of the K-FA  
 331 sorbent in presence of the Li<sub>2</sub>CO<sub>3</sub> sorption promoter (10 wt%), the process became feasible at  
 332 5 minutes sorption time in presence of pure CO<sub>2</sub> stream, with only 12 vessels in parallel  
 333 required for the CO<sub>2</sub> uptake, which would result in reduced capital costs. As expected, the  
 334 CO<sub>2</sub> sorption capacity in presence of diluted CO<sub>2</sub> stream (14% CO<sub>2</sub> balanced with N<sub>2</sub>) is  
 335 lower than in presence of pure CO<sub>2</sub> and this affects the foot-print of the hypothetical CO<sub>2</sub>  
 336 capture plant, where 20 reactors would be required.

337

338 **Table 3.** CO<sub>2</sub> sorption capacity at different times and number of reactors required to capture 90% of CO<sub>2</sub> from a  
 339 500 MW coal-fired power plant with 90% CO<sub>2</sub> capture (~ 419,000 kg CO<sub>2</sub>/h). na: non available.

<b>CO<sub>2</sub> sorption, mmol CO<sub>2</sub>/g sorbent</b>				
<b>Time, min</b>	<b>5</b>	<b>10</b>	<b>15</b>	<b>30</b>
K-FA 1:1	2.38	2.4	2.4	2.4
K-FA 2:1	1.44	1.58	1.67	1.78
<b>Reactors required for CO<sub>2</sub> sorption</b>				
K-FA 1:1 - 100%CO <sub>2</sub>	12	24	35	71
K-FA 1:1 - 14%CO <sub>2</sub>	20	51	na	na

340

341

342 Amount of sorbents can be lowered by employing rapid thermal swing chemisorption  
 343 (RTSC) process that utilizes shell and tube type vessels to minimize heating and cooling time  
 344 (Lee and Sircar, 2008). Calculations indicated a 24% reduction in capital cost and a 78%

345 reduction in operating cost relative to conventional MEA technology may be achievable  
346 (Quinn et al, 2012). For example, the K-FA sorbent able to load 2.38 mmol CO<sub>2</sub>/g sorbent  
347 would result in 0.37 t to be loaded in the RTSC. Further works are required to evaluate the  
348 potential use of these sorbents with rapid sorption/desorption processes in presence of  
349 moisture.

350

## 351 **Conclusions**

352 Potassium-fly ash (K-FA) CO<sub>2</sub> chemisorption at high temperature was evaluated using  
353 isothermal and cyclic thermo-gravimetric analyses in presence of 100% and 14% CO<sub>2</sub>.  
354 Lithium carbonate and calcium hydroxide were also evaluated as CO<sub>2</sub> sorption promoters.  
355 Temperature strongly affected the performance of the K-FA sorbents, resulting in a CO<sub>2</sub>  
356 uptake of 1.45 mmol CO<sub>2</sub>/g sorbent for K-FA 1:1 at 700°C. The CO<sub>2</sub> sorption was enhanced  
357 by the presence of lithium carbonate (10 wt%), with the K-FA 1:1 capturing 2.38 mmol  
358 CO<sub>2</sub>/g sorbent at 700°C in 5 minutes. The presence of 10% Li<sub>2</sub>CO<sub>3</sub> also accelerated sorption  
359 and desorption. The results suggest that the increased uptake of CO<sub>2</sub> and faster reaction rates  
360 in presence of K-FA can be ascribed to the formation of K-Li eutectic phase, which favours  
361 the diffusion of potassium and CO<sub>2</sub> in the material matrix. The cyclic experiments showed  
362 that the K-FA materials maintained stable CO<sub>2</sub> uptake and reaction rates over 10 cycles.  
363 Thanks to the rapid CO<sub>2</sub> sorption/desorption of the K-FA sorbent with Li<sub>2</sub>CO<sub>3</sub> (10 wt%), the  
364 process would require only 12 fix bed units for the sorption of 90% of the CO<sub>2</sub> emitted in a  
365 500 MW coal power plant. As expected, the CO<sub>2</sub> sorption capacity in presence of 14% CO<sub>2</sub>  
366 affects the foot-print of the hypothetical CO<sub>2</sub> capture plant, where 20 reactors would be  
367 required.

368

## 369 **Acknowledgements**

370 The authors thank the Centre for Innovation in Carbon Capture and Storage, Heriot-Watt  
371 University (EPSRC Grant No. EP/F012098/2) for support and logistics.

372

## 373 **References**

374 - de Kroon AP, Schäfer GW, Aldinger F (2001), Crystallography of potassium  
375 aluminate K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>, Journal of Alloys and Compounds, 314;1-2:147-153.



- 376 - Flores-Martínez MT, Pfeiffer H (2015), CO<sub>2</sub> chemisorption and cyclability analyses  
377 in  $\alpha$ -Li<sub>5</sub>AlO<sub>4</sub>: effects of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> addition, Greenhouse Gas Sci Technol.  
378 5:1–11.
- 379 - Hayashi, H.; Taniuchi, J.; Furuyashiki, N; Sugiyama, S.; Hirano, S.; Shigemoto, N.;  
380 and T Nonaka (1998). Efficient Recovery of Carbon Dioxide from Flue Gases of  
381 Coal-Fired Power Plants by Cyclic Fixed-Bed Operations over K<sub>2</sub>CO<sub>3</sub>-on-Carbon.  
382 Ind. Eng. Chem. Res., 37, 185-191, 1998.
- 383 - Hindryawati N, Maniam GP, Karim Md.R., Chong K.kF. (2014), Transesterification  
384 of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as  
385 potential solid base catalyst, Engineering Science and Technology, an International  
386 Journal, 17, 95-103.
- 387 - Hoffman JS, Pennline HW (2001), Study of Regenerable Sorbents for CO<sub>2</sub> Capture  
388 National Energy Technology Laboratory, DOE,  
389 [http://www.netl.doe.gov/publications/proceedings/01/carbon\\_seq/3b2.pdf](http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/3b2.pdf)
- 390 - Kalapathy U, Proctor A, Shultz J (2000), A simple method for production of pure  
391 silica from rice hull ash, Bioresour. Technol. 73;257-262.
- 392 - Kato M, Nakagawa K, Essaki K, Maezawa Y, Takeda Sh, Kogo R, Hagiwara Y  
393 (2005) Novel CO<sub>2</sub> absorbents using lithium containing oxide Int J Appl Ceram  
394 Technol 2:467–475.
- 395 - Lee K.B., Sircar S. (2008), Removal and recovery of compressed CO<sub>2</sub> from flue gas  
396 by a novel thermal swing chemisorption process. AIChE J.;54:2293-2302.
- 397 - Leung D.Y.C., Caramanna G., Maroto-Valer M.M. (2014), An overview of current  
398 status of carbon dioxide capture and storage technologies, Renewable and Sustainable  
399 Energy Reviews;39:426-443.
- 400 - Manzoor S., A. Korre, S. Durucan, A. Simperler (2014), Atmospheric Chemistry  
401 Modelling of Amine Emissions from Post Combustion CO<sub>2</sub> Capture Technology,  
402 Energy Procedia, 63, 822–829.
- 403 - Maroño M, Torreiro Y, Montenegro L, Sánchez J (2014). Lab-scale tests of different  
404 materials for the selection of suitable sorbents for CO<sub>2</sub> capture with H<sub>2</sub> production in  
405 IGCC processes, Fuel 116; 861-870.
- 406 - Nalette, T., Bibara, P., Aylward J (1992). Preparation of high capacity unsupported  
407 regenerable CO<sub>2</sub> sorbent. US Patent No. 5,079,209.

- 408 - Olivares-Marín M, Drage TC, Maroto-Valer MM (2010) Novel lithium-based  
409 sorbents from fly ashes for CO<sub>2</sub> capture at high temperatures Int J Greenh Gas Con  
410 4:623–629.
- 411 - Onischak, J.; and B. Baker (1978). Development of a Prototype Regenerable Carbon  
412 Dioxide Absorber for Portable Life Support Systems. J. Eng. Ind., 100(3), 383-385,  
413 1978.
- 414 - Ortiz-Landeros J , Ávalos-Rendón TL , Gómez-Yáñez C, Pfeiffer H (2012), Analysis  
415 and perspectives concerning CO<sub>2</sub> chemisorption on lithium ceramics using thermal  
416 analysis. J Therm Anal Calorim 108:647–655.
- 417 - Quinn R, Kitzhoffer R.J., Hufton J.R., Golden T.C. (2012), Ind.Eng.Chem.Res., 51,  
418 9320-9327.
- 419 - Rana Sabouni, Hossein Kazemian, Sohrab Rohani (2014), Carbon dioxide capturing  
420 technologies: A review focusing on metal organic framework materials (MOFs),  
421 Environ Sci Pollut Res 21:5427–5449
- 422 - Ridha FN, Yang YX, Webley PA (2009), Adsorption characteristics of a fully  
423 exchanged potassium chabazite zeolite prepared from decomposition of zeolite Y,  
424 Microporous Mesoporous Mater., 117, 497.
- 425 - Rodríguez MT, Pfeiffer H (2008) Sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>): A thermo-kinetic  
426 analysis of its CO<sub>2</sub> chemical sorption. Thermochim Acta 473:92–95.
- 427 - Samanta A., Zhao A.N., Shimizu G.K.H, Sarkar P., Gupta R. (2012), Post-  
428 Combustion CO<sub>2</sub> Capture Using Solid Sorbents: A Review, Ind. Eng. Chem. Res. ;  
429 51,(4):1438-1463.
- 430 - Sanna A, Ramli I, Maroto-Valer MM (2014) Novel Na-silicates CO<sub>2</sub> sorbents from  
431 fly ash, Energy Procedia, 63, 739-744.
- 432 - Sanna A, Ramli I, Maroto-Valer MM (2015), Development of sodium/lithium/fly ash  
433 sorbents for high temperature post-combustion CO<sub>2</sub> capture, Appl Energy, 156, 197-  
434 206.
- 435 - Seggiani M, Puccini M and Vitolo S (2011), High-temperature and low concentration  
436 CO<sub>2</sub> sorption on Li<sub>4</sub>SiO<sub>4</sub> based sorbents: Study of the used silica and doping method  
437 effects . Int J Greenhouse Gas Control 5: 741–748.
- 438 - Seggiani M, Puccini M, Vitolo S (2013) Int J Greenh Gas Con 17:25–31.
- 439 - The Financialist, The Precious Mobile Metal (2014). Credit Suisse. 9 June 2014.

- 440 - Thuadaij N, Nuntiya A (2008), Preparation of nanosilica powder from rice husk ash  
441 by precipitation method, *Chiang Mai J. Sci.* 35; 206-211
- 442 - Vega F., Sanna A., Cortés V., Navarrete B., Maroto-Valer M.M. (2014), Degradation  
443 of amine-based solvents in CO<sub>2</sub> capture process by chemical absorption. *Greenhouse*  
444 *Gases: Science and Technology*, 4, 6, 707-733.
- 445 - Walton KS, Abney MB, LeVan MD (2006), CO<sub>2</sub> adsorption in Y and X zeolites  
446 modified by alkali metal cation exchange, *Microporous Mesoporous Mater*, 91, 78.
- 447 - Yazhenskikh E, Hack K, Müller M (2008), Critical Thermodynamic Evaluation of  
448 Oxide Systems Relevant to Fuel Ashes and Slags, Part 4: Sodium Oxide - Potassium  
449 Oxide – Silica, *Calphad* 32:506-513.
- 450 - Zhao C, Chen X, Anthony EJ, Jiang X, Duan L, Wu Y, et al. (2013). Capturing CO<sub>2</sub>  
451 in flue gas from fossil fuel-fired power plants using dry regenerable alkali metalbased  
452 sorbent. *Prog Energy Combust Sci* 3;39(6):515–34.
- 453 - Zhao C, Guo Y, Li C, Lu S (2014), Removal of low concentration CO<sub>2</sub> at ambient  
454 temperature using several potassium-based sorbents, *Applied Energy* 124; 241–247.
- 455 - Zhao CW, Chen XP, Zhao CS, (2011). Carbonation and active-component-  
456 distribution behaviors of several potassium-based sorbents. *Ind Eng Chem Res*;  
457 50(8):4464–70.
- 458
- 459