KOH capture by coal fly ash

Wang, Guoliang; Jensen, Peter Arendt; Wu, Hao; Frandsen, Flemming Jappe; Laxminarayan, Yashasvi; Sander, Bo; Glarborg, Peter

Published in:
Fuel

Link to article, DOI:
[10.1016/j.fuel.2018.12.088](https://doi.org/10.1016/j.fuel.2018.12.088)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Wang, G., Jensen, P. A., Wu, H., Frandsen, F. J., Laxminarayan, Y., Sander, B., & Glarborg, P. (2019). KOH capture by coal fly ash. *Fuel*, 242, 828 - 836. <https://doi.org/10.1016/j.fuel.2018.12.088>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

KOH Capture by Coal Fly Ash

Guoliang Wang ^{a*}, Peter Arendt Jensen ^a, Hao Wu ^a, Flemming Jappe Frandsen ^a, Yashasvi
Laxminarayan ^a, Bo Sander ^b, Peter Glarborg ^a

^a Department of Chemical and Biochemical Engineering, Technical University of Denmark,
Søltofts Plads, Building 229, DK-2800 Kgs. Lyngby, Denmark

^b Ørsted Bioenergy & Thermal Power A/S, Kraftværksvej 53, 7000 Fredericia, Denmark

*Corresponding author email-id: guow@kt.dtu.dk

Permanent address:

Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts
Plads, Building 229, DK-2800 Kgs. Lyngby, Denmark

Abstract:

The KOH-capture reaction by coal fly ash at suspension-fired conditions was studied through entrained flow reactor (EFR) experiments and chemical equilibrium calculations. The influence of KOH-concentration (50-1000 ppmv), reaction temperature (800-1450 °C), and coal fly ash particle size ($D_{50} = 6.03\text{-}33.70\text{ }\mu\text{m}$) on the reaction was investigated. The results revealed that, at 50 ppmv KOH (molar ratio of $\text{K}/(\text{Al}+\text{Si}) = 0.048$ of feed), the measured K-capture level (C_K) of coal fly ash was comparable to the equilibrium prediction, while at 250 ppmv KOH and above, the measured data were lower than chemical equilibrium. Similar to the KOH-kaolin reaction reported in our previous study, leucite (KAlSi_2O_6) and kaliophilite (KAlSiO_4) were formed from the KOH-coal fly ash reaction. However, coal fly ash captured KOH less effectively compared to kaolin at 250 ppmv KOH and above. Studies at different temperatures showed that, at 800 °C, the KOH-coal fly ash reaction was probably kinetically controlled. At 900-1300 °C it was diffusion limited, while at 1450 °C, it was equilibrium limited to some extent. At 500 ppmv KOH (molar ratio of $\text{K}/(\text{Al}+\text{Si}) = 0.481$), and a gas residence time of 1.2 s, 0.063 g K/(g additive) and 0.087 g K/(g additive) was captured by coal fly ash ($D_{50} = 10.20\text{ }\mu\text{m}$) at 900 and 1450 °C, respectively. Experiments with coal fly ash of different particle sizes showed that a higher K-capture level were obtained using finer particle sizes, indicating some internal diffusion control of the process.

Keywords: Coal fly ash; potassium capture; biomass combustion; additive; KOH

1 Introduction

Existing coal suspension-fired boilers have been converted to biomass combustion to increase the share of renewable power and district heat production in Denmark [1, 2]. Compared to traditional biomass grate-fired power plants, biomass suspension-fired power plants have higher efficiency, and they can compensate for the fluctuations of the wind power production [3]. However,

the alkali elements (mainly K) in biomass fuels to a high degree evaporates during combustion in PF (pulverized fuel) boilers [4-7], and are present in the gas phase as KOH, KCl or K₂SO₄ [8-10]. When the flue gas is cooling down, these K-compounds condense and may form sticky deposit on super-heater and reheater tubes, resulting in accelerated deposit formation as well as corrosion. Additionally, K-salt aerosols formed from nucleation and condensation of gaseous K-species can deteriorate the performance of de-NO_x SCR catalyst through physical deposition and chemical poisoning [11-14].

One option to deal with these alkali-induced problems is to inject additives that can react with volatile alkali species to form less problematic compounds with higher melting points. Various additives have been investigated, and they can largely be categorized into four groups: Al-Si based [3, 15-18], S-based [19-21], P-based [22] and Ca-based [23], according to the major elements that are present in the additives [3, 24]. Among the different additives, coal fly ash was the only one that has been commercially utilized in full-scale suspension-fired boilers due to its low cost and high effectiveness [1, 2, 25].

Coal fly ash is a solid residue from combustion of coal. Approximately 500 million tons of coal fly ash are produced worldwide each year [26]. Coal fly ash could be an environmental concern if not handled properly [26]. The mineralogical composition of coal fly ash is quite complex, depending on the parental coal and the combustion technology. The dominant mineral phases include quartz, mullite, illite and siderite [27]. The effectiveness of coal fly ash in capturing volatile K-species from biomass has been observed in co-combustion of coal and biomass [28-30].

The K-capture reaction by coal fly ash was studied by Wu and co-workers in a full-scale biomass suspension-fired boiler [1, 2]. The impact of injection of coal fly ash in different amounts on the deposition behavior, deposit composition and the formation of aerosols was investigated. With the addition of coal fly ash, the amount of aerosols formed was greatly suppressed, with its

composition changed from K-S-Cl rich to Ca-P-Si rich [2]. The composition of the ash deposit is also significantly influenced. The amount of K_2SO_4 in inner layer deposit collected from high-temperature flue gas (1300 °C) was greatly reduced. KCl, KOH, and K_2CO_3 completely disappeared, when adding coal fly ash. The large outer deposit also transferred from K-Ca-Si rich to Si-Al rich, resulting in an easier and more frequent removal of the deposits. In the deposits formed at low-temperature flue gas (800 °C), KCl disappeared, and the content of KOH and K_2CO_3 was significantly decreased. The corrosion risk was considerably decreased consequently. However, because of the complexity of the full-scale system, no quantitative data such as the potassium capture amount of per unit of coal fly ash could be obtained.

Quantitative and detailed study on K-capture reaction by coal fly ash at high-temperature conditions is still rare. To the authors' knowledge, the only two quantitative studies on K-capture by coal fly ash were both conducted in fixed bed reactors, where coal fly ash pellets with a diameter of 1.5 mm or piles of coal ash were utilized [15, 31]. However, the residence time of coal fly ash in these fixed bed reactors was in an order of hours, significantly larger than that of biomass suspension-fired boilers, where coal fly ash particles only stay a few seconds in the flue gas [1, 2].

The objective of this work is to study quantitatively the K-capture behavior of coal fly ash at well-controlled conditions in suspension, and to understand the influence of reaction conditions. This paper focuses on the KOH capture by coal fly ash. Results on K_2CO_3 , KCl and K_2SO_4 capture by coal fly ash will be published in another paper.

2 Experimental

2.1 Materials

A coal fly ash from the unit 2 of Asnæsværket Power Plant (ASV2), Denmark was utilized in this work. The ASV2 coal fly ash was sieved to 0-32 μm and 32-45 μm , named as ASV2CFA0-32

71 and ASV2CFA32-45, respectively. Additionally, the ASV2CFA0-32 was ground in a ball mill to
72 get a finer coal ash sample, named as ASV2CFAGR. The three ash samples were all analyzed with
73 a Malvern 3000 particle size analyzer. The median diameter (D_{50}) of ASV2CFA0-32,
74 ASV2CFA32-45 and ASV2CFAGR was 10.20 μm , 33.70 μm and 6.03 μm , respectively. The D_{50} of
75 ASV2CFAGR is comparable with that of kaolin (5.47 μm) and mullite (5.90 μm) utilized in our
76 previous studies [32, 33]. A sieving analysis showed that ASV2CFA0-32 contributed 63.0 wt. % of
77 the ASV2 coal fly ash, while ASV2CFA32-45 made up 14.4 wt. %. The three coal fly ashes size
78 fractions were also subjected to ICP-OES analysis, with the results summarized in Table 1. The
79 three ash size fractions had similar composition and were all rich in Al and Si. The molar ratio of
80 $(\text{K}+\text{Na})/(\text{Al}+\text{Si})$ of the three ash fractions was around 0.02, indicating that there was a large surplus
81 of Al and Si in the ashes which could participate the K-capture reaction. The coal fly ashes was also
82 analyzed with XRD (X-ray Diffraction), and the results showed that mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and
83 quartz (SiO_2) were the main crystalline phases, with no crystalline alkali or alkali earth species
84 detected. This indicated that the small amounts of Na, K, Ca and Mg detected by ICP-OES were
85 present in amorphous species.

86 **2.2 Setup**

87 The DTU Entrained Flow Reactor (EFR) (Figure 1) utilized in this study, can simulate the
88 conditions in suspension-fired boilers. It consists of a gas supply system, a liquid/slurry sample
89 feeding system, a gas preheater, a vertical reactor tube, a bottom chamber and a particle and flue gas
90 sampling system. The vertical reactor tube is 2 m long and the inner diameter is 79 mm. It can be
91 heated up to 1450 $^{\circ}\text{C}$ by 7 electrical heating elements.

92 Instead of feeding solid KOH powder and coal fly ash directly into the reactor [19], solid KOH
93 and coal fly ashes were mixed with deionized water, to make a homogeneous slurry. The slurry was
94 subsequently fed into the reactor through water-cooled feeding probe, with a feeding rate varying

95 from 3.2 to 6.2 g/min. The slurry was subsequently atomized by a 30 NL/min primary air. The
96 atomized slurry droplets were mixed with preheated secondary air (40-87 NL/min) and subsequently
97 vaporized. KOH evaporated and reacted with coal fly ash in the reactor tube. Solid particles and
98 aerosols were collected by a cyclone (with a cut-off diameter of 2.3 μm) and a metal filter (with a
99 pore size of 0.8 μm), respectively. The cyclone and filter were heated to 200 °C to avoid
100 condensation of water vapor. Detailed information on the EFR reactor and the slurry feeding system
101 can be found elsewhere [32, 33].

102 **2.3 Experimental matrix**

103 The conditions of the EFR experiments of KOH capture by coal fly ashes are summarized in
104 Table 2. The influence of the KOH-concentration, the molar ratio of K/(Al+Si) in reactants, the
105 reaction temperature and the coal fly ash particle size on the KOH-capture reaction were
106 investigated.

107 In the experimental series (A) of Table 2, the concentration of coal fly ash in the feeding slurry
108 was kept constant while the feed amount of KOH was varied, to investigate the effect of KOH
109 concentration in flue gas (50-1000 ppmv) and the molar ratio of K/(Al+Si) in reactants (0.048-
110 0.961). In series (B), the temperature in reactor was changed from 800 to 1450 °C. Two different
111 KOH concentrations in the flue gas were studied: 50 ppmv and 500 ppmv. In series (C), the
112 influence of coal fly ash particle size on the K-capture reaction was studied, using ASV2CFAGR
113 ($D_{50} = 6.03 \mu\text{m}$), ASV2CFA0-32 ($D_{50} = 10.20 \mu\text{m}$) and ASV2CFA32-45 ($D_{50} = 33.70 \mu\text{m}$). The
114 results were also compared to data from our previous study on KOH capture by kaolin and mullite
115 [32, 33]. The gas residence time in the reactor was kept at 1.2 s in all the experiments.

116 **2.4 Analytical methods**

117 The collected solid samples were subjected to ICP-OES (Inductively Coupled Plasma Atomic
118 Emission Spectroscopy) to quantify the amount of potassium captured by coal fly ash. The

119 concentrations of major elements were determined according to the Danish Standard DS/EN 15290
120 (Solid Biofuels- Determination of Major Elements). The concentration of water-soluble K and Cl
121 was analyzed according to the standard DS/EN ISO 16995 (Solid Biofuels- Determination of water-
122 soluble Chloride, Sodium and Potassium).

123 Two parameters were defined to quantify the K-capture degree by coal fly ash: the K-
124 conversion (X_K), and the K-capture level (C_K). X_K is the percentage (%) of input K-compound
125 (KOH) chemically captured by additives (coal fly ash) forming water-insoluble K-aluminosilicate.
126 C_K is the mass of potassium captured by 1 g of additive (coal fly ash) (g K/g additive). Details of
127 the calculation method can be found in our previous work [32, 33].

128 Additionally, solid products were also analyzed with XRD (X-ray diffraction analysis) to
129 determine the mineralogical composition. Samples collected from the EFR experiments were
130 washed with deionized water at room temperature for 24 hours to remove the water-soluble
131 compounds (like unreacted K-salts) and then filtered and dried. The XRD spectra were obtained
132 with a Huber diffractometer, and the main crystalline phases were identified with JADE 6.0 using
133 database of PDF2-2004.

134 **2.5 Equilibrium calculation**

135 Chemical equilibrium calculations have been widely utilized to investigate the speciation of
136 alkali as well as the interaction between alkali and coal ash minerals during combustion [28-30]. In
137 the present study, global equilibrium calculations were carried out using the equilibrium module of
138 FactSage 7.0. Experimental results and equilibrium calculation data were compared to better
139 understand the results.

140 The chemical equilibrium calculations were performed at atmospheric pressure in the
141 temperature range of 500-1800 °C. Four databases including FactPS, FToxid, FTsalt and FTpulp
142 were employed. Gas, liquid and solid compound species were selected for the equilibrium

calculations. Detailed information about the databases [34] and calculation settings are included in the supplementary material. The calculation results of key points are summarized in Table 3.

3 Results and discussion

3.1 Representativeness of solid product samples

Although the solid samples obtained from the sampling system (sampling tube, cyclone, and filter) were carefully collected, the mass balance for each experiment only closed within about 58 - 75 %. The difference was due to the deposition on the inner wall of the vertical reactor tube and other places. The calculation of K-capture level (C_K) and K-conversion (X_K) was based on the assumption that the collected samples are representative. The representativeness of the product samples was examined by comparing the molar ratio of K/(Al+Si) in products with that of the fed reactants. The result basing on ICP-OES analysis is shown in Figure 2. It shows that the molar ratio of K/(Al+Si) in the collected solid samples is close to that of fed reactants, suggesting that the solid samples are representative.

3.2 KOH capture by coal fly ash

3.2.1 Equilibrium calculations

The equilibrium calculation results of KOH capture by ASV2CFA0-32 at different temperatures (800-1450 °C) and KOH concentrations (50-1000 ppmv) are summarized in Table 3. Results that are more detailed can be found in the supplementary material.

The calculations indicate that the type of the K-aluminosilicates formed from the KOH-capture reaction changes with the K-concentration or the molar ratio of K/(Al+Si) in reactants. At 50 ppmv KOH (molar K/(Al+Si) in reactant was 0.048), sanidine ($KAlSi_3O_8$) with K:Al:Si = 1:1:3 was predicted as the main K-aluminosilicate through the whole temperature range 800-1450 °C. When the KOH concentration increased to 250 ppmv, leucite ($KAlSi_2O_6$) with a molar ratio of K:Al:Si =

166 1:1:2 became the dominant K-aluminosilicate. At 500, 750 and 1000 ppmv KOH, kaliophilite
167 (KAlSiO_4) with a molar ratio of K:Al:Si = 1:1:1 was the main K-aluminosilicate product.

168 3.2.2 Impact of KOH concentration

169 The measured K-capture level (C_K) and K-conversion (X_K) of KOH capture by ASV2CFA0-32
170 at different KOH concentrations (50-1000 ppmv) and 1300 °C are compared with equilibrium
171 calculations in Figure 3. For 50 ppmv KOH, the measured C_K (0.022 g K/(g additive)) and X_K
172 (95 %) of ASV2CFA0-32 are close to the equilibrium values. However, the experimental C_K and
173 X_K become remarkably lower than the equilibrium data at 250 ppmv KOH and above. As the KOH-
174 concentration in the flue gas increases from 50 ppmv to 500 ppmv, although the K-capture level
175 (C_K) increased considerably from 0.022 g K/(g additive) to 0.074 g K/(g additive), K-conversion
176 (X_K) decreased sharply from 95 % to 32 %. With a further increase in KOH to 750 and 1000 ppmv,
177 no obvious increase of C_K was observed, and the K-conversion (X_K) dropped to 16 % at 1000 ppmv,
178 showing that most KOH remained unreacted in this case. The difference between equilibrium data
179 and experimental data implied that only part of the coal fly ash participated in the K-capture
180 reaction.

181 Also, the measured C_K and X_K of KOH reaction with kaolin from our previous study [33] are
182 included for comparison in Figure 3. The experiments of KOH capture by kaolin were conducted at
183 1100 °C, while the experiments with ASV2CFA0-32 were conducted at 1300 °C. Although the
184 reaction temperature was different, the results are still comparable, because the K-capture behavior
185 of kaolin at 1100 °C and 1300 °C is similar according to our previous study [33]. The results show
186 that the measured C_K and X_K of ASV2CFA0-32 were considerably lower than that of kaolin. There
187 may be several reasons for the lower efficiency of the coal fly ash compared to kaolin. One possible
188 reason is that the main mineral phase of coal fly ash, mullite, is less reactive towards potassium than
189 kaolin and metakaolin. Another possible reason is that the BET surface area of ASV2CFA0-32

190 (8.04 m²/g) is smaller than that of kaolin (12.70 m²/g), and the median diameter of ASV2CFA0-32
191 (10.20 μm) is larger than that of kaolin (5.47 μm). Consequently, there were fewer active sites for
192 KOH-capture in ASV2CFA0-32 [33]. In addition, diffusion limitations for KOH inside the coal fly
193 ash particles may have also played a role, resulting in an incomplete consumption of mullite in the
194 coal fly ash case. The incomplete consumption of mullite is supported by the XRD results shown in
195 Figure 4, in which peaks corresponding to mullite were detected in the KOH-reacted coal fly ash.

196 The XRD spectra of water-washed KOH-reacted ASV2CFA0-32 at 50 ppmv, 250 ppmv and
197 500 ppmv KOH are compared in Figure 4. At 50 ppmv KOH, only mullite and quartz originated
198 from the raw coal fly ash were detected. No crystalline K-aluminosilicate was detected, although
199 sanidine (KAlSi₃O₈) was predicted by the equilibrium calculations. This is probably because either
200 the content of K-aluminosilicate in the products was too low to be detected, or amorphous K-
201 aluminosilicates were formed which cannot be detected by XRD. In the 250 ppmv sample, leucite
202 (KAlSi₂O₆) was detected as the main K-aluminosilicate product. In the 500 ppmv sample,
203 kaliophilite (KAlSiO₄) was present as the dominant K-aluminosilicate. The type of K-
204 aluminosilicates detected by XRD, generally agrees with the equilibrium results as shown in Table
205 3. Notably, mullite was detected in all the three KOH-reacted coal fly ash samples, showing that
206 part of the mullite remained unreacted in those samples. This is different from what was observed in
207 the study of KOH capture by kaolin, where a full conversion of kaolin to K-aluminosilicate was
208 observed and no mullite was detected in the product samples at 500 ppmv KOH and above with a
209 reaction temperature of 1100 °C [33].

210 3.2.3 Impact of reaction temperature

211 The measured K-capture level (C_K) and K-conversion (X_K) of KOH capture by ASV2CFA0-32
212 at different reaction temperatures (800-1450 °C) are compared with the equilibrium calculation
213 results in Figure 5. KOH concentrations of 50 ppmv and 500 ppmv in the flue gas were studied. The

214 C_K and X_K of KOH capture by kaolin at the same conditions [33] are included as well for
215 comparison. As shown in Figure 5 (A) and (B), at 500 ppmv KOH, the measured C_K and X_K of
216 KOH capture by ASV2CFA0-32 were both significantly lower than equilibrium data. At 800 °C,
217 the K-capture level (C_K) was only 0.025 g K/(g additive), with 11 % of KOH captured as K-
218 aluminosilicate. When the temperature increased to 900 °C, C_K increased significantly to 0.063 g
219 K/(g additive), with 27 % of KOH converted to K-aluminosilicate. At temperatures of 900-1100 °C,
220 the C_K stayed constant. However, when the reaction temperature increased further to 1300 °C and
221 1450 °C, C_K increased by 38 % reaching 0.087 g K/(g additive), with 37 % of fed KOH chemically
222 bonded by coal fly ash as K-aluminosilicate at 1450 °C.

223 At 50 ppmv KOH, the measured C_K and X_K of ASV2CFA0-32 were close to the equilibrium
224 predictions; see Figure 5 (C) and (D). The C_K and X_K were both constant and independent of the
225 reaction temperature in the temperature range of 900-1300 °C. The C_K was around 0.019 g K/(g
226 additive), with about 94 % KOH converted to K-aluminosilicate.

227 Comparison of results of KOH-ASV2CFA0-32 and KOH-kaolin in Figure 5 shows that, at 500
228 ppmv KOH, the C_K and X_K of ASV2CFA0-32 were considerably lower than that of kaolin, showing
229 that coal fly ash (ASV2CFA0-32) captures KOH less effectively in this case. Additionally, the trend
230 of the C_K and X_K of kaolin and ASV2CFA0-32 at 500 ppmv was obviously different. For kaolin, C_K
231 and X_K firstly increased and then decreased when the reaction temperature was changed from
232 800 °C to 1450 °C, reaching a peak at 1300 °C. The C_K and X_K of ASV2CFA0-32 increased sharply
233 when the temperature increased from 800 °C to 900 °C, and it stayed constant at 900-1100 °C.
234 When the reaction temperature increased further to 1300 °C and 1450 °C, they increased again,
235 probably because the melting of the coal fly ash particles accelerated the internal diffusion of KOH.
236 However, at 50 ppmv KOH, the C_K and X_K of ASV2CFA0-32 were comparable to that of kaolin.
237 The trend at different temperatures of the two additives (kaolin and ASV2CFA) was also the same.

238 The XRD spectra of water-washed 500 ppmv KOH-reacted coal fly ash at different
239 temperatures (800-1450 °C) are compared in Figure 6. Additionally, experiments feeding only coal
240 fly ash (ASV2CFA0-32) without KOH were carried out at 1100 °C, 1300 °C and 1450 °C. The
241 XRD spectra of the residues were the same as that of the raw ASV2CFA0-32, with only mullite and
242 quartz being detected. This reveals that, without KOH addition, no large change of the
243 mineralogical composition of the coal fly ash took place.

244 The results in Figure 6 show that, with KOH addition, at 800 °C and 900 °C, the spectra were
245 almost the same as that of the parental coal fly ash, with only mullite and quartz detected although
246 chemically captured K was detected by the ICP analysis (Figure 5). This shows that the formed K-
247 aluminosilicate remained in amorphous phase, or that the concentration of crystalline phase was too
248 low to be detected. In the 1100 °C sample, crystalline kaliophilite (KAlSiO_4) was detected. When
249 the reaction temperature increased further to 1300 °C and 1450 °C, the peaks of kaliophilite
250 (KAlSiO_4) became stronger, indicating that more crystalline kaliophilite (KAlSiO_4) was formed.
251 Notably, mullite and quartz were detected in all the product samples, showing an incomplete
252 conversion of the coal fly ash (ASV2CFA). This supports the results that the measured K-capture
253 level (C_K) and K-conversion (X_K) were considerably lower than those predicted by equilibrium
254 calculations. In our previous study on KOH capture by kaolin [33], full conversion of kaolin into K-
255 aluminosilicate was observed. The difference between kaolin and ASV2CFA0-32 indicates that, the
256 controlling mechanisms of KOH-capture reaction by coal fly ash and kaolin in the EFR are different.
257 In the KOH-kaolin system, the reaction was equilibrium limited, while the KOH-coal fly ash
258 reaction was probably diffusion or kinetically controlled.

259 **3.2.4 Impact of coal fly ash particle size**

260 The K-capture level (C_K) and K-conversion (X_K) of KOH by ASV2 coal fly ash of different
261 particle sizes are compared in Figure 7. At 800 °C, the C_K and X_K of ASV2 coal fly ash of different

particle sizes are almost independent of different particle size, probably due to a kinetically controlled reaction at this temperature. When the reaction temperature increased to 900 °C and above, the C_K of the finer coal fly ash (ASV2CFAGR) was significantly higher than that of normal coal fly ash (ASV2CFA0-32). The C_K and X_K of coarse coal fly ash (ASV2CFA32-45) were lower than that of ASV2CFA0-32. This indicates that at 900-1300 °C, the reaction was diffusion-influenced.

3.2.5 KOH capture by kaolin, mullite and coal fly ash

The measured K-capture level (C_K) and K-conversion (X_K) of KOH-coal fly ash (ASV2CFA0-32 and ASV2CFAGR) obtained at different temperatures are compared with the experimental results of KOH-kaolin and mullite from our previous study [33] in Figure 8. The mullite sample was generated by heating kaolin at 1100 °C for 24 hours [33]. The median diameter D_{50} of ASV2CFAGR ($D_{50} = 6.02 \mu\text{m}$) was comparable to that of the kaolin ($D_{50} = 5.47 \mu\text{m}$) and mullite powder ($D_{50} = 5.90 \mu\text{m}$), while the D_{50} of ASV2CFA0-32 was somewhat larger (10.2 μm). The BET surface area of kaolin (12.7 m^2/g) was higher than those of mullite (5.30 m^2/g) and ASV2CFAGR (9.07 m^2/g). The main mineral phase of the mullite powder and the ASV2 coal fly ash (ASV2CFAGR, ASV2CFA0-32) was mullite, whereas it was kaolinite for kaolin powder.

The results show that at 800 °C, the C_K of ASV2CFA0-32, ASV2CFAGR and mullite was at the same level, about 0.020 g K/(g additive), while the value for kaolin was much higher at 0.167 g K/(g additive). One possible reason is that the BET surface areas of coal fly ash and mullite were smaller than that of kaolin, resulting in a smaller amount of reactive spots and a slower internal diffusion of KOH. Another possible reason is that the kinetics of the KOH-capture reaction by mullite and kaolinite are different and it is probably slower for mullite than that of kaolinite or metakaolin. Considering that the BET surface area and median diameter D_{50} of ASV2CFAGR were comparable to those of kaolin but that the C_K of kaolin was still considerably higher than that of

286 ASV2CFAGR, the difference of the kinetics of KOH-capture by kaolinite and mullite might be the
287 main reason for the observed difference of C_K at 800 °C.

288 In the temperature range 900-1300 °C, the C_K of coal fly ashes, mullite and kaolin all increased
289 with increasing temperature, but the C_K of coal fly ash and mullite was both considerably lower
290 than that of kaolin. When the temperature increased further to 1450 °C, the C_K of mullite increased
291 significantly, and it became comparable to that of kaolin. However, there is a less pronounced
292 increase in C_K for the two ASV2 coal fly ashes. At 1450 °C, the relatively lower C_K of the two
293 ASV2 coal fly ashes may be partly due to the equilibrium limit as shown in Figure 9, and partly due
294 to internal diffusion limitations. In summary, the KOH-capture reaction by kaolin, mullite and coal
295 fly ash at 800 °C were all kinetically controlled. At 900-1300 °C, KOH capture by mullite and coal
296 fly ash were more diffusion-influenced. At 1450 °C, KOH capture by kaolin, and mullite was
297 limited by equilibrium, while it is diffusion influence for coal fly ash (ASV2CFA0-32 and
298 ASV2CFAGR).

299 **4 Conclusions**

300 The KOH-capture reaction by coal fly ash was studied by entrained flow reactor experiments
301 and equilibrium calculations. The impacts of KOH-concentration, molar ratio of K/(Al+Si) in
302 reactants, reaction temperature and particle size of coal fly ash were investigated. The results of
303 KOH-capture experiments using coal fly ash were also compared with that of kaolin and mullite
304 from our previous studies [33].

305 The experimental results at different KOH concentrations (different molar ratio of K/(Al+Si) in
306 feed) with a reaction temperature of 1300 °C, and a gas residence time of 1.2 s showed that, the K-
307 capture level (C_K) of coal fly ash increased with the KOH concentration at 50-500 ppmv KOH
308 ($K/(Al+Si) = 0.048-0.481$), but no further increase of K-capture level (C_K) was observed at a K-

309 concentration of 750-1000 ppmv. At 50 ppmv KOH, the measured K-capture level (C_K) of coal fly
310 ash was comparable to the equilibrium calculation data and the experimental C_K of kaolin from our
311 previous study [33]. However, at 250 ppmv KOH and above (molar $K/(Al+Si) \geq 0.240$), the
312 measured C_K was lower than the equilibrium data. The main alkali product species formed were
313 leucite ($KAlSi_2O_6$) at 250 ppmv, and kaliophilite ($KAlSiO_4$) at 500 ppmv. Although the types of
314 formed K-aluminosilicates (predicted by equilibrium calculations) agreed with those of the KOH-
315 kaolin reaction, coal fly ash captured KOH less effectively at 250 ppmv KOH and above (molar
316 $K/(Al+Si) \geq 0.240$).

317 At 500 ppmv KOH ($K/(Al+Si) = 0.481$), when the temperature changed from 800 to 1450 °C,
318 C_K of the coal fly ash generally increased from 0.025 g K/(g additive) to 0.087 g K/(g additive). The
319 K-capture level (C_K) of coal fly ash was lower than that of kaolin throughout the whole temperature
320 range studied. At 800 °C, with a median particle size of 10.20 μm , the KOH-capture reaction by
321 coal fly ash was probably kinetically controlled. At 900-1300 °C, the K-capture level increased with
322 the decreased particle size and was probably transport or kinetically limited. At 1450 °C the
323 reaction was limited by equilibrium as well. The gradual increase of C_K at 900-1450°C may be
324 caused by the increased internal or external transport of KOH.

325 At 50 ppmv KOH ($K/(Al+Si) = 0.048$), representative for the gaseous potassium level in wood
326 suspension-fired plants, C_K of coal fly ash (around 0.02 g K/(g additive)) was comparable to the
327 equilibrium data. Results of the reaction between KOH and coal fly ash of different particle sizes at
328 900-1300 °C showed that, decreasing the coal fly ash particle size from $D_{50} = 10.20 \mu m$ to $D_{50} =$
329 $6.03 \mu m$ could increase the K-capture level (C_K) from 0.05 to 0.08 g K/(g additive).

330 **5 Acknowledgment**

331 This work is part of the project ‘Flexible use of Biomass on PF fired power plants’ funded by
332 Energinet.dk through the ForskEL programme, Ørsted Bioenergy & Thermal Power A/S and DTU.

333 **6 Funding:**

334 This work was supported by Energinet.dk [ForskEL - project number. 2014-1-12150], Ørsted
335 Bioenergy & Thermal Power A/S and DTU.

336 **Supplementary material:** Detailed results of the equilibrium calculation of KOH capture by
337 coal fly ash are included in the supplementary material.

7 References

- [1] Wu H, Bashir M S, Jensen P A, Sander B, Glarborg P. Impact of coal fly ash addition on ash transformation and deposition in a full-scale wood suspension-firing boiler. *Fuel* 2013; 113: 632-643.
- [2] Damoe A J, Wu H, Frandsen F J, Glarborg P, Sander B. Impact of Coal Fly Ash Addition on Combustion Aerosols (PM 2.5) from Full-Scale Suspension-Firing of Pulverized Wood. *Energy Fuels* 2014; 28: 3217-3223.
- [3] Wu H, Glarborg P, Frandsen F J, Dam-Johansen K, Jensen P A. Dust-Firing of Straw and Additives: Ash Chemistry and Deposition Behavior. *Energy Fuels* 2011; 25: 2862-2873.
- [4] Christensen K A, Stenholm M, Livbjerg H. The formation of submicron aerosol particles, HCl and SO₂ in straw-fired boilers. *J. Aerosol Sci* 1998; 29: 421-444.
- [5] Dayton D C, French R J, Milne T A. Direct Observation of Alkali Vapor Release during Biomass Combustion and Gasification. 1. Application of Molecular Beam/Mass Spectrometry to Switchgrass Combustion. *Energy Fuels* 1995; 9: 855-865.
- [6] Vassilev S V, Baxter D, Andersen L K, Vassileva C G. An overview of the composition and application of biomass ash. *Fuel* 2013; 105: 19-39.
- [7] Gao X, Yani S, Wu H. Emission of Inorganic PM₁₀ during the Combustion of Spent Biomass from Mallee Leaf Steam Distillation. *Energy Fuels* 2015; 29: 5171-5175.
- [8] Johansen J M, Aho M, Paakkinen K, Taipale R, Egsgaard H, Jakobsen J G, Frandsen F J, Glarborg P. Release of K, Cl, and S during combustion and co-combustion with wood of high-chlorine biomass in bench and pilot scale fuel beds. *Proc. Combust. Inst.* 2013; 34: 2363-2372.
- [9] Yin C, Rosendahl L A, Kær S K. Grate-firing of biomass for heat and power production. *Prog. Energy Combust. Sci.* 2008; 34: 725-754.
- [10] Damoe A J, Jensen P A, Frandsen F J, Wu H, Glarborg P. Fly Ash Formation during Suspension Firing of Biomass: Effects of Residence Time and Fuel Type. *Energy Fuels* 2017; 31: 555-570.
- [11] Zheng Y, Jensen A D, Johnsson J E. Deactivation of V₂O₅-WO₃-TiO₂ SCR catalyst at a biomass-fired combined heat and power plant. *Appl. Catal., B: Environ.* 2005; 60: 253-264.

364 [12] Zheng Y, Jensen A D, Johnsson J E. Laboratory Investigation of Selective Catalytic Reduction
 365 Catalysts: Deactivation by Potassium Compounds and Catalyst Regeneration. *Ind. Eng. Chem. Res.* 2004;
 366 43: 941-947.

367 [13] Castellino F, Rasmussen S B, Jensen A D, Johnsson J E, Fehrmann R. Deactivation of vanadia-based
 368 commercial SCR catalysts by polyphosphoric acids. *Appl. Catal., B: Environ.* 2008; 83: 110-122.

369 [14] Castellino F, Jensen A D, Johnsson J E, Fehrmann R. Influence of reaction products of K-getter fuel
 370 additives on commercial vanadia-based SCR catalysts Part I. Potassium phosphate. *Appl. Catal., B: Environ.*
 371 2009; 86: 196-205.

372 [15] Zheng Y, Jensen P A, Jensen A D. A kinetic study of gaseous potassium capture by coal minerals in a
 373 high temperature fixed-bed reactor. *Fuel* 2008; 87: 3304-3312.

374 [16] Wang L, Becidan M, Skreiberg Ø. Sintering Behavior of Agricultural Residues Ashes and Effects of
 375 Additives. *Energy Fuels* 2012; 26: 5917-5929.

376 [17] Uberoi M, Punjak W A, Shadman F. The kinetics and mechanism of alkali removal from flue gases by
 377 solid sorbents. *Prog. Energy Combust. Sci.* 1990; 16: 205-211.

378 [18] Tran K-Q, Iisa K, Steenari B-M, Lindqvist O. A kinetic study of gaseous alkali capture by kaolin in the
 379 fixed bed reactor equipped with an alkali detector. *Fuel* 2005; 84: 169-175.

380 [19] Iisa K, Lu Y, Salmenoja K. Sulfation of Potassium Chloride at Combustion Conditions. *Energy Fuels*
 381 1999; 13: 1184-1190.

382 [20] Zeuthen J H, Jensen P A, Jensen J P, Livbjerg H. Aerosol Formation during the Combustion of Straw
 383 with Addition of Sorbents. *Energy Fuels* 2007; 21: 699-709.

384 [21] Davidsson K O, Steenari B M, Eskilsson D. Kaolin Addition during Biomass Combustion in a 35 MW
 385 Circulating Fluidized-Bed Boiler. *Energy Fuels* 2007; 21: 1959-1966.

386 [22] De Fusco L, Boucquey A, Blondeau J, Jeanmart H, Contino F. Fouling propensity of high-phosphorus
 387 solid fuels: Predictive criteria and ash deposits characterization of sunflower hulls with P/Ca-additives in a
 388 drop tube furnace. *Fuel* 2016; 170: 16-26.

389 [23] Wu H, Castro M, Jensen P A, Frandsen F J, Glarborg P, Dam-Johansen K, Røkke M, Lundtorp K.
390 Release and Transformation of Inorganic Elements in Combustion of a High-Phosphorus Fuel. *Energy Fuels*
391 2011; 25: 2874-2886.

392 [24] Wang L, Hustad J E, Skreiberg Ø, Skjevrak G, Grønli M. A Critical Review on Additives to Reduce
393 Ash Related Operation Problems in Biomass Combustion Applications. *Energy Procedia* 2012; 20: 20-29.

394 [25] Bashir M S, Characterization and Quantification of Deposit Build-up and Removal in Straw
395 Suspension-Fired Boilers, in: Department of Chemical and Biochemical Engineering, Technical University
396 of Denmark, Copenhagen, 2012.

397 [26] Ahmaruzzaman M. A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* 2010; 36: 327-
398 363.

399 [27] Blissett R S, Rowson N A. A review of the multi-component utilization of coal fly ash. *Fuel* 2012; 97:
400 1-23.

401 [28] Zheng Y, Jensen P A, Jensen A D, Sander B, Junker H. Ash transformation during co-firing coal and
402 straw. *Fuel* 2007; 86: 1008-1020.

403 [29] Wei X, Lopez C, von Puttkamer T, Schnell U, Unterberger S, Hein K R G. Assessment of
404 Chlorine-Alkali-Mineral Interactions during Co-Combustion of Coal and Straw. *Energy Fuels* 2002; 16:
405 1095-1108.

406 [30] Dayton D C, Belle-Oudry D, Nordin A. Effect of Coal Minerals on Chlorine and Alkali Metals Released
407 during Biomass/Coal Cofiring. *Energy Fuels* 1999; 13: 1203-1211.

408 [31] Liu Y, Duan X, Cao X, Che D, Liu K. Experimental study on adsorption of potassium vapor in flue gas
409 by coal ash. *Powder Technol.* 2017; 318: 170-176.

410 [32] Wang G, Jensen P A, Wu H, Frandsen F J, Sander B, Glarborg P. Potassium Capture by Kaolin, Part 2:
411 K_2CO_3 , KCl and K_2SO_4 . *Energy Fuels* 2018; 32: 3566-3578.

412 [33] Wang G, Jensen P A, Wu H, Frandsen F J, Sander B, Glarborg P. Potassium Capture by Kaolin, Part 1:
413 KOH. *Energy Fuels* 2018; 32: 1851-1862.

414 [34] Bale C W, Bélisle E, Chartrand P, Decterov S A, Eriksson G, Hack K, Jung I H, Kang Y B, Melançon J,
415 Pelton A D, Robelin C, Petersen S. FactSage thermochemical software and databases — recent
416 developments. Calphad. 2009; 33: 295-311.

417

418 **Figures**

419

420

421 Figure 1. Schematic of the Entrained Flow Reactor (EFR).

422

423 Figure 2. Comparison of $K/(Al+Si)$ in collected solid products and reactants fed into the EFR.

424 Figure 3. K-capture level (C_K) and K-conversion (X_K) of KOH-capture by ASV2CFA0-32 and
 425 kaolin ($D_{50} = 5.47\mu m$) [33] at KOH concentrations from 50 to 1000 ppmv. Molar ratio of $K/(Al+Si)$
 426 in the reactants varied from 0.048 to 0.961. Reaction temperature for ASV2CFA0-32 was 1300 °C
 427 and reaction temperature of kaolin was 1100 °C; gas residence time was 1.2 s. Equilibrium
 428 calculation results for KOH capture by ASV2CFA0-32 are included for comparison.

429

430 Figure 4. XRD spectra of water-washed KOH-reacted ASV2CFA0-32 at 50 ppmv, 250 ppmv and
 431 500 ppmv KOH. The reaction temperature was 1300 °C; the molar ratio of K/(Al+Si) in the
 432 reactants was 0.048, 0.240 and 0.481; the gas residence time was 1.2 s.

433

435 Figure 5. Comparison of K-capture level (C_K) and K-conversion (X_K) of KOH capture by
436 ASV2CFA0-32 and kaolin ($D_{50} = 5.47\mu\text{m}$) [33] at temperatures 800-1450 °C. The KOH
437 concentration was 500 ppmv (molar ratio of $\text{K}/(\text{Al}+\text{Si}) = 0.481$) in (A) and (B), and 50 ppmv (molar
438 ratio of $\text{K}/(\text{Al}+\text{Si}) = 0.048$) in (C) and (D). The gas residence time was 1.2 s, and equilibrium
439 results of KOH capture by ASV2CFA0-32 are included for comparison.

440

441 Figure 6. XRD spectra of water washed KOH-reacted ASV2CFA0-32 samples at different
 442 temperatures (800-1450 °C). The KOH-concentration was 500 ppmv, with molar ratio of K/(Al+Si)
 443 in reactants of 0.481. The gas residence time was 1.2 s.

444

(A) K-capture level (C_K) (B) K-conversion (X_K)

446 Figure 7. Comparison of K-capture level (C_K) and K-conversion (X_K) of KOH capture by
447 ASV2 coal fly ash of different particle sizes: ASV2CFAGR ($D_{50} = 6.03 \mu\text{m}$), ASV2CFA0-32 (D_{50}
448 $= 10.20 \mu\text{m}$), and ASV2CFA32-45 ($D_{50} = 33.70 \mu\text{m}$). The reaction temperature was 1300 °C; the
449 gas residence time was 1.2 s; the KOH concentration in the flue gas was 500 ppmv, with a molar
450 K/(Al+Si) ratio of 0.481. Equilibrium calculation results are included for comparison.

Figure 8. Comparison of K-capture level (C_K) and K-conversion (X_K) of ASV2 coal fly ashes of different particle size (ASV2CFA0-32 and ASV2CFAGR), kaolin and mullite [33]. The KOH concentration was 500 ppmv in all experiments, with molar K/(Al+Si) ratio of 0.481. Gas residence time was 1.2 s.

Figure 9. Comparison of equilibrium calculated K-capture level (C_K) of KOH capture by kaolin [33] and ASV2CFA0-32. The KOH concentration was 500 ppmv in the flue gas, with a molar K/(Al+Si) ratio of 0.481.

463 **Tables**

464 Table 1. Characteristics of the coal fly ashes.

Name	ASV2CFAGR	ASV2CFA0-32	ASV2CFA32-45
particle size (µm)	0-32	0-32	32-45
D ₅₀ (µm)	D ₅₀ = 6.03	D ₅₀ = 10.20	D ₅₀ = 33.70
BET surface area (m ² /g)	9.07	8.04	3.41
O (wt. % dry base)	46.60	46.60	45.06
S (wt. % dry base)	0.26	0.26	0.21
P (wt. % dry base)	0.64	0.64	0.57
Si (wt. % dry base)	22.0	22.0	21.0
Al (wt. % dry base)	14.0	14.0	13.0
Fe (wt. % dry base)	2.9	2.9	3.0
Ca (wt. % dry base)	4.50	4.50	5.2
Mg (wt. % dry base)	0.97	0.97	0.88
Na (wt. % dry base)	0.27	0.27	0.2
K (wt. % dry base)	0.87	0.87	0.67
Ti (wt. % dry base)	0.88	0.88	0.74

465

466

467

468 Table 2. Conditions of the experiments in the Entrained Flow Reactor (EFR).

Experimental series	K-species	additives	D ₅₀ of additives /μm	Temp./°C	Gas residence time/s	K in gas /ppmv	K/(Al+Si)
(A) KOH-capture by CFA (impact of K-concentration)	KOH	ASV2CFA0-32	10.20	1300	1.2	50	0.048
						250	0.240
						500	0.481
						750	0.721
						1000	0.961
(B) KOH-capture by CFA (impact of temperature)	KOH	ASV2CFA0-32	10.20	800	1.2	50, 500	0.481
				900			
				1100			
				1300			
				1450			
(C) KOH-capture by CFA (impact of CFA particle size)	KOH	ASV2CFAGR0-32	6.03	1300	1.2	500	0.481
		ASV2CFA0-32	10.20				
	KOH	AMVCFA0-32	33.70				

469

470

471

472 Table 3. Equilibrium calculation results of KOH capture by coal fly ash (ASV2CFA0-32).

Input conditions	Temp. /°C	K-species appearing	Al-con. /%	Si-con. /%	C _K /%	C _K /(g K/(g additive))
50 ppmv KOH, K/(Al+Si) =0.048	800	100 % KAlSi ₃ O ₈	12	24	100	0.023
	900	100 % KAlSi ₃ O ₈	12	24	100	0.023
	1100	100 % KAlSi ₃ O ₈	12	24	100	0.023
	1300	100 % KAlSi ₃ O ₈	12	24	100	0.023
	1450	98 % KAlSi ₃ O ₈ + 1 % KOH + 1 % KCl	12	24	98	0.023
250 ppmv KOH, K/(Al+Si) =0.240	800	100 % KAlSi ₂ O ₆	60	81	100	0.117
	900	100 % KAlSi ₂ O ₆	60	80	100	0.116
	1100	98 % KAlSi ₂ O ₆ + 1 % KOH	60	80	98	0.115
	1300	93 % KAlSi ₂ O ₆ + 6 % KOH	56	75	93	0.108
	1450	93 % KAlSi ₂ O ₆ + 6 % KOH	56	75	93	0.109
500 ppmv KOH, K/(Al+Si) =0.481	800	72 % KAlSiO ₄ + 10 % KAlSi ₂ O ₆	100	75	83	0.193
	900	71 % KAlSiO ₄ + 12 % KAlSi ₂ O ₆ + 2 % KOH	100	77	83	0.193
	1100	55 % KAlSiO ₄ + 28 % KAlSi ₂ O ₆ + 15 % KOH	100	89	83	0.193
	1300	55 % KAlSiO ₄ + 28 % KAlSi ₂ O ₆ + 16 % KOH	100	90	83	0.193
	1450	57 % KAlSi ₂ O ₆ + 42 % KOH	69	92	57	0.133
750 ppmv KOH, K/(Al+Si) =0.721	800	55 % KAlSiO ₄ + 41 % K ₂ SiO ₃ + 2 % KOH	100	67	55	0.193
	900	55 % KAlSiO ₄ + 36 % K ₂ SiO ₃ + 2 % K ₂ Si ₂ O ₅ + 4 % KOH	100	67	55	0.193
	1100	55 % KAlSiO ₄ + 18 % K ₂ Si ₂ O ₅ + 24 % KOH	100	67	55	0.193
	1300	36 % KAlSiO ₄ + 19 % KAlSi ₂ O ₆ + 44 % KOH	100	90	55	0.193
	1450	29 % KAlSiO ₄ + 23 % KAlSi ₂ O ₆ + 47 % KOH	94	91	52	0.181
1000 ppmv KOH, K/(Al+Si) =0.961	800	32 % KAlSiO ₄ + 9 % KAlO ₂ + 52 % K ₂ SiO ₃ + 4 % KOH	78	52	32	0.151
	900	41 % KAlSiO ₄ + 1 % KAlO ₂ + 36 % K ₂ SiO ₃ + 21 % KOH	99	66	41	0.191
	1100	41 % KAlSiO ₄ + 15 % K ₂ Si ₂ O ₅ + 41 % KOH	100	67	41	0.193
	1300	27 % KAlSiO ₄ + 14 % KAlSi ₂ O ₆ + 58 % KOH	100	90	41	0.193
	1450	27 % KAlSiO ₄ + 14 % KAlSi ₂ O ₆ + 58 % KOH + 1 % K	100	90	41	0.193

473