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KOH Capture by Coal Fly Ash

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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 ($D_{50} = 6.03-33.70 \mu\text{m}$) on the reaction was investigated. The results revealed that, at 50 ppmv KOH (molar ratio of K/(Al+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$_2$O$_6$) 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 K/(Al+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 ($D_{50} = 10.20 \mu\text{m}$) 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 K$_2$SO$_4$ [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 $\text{K}_2\text{SO}_4$ in inner layer deposit collected from high-temperature flue gas (1300 °C) was greatly reduced. KCl, KOH, and $\text{K}_2\text{CO}_3$ 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 $\text{K}_2\text{CO}_3$ 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 $\text{K}_2\text{CO}_3$, KCl and $\text{K}_2\text{SO}_4$ 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
and ASV2CFA32-45, respectively. Additionally, the ASV2CFA0-32 was ground in a ball mill to get a finer coal ash sample, named as ASV2CFAGR. The three ash samples were all analyzed with a Malvern 3000 particle size analyzer. The median diameter ($D_{50}$) of ASV2CFA0-32, ASV2CFA32-45 and ASV2CFAGR was 10.20 μm, 33.70 μm and 6.03 μm, respectively. The $D_{50}$ of ASV2CFAGR is comparable with that of kaolin (5.47 μm) and mullite (5.90 μm) utilized in our previous studies [32, 33]. A sieving analysis showed that ASV2CFA0-32 contributed 63.0 wt. % of the ASV2 coal fly ash, while ASV2CFA32-45 made up 14.4 wt. %. The three coal fly ashes size fractions were also subjected to ICP-OES analysis, with the results summarized in Table 1. The three ash size fractions had similar composition and were all rich in Al and Si. The molar ratio of $(K+Na)/(Al+Si)$ of the three ash fractions was around 0.02, indicating that there was a large surplus of Al and Si in the ashes which could participate the K-capture reaction. The coal fly ashes was also analyzed with XRD (X-ray Diffraction), and the results showed that mullite ($3Al_2O_3\cdot2SiO_2$) and quartz ($SiO_2$) were the main crystalline phases, with no crystalline alkali or alkali earth species detected. This indicated that the small amounts of Na, K, Ca and Mg detected by ICP-OES were present in amorphous species.

### 2.2 Setup

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

Instead of feeding solid KOH powder and coal fly ash directly into the reactor [19], solid KOH and coal fly ashes were mixed with deionized water, to make a homogeneous slurry. The slurry was subsequently fed into the reactor through water-cooled feeding probe, with a feeding rate varying
from 3.2 to 6.2 g/min. The slurry was subsequently atomized by a 30 Nl/min primary air. The atomized slurry droplets were mixed with preheated secondary air (40-87 Nl/min) and subsequently vaporized. KOH evaporated and reacted with coal fly ash in the reactor tube. Solid particles and aerosols were collected by a cyclone (with a cut-off diameter of 2.3 \( \mu m \)) and a metal filter (with a pore size of 0.8 \( \mu m \)), respectively. The cyclone and filter were heated to 200 °C to avoid condensation of water vapor. Detailed information on the EFR reactor and the slurry feeding system can be found elsewhere [32, 33].

2.3 Experimental matrix

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

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

2.4 Analytical methods

The collected solid samples were subjected to ICP-OES (Inductively Coupled Plasma Atomic Emission Spectroscopy) to quantify the amount of potassium captured by coal fly ash. The
concentrations of major elements were determined according to the Danish Standard DS/EN 15290 (Solid Biofuels- Determination of Major Elements). The concentration of water-soluble K and Cl was analyzed according to the standard DS/EN ISO 16995 (Solid Biofuels- Determination of water-soluble Chloride, Sodium and Potassium).

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

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

2.5 Equilibrium calculation

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

The chemical equilibrium calculations were performed at atmospheric pressure in the temperature range of 500-1800 °C. Four databases including FactPS, FToxid, FTsalt and FTpulp 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$_3$O$_8$) 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$_2$O$_6$) with a molar ratio of K:Al:Si =
1:1:2 became the dominant K-aluminosilicate. At 500, 750 and 1000 ppmv KOH, kaliophilite (KAlSiO$_4$) with a molar ratio of K:Al:Si = 1:1:1 was the main K-aluminosilicate product.

3.2.2 Impact of KOH concentration

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

Also, the measured $C_K$ and $X_K$ of KOH reaction with kaolin from our previous study [33] are included for comparison in Figure 3. The experiments of KOH capture by kaolin were conducted at 1100 °C, while the experiments with ASV2CFA0-32 were conducted at 1300 °C. Although the reaction temperature was different, the results are still comparable, because the K-capture behavior of kaolin at 1100 °C and 1300 °C is similar according to our previous study [33]. The results show that the measured $C_K$ and $X_K$ of ASV2CFA0-32 were considerably lower than that of kaolin. There may be several reasons for the lower efficiency of the coal fly ash compared to kaolin. One possible reason is that the main mineral phase of coal fly ash, mullite, is less reactive towards potassium than kaolin and metakaolin. Another possible reason is that the BET surface area of ASV2CFA0-32
(8.04 m$^2$/g) is smaller than that of kaolin (12.70 m$^2$/g), and the median diameter of ASV2CFA0-32 (10.20 μm) is larger than that of kaolin (5.47 μm). Consequently, there were fewer active sites for KOH-capture in ASV2CFA0-32 [33]. In addition, diffusion limitations for KOH inside the coal fly ash particles may have also played a role, resulting in an incomplete consumption of mullite in the coal fly ash case. The incomplete consumption of mullite is supported by the XRD results shown in Figure 4, in which peaks corresponding to mullite were detected in the KOH-reacted coal fly ash.

The XRD spectra of water-washed KOH-reacted ASV2CFA0-32 at 50 ppmv, 250 ppmv and 500 ppmv KOH are compared in Figure 4. At 50 ppmv KOH, only mullite and quartz originated from the raw coal fly ash were detected. No crystalline K-aluminosilicate was detected, although sanidine (KAlSi$_3$O$_8$) was predicted by the equilibrium calculations. This is probably because either the content of K-aluminosilicate in the products was too low to be detected, or amorphous K-aluminosilicates were formed which cannot be detected by XRD. In the 250 ppmv sample, leucite (KAlSi$_2$O$_6$) was detected as the main K-aluminosilicate product. In the 500 ppmv sample, kaliophilite (KAlSiO$_4$) was present as the dominant K-aluminosilicate. The type of K-aluminosilicates detected by XRD, generally agrees with the equilibrium results as shown in Table 3. Notably, mullite was detected in all the three KOH-reacted coal fly ash samples, showing that part of the mullite remained unreacted in those samples. This is different from what was observed in the study of KOH capture by kaolin, where a full conversion of kaolin to K-aluminosilicate was observed and no mullite was detected in the product samples at 500 ppmv KOH and above with a reaction temperature of 1100 °C [33].

3.2.3 Impact of reaction temperature

The measured K-capture level ($C_K$) and K-conversion ($X_K$) of KOH capture by ASV2CFA0-32 at different reaction temperatures (800-1450 °C) are compared with the equilibrium calculation results in Figure 5. KOH concentrations of 50 ppmv and 500 ppmv in the flue gas were studied. The
C\textsubscript{K} and X\textsubscript{K} of KOH capture by kaolin at the same conditions [33] are included as well for comparison. As shown in Figure 5 (A) and (B), at 500 ppmv KOH, the measured C\textsubscript{K} and X\textsubscript{K} of KOH capture by ASV2CFA0-32 were both significantly lower than equilibrium data. At 800 °C, the K-capture level (C\textsubscript{K}) was only 0.025 g K/(g additive), with 11 % of KOH captured as K-aluminosilicate. When the temperature increased to 900 °C, C\textsubscript{K} increased significantly to 0.063 g K/(g additive), with 27 % of KOH converted to K-aluminosilicate. At temperatures of 900-1100 °C, the C\textsubscript{K} stayed constant. However, when the reaction temperature increased further to 1300 °C and 1450 °C, C\textsubscript{K} increased by 38 % reaching 0.087 g K/(g additive), with 37 % of fed KOH chemically bonded by coal fly ash as K-aluminosilicate at 1450 °C.

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

Comparison of results of KOH-ASV2CFA0-32 and KOH-kaolin in Figure 5 shows that, at 500 ppmv KOH, the C\textsubscript{K} and X\textsubscript{K} of ASV2CFA0-32 were considerably lower than that of kaolin, showing that coal fly ash (ASV2CFA0-32) captures KOH less effectively in this case. Additionally, the trend of the C\textsubscript{K} and X\textsubscript{K} of kaolin and ASV2CFA0-32 at 500 ppmv was obviously different. For kaolin, C\textsubscript{K} and X\textsubscript{K} firstly increased and then decreased when the reaction temperature was changed from 800 °C to 1450 °C, reaching a peak at 1300 °C. The C\textsubscript{K} and X\textsubscript{K} of ASV2CFA0-32 increased sharply when the temperature increased from 800 °C to 900 °C, and it stayed constant at 900-1100 °C. When the reaction temperature increased further to 1300 °C and 1450 °C, they increased again, probably because the melting of the coal fly ash particles accelerated the internal diffusion of KOH. However, at 50 ppmv KOH, the C\textsubscript{K} and X\textsubscript{K} of ASV2CFA0-32 were comparable to that of kaolin. The trend at different temperatures of the two additives (kaolin and ASV2CFA) was also the same.
The XRD spectra of water-washed 500 ppmv KOH-reacted coal fly ash at different temperatures (800-1450 °C) are compared in Figure 6. Additionally, experiments feeding only coal fly ash (ASV2CFA0-32) without KOH were carried out at 1100 °C, 1300 °C and 1450 °C. The XRD spectra of the residues were the same as that of the raw ASV2CFA0-32, with only mullite and quartz being detected. This reveals that, without KOH addition, no large change of the mineralogical composition of the coal fly ash took place.

The results in Figure 6 show that, with KOH addition, at 800 °C and 900 °C, the spectra were almost the same as that of the parental coal fly ash, with only mullite and quartz detected although chemically captured K was detected by the ICP analysis (Figure 5). This shows that the formed K-alumino-silicate remained in amorphous phase, or that the concentration of crystalline phase was too low to be detected. In the 1100 °C sample, crystalline kaliophilite (KAlSiO₄) was detected. When the reaction temperature increased further to 1300 °C and 1450 °C, the peaks of kaliophilite (KAlSiO₄) became stronger, indicating that more crystalline kaliophilite (KAlSiO₄) was formed. Notably, mullite and quartz were detected in all the product samples, showing an incomplete conversion of the coal fly ash (ASV2CFA). This supports the results that the measured K-capture level (Cₖ) and K-conversion (Xₖ) were considerably lower than those predicted by equilibrium calculations. In our previous study on KOH capture by kaolin [33], full conversion of kaolin into K-alumino-silicate was observed. The difference between kaolin and ASV2CFA0-32 indicates that, the controlling mechanisms of KOH-capture reaction by coal fly ash and kaolin in the EFR are different. In the KOH-kaolin system, the reaction was equilibrium limited, while the KOH-coal fly ash reaction was probably diffusion or kinetically controlled.

3.2.4 Impact of coal fly ash particle size

The K-capture level (Cₖ) and K-conversion (Xₖ) of KOH by ASV2 coal fly ash of different particle sizes are compared in Figure 7. At 800 °C, the Cₖ and Xₖ 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 ($D_{50} = 6.02 \mu m$) was comparable to that of the kaolin ($D_{50} = 5.47 \mu m$) and mullite powder ($D_{50} = 5.90 \mu m$), while the $D_{50}$ of ASV2CFA0-32 was somewhat larger (10.2 $\mu m$). 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
ASV2CFAGR, the difference of the kinetics of KOH-capture by kaolinite and mullite might be the main reason for the observed difference of C_K at 800 °C.

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

4 Conclusions

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

The experimental results at different KOH concentrations (different molar ratio of K/(Al+Si) in feed) with a reaction temperature of 1300 °C, and a gas residence time of 1.2 s showed that, the K-capture level (C_K) of coal fly ash increased with the KOH concentration at 50-500 ppmv KOH (K/(Al+Si) = 0.048-0.481), but no further increase of K-capture level (C_K) was observed at a K-
concentration of 750-1000 ppmv. At 50 ppmv KOH, the measured K-capture level \( (C_K) \) of coal fly ash was comparable to the equilibrium calculation data and the experimental \( C_K \) of kaolin from our previous study [33]. However, at 250 ppmv KOH and above (molar \( K/(Al+Si) \geq 0.240 \)), the measured \( C_K \) was lower than the equilibrium data. The main alkali product species formed were leucite (\( KAlSi_2O_6 \)) at 250 ppmv, and kaliophilite (\( KAISiO_4 \)) at 500 ppmv. Although the types of formed K-aluminosilicates (predicted by equilibrium calculations) agreed with those of the KOH-kaolin reaction, coal fly ash captured KOH less effectively at 250 ppmv KOH and above (molar \( K/(Al+Si) \geq 0.240 \)).

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

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

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

6 Funding:

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


Figure 1. Schematic of the Entrained Flow Reactor (EFR).
Figure 2. Comparison of K/(Al+Si) in collected solid products and reactants fed into the EFR.

Figure 3. K-capture level (C_K) and K-conversion (X_K) of KOH-capture by ASV2CFA0-32 and kaolin (D_{50} = 5.47 μm) [33] at KOH concentrations from 50 to 1000 ppmv. Molar ratio of K/(Al+Si) in the reactants varied from 0.048 to 0.961. Reaction temperature for ASV2CFA0-32 was 1300 °C and reaction temperature of kaolin was 1100 °C; gas residence time was 1.2 s. Equilibrium calculation results for KOH capture by ASV2CFA0-32 are included for comparison.
Figure 4. XRD spectra of water-washed KOH-reacted ASV2CFA0-32 at 50 ppmv, 250 ppmv and 500 ppmv KOH. The reaction temperature was 1300 °C; the molar ratio of K/(Al+Si) in the reactants was 0.048, 0.240 and 0.481; the gas residence time was 1.2 s.
Figure 5. Comparison of K-capture level (C_K) and K-conversion (X_K) of KOH capture by ASV2CFA0-32 and kaolin (D_{50} = 5.47 μm) [33] at temperatures 800-1450 °C. The KOH concentration was 500 ppmv (molar ratio of K/(Al+Si) = 0.481) in (A) and (B), and 50 ppmv (molar ratio of K/(Al+Si) = 0.048) in (C) and (D). The gas residence time was 1.2 s, and equilibrium results of KOH capture by ASV2CFA0-32 are included for comparison.
Figure 6. XRD spectra of water washed KOH-reacted ASV2CFA0-32 samples at different temperatures (800-1450 °C). The KOH-concentration was 500 ppmv, with molar ratio of K/(Al+Si) in reactants of 0.481. The gas residence time was 1.2 s.
Figure 7. Comparison of K-capture level ($C_K$) and K-conversion ($X_K$) of KOH capture by ASV2 coal fly ash of different particle sizes: ASV2CFAGR ($D_{50} = 6.03 \ \mu m$), ASV2CFA0-32 ($D_{50} = 10.20 \ \mu m$), and ASV2CFA32-45 ($D_{50} = 33.70 \ \mu m$). The reaction temperature was 1300 °C; the gas residence time was 1.2 s; the KOH concentration in the flue gas was 500 ppmv, with a molar K/(Al+Si) ratio of 0.481. Equilibrium calculation results are included for comparison.
Figure 8. Comparison of K-capture level (C\textsubscript{K}) and K-conversion (X\textsubscript{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\textsubscript{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.
Table 1. Characteristics of the coal fly ashes.

<table>
<thead>
<tr>
<th>Name</th>
<th>ASV2CFAGR</th>
<th>ASV2CFA0-32</th>
<th>ASV2CFA32-45</th>
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</thead>
<tbody>
<tr>
<td>particle size (µm)</td>
<td>0-32</td>
<td>0-32</td>
<td>32-45</td>
</tr>
<tr>
<td>D$_{50}$ (µm)</td>
<td>D$_{50}$ = 6.03</td>
<td>D$_{50}$ = 10.20</td>
<td>D$_{50}$ = 33.70</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>9.07</td>
<td>8.04</td>
<td>3.41</td>
</tr>
<tr>
<td>O (wt. % dry base)</td>
<td>46.60</td>
<td>46.60</td>
<td>45.06</td>
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<tr>
<td>S (wt. % dry base)</td>
<td>0.26</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>P (wt. % dry base)</td>
<td>0.64</td>
<td>0.64</td>
<td>0.57</td>
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<tr>
<td>Si (wt. % dry base)</td>
<td>22.0</td>
<td>22.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Al (wt. % dry base)</td>
<td>14.0</td>
<td>14.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Fe (wt. % dry base)</td>
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<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Ca (wt. % dry base)</td>
<td>4.50</td>
<td>4.50</td>
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<tr>
<td>Mg (wt. % dry base)</td>
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<td>0.97</td>
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<td>Na (wt. % dry base)</td>
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<tr>
<td>Ti (wt. % dry base)</td>
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Table 2. Conditions of the experiments in the Entrained Flow Reactor (EFR).

<table>
<thead>
<tr>
<th>Experimental series</th>
<th>K-species</th>
<th>additives</th>
<th>D_{50} of additives /μm</th>
<th>Temp./°C</th>
<th>Gas residence time/s</th>
<th>K in gas /ppmv</th>
<th>K/(Al+Si)</th>
</tr>
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<tbody>
<tr>
<td>(A) KOH-capture by CFA (impact of K-concentration)</td>
<td>KOH</td>
<td>ASV2CFA0-32</td>
<td>10.20</td>
<td>1300</td>
<td>1.2</td>
<td>50</td>
<td>0.048</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>250</td>
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<td>500</td>
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<td>750</td>
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<td></td>
<td>1000</td>
<td>0.961</td>
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<td>(B) KOH-capture by CFA (impact of temperature)</td>
<td>KOH</td>
<td>ASV2CFA0-32</td>
<td>10.20</td>
<td>800</td>
<td>1.2</td>
<td>50, 500</td>
<td>0.481</td>
</tr>
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<td>900</td>
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<td></td>
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<td>(C) KOH-capture by CFA (impact of CFA particle size)</td>
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<td>ASV2CFAGR0-32</td>
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<td>1300</td>
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<tr>
<td></td>
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Table 3. Equilibrium calculation results of KOH capture by coal fly ash (ASV2CFA0-32).

<table>
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<tr>
<th>Input conditions</th>
<th>Temp. /°C</th>
<th>K-species appearing</th>
<th>Al-con. /%</th>
<th>Si-con. /%</th>
<th>C_K/%</th>
<th>C_K/(g K/(g additive))</th>
</tr>
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<tbody>
<tr>
<td>50 ppmv KOH, K/(Al+Si) =0.048</td>
<td>800</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>12</td>
<td>24</td>
<td>100</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>12</td>
<td>24</td>
<td>100</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>12</td>
<td>24</td>
<td>100</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>12</td>
<td>24</td>
<td>100</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>98 % KAISi$_2$O$_8$ + 1 % KOH + 1 % KCl</td>
<td>12</td>
<td>24</td>
<td>98</td>
<td>0.023</td>
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<tr>
<td>250 ppmv KOH, K/(Al+Si) =0.240</td>
<td>800</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>60</td>
<td>81</td>
<td>100</td>
<td>0.117</td>
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<td>900</td>
<td>100 % KAISi$_2$O$_8$</td>
<td>60</td>
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<td>100</td>
<td>0.116</td>
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<td>93 % KAISi$_2$O$_8$ + 6 % KOH</td>
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<td>75</td>
<td>93</td>
<td>0.109</td>
</tr>
<tr>
<td>500 ppmv KOH, K/(Al+Si) =0.481</td>
<td>800</td>
<td>72 % KAISiO$_4$ + 10 % KAISi$_2$O$_8$</td>
<td>100</td>
<td>75</td>
<td>83</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>71 % KAISiO$_4$ + 12 % KAISi$_2$O$_8$ + 2 % KOH</td>
<td>100</td>
<td>77</td>
<td>83</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
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<td>55 % KAISiO$_4$ + 28 % KAISi$_2$O$_8$ + 15 % KOH</td>
<td>100</td>
<td>89</td>
<td>83</td>
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<td>55 % KAISiO$_4$ + 28 % KAISi$_2$O$_8$ + 16 % KOH</td>
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<td>90</td>
<td>83</td>
<td>0.193</td>
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<td>57 % KAISi$_2$O$_8$ + 42 % KOH</td>
<td>69</td>
<td>92</td>
<td>57</td>
<td>0.133</td>
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<tr>
<td>750 ppmv KOH, K/(Al+Si) =0.721</td>
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<td>55 % KAISiO$_4$ + 41 % K$_2$SiO$_3$ + 2 % KOH</td>
<td>100</td>
<td>67</td>
<td>55</td>
<td>0.193</td>
</tr>
<tr>
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<td>55 % KAISiO$_4$ + 36 % K$_2$SiO$_3$ + 2 % K$_2$Si$_2$O$_5$ + 4 % KOH</td>
<td>100</td>
<td>67</td>
<td>55</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>55 % KAISiO$_4$ + 18 % K$_2$Si$_2$O$_5$ + 24 % KOH</td>
<td>100</td>
<td>67</td>
<td>55</td>
<td>0.193</td>
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<td>91</td>
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<td>52</td>
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<td>0.151</td>
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<tr>
<td></td>
<td>900</td>
<td>41 % KAISiO$_4$ + 1 % KAlO$_2$ + 36 % K$_2$SiO$_3$ + 21 % KOH</td>
<td>99</td>
<td>66</td>
<td>41</td>
<td>0.191</td>
</tr>
<tr>
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<td>1100</td>
<td>47 % KAISiO$_4$ + 15 % K$_2$Si$_2$O$_5$ + 41 % KOH</td>
<td>100</td>
<td>67</td>
<td>41</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>27 % KAISiO$_4$ + 14 % KAISi$_2$O$_8$ + 58 % KOH</td>
<td>100</td>
<td>90</td>
<td>41</td>
<td>0.193</td>
</tr>
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<td></td>
<td>1450</td>
<td>27 % KAISiO$_4$ + 14 % KAISi$_2$O$_8$ + 58 % KOH + 1 % K</td>
<td>100</td>
<td>90</td>
<td>41</td>
<td>0.193</td>
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