ABSTRACT: A method to simulate the reaction between gaseous K-species and solid additives, at suspension fired conditions has been developed, using an entrained flow reactor (EFR). A water slurry containing solid additives (kaolin or coal fly ash) and KCl, is injected into the EFR and the solid products are collected from the cyclone and filter. The K-capture reaction is evaluated by determining the fraction of water-insoluble K in the products. The results showed that KCl can effectively be captured by kaolin and coal fly ash, forming water-insoluble K-aluminosilicates. The amount of K, captured per gram of additives, rose when increasing the molar ratio of K/(Al+Si) in the reactants. A change of the reaction temperature, from 1100 °C to 1450 °C, did not significantly influence the extent of the reaction, which is in contradiction to the trend observed in previous fixed-bed reactor studies. The method using the EFR, developed in this study, will be applied for further studies on the reaction of different additives and alkali species.

Keywords: Alkali, Additives, Boiler, Combustion, Fouling
sampling system and caught by a cyclone and a metal filter.

Figure 2: Sources of K in collected solid products

As shown in Figure 2, in the collected solid products, both water-soluble K (A) and water-insoluble K exist, and the water-insoluble K originates from two different sources: formation by K-capturing reaction (B) and being brought in by solid additives (C).

The concentration of water-soluble K and water-insoluble K in the solid products was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis. The extent of reaction between KCl and solid additives under different conditions was evaluated by the amount of water-insoluble K formed.

In order to quantify the extent of K-capturing reaction, two parameters are defined: K-conversion fraction ($X_K$) and K-capturing level ($C_K$). $X_K$ is defined as the percentage of KCl which is transformed into water-insoluble K-aluminosilicate (%), while $C_K$ is defined as the mass of K captured by 1 g solid additives during the reaction (g K/g additive). These two parameters are calculated as below.

\[ X_K = \frac{B}{D} \times 100\% \quad (1) \]
\[ C_K = \frac{n_{KCl} M_K X_K}{m_{ad}} \quad (2) \]

Where B is the amount of water-insoluble K formed by K-capturing reaction, and D is the amount of K from KCl which is fed into the reactor, as shown in Figure 2. $n_{KCl}$ is the molar amount of KCl fed into the reactor; $M_K$ is the molar mass of K (g/mol); $m_{ad}$ is the mass of solid additives fed into the reactor (g).

The utilized quantification method is based on the assumption that collected solid samples are representative, which means that the collected and uncollected products have the same constituents. The representativeness of collected samples was checked by comparing the molar ratio of K/Al in reactants and that in collected products, with results of four tests shown in Figure 3. The results show that the molar ratio of K/Al in reactants is close to that of the collected solid samples, indicating that the collected solid samples are representative, and the aforementioned quantifying method can be used for evaluating the reaction.

3.2 Experimental Matrix

Two types of solid additives including pulverized kaolin ($D_{50} = 5.47$ µm), and, coal fly ash from Asnæsværket Power Plant, Denmark (ASV2), were utilized in this study. The impact of different parameters, such as reaction temperature, solid additive particle size, and the molar ratio of K/(Al+Si) in reactants, were investigated in the present study. The molar ratio of K/(Al+Si) in the reactants was changed by adjusting the concentration of KCl and solid additives in utilized slurries. The ASV2 coal fly ash, sieved to 0-32 µm and 32-45 µm, was injected into the reactor to investigate the influence of solid additive particle size on the reaction. Different reaction temperatures of 1100 °C, 1300 °C and 1450 °C, were obtained by adjusting the heating power of the electrically heating elements of the EFR. The experimental matrix is shown in Table I.

Table I: Experimental matrix

<table>
<thead>
<tr>
<th>Additive</th>
<th>Temp./°C</th>
<th>K/(Al + Si) molar ratio</th>
<th>Gas residence time /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin ($D_{50} = 5.47\mu m$)</td>
<td>1100</td>
<td>0.06</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>0.46</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.06</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.22</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.46</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.66</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>0.06</td>
<td>0.7</td>
</tr>
<tr>
<td>Coal ash (0-32 µm)</td>
<td>1100</td>
<td>0.06</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.06</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.48</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>0.06</td>
<td>0.7</td>
</tr>
<tr>
<td>Coal ash (32-45 µm)</td>
<td>1300</td>
<td>0.06</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>0.47</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

3.1 Representativeness of collected products

The representativeness of collected solid samples is checked by comparing the molar ratio of K/Al in reactants and that in collected products, with results of four tests shown in Figure 3. The results show that the molar ratio of K/Al in reactants is close to that of the collected solid samples, indicating that the collected solid samples are representative, and the aforementioned quantifying method can be used for evaluating the reaction.

Additionally, the morphology of reacted solid products is studied with SEM (Scanning Electron Microscopy), in order to obtain an understanding of the mechanism of the reaction.

Figure 3: molar ratio of K/Al in reactant and product (all the four experiments are conducted at 1300 °C)
3.2 Impact of molar ratio of K/(Al+Si) in reactants

For kaolin and coal fly ash, the active elements for capturing K-species are Al and Si. Therefore, the molar ratio of K/(Al+Si) indicates the relative amount of “active component” of additive to K-species in reactants. In addition, the K-capturing efficiency of different additives can be evaluated by comparing the value of $C_K$, at the same molar ratio of K/(Al+Si) in reactants.

Figure 4 shows that, for kaolin, with the increase of the molar ratio of K/(Al+Si) from 0.06 to 0.66 in the reactants, the conversion of KCl decreased from around 90 % to 30 %, implying more KCl stayed unreacted. For coal fly ash, it behaved similarly as kaolin in the EFR. Comparing to K-capture by coal fly ash in full-scale boilers where the K-conversion is about 99 % at similar molar ratio of K/(Al+Si), the X_K in the EFR is significantly lower. One possible reason for this is that the residence time in the EFR (< 1 s) is relatively shorter than that in full-scale boilers.

The results also show that kaolin is more reactive for K-capturing, compared to coal fly ash, which is due to the fact that in coal fly ash, the active elements Al and Si, are present in the form of mullite instead of kaolinite, and mullite has been proven to be less active than kaolinite for K-species capturing reaction [4]. The presence of mullite was confirmed by the X-ray diffraction (XRD) analysis of the coal ash.

3.3 Impact of temperature

To understand the influence of local temperature on the K-capturing reaction, experiments were conducted at 1100 °C, 1300 °C and 1450 °C with kaolin and coal fly ash as additives.

Reacted kaolin particles are analysed by SEM (see Figure 5). Solid products collected from 1100 °C predominantly existed as flakes, while mainly spherical kaolin particles were collected from experiments at 1300°C, implying that the eutectic melting point of the solid product is between 1100 °C and 1300 °C.

Additionally, the solid products collected from experiments conducted with kaolin and coal fly ash were quantitatively analysed by ICP-OES as shown in Figure 6 and Figure 7, respectively. For comparison, data gained from fixed bed reactor by Zheng [4] are also included. The results show that changing reaction temperature from 1100 °C to 1450 °C, does not pose significant impact on the extent of K-capture reaction in the EFR. However, in
Another interesting result is that $C_K$ in the EFR is lower than 10 g K/g additive, compared to less than 0.05 g K/g additive in the fixed-bed reactor at 1000 ppm KCl. At 50 ppm KCl in the EFR, kaolin can reach similar K-capturing levels with that in the fixed-bed reactor at 1000 ppm KCl. The results imply that dispersed kaolin particles in flue gas can capture gaseous KCl much more efficiently than additives in the form of pellets which was widely employed in previous studies [2, 8, 11]. However, the $C_K$ in EFR is still lower than the theoretical maximum value (0.3 g K/g kaolin) which is calculated according to the following reaction R1 and R2, indicating a possible improvement in utilizing solid additives under suspension-fired conditions.

$$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \xrightarrow{450-700^\circ\text{C}} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O} (g) \quad \text{R1}$$

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{KCl} + \text{H}_2\text{O} \rightarrow K_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{HCl} (g) \quad \text{R2}$$

4 CONCLUSIONS

A method of simulating the reaction of capturing gaseous K-species, by solid additives under suspension-fired conditions was developed, using an entrained flow reactor (EFR). The method makes it possible to investigate the influence of reaction temperature, residence time, additive particle size, and alkali concentration on the K-capturing reaction by different additives. Kaolin and coal fly ash, were employed in the present study.

The results showed that under suspension-fired conditions, kaolin powder and coal fly ash can effectively capture corrosive gaseous KCl in flue gas. The K-capturing level of kaolin rose with increasing molar ratio of K/(Al+Si) in reactants.

When changing reaction temperature from 1100 °C to 1450 °C, the K-capturing behaviour of kaolin and coal fly ash in the EFR differed from that observed in fixed-bed reactors, indicating a different reaction controlling mechanism for K-capturing reaction by dispersed solid additives. A detailed explanation of these observations needs further experimental investigation and analysis.

5 FUTURE WORK

The developed method using the EFR in this study will be used for future systematic quantitative investigation of different solid additives. The experimental data gained in this study will be used for developing a mathematical model describing the K-species capture and providing recommendations for optimal use of the additives in suspension-fired full-scale boilers.

6 ACKNOWLEDGEMENTS

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7 REFERENCES