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Use of aluminosilicate sorbents to control KCl vapors in biomass combustion gases

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Abstract

Lab-scale investigations were conducted into the impact of additives on the abatement of chlorine corrosion induced by combustion or co-firing of agricultural biofuels in boilers. The effect of potassium retention and chlorine liberation was examined by applying domestic aluminosilicates. The following additives were examined: kaolin, bentonite, halloysite and lignite fly ash. The samples of potassium chloride and the additive mixtures were heated in a muffle furnace in the temperature range 600–1000°C. The sintered samples obtained were examined for chlorine content, potassium retention and crystalline structure. Three mineral additives (kaolin, bentonite and halloysite) appeared to be effective in potassium binding at high temperature melting potassium aluminosilicates and in liberating chlorine in the temperature range 800–1000°C. Aluminosilicate type lignite fly ash can be considered as a very effective and inexpensive additive that prevents chlorine corrosion during biomass co-firing.

Keywords: Chlorine corrosion, Additives, Aluminosilicates

1. Introduction

Biomass-based solid fuels often contain a high content of potassium and chlorine [1]. During biomass combustion potassium easily evaporates and is released into flue gas, mainly as: HCl(g), KCl(g), KOH(g) and K(g). The others can be retained in slag and ash.

Combustion or co-firing of this type of biomass in boilers can lead to chlorine corrosion of the heat exchanging surfaces due to condensation of potassium chloride KCl(g) into deposit [2]. The low melting temperature of potassium chloride (774°C) can promote the processes of furnace wall slagging and the fouling of superheaters. The hazard of chlorine corrosion and slagging is reduced if potassium chloride is converted into sulfate or retained by aluminosilicates before reaching the tubes of a superheater [2, 3].

The objective of these studies was to evaluate the possibility of immobilizing potassium and releasing chlorine in the form of HCl by the reaction of KCl and selected domestic aluminosilicates in a lab-scale process. Motivations for the studies were the properties of aluminosilicates of the kaolinite and montmorillonite groups, which have the ability to trap alkali metals at a temperature range of 600–1000°C.

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2. Mechanisms of potassium binding and chlorine liberation

The mechanism of potassium binding and chlorine liberation due to reactions of aluminosilicates and potassium chlorine is explained with reference to kaolinite ($Al_4Si_4O_{10}(OH)_8$). This mineral, a basic component of kaolin and other clay minerals [4, 5], is in the kaolinite-serpentine group.

In the temperature range of 400–1000°C kaolinite undergoes transformation through the process of de-hydroxylation, in which water is formed and liberated as a result of chemical reactions between hydroxyl radicals and protons resulting from dissociation of less thermally durable OH groups [4].

De-hydroxylation destroys the primary structure of kaolinite and an amorphous anhydride is formed called meta-kaolinite ($Al_2O_3 \cdot 2SiO_2$). The residue readily reacts with alkali, which are absorbed, and forms crystalline potassium aluminosilicates. For instance, when meta-kaolinite reacts with potassium chloride, potassium aluminosilicate is formed and hydrogen chloride is released:

$$Al_2O_3 \cdot 2SiO_2 + 2KCl + H_2O \rightarrow \tag{1}$$

$$K_2Al_2Si_2O_8 + 2HCl \tag{2}$$

Including the process of kaolinite de-hydroxylation and meta-kaolinite-KCl reaction, one can denote:

$$Al_2Si_2O_5(OH)_4 + 2KCl + 2SiO_2 \rightarrow \tag{3}$$

$$2KAlSi_2O_6 + 2H_2O + 2HCl \tag{4}$$

The potassium aluminosilicates: kalsilite ($K_2Al_2Si_2O_8$) and leucyt ($KAlSi_2O_6$) are both characterized by a high melting temperature (1684 and 1686±5°C, respectively) [6], which could increase by a couple hundred degrees the melting temperature of ash, preventing corrosion and slagging [7].

3. Characteristics of additives

The minerals used belong to the wide class of aluminosilicates having the common formula $Al_4Si_4O_{10}(OH)_8$. The main diversity between them lies in their differing crystalline structures [4, 5]. To evaluate the ability of potassium retention by selected aluminosilicates, laboratory investigations were conducted by applying three minerals and one fly ash. The selection of these materials was based on their properties at elevated temperatures [3, 8, 9]. These were:

- halloysite PS,
- bentonite S-130,
- kaolin,
- lignite fly ash.

Table 1: Chemical analysis of the mineral additives and lignite fly ash

Component, mas.%	Kaolin	Bentonite	Halloysite	Fly ash
SiO_2	52.1	61.6	32.0	57.4
Al_2O_3	34.1	19.1	26.0	36.7
Fe_2O_3	0.6	2.4	22.0	1.3
CaO	0.1	1.8	-	0.6
MgO	0.1	3.7	-	0.3
Na_2O	0.0	2.7	-	1.0
K_2O	0.6	0.9	-	1.5
TiO_2	-	-	-	1.3
LOI*	11.8	7.1	-	-

*LOI—Loss of Ignition

3.1. Kaolin

Kaolin is a common raw material used in several applications. The main mineral of kaolin is kaolinite. Kaolin was delivered by the company KSM Surmin-Kaolin S.A. of Nowogrodziec. The raw material was cleaned of sand and hematite, enriched, homogenized, whitened, dried and ground to get bulk density of approx. 300 kg/m^3. The chemical composition of the product is shown in Table 1.

3.2. Halloysite

Halloysite is a rare mineral belonging to the kaolinite group. Its theoretical chemical composition is expressed by the formula $Al_4[Si_4O_{10}](OH)_8$. This mineral has a layered structure, in which particular plates are separated by spaces. Between the plates cations of alkali metals can penetrate and become immobilized due to chemisorption. Halloysite has an inner area surface ten times bigger than kaolinite, which makes it a very reactive material [4].

Halloysite (trade name PS) was used in the investigations (Table 1). It was delivered by the company INTERMARK of Gliwice (the raw material was mined in the "Dunino" mine near Legnica). Halloysite underwent calcination.

3.3. Bentonite

Bentonite is an aluminosilicate of clay and montmorillonite rocks characterized by high absorption ability. The bentonite used in the investigations (trade name S-130) was received from the company Polroc I Sp. z o.o. of Gliwice. The raw material was dried at a temperature below 70°C, ground and granulated. The montmorillonite content ranged from 65 to 85%. The main components of bentonite are shown in Table 1.

3.4. Lignite fly ash

Fly ash was prepared from lignite received from the Turów lignite mine. The mass content of the mineral matter in lignite was 49.8%. The lignite was dried, milled and the fraction of particles of a size below 200 μm was separated. To obtain ash the separated fraction was heated in a muffle furnace at a temperature of 815°C for two hours. Chemical analysis showed that the ash produced is of an aluminosilicate type with a small amount of alkalis (Table 1).

4. Experimental

The samples of potassium chloride and the selected additive mixtures at 5 mass ratios were heated at temperatures of 600, 815 and 1000°C for 2 hours in a CZYLOK FCF 5 SM type muffle furnace. The sintered samples were cooled, ground and sent to the laboratory in order to assay:

- chlorine content,
- potassium content,
- crystalline structure.

The chlorine content in a sintered sample (c_m) was determined according to the Polish standard PN-ISO 9297: 1944 [10] in the Institute of Environmental Protection Engineering of Wrocław University of Technology. The potassium content in a sintered sample was determined using the SEM/EDS method (Scanning Electron Microscope SEM coupled with Energy Dispersive X-ray Spectrometer EDS) in the Electrotechnics Institute of Wrocław. A crystallographic analysis of sintered samples was performed in the same Institute, using the XRD technique (X-Ray Diffraction).

5. Results

5.1. Chlorine release

The chlorine content in a sintered sample (c_m) was compared with the forecasted chlorine content (c_{ref}) in a sample of the mixture of KCl and an additive at the given additive ratio R. The effectiveness of chlorine removal (chlorine loss) from a sintered sample U_{Cl} was calculated from the following formula:

$$U_{Cl} = \left(1 - \frac{c_m}{c_{ref}}\right) \cdot 100\% \tag{5}$$

The forecasted mass content of chlorine c_{ref} was determined on the basis of the KCl mass ratio in the mixture and the atomic masses of potassium K (u_K = 39.098) and chlorine Cl (u_{Cl} = 35.453). The additive ratio R is the ratio of an additive mass mad to the mass of the mixture of KCl (m_{KCl}) and an additive:

$$R = \frac{m_{ad}}{m_{ad} + m_{KCl}} \tag{6}$$

5.1.1. Halloysite additive

The effect of the halloysite PS additive on the effectiveness of chlorine removal from the sintered sample at the temperatures of 600, 815 and 1000°C is presented in a bar chart (Fig. 1). However, only the rise in furnace temperature up to 1000°C resulted in a considerable improvement in the effectiveness of chlorine release from the sintered samples. A strong impact of halloysite PS on chlorine liberation ($R \geq 50\%$ the effectiveness of chlorine removal achieved roughly 95%) at the same temperature was observed.

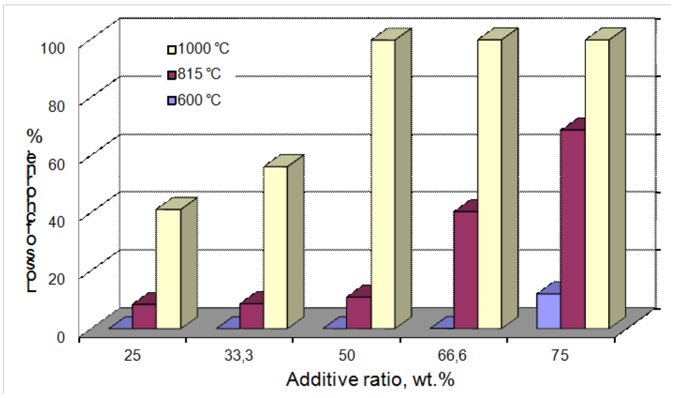

Figure 1: Effectiveness of chlorine removal by halloysite PS additive

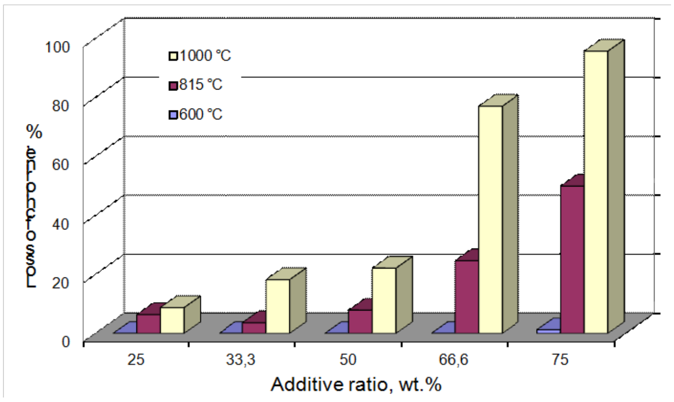

Figure 2: Effectiveness of chlorine removal by bentonite S-130 additive

5.1.2. *Bentonite additive*

The effects of the use of bentonite S-130 (Tab. 1) on the effectiveness of chlorine removal from the sintered samples were similar to those of the halloysite PS additive. For instance, when the bentonite ratio *R* was 75% the chlorine loss U_{Cl} was between 30 and 40% at 815°C and approx. 85% at the temperature of 1000°C (Fig. 2).

5.1.3. *Kaolin additive*

Taking into consideration the results of investigations when halloysite and bentonite were used, in these investigations the temperature in the muffle furnace was limited to 815 and 1000°C. At the temperature of 815°C chlorine was effectively liberated for the kaolin ratio $R \geq 66.6\%$, but at the temperature of 1000°C almost 90% of the chlorine was released for the kaolin ratio $R = 50\%$ (Fig. 3).

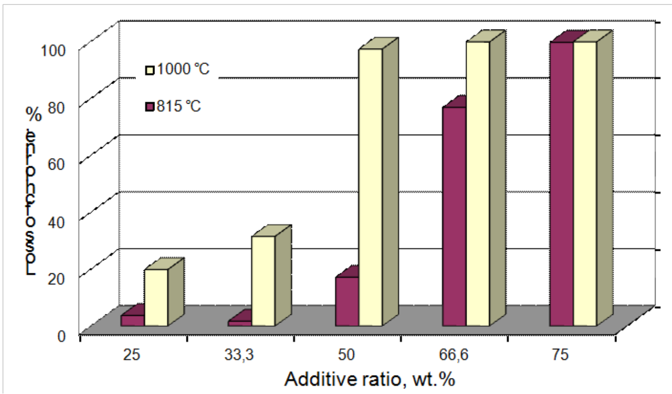

Figure 3: Effectiveness of chlorine removal by kaolin additive

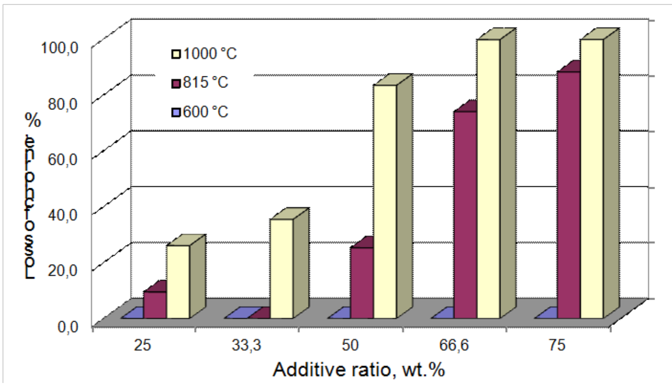

Figure 4: Effectiveness of chlorine removal by fly ash additive

5.1.4. *Fly ash additive*

Promising results were gained by applying lignite fly ash additive. The temperature of 600°C was too low to notice any visible effect. For the fly ash ratio $R = 50\%$ chlorine loss was approx. 20% at the temperature of 815°C, however at the temperature of 1000°C almost $U_{Cl} = 75\%$ was reached (Fig. 4).

5.1.5. *Discussion of the obtained results*

Because of the insignificant effect of chlorine release from the sintered samples of potassium chloride and additives mixtures at the temperature of 600°C, the effectiveness of the additives was compared on the basis of the results obtained at the temperatures of 815 and 1000°C (Fig. 5 and 6).

At the temperature of 815°C the effectiveness of chlorine removal from the sintered samples was not significant. For instance, for the additive ratio of 50% only fly ash liberated 20% of chlorine (Fig. 5). Far greater effectiveness was achieved for the additive ratio $R = 75\%$. At this temperature kaolin ap-

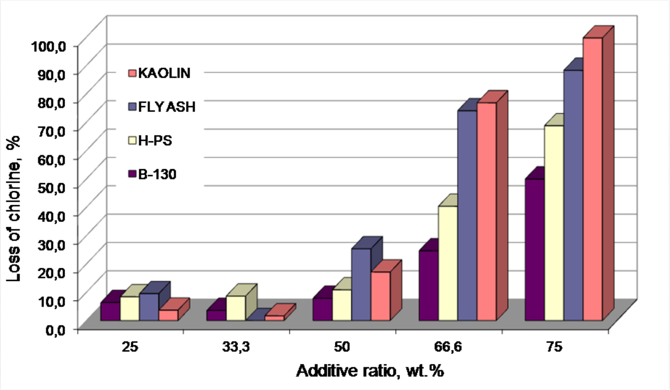

Figure 5: Effectiveness of chlorine release by additives at the temperature of 815°C (B—bentonite, H—halloysite)

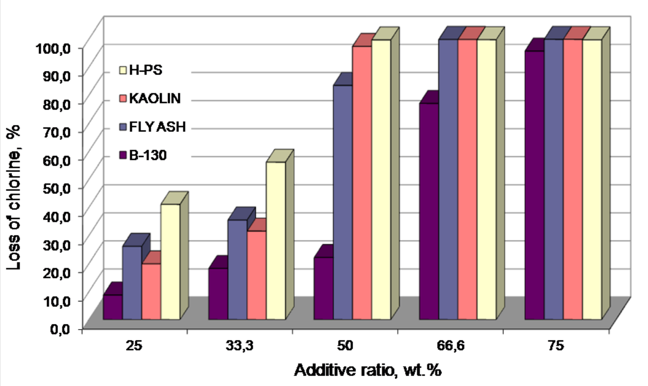

Figure 6: Effectiveness of chlorine release by additives at the temperature of 1000°C (B—bentonite, H—halloysite)

peared to be the best additive, but fly ash was only about 10% worse.

Increasing the temperature up to 1000°C markedly improved the effectiveness of chlorine removal by the additives (Fig. 6). For the additive ratio R = 50% the best effectiveness UCl was achieved by halloysite PS, kaolin and fly ash and when R increased to 66.6% almost 100% chlorine was liberated. For the additive ratio $R \geq 75\%$ each of the additives used caused almost complete removal of chlorine from the sintered samples.

5.2. *Elementary analysis of sintered samples*

In order to estimate the effectiveness of potassium binding by the additives SEM EDS analysis of the sintered samples was conducted. Only samples of 50/50 mixtures of potassium chlorine and an additive heated at the temperature of 1000°C were selected for these investigations.

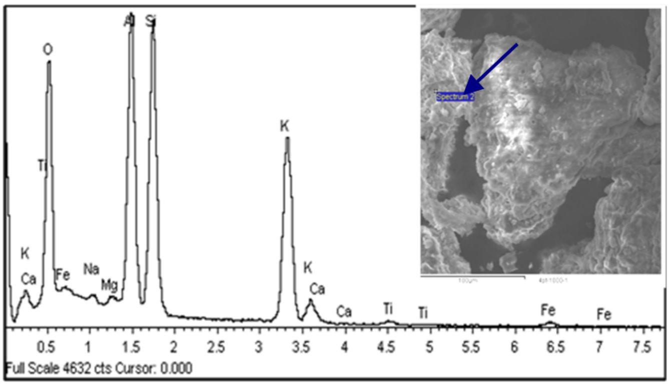

Figure 7: SEM image and X-ray spectrum recorded from the sintered sample of KCl and fly ash mixture

Table 2: Elementary analysis of the sintered samples of mixtures of KCl and additives (temperature of 1000°C)

Additive	Halloysite	Bentonite	Fly ash	Kaolin
Element		mas. %		
O	47.94	47.01	51.35	42.15
Na	0.46	4.44	0.64	-
Al	12.84	6.84	13.97	13.73
Si	14.73	22.84	16.81	18.01
P	0.44	-	-	-
K	18.71	13.14	15.31	24.79
Ti	0.35	-	0.43	0.36
Fe	4.52	1.60	0.77	-
Mg	-	4.44	0.34	-
Ca	-	3.53	0.39	-
Cl	-	0.59	-	0.96

Figure 7 shows the microscopic photo and the X-ray spectrum for the sintered sample of the KCl and fly ash mixture. The results of elementary analysis of the sintered samples for all additives are presented in Table 2. The high content of potassium in the sintered samples (13–14%) should be noted. This result shows a substantial increase compared to the initial level of potassium in the additives (Table 1).

5.3. *Crystallographic analysis of sintered samples*

The X-ray powder diffraction technique was applied to identify the crystalline phases in the same sintered samples analysed in the previous section

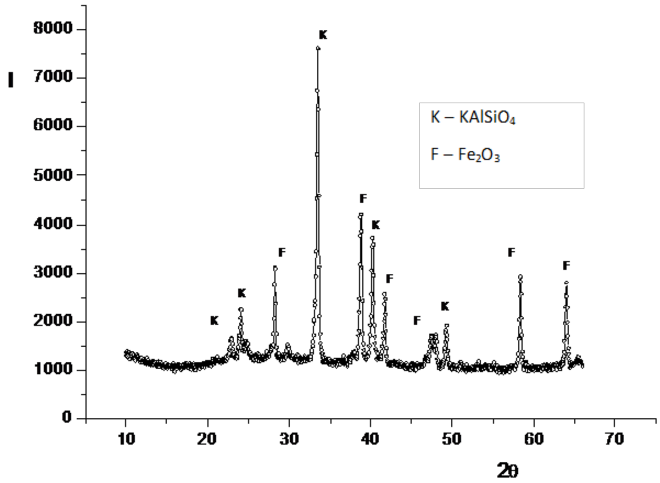

Figure 8: XRD spectra of the sample of halloysite (50%) and KCl (50%) mixture sintered at the temperature of 1000°C

Table 3: Potassium aluminosilicates identified in sintered samples

Additive	Primary component	Secondary component
halloysite PS	$KAlSiO_4$ kalsilite	Fe_2O_3 hematite
bentonite S-130	$K_4Al_2Si_2O_9$	Fe_2O_3 hematite
kaolin	$KAlSiO_4$ kalsilite	SiO_2 quartz
fly ash	$KAlSiO_4$ kalsilite	SiO_2 quartz

(5.2). An example of the XRD spectra of the sample of the halloysite PS (50%) and KCl (50%) mixture heated at the temperature of 1000°C is shown in Fig. 8.

The major crystalline components identified in the sintered samples are shown in Table 3. In every case studied crystalline potassium aluminosilicates were in the dominant part in the sintered samples.

6. Summary/Conclusions

The experimental studies conducted proved that aluminosilicates have the ability to bind potassium and liberate chlorine from alkali chlorides. These properties are very useful for preventing chlorine corrosion and reducing slagging and fouling in biomass combustion and co-firing boilers. The results obtained lead one to the following conclusions:

Kaolin, halloysite and bentonite from domestic mineral deposits react with potassium chloride, effectively binding potassium in high melting temperature potassium aluminosilicates and liberating chlorine in the form of HCl in the temperature range 800–1000°C.

Lignite fly ash of the aluminosilicate type can compete in potassium retention with commercial aluminosilicates.

The effectiveness of the additives used in potassium retention and chlorine release essentially depends on the temperature, which should be approx. 1000°C to achieve almost entire removal of chlorine.

Taking into account the results of the studies conducted, the selected additives could be ordered as follows:

$$halloysite > kaolin > flyash > bentonite$$

Acknowledgments

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