

Potassium and chlorine distributions in high temperature halloysite formed deposits

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Abstract. The paper presents results of investigations on KCl interaction with halloysite under high temperature conditions. Halloysite is an aluminosilicate that can be used as a fuel additive to prevent chlorine corrosion and formation of low melting corrosive deposits during combustion of biomass. It is claimed that an increase of the emission of gaseous chlorine as HCl(g) and decrease of chlorine share in the ash as result of KCl and halloysite interaction should be expected. During presented tests the mixtures of KCl and halloysite with different ratios were thermally decomposed in a muffle furnace at high temperatures of 900°C and 1100°C. Then, the analyses of potassium and chlorine contents in the formed solid residues were determined. Besides, it has been proved that halloysite addition changes the ash deposit structure as well as increases the ash fusion temperatures. This was supported by performing phase equilibrium calculations for the investigated different halloysite/KCl mixtures. The positive effects of halloysite on potassium capture while reducing chlorine content in solid residue to prevent formation of corrosive deposits have been confirmed.

1 Introduction

Biomass is considered to be a “difficult” fuel due to its physical and chemical properties. Comparing with coal, the biomass contains on average about twice as much carbon, four times more oxygen, less sulfur and nitrogen, and significantly more chlorine[1]. Biomass ash differs from hard coal ash: the main components of biomass ash are SiO₂, CaO, K₂O while hard coal ash SiO₂, Al₂O₃, Fe₂O₃. Ash forming elements in agricultural biomass originate in a large amount from alkali salts, quartz whereas in coal mostly from aluminosilicates, pyrites and other minerals. The increased presence of alkali salts in biomass may lead to formation of low melting alkali chloride deposits which can significantly increase corrosion rates of boiler heat exchange surfaces, The interaction of alkali elements with aluminosilicates, quartz may decrease (for low (Al₂O₃+SiO₂)/K₂O ratios) the melting temperature of ash particles and cause increased slagging and fouling

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risk. To prevent abovementioned ash-related problems, the use of various additives are being investigated, which can reduce biomass impacts on ash deposition and prevent from formation of corrosive deposits.

Fuel additives refer to a group of chemicals or minerals which can change the ash chemistry, decrease concentration of problematic species or raise melting temperatures of the ash. Chemical binding is claimed to be the most important effect of additives, due to converting problematic ash elements into high-temperature stable substances [5]. In order to prevent chlorine induced corrosion and ash deposition in biomass-fired boilers selected fuel additives can be used. In general they can be classified in two groups [2,3,6]:

- a) Additives which influence gas K-S-Cl chemistry and aerosols formation. Various aluminosilicate based minerals can be used to capture alkali metals: kaolinite, bentonite, bauxite or halloysite (eq. 1.1). Application of aluminosilicates as fuel additives aims to increase ash melting temperatures and, as a result, to prevent ash agglomeration, fouling and slagging tendencies.



More stable and high-melting species can be formed by mono-calcium phosphate (eq. 1.2)



On the other side alkali chlorides can be transformed to the gas phase to alkali sulphates, which are characterized by higher melting temperatures and less corrosive effect (eq. 1.3)



- b) Additives which change the physical and chemical properties of the ash making it easy to remove by soot-blowers, for example copper oxychloride $3\text{CuO} \cdot \text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ which is claimed to reduce slagging by making ash deposits soft and friable [7].

The aim of presented study was to investigate thermo-chemical interactions between additive and KCl at high temperature and to determine the influence of halloysite addition on chlorine and potassium distributions for different halloysite/KCl ratios and two temperature levels. The results obtained will provide better knowledge on halloysite behavior under high temperature conditions and will help to optimize additive dosage when utilizing high chlorine content agricultural biomass.

2 Materials

2.1 Halloysite specification

Halloysite is a rather rare aluminosilicate clay mineral classified to the kaolin sub group with a chemical composition similar to kaolinite. As a combustion additive it can be used to capture alkali metals according to (eq. 1.1). In its fully hydrated form the halloysite formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. What differs halloysite from kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is that it contains additional water molecules between the layers. Kaolinite most commonly occurs in platy forms while halloysite has a tubular morphology [8] which can be seen in Figure 1.

Halloysite is often observed in a partly dehydrated state since it loses its interlayer water molecules easily above 60°C [8]. Halloysite is not as commonly used as kaolinite, however it becomes increasingly important in nanotechnology applications due to its tubular structure. Its inner specific surface can be ten times bigger than kaolinite [10] and reaches approximately 70–85 m²/g. It is a mineral of low hardness (1–2 in Mohs scale) and high temperature resistance. Halloysite is characterized by the ability of ions absorption both on the outer surface and inside the crystal [11]. Consequently halloysite can be claimed to be a more effective fuel additive than kaolinite. High reactivity of halloysite is a consequence of phase change temperature above 550 °C, which allows the formation of high melting compounds with alkali metals.

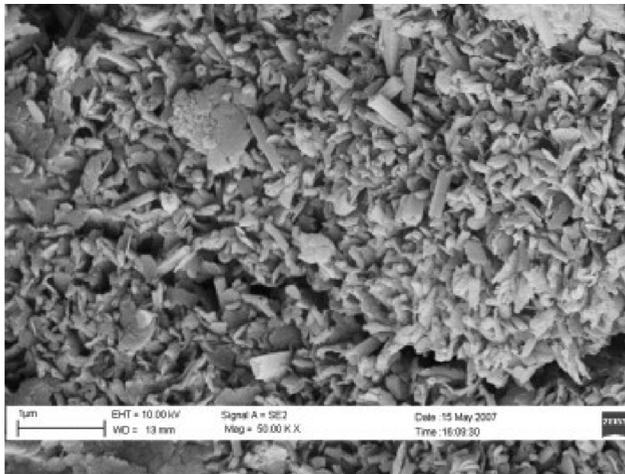


Fig. 1. Nanotubular structure of halloysite

3 Process parameters and setup

3.1 Experimental stand scheme and description

Tests were carried out in a muffle furnace (Czylok manufacture). The furnace allows to reach a stable temperature level up to 1400°C.

3.2 Tests parameters

The mixtures of halloysite/KCl were prepared in three mass ratios as follows:

- Ratio 2,
- Ratio 5,
- Ratio 20.

Mixtures were placed in ceramic boats and heated at two temperature levels: 900°C and 1100°C for 90 minutes. After thermal decomposition samples were collected and analyzed for Cl and K content (Oxides Analysis) as well as characteristic ash fusion temperatures. Analysis were performed in certified laboratory using procedures:

- Initial Deformation Temperature (DT), Softening Temperature (ST), Hemisphere temperature (HT), Flow temperature (FT) in two atmospheres: reducing and oxidative – PN-ISO 540:2001

- Ash Oxides Analysis - Plasma Spectrophotometry; Thermo iCAP 6500 Duo ICP
- Total Chlorine Content – PN-ISO 540:2001

3.3. Phase equilibrium calculations

The phase equilibrium calculations were carried out with the aid of FactSage 7.2 thermo-chemical software and databases which are based on a minimization of Gibbs free energy. The used thermo-chemical databases (SLAG-A, FToxid, FTSalt, and FactPS) allow to analyze, under high temperature conditions, the slag phase formation, but also condensation through the liquid/melt formation of salts. The calculations were performed in the air atmosphere, and temperature range between 700°C-1700°C with 25°C intervals.



Fig. 2. Sample decomposed in 900°C – ratio 5



Fig. 3. Sample decomposed in 1100°C – ratio 5

Table 1. For Oxides analysis for halloysite/KCl mixtures

Sample	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	P ₂ O ₅	Na ₂ O	K ₂ O	Cl	Al ₂ O ₃ / K ₂ O
Ratio 2	25,5	5,51	22,3	0,9	0,31	0,16	0,34	0,14	20,6	16,2	1,08
Ratio 2 900°C	36,1	6,98	28,7	1,16	0,42	0,2	0,44	0,39	23	0,87	1,25
Ratio 2 1100°C	38,6	7,39	30,5	1,24	0,47	0,23	0,48	0,18	20	0,7	1,53
Ratio 5	34,7	6,88	28,3	1,14	0,38	0,19	0,43	0,12	12	7,48	2,36
Ratio 5 900°C	41,2	8,04	33,2	1,33	0,45	0,23	0,5	0,2	14,1	0,02	2,35
Ratio 5 1100°C	40,7	7,85	33,3	1,34	0,45	0,23	0,49	0,17	15	0,02	2,22
Ratio 20	40,7	7,8	32,3	1,29	0,45	0,22	0,48	0,11	3,3	0,87	9,76
Ratio 20 900°C	48,6	9,02	36,5	1,47	0,5	0,25	0,54	0,15	4,01	0,02	9,10
Ratio 20 1100°C	46,4	9,18	36,7	1,47	0,49	0,25	0,54	0,15	4,34	0,02	8,46

Comparing the compositions of the halloysite/KCl mixtures before and after thermal exposures in 900°C and 1100°C, it could be observed that most of the chlorine originated from KCl was released from the samples after heating whereas potassium remained in solid residue bounded with additive. In addition, the ratio of Al₂O₃/K₂O was calculated which may indicate relatively how much K (as KCl) vaporized, in relation to a thermal stable Al₂O₃, from the original sample in different ratios, and under 900°C and 1100°C. This is especially visible for Ratio 2, for which it is postulated, that some KCl unreacted with halloysite (due to KCl excess) completely vaporized from the sample during the heating.

Table 2. Characteristic ash fusion temperatures for halloysite/KCl mixtures

Sample	Initial Deformation Temperature (DT), °C	Softening Temperature (ST), °C	Hemisphere temperature (HT), °C	Flow temperature (FT), °C
Ratio 2	1380/1390	1420/1440	1450/1450	1480/1480
Ratio 2 900°C	1410/1420	1430/1450	1440/1460	1490/1480
Ratio 2 1100°C	1430/1450	1450/1460	1460/1470	1480/1500
Ratio 5	1390/1390	1410/1430	1420/1470	1470/>1500
Ratio 5 900°C	1370/1320	1420/1410	1430/1460	1490/>1500
Ratio 5 1100°C	1400/1390	1420/1410	1440/1470	1500/>1500
Ratio 20	>1500/>1500	>1500/>1500	>1500/>1500	>1500/>1500
Ratio 20 900°C	>1500/>1500	>1500/>1500	>1500/>1500	>1500/>1500
Ratio 20 1100°C	>1500/1400	>1500/>1500	>1500/>1500	>1500/>1500

Concerning the impact of halloysite/KCl ratios on the ash fusion temperatures (AFT), the increase of AFT has been observed for higher ratios of halloysite in the mixtures, as shown in Table 2.

Apart from the lab experimental tests, the phase equilibrium calculations were performed to determine formation of slag (or liq), solid (s), and gas (g) phases which may occur during the interaction between halloysite and KCl, and halloysite transformation, in temperature range between 700°C-1700°C, in air atmosphere, and halloysite/KCl ratios of 2, 5 and 20 as shown in Figures 4-6, respectively. In the following figures only these phases which contain K or Cl are displayed.

Analyzing the impact of KCl on slag formation of halloysite, an increase of halloysite/KCl ratio led to shifting the maximum slag levels to higher temperatures, which corresponds to the measured ash flow temperatures of investigated halloysite/KCl mixtures. This confirmed the positive impact of halloysite on increasing the ash flow melting temperature. However, in turn, this led to higher slag levels calculated for lower temperature range between 900°C -1200°C for mixture with higher halloysite ratio. This is not in good agreement with the measured initial deformation temperatures of investigated mixtures. The reason may be that there is too short exposure time during AFT test, and at lower temperature KCl needs more time to affect the slag matrix of transforming additive. To support this statement, the sintered structure of the halloysite/KCl, heat treated at 1100°C for 90 min can be seen in Figure 3, which could be originated from the existing slag phase as determined by the phase equilibrium analysis.

As far as potassium distribution is concerned, potassium is partially dissolved in the slag phase, partially forms K-alumina(silicates), or if unreacted with transforming halloysite additive may exist in gas phase as KCl(g) and then, as temperature drops, may further forms molten salt KCl(liq) at around 900°C -750°C, and solid phase KCl(s), as shown in Figure 4.

After reacting of an additive with potassium the remaining form KCl chlorine forms HCl(g) with the water released during the halloysite decomposition.

Based on the carried out phase equilibrium calculations, it could be observed that for the ratio of halloysite/KCl=20, the KCl was completely removed from the system, resulting in formation of $\text{KAlSi}_3\text{O}_8(\text{s})$ and $\text{HCl}(\text{g})$, and increasing slightly the slag % in temperature range of 900°C -1200°C, whilst shifting the complete ash melting to the higher temperature far above 1500°C. In case of ratio halloysite/KCl=5, potassium chloride may exist in gas phase at higher temperature range above 1200°C, however during the temperature drop will further convert to form $\text{HCl}(\text{g})$ and K-alumina-silicates. In real combustion systems, kinetics and reagent mixing will play crucial role. The higher risk of KCl condensation and formation of corrosive deposit at temperature range of 700°C -900°C was identified for halloysite/KCl ratio = 2,. Furthermore, from the mass balance of samples taken for the experiments, in the mixture with ratio of halloysite/KCl=2 the highest mass loss were determined after sample heating both in 900°C and 1100°C. This can be confirmed with measured mass losses in the samples due to KCl evaporation from the system.

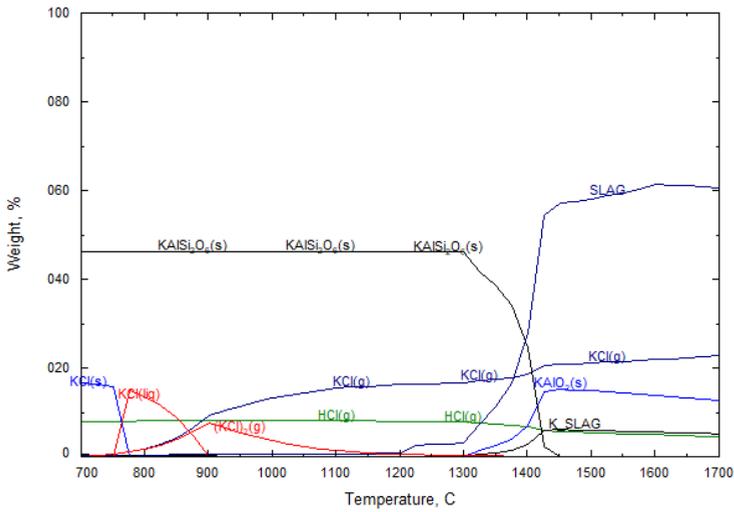


Fig. 4. Phase distribution calculated for ratio Halloysite/KCl = 2

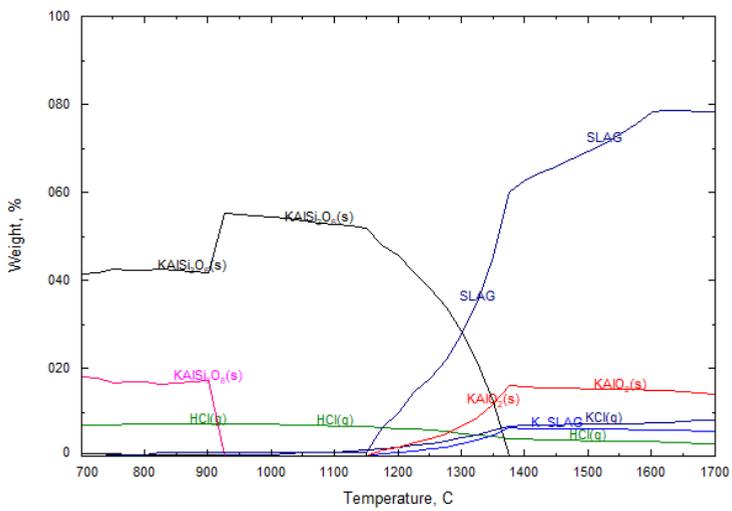


Fig. 5. Phase distribution calculated for ratio Halloysite/KCl = 5

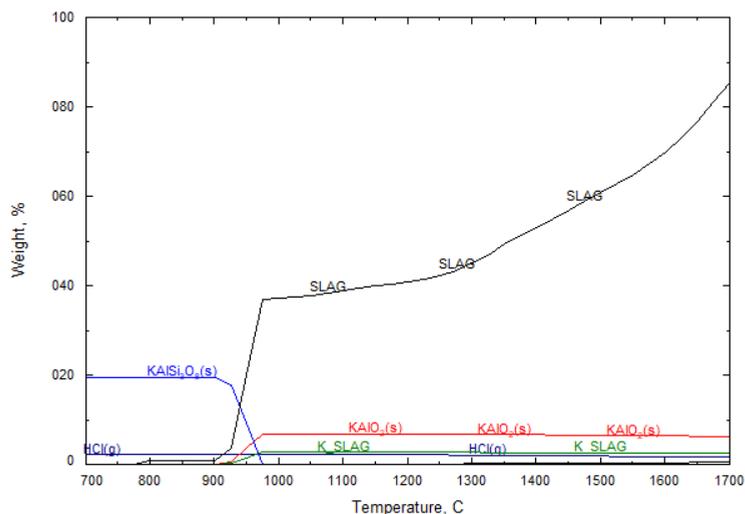


Fig. 6. Phase distribution calculated for ratio Halloysite/KCl = 20

4 Conclusions

Utilization of mineral additives, such as halloysite, to prevent slagging/fouling and corrosion issues is a promising measure when firing agricultural biomass. However, to achieve good process efficiency with additive use, an excess of additive is required. Therefore, determination of proper additive/fuel ratio is important for the optimization of process conditions and decreasing costs of additive dosage.

The first results presented in this study confirmed that the halloysite has the positive impact on increasing the ash flow melting temperature. Furthermore, for increased halloysite/KCl ratios, chlorine was completely released as HCl to the gas phase whereas potassium was captured by decomposed additive. As a result, the formation of KCl corrosive deposits is prevented.

It should be noted, that the performed experimental tests were carried out during a long exposure (90 min) in a muffle furnace allowing enough time for halloysite and KCl to interact. Based on ongoing research experience not only the temperature and additive/KCl ratio is important, but also residence time seems to be crucial for the efficient interaction between additive and KCl. Therefore, more studies are still needed to further understand the mechanisms involved when firing alkali-rich biomass with additive dosage. Laboratory scale tests presented in this paper are an introduction to further tests, which are planned to be conducted in a semi-industrial combustion unit.

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