

Effect of ammonium sulphate addition on the combustion of high chlorine and potassium biomass in a 12 MW_{th} CFB – ash and species balance

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1. Introduction

Combustion of biomass with high alkali and chlorine contents may induce ash related problems such as ash deposition and corrosion in the superheaters [1-3] and agglomeration of bed materials in a fluidized bed boiler [4]. The ash related problems are primarily due to the formation of a significant amount of alkali chlorides during the combustion of biomass [1,3]. In fluidized bed combustion, the reaction between alkali chlorides and silica rich sand can generate low-melting point alkali silicates on the surface of the bed particles which may lead to bed agglomeration [4]. The alkali chlorides may enhance the stickiness of fly ash particles and increase the ash deposition rate on the superheaters [2,3,5]. The deposited alkali chlorides may increase the corrosion rate of superheaters, as the chlorides may form low melting point eutectics and cause aggressive liquid-phase corrosion [6]. In addition, the deposited alkali chlorides on the superheaters may undergo sulphation reactions and release gaseous chlorine with high local concentration near the metal surface which may result in accelerated oxidation and corrosion of the superheaters [3].

Injection of additives such as sulfur compounds during the combustion of problematic biomass is possible solution to minimize the ash related problems [4,11-13]. The reactions between the sulfur additive and alkali chlorides form alkali sulphates and the chlorine is released into gas phase as HCl. The alkali sulphates have higher melting points than the corresponding alkali chlorides and will therefore have a smaller tendency to stick to the superheaters as deposits. The deposit formation and the corrosion potential of the superheaters can therefore be minimized.

Another solution may be to co-fire the problematic biomass with coal [7-9], or other less problematic fuels such as peat, rice husk and sewage sludge [1,2,5,10]. The synergy effects between different fuels, either chemically or physically, may reduce the ash deposition and corrosion problems in the boilers [5,7,9,10].

In this study, co-firing of different biomass fuels and the effects of ammonium sulphate addition were investigated in a 12 MW_{th} circulating fluidized bed (CFB) boiler at Chalmers University of Technology. During a two day-testing period, wood chips and straw pellets were co-combusted on the first day, and the effects of ammonium sulfate injection were evaluated under similar fuel condition on the second day. The work presented here focuses on the ash and elemental mass balances in the experiments as well as the distribution and molar ratio of different elements in different ash samples. Effects of ammonium sulfate addition on

the reactions of potassium and chlorine in the biomass fuels will be discussed based on the results.

2. Experimental

2.1 Setup

The combustion of biofuels has been carried out in a 12MW_{th} circulating fluidised bed (CFB) boiler (Figure 1). Fuel and sand (1a-c) is fed into the combustion chamber (3) (cross section 2.25 m² x height 13.6m) where the fuel is combusted at ~800 °C. The bed material and the exhaust gases are separated in the primary cyclone (6). The bed material is re-circulated in the combustion chamber. The alkali chlorides concentration of the hot gases are measured (9) before they enter convection pass (10), where they are cooled to ~150 °C. The flue gases are cleaned in the secondary cyclone (12) and in the bag filter (13), where the ash is separated from the gas. The gas composition is analysed before and after the gas cleaning (11, 14). Afterwards, the gases are released through the stack. The boiler operation conditions are listed in Table 1.

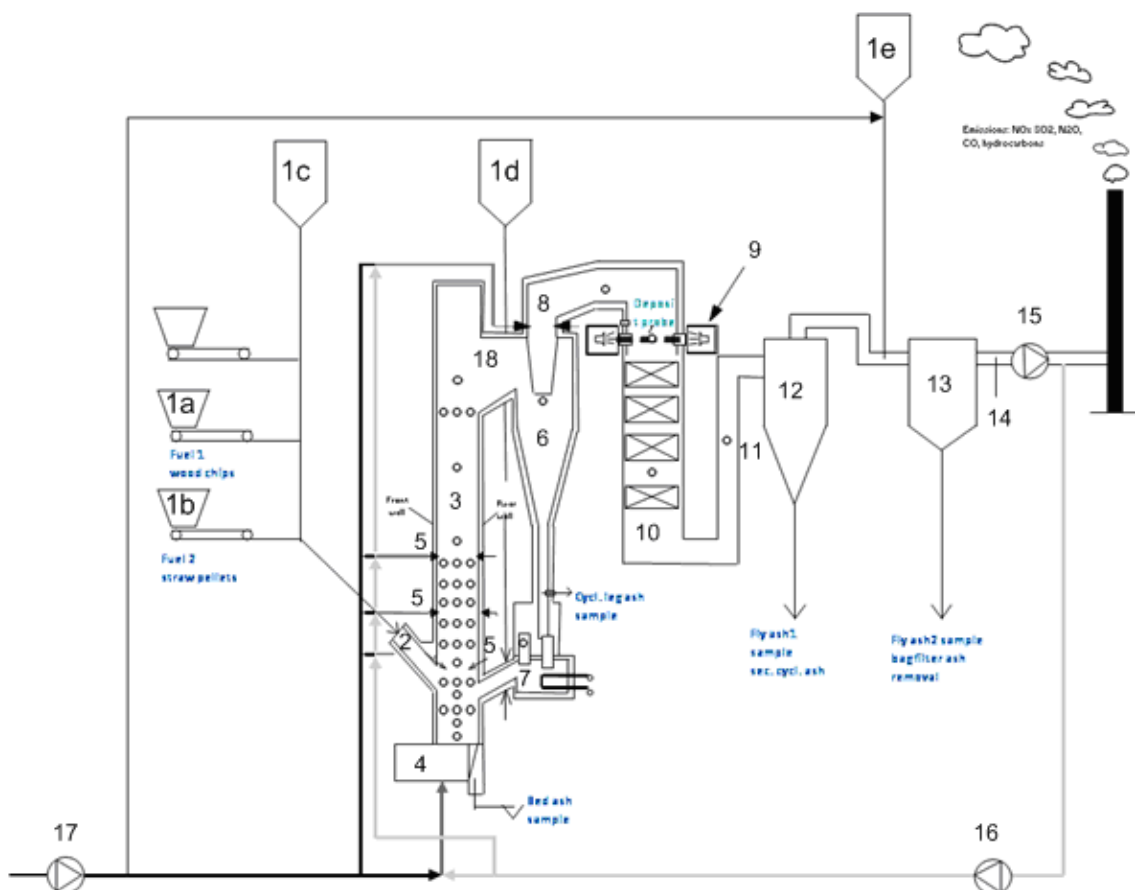


Figure 1. The 12 MW boiler. 1a fuel bunker (wood chips), 2b fuel bunker (straw pellets), 1c sand bin, 1d lime bin, 1e hydrated lime bin, 2 fuel feed chute, 3 combustion chamber, 4 air plenum, 5 secondary air inlet, 6 primary cyclone, 7 particle cooler, 8 cyclone exit duct, 9 IACM instrument, 10 convection pass, 11 measurement hole, 12 secondary cyclone, 13 bag filter, 14 gas-extraction probe, 15 flue gas fan, 16 flue gas recirculation fan, 17 air fan, 18 injection point for ammonium sulphate.

Table 1. Operational condition of the boiler. * Operation conditions from [2].

Parameter	Day 1 (Wood +straw)	Day 2 (Wood+straw+Amsulf)
Wood chips (kg/h, dry basis)	897	979
Straw pellets (kg/h, dry basis)	271	273
Ammonium sulphate (kg/h)	0	12.3
Weight percentage of straw (% of load)	23	22
Bed temperature top (°C)*	850	850
Bed temperature bottom (°C)*	870	870
Primary cyclone outlet temperature* (°C)	820	820
Flue gas temperature after bag filter* (°C)	150	150
Primary air/secondary air (%)*	50	50
Fluidization velocity (m/s)*	4.5	4.5
Bed turnover high (kg/h)*	80	80

2.2 Fuels

Table 2 shows the properties of the two fuels used in the experiments, wood chips and straw pellets. The fuels have similar lower heating value on a dry, ash free basis (daf). However, there is a large difference between the moisture content of the fuels, 42wt% for wood and 13wt% for straw. The most important difference between the fuels is in the ash content and the chlorine and alkali content. Compared to wood, the straw has approximately 8 times higher ash fraction on dry basis, and the ash from straw has higher chlorine and alkali contents, especially potassium. A combination of this gives a significantly higher chlorine and alkali content in the boiler system when increasing the share of straw as fuel.

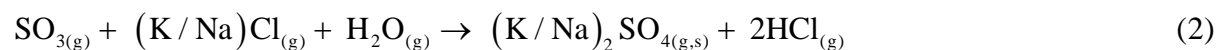
2.3 Additive

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is added to the boiler system to reduce unwanted deposits of alkali chlorides and superheater corrosion in the convection heat exchangers. Ammonium sulphate is added in the high temperature zone between the boiler and primary cyclone, as seen in Figure 1 point 18. Because of the low decomposition temperature of ammonium sulphate (see

Table 3) and the high temperature at the injection position ($\sim 870^\circ\text{C}$ [14]), ammonium sulphate is assumed to decompose instantaneously when added to the system by the following reaction [6]:



The SO_3 from the decomposition of ammonium sulphate can undergo sulphation reactions with gaseous KCl and NaCl through the following global reaction [6]:



More detailed mechanism for the reaction above can be found in [15]. As shown in

Table 3, the formed alkali sulphates generally have higher melting temperatures than their chlorides. Therefore, the deposition propensity of fly ashes would be reduced by the sulphation reaction shown in Eq. 2. In addition, since the alkali sulphates are much less corrosive than the alkali chlorides [6], the corrosion potential of the superheaters can also be decreased by the sulphation reaction.

Table 2. Fuel properties.

	Wood chips	Straw pellets
Proximate analysis (wt%, as received)		
Combustibles	58.15	83.63
Moisture	41.59	13.12
Ash	0.26	3.25
Ultimate analysis (wt%, daf)		
C	50.20	49.40
H	6.00	6.20
N	0.13	0.90
S	0.01	0.10
Cl	0.01	0.19
O	43.60	43.20
Low heating value (MJ/kg, daf)	18.69	18.45
Ash analysis (wt% of dry ash)		
K	11.30	15.10
Na	0.64	0.79
Al	0.81	0.84
Si	3.30	20.10
Fe	1.77	0.60
Ca	21.30	6.85
Mg	3.47	2.80
P	1.79	2.33
Ti	0.07	0.05
Ba	0.27	0.10
Mn	1.39	0.10

Table 3. Melting temperature of the compound of interest in relation to the sulphation reaction [16]

Compound	Melting temperature (°C)
(NH ₄) ₂ SO ₄	280 (decomposition)
KCl	771
NaCl	800.7
CaCl ₂	775
K ₂ SO ₄	1069
Na ₂ SO ₄	884
CaSO ₄	1460

2.4 Mass balance calculation

Mass balance calculation is performed for ash and major inorganic elements, both for the experiments with and without the addition of ammonium sulphate. The calculation method is described in detailed in Appendix C. For ash or a specific element, the overall mass balance in the experiments is calculated from:

$$Mass\ balance_i(\%) = \frac{Mass_{i,out} + Mass_{i,acc}}{Mass_{i,in}} \cdot 100\% \quad (3)$$

where i denotes the ash or the element of interest; $Mass_{in}$ is the ash/element introduced to the boiler via the fuels or additive; $Mass_{out}$ is the ash/element leaving the boiler as secondary cyclone ash (position 12 in Figure 1), bag filter ash (position 13 in Figure 1), and gaseous emission; $Mass_{acc}$ is the ash/element accumulated in the boiler.

A few assumptions are made in the calculation of ash and elemental mass balances [17]. Since the actual amount of ash accumulated in the boiler cannot be measured directly, the ash accumulated in the boiler is calculated from the difference between the ash inflow and ash outflow. The composition of the accumulated ash is assumed to be the same as the secondary cyclone ash, as it is difficult to find a representative accumulated ash sample.

3. Results and discussion

3.1 Mass balance

The mass balances for ash and the major inorganic elements are obtained by using the method described in Appendix C, and the detailed results are given in Appendix B. Since the amount of accumulated ash is calculated from the difference in the ash inflow and ash outflow, the ash balance naturally adds up to 100%. In this study, the main elements of interest are K, Na, Ca, Cl and S. The elemental balances for those elements are presented in Figure 2. It is shown that only the species balance for S adds up close to 100% both for the experiments with and without additive. The balances for the rest of elements are in general not satisfactory. The Cl recovery is 53% during the experiment without the addition of ammonium sulphate (AmSulf) and 129% with AmSulf addition. Similarly, the balance for K only adds to 21% at experiment day 1, while its balance is increased to 50% with the addition of AmSulf at day 2. For Ca, its elemental balance adds up to 136% at day 1 and 154% at day 2. The obtained Na balance is close to 64% at day 1 and 108% at day 2.

The general unsatisfactory elemental balances on K, Na and Cl are most likely caused by the assumption that the accumulated ash has the same composition as the second cyclone ash. This assumption is inappropriate since alkali chlorides may be more likely to be retained in the boiler, as agglomerates or deposits, than other ash forming species. Therefore, the actual accumulated ash would have higher alkali chloride content than that of secondary cyclone ash. This can explain the low recoveries of K, Na and Cl obtained at day 1 experiment, since the formation and the retention of alkali chlorides in the boiler would be significant during co-

combustion of straw and wood. In other words, the accumulated ash in day 1 would have much higher alkali and chlorine contents than the secondary cyclone ash. In day 2 experiment, the injection of AmSulf would reduce the formation of alkali chlorides, and result in less retention of alkali and chlorine in the boiler. As a consequence, the obtained recoveries of Cl, K and Na in day 2 are generally increased compared to day 1.



Figure 2. Mass balance of ash and different element in the experiments of day 1 (straw + wood) and day 2 (straw + wood + AmSulf).

Another assumption applied in the balance calculation is that the amount of accumulated ash equals to the difference between ash inflow and outflow. This assumption may also deviate from the practical situation, for instance due to dust emissions, which can influence the elemental balances. However, compared to the inappropriate assumption on the composition of the accumulated ash, the effect of this assumption on the elemental balances is believed to be less significant, especially for K, Na and Cl.

Measurement uncertainties on the fuel and ash compositions may also influence the elemental balance, especially for element with low content. The observed over recoveries of Ca may be related with the measurement errors on the fuel/ash compositions. However, for the K and Cl balances, the influence of measurement uncertainties may not be very significant compared to the errors introduced by the composition of accumulated ash.

3.2 Distribution of elements

The balances shown in Figure 2 imply that it is not appropriate to assume the ash accumulated in the boiler has the same composition as the secondary cyclone ash. To estimate the actual composition of the accumulated ash and the distribution of different elements in the secondary cyclone ash, bag filter ash, accumulated ash and gaseous emission, the following equation is used to calculate the percentage of ash or element that is accumulated in the boiler:

$$Accumulation_i(\%) = \left(1 - \frac{Mass_{i,out}}{Mass_{i,in}}\right) \cdot 100\% \quad (4)$$

where i denotes the ash or the element of interest.

By applying Eq. 4, it is assumed that both the ash and elemental balances are 100% for the experiments. However, it is noticed that elements such as Cl and Ca sometimes give negative values for the accumulated fraction. These negative values are likely caused by the measurement errors on the mass flow rates or the composition of fuel and ash. However, the negative values indicate that the accumulation of those elements is not significant, thus majority of those elements would result in secondary cyclone, bag filter, and emission. As a result, in case that the accumulated fraction of a species shows a negative value, it would be reasonable to assume that this species do not accumulate in the boiler. With this assumption and Eq. 4, the distributions of ash, K, Na, Ca, S, and Cl in secondary cyclone, bag filter, emission, and accumulated ash are calculated and presented in Figure 3.

As shown in Figure 3, when straw and wood are co-fired in the circulating fluidized bed boiler, a majority of the alkalis and chlorine in the fuel mixture is accumulated in the boiler, approximately 90% for K, 65% for Na and 60% for Cl. The accumulated alkalis may consist of two parts i.e. the part which has reacted with the silica rich sands in the bed and the part which has formed deposits in the furnace and convective section of the boiler. The accumulated chlorine would be mainly in the deposits. In comparison with alkalis and chlorine, less calcium and sulfur are accumulated in the boiler. About 50% of the ashes are found in the accumulation fraction which may imply that ash deposition in the boiler may be severe for this fuel mixture.

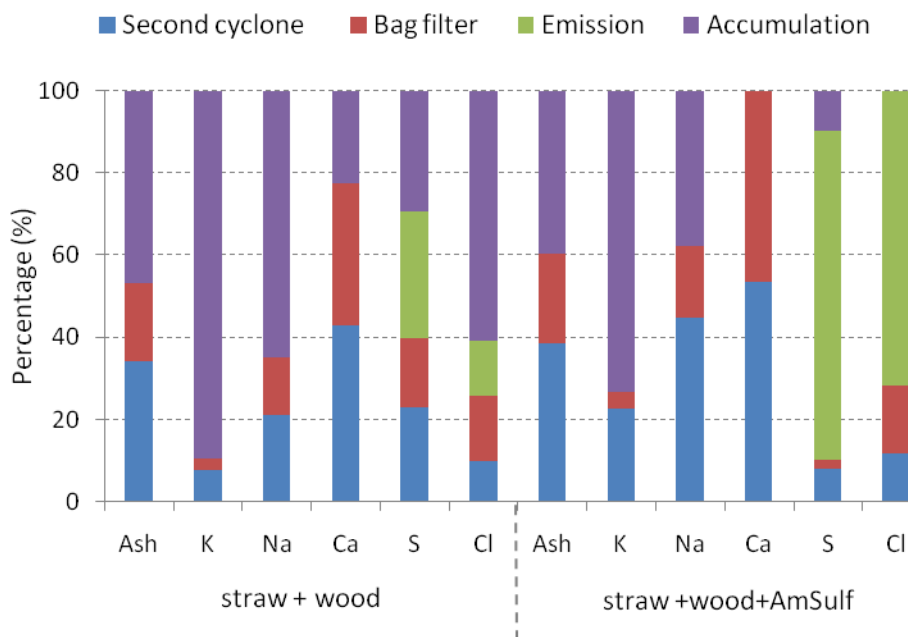


Figure 3. Distributions of K, Na, Ca, S and Cl in the experiments of day 1 (straw + wood) and day 2 (straw + wood + AmSulf).

With the addition of ammonium sulfate, it is shown that about 70% of the chlorine in the fuel mixture is emitted as flue gas and the percentage of K and Na accumulated in the boiler (about 75% and 40%) is decreased compared to that in day 1 experiment. The decrease of Cl, K and Na in the accumulated fractions is probably due to the sulphation reaction between alkali chlorides and the SO_3 released from the decomposition of ammonium sulfate, which is shown in Eq. 2. In addition, sulphation reaction may also happen on the condensed/deposited alkali chlorides and the gaseous sulfur species (SO_2 or SO_3) [6], which may further reduce the percentage of Cl accumulated in the boiler. Although the percentage of emitted chlorine is significantly increased with the addition of ammonium sulphate, about 30% of chlorine still results in secondary cyclone ash and bag filter ash. It shows that not all of the chlorides generated from the combustion have been reacted to sulphates according to Eq. 2. The ICAM analysis (not shown) confirms that alkali chlorides still present in the flue gas (about 9 ppm) before entering the convective section, when ammonium sulphate is added. The alkali chlorides would form deposits on the superheaters. However, the deposited solid phase alkali chlorides may undergo sulphation reaction and release chlorine to the gas phase. Therefore, the nearly no accumulation of chlorine in the boiler during ammonium sulphate addition is most likely a result of both gaseous and solid phase sulphation reactions.

The percentage of ashes accumulated in the boiler is also reduced with the addition of ammonium sulfate which indicates that the ash deposition problem in day 2 experiment may be mitigated compared to that of day 1 experiment. About 80% of sulfur in the fuel mixture and ammonium sulfate is emitted as SO_2 in the flue gas, implying that only a small fraction of sulfur has participated in the sulphation reactions. Majority of Ca is found in secondary cyclone and bag filter which shows that the accumulation of Ca in the boiler is not significant for day 2 experiment. However, in day 1, a certain fraction of Ca is probably deposited in the boiler, possibly in a form of CaCl_2 . Besides, part of Ca in the fuels may be retained in the CFB boiler as a calcium rich layer on the surface of the bed material [4].

3.3 Molar ratio

Molar ratios of different species in the fuel have been used as parameters which indicate the ash deposition or corrosion behavior of the fuel [7,13,18,19]. A number of those parameters are given in Table 4. The S/Cl ratio was used in [18] which suggested that the corrosion caused by chlorine would be negligible if the S/Cl ratio in the fuel exceeded 4. Robinson et al found that if the molar ratio of $2\text{S}/(\text{K}+\text{Na})$ was higher than 4, the chlorine content in the deposits was negligible [19]. A critical value above 8-10 for the molar ratio of reactive $(\text{Al}+\text{Si})/\text{Cl}$ has been proposed by Aho et al. [13] to prevent the Cl in the deposits.

As shown in Table 4, for the fuel mixture used in day 1 experiment, the molar ratio of S/Cl, $2\text{S}/(\text{K}+\text{Na})$, and $(\text{Al}+\text{Si})/\text{Cl}$ is about 0.69, 0.41, and 5.01 respectively. According to [13,18,19], these molar ratios imply that the presence of Cl in the deposits as well as the corrosion induced by chlorine may be severe for the fuel mixture. The molar ratio of S/Cl shows a deficiency of sulfur compared to chlorine, indicating the sulfur in the fuel mixture may not be sufficient to sulphate all of the chlorides generated from combustion. The molar ratio of S/Ca is higher than that of $2\text{S}/(\text{K}+\text{Na})$, implying that the reactions between calcium

and sulfur species may compete with the reaction between alkalis and sulfur species. Therefore, even less sulfur may be available for reaction with alkali chlorides.

With the addition of ammonium sulphate in day 2 experiment, the molar ratio of S/Cl and 2S/(K+Na) in the fuel and additive mixture becomes about 6.30 and 3.69 respectively. Both molar ratios indicate that the Cl content in the deposits and the corrosion caused by chlorine would be negligible [18,19]. The molar ratio of S/(Ca+K/2+Na/2) is about 1.52, which confirms that the sulfur in the mixture surpluses the capture potential of alkali and earth alkali species in the fuels.

Table 4. Molar ratios of chlorides or sulfates compounds in fuel mixture, second cyclone ash, bag filter ash, and bottom ash.

Molar ratio	without (NH ₄) ₂ SO ₄ addition (day 1)				with (NH ₄) ₂ SO ₄ addition (day 2)		
	Fuel Mixture	Second cyclone ash	Bag filter ash	Bottom ash	Fuel Mixture	Second cyclone ash	Bag filter ash
Cl/(K+Na)	0.29	0.33	1.33	0.01	0.29	0.16	1.12
2S/(K+Na)	0.41	1.05	1.93	0.03	3.69	1.20	1.65
S/Cl	0.69	1.61	0.73	2.21	6.30	3.72	0.74
S/Ca	0.29	0.16	0.14	0.01	2.58	0.38	0.12
S/(Ca+K/2+Na/2)	0.17	0.14	0.13	0.01	1.52	0.29	0.11
(Al+Si)/Cl	5.01	17.95	3.37	5416	4.97	21.85	4.49
K/Si	0.66	0.15	0.21	0.02	0.67	0.26	0.19

The molar ratios in the fuel mixture from day 1 and day 2 show significant differences, especially on the sulfur related ratios. The information obtained from the fuel molar ratios is that day 1 experiment may cause severe chlorine related ash problems and day 2 experiment may reduce the problems by addition of ammonium sulphate. However, one should be aware that those molar ratios can only provide a rough estimation about the fuel ash behavior. In practical situation, the association of different species in the fuels [20], the release of those species from the fuels [21], and the further reactions in a complicated combustion system also significantly affect the fuel ash behavior in combustion.

The molar ratios in the collected ash samples are also presented in Table 4. Compared to day 1 experiment, the molar ratio of Cl/(K+Na) is significantly decreased and the molar ratio of 2S/(K+Na) is increased in the secondary cyclone ash from day 2 experiment. This shows the effect of sulphation reaction proposed in Eq. 2. Compared to the secondary cyclone ash, the molar ratios of Cl/(K+Na) and 2S/(K+Na) are generally higher in the bag filter ash. It is probably because the bag filter ash contains more aerosols formed from combustion which mostly consist of volatile species such as alkali chlorides and sulphates [4,22]. Only the

bottom ash from day 1 experiment has been analyzed. The $\text{Cl}/(\text{K}+\text{Na})$ and $2\text{S}/(\text{K}+\text{Na})$ ratios are very small compared to the secondary cyclone ash and the bag filter ash. This is probably because the bottom ash is dominated by the bed material with high Si content. The silica in bed material would react with the alkali species such as alkali chlorides and sulphates which release Cl and S to the gas phase [7]. Therefore, the alkalis in the bottom ash mostly exist as silicates and the presence of chlorides or sulphates is negligible.

4. Conclusion

Combustion of biomass with high alkali and chlorine contents may induce ash related problems such as ash deposition and corrosion in the superheaters and agglomeration of bed materials in a fluidized bed boiler. Sulfur additives undergo sulphation reactions with alkali chlorides forming less problematic alkali sulphates and release chlorine as HCl in the gas phase. Experiments were conducted in a CFB boiler co-combusting straw and wood with and without addition of ammonium sulphates.

Mass balances of the ash and major inorganic element were made. Only the mass balance for sulfur closed acceptable to about 100%. The general unsatisfactory mass balances of other elements such as K, Cl and Na indicate that the assumption of the accumulated ash composition equaling to that of secondary cyclone ash does not seem adequate. However, the mass balances clearly show that the addition of ammonium sulphate has converted part of alkali chlorides to alkali sulphates.

The distribution of the different elements in the secondary cyclone ash, bag filter ash, accumulated ash, and emissions is estimated. It is found that the majority of alkali and chlorides are accumulated in the boiler when no additive is used. The ammonium sulphate additive significantly reduces this accumulation, however approximately 30% of the chlorine which is found in secondary cyclone ash and bag filter ash does not undergo the gaseous sulphation reaction despite a large excess of sulfur present. The nearly no accumulation of chlorine in the boiler is most likely a result of both solid phase and gaseous sulphation reaction.

Molar ratios of the elements of interest are made for the fuel mixture and ash samples. The increase of sulphate containing molar ratios when adding ammonium sulphate in the second day experiments indicate that the corrosion and deposits caused by alkali chlorine is negligible.

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Appendix A Ash composition from different experiments

Table A 1. Ash analysis from day 1 experiment without AmSulf addition

Ash analysis (g/kg ash)	Second cyclone ash	Bag filter ash	Bottom bed ash
K	32.2	18.9	11.8
Na	4.64	5.40	1.81
Al	13.9	24.8	3.11
Si	154	64.8	427
Fe	38.2	123	1.91
Ca	137	197	18.1
Mg	14.6	23.5	3.912
P	9.71	13.9	2.106
Ti	1.40	4.55	0.502
Ba	1.19	3.18	0.40
Mn	6.80	12.1	2.0
S	17.3	22.2	0.20
Cl	11.9	33.9	0.10

Table A 2. Ash analysis from day 1 experiment without AmSulf addition.

Ash analysis (g/kg ash)	Second cyclone ash	Bag filter ash	Bottom bed ash
K	68.3	20.5	11.8
Na	7.2	5.0	1.81
Al	11.7	28.0	3.11
Si	191.1	75.5	427
Fe	17.9	117.6	1.91
Ca	130.2	203.7	18.1
Mg	23.1	21.5	3.912
P	17.1	12.0	2.106
Ti	0.9	3.9	0.502
Ba	1.3	2.6	0.40
Mn	5.0	10.8	2.0
S	39.5	19.6	0.20
Cl	11.7	29.4	0.10

Appendix B Ash and elemental balance for different experiments

Table A 3. Ash and elemental balances for day 1 experiment in the CFB boiler without AmSulf addition.

Species	In [kg/s]				Out [kg/s]		Acc. kg/s]	Balance (%)
	Wood	Straw	Additive	Sec. Cycl.	Bag filter	Emissions	Conv.	
Ash	3.99	10.15	-	4.82	2.71	-	6.61	100
K	0.45	1.53	-	0.15	0.05	-	0.21	21.1
Na	0.03	0.08	-	0.02	0.01	-	0.03	64.0
Ca	0.85	0.70	-	0.66	0.53	-	0.91	136
S	0.09	0.27	-	0.08	0.06	0.11	0.11	102
Cl	0.09	0.49	-	0.06	0.09	0.08	0.08	52.8
Mg	0.14	0.28	-	0.07	0.06	-	0.10	54.5
P	0.07	0.24	-	0.05	0.04	-	0.06	48.3
Ti	0.00	0.01	-	0.01	0.01	-	0.01	361
Ba	0.01	0.01	-	0.01	0.01	-	0.01	106
Mn	0.06	0.01	-	0.03	0.03	-	0.04	168
Al	0.03	0.09	-	0.07	0.07	-	0.09	192
Si	0.13	2.04	-	0.74	0.18	-	1.02	89.3
Fe	0.07	0.06	-	0.18	0.33	-	0.25	585

Table A 4. Ash and elemental balances for day 2 experiment in the CFB boiler with AmSulf addition.

Species	In				Out		Acc. [kg/s]	Balance (%)
	Wood	Straw	Additive	Sec. Cycl.	Bag filter	Emissions	Conv.	
Ash	4.36	10.22	2.99	6.79	3.80	-	6.98	100
K	0.49	1.54	-	0.46	0.08	-	0.48	50.0
Na	0.03	0.08	-	0.05	0.02	-	0.05	108
Ca	0.93	0.70	-	0.88	0.77	-	0.91	158
S	0.10	0.27	2.99	0.27	0.07	2.69	0.28	98.5
Cl	0.10	0.49	-	0.08	0.11	0.49	0.08	129
Mg	0.15	0.29	-	0.16	0.08	-	0.16	91.2
P	0.08	0.24	-	0.12	0.05	-	0.12	88.8
Ti	0.00	0.01	-	0.01	0.01	-	0.01	327
Ba	0.01	0.01	-	0.01	0.01	-	0.01	125
Mn	0.06	0.01	-	0.03	0.04	-	0.04	155
Al	0.04	0.09	-	0.08	0.11	-	0.08	221
Si	0.14	2.06	-	1.30	0.29	-	1.33	133
Fe	0.08	0.06	-	0.12	0.45	-	0.13	501

Appendix C Ash and elemental balance calculations

In the mass balance calculation, it is assumed that the ash is introduced into the system through the fuels, wood and straw, and from the ammonium sulphate (AmSulf). The mass inflow of ash or a specific element is calculated through the following equation:

$$Mass_{i,in} (kg / s) = Straw_{i,in} (kg / s) + Wood_{i,in} (kg / s) + AmSulf_{i,in} (kg / s) \quad (A1)$$

where *i* denotes the ash or the element of interest. The ash/element inflow from the fuel (kg/s), $Straw_{i,in}$ or $Wood_{i,in}$, is calculated by multiplying the fuel flow rate (kg/s) with the ash/element content in the fuel (wt%). For AmSulf, only the S in this additive is an ash input.

Ash is leaving the system only as secondary cyclone ash and as filter bag ash. The bottom ash, which is normally part of ash outflow, was accumulated in the boiler during the experiments. For some of the ash forming elements such as S and Cl, part of them may leave the system as gaseous emission. As a result, the overall ash/element outflow can be calculated as:

$$Mass_{i,out} (kg / s) = Secondcyclone_{i,out} (kg / s) + Bagfilter_{i,out} (kg / s) + Emission_{i,out} (kg / s) \quad (A2)$$

where *i* denotes the ash or the element of interest. The ash outflows (kg/s), $Secondcyclone_{ash,out}$ and $Bagfilter_{ash,out}$, are obtained during the experiments. For a specific element, its outflow is calculated from the ash outflows and the composition of the ashes which are given in Appendix A. For Cl and S, the emissions of HCl and SO₂ are included as part of elemental outflows.

Since the ash accumulated in the furnace and convective section cannot be measured, the ash accumulation is calculated from the difference in the ash inflow and outflow:

$$Mass_{ash,acc} (kg / s) = Mass_{ash,in} (kg / s) - Mass_{ash,out} (kg / s) \quad (A3)$$

The accumulated ash is assumed to have the same composition as the second cyclone ash, thus the elemental accumulation can be calculated as:

$$Mass_{i,acc} (kg / s) = Mass_{ash,acc} (kg / s) \cdot X_{i,secondcyclone} (wt\%) \quad (A4)$$

where *i* denotes the element of interest and $X_{i,secondcyclone}$ is the content of the element in second cyclone ash (wt%).

The total mass balance for ash or a specific element in the experiments can be obtained as:

$$Massbalance_i (\%) = \frac{Mass_{i,out} + Mass_{i,acc}}{Mass_{i,in}} \cdot 100\% \quad (A5)$$

where *i* denotes the ash or the element of interest.