

Aspects on the Flue Gas Chemistry of KCl, NO and CO During Injection of Ammonium Sulphate – An Experimental Approach

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Abstract

Sulphate containing additives, such as ammonium sulphate (AS, $(\text{NH}_4)_2\text{SO}_4$), are used for sulphation of KCl during biomass combustion. Another aspect with injection of AS is that a significant NO_x reduction is achieved but it may also have an impact on other flue gas components such as CO. The concentration of oxygen and the presence of volatile combustibles could also have an effect on the flue gas chemistry involving KCl, NO and CO. This paper is based on results obtained from two measurement campaigns during co-combustion of wood chips and straw pellets in a 12 MW circulating fluidised bed (CFB) boiler. In the first campaign, the NO reduction performance of AS, ammonia and urea was compared. In the second one, AS was injected at three positions in the boiler i.e. in the upper part of the combustion chamber, in the cyclone inlet, and in the cyclone. The impact of AS on the flue gas chemistry was investigated at three air excess ratios ($\lambda = 1.1, 1.2$ and 1.4). Several measurement tools including, IACM (on-line measurements of gaseous alkali chlorides) and gas analysis were applied. The position for injection of AS as well as the different air excess ratios had a great impact on the flue gas chemistry for especially KCl and NO.

1. Introduction

High levels of potassium chloride (KCl) in flue gas during combustion of a biomass fuel can enhance deposit formation and a high content of KCl in the deposits may accelerate superheater corrosion. These operational problems can be reduced by sulphur/sulphate containing additives which convert KCl to a less corrosive alkali sulphate [1-8]. In [1-4, 8, 9] results are presented from experiments when using elemental sulphur (S) and/or ammonium sulphate (AS, $(\text{NH}_4)_2\text{SO}_4$). AS lowered the concentration of gaseous KCl and simultaneously reduced the chlorine content in the deposits significantly better than sulphur [3]. AS can, in parallel to the sulphation of KCl be used as an additive for SNCR (selective non-catalytic reduction) of NO. The SNCR technology was introduced for NO_x emission control in coal-fired boilers but is now applied for various types of boilers and fuels including biomass [10-12]. The most commonly used SNCR additives are ammonia (NH_3) and urea ($\text{CO}(\text{NH}_4)_2$). Their performance can be improved and altered by a number of strategies [10, 13-17].

The influence of oxygen and combustibles on the sulphation of gaseous KCl [8] and the deposit chemistry [9] during injection of AS were investigated in previous papers. The experimental work was carried out in a full-scale CFB boiler and this measurement campaign is referred to as *Sulphation*. The NO reduction obtained from AS and the conventional SNCR additives NH_3 and urea was compared in [2]. This measurement campaign was carried out in the same CFB boiler and is referred to as *SNCR*. There are known interactions between the volatile combustibles and trace species, including K, S, Cl, and N during combustion [18]. The scope of the present paper is an improved understanding of these interactions. The strategy applied is to compare results obtained in [2] and [8] with a wider approach on aspects of the flue gas chemistry of especially KCl and NO during injection of AS.

2. Theory

Interactions occur between the CH oxidation and the chemistry of K, S, N and Cl during combustion, [18]. Many of these interactions concern the so-called “chain carrying radicals”, which include the radical pool of hydroxyl (OH), oxygen (O) and hydrogen (H) radicals. The chain branching reaction (R1) in Table 1 is the most important reaction for radical production. Light volatile hydrocarbons are oxidised in a series of steps by the chain carrying radicals and finally CO is formed in the last step. CO is further oxidised to CO_2 mainly by a hydroxyl radical (R2). The reaction between hydrocarbon radicals and chain carrying radicals is normally faster than R2 [19]. This leads to an accumulation of

CO, which starts to oxidise when the hydrocarbon oxidation is completed. Thus, the presence of combustibles has a large influence over the O/H radical pool.

Reactions of particular interest in this paper involve the O/H radical pool, reduction of NO by SNCR, and sulphation of gaseous KCl. NO reduction by NH₃ is initiated by an OH radical (R4) and the formation of OH radicals can be promoted or inhibited by additives [14, 15, 17, 19]. Additionally, these additives can alter the temperature window for NO reduction by SNCR. Sulphation of gaseous KCl is more efficient in the presence of SO₃ rather than SO₂ [3]. Ammonium sulphate (AS) is proposed to decompose into NH₃ and SO₃ according to (R3) when injected into the boiler [8]. The overall sulphation reaction of KCl by SO₃ may be described as follows (R5). The oxidation of SO₂ to SO₃ (global reaction R6) involves recombination of SO₂ with O or OH radicals and it may involve HOSO₂ as an intermediate (R7, R8), and SO₃ may be reduced by H radicals (R9). R9 is a fast reaction and the presence of H radicals can thus have a great influence on the efficiency of the sulphation of KCl. Calculations concerning the reactions of SO₃ with the O/H radical pool were presented in [20]. Furthermore, the presence of KCl may consume OH radicals and inhibit oxidation of CO by (R10) [19].

Table 1 Reactions of interest

Description of reaction	Number and reaction
Chain branching reaction	(R1) $H + O_2 \rightleftharpoons OH + O$
Oxidation of CO by a hydroxyl radical	(R2) $CO + OH \rightleftharpoons CO_2 + H$
Interference of alkali on CO oxidation	(R10) $K + OH + M \rightleftharpoons KOH + M$
Decomposition of ammonium sulphate	(R3) $(NH_4)_2SO_4 \rightarrow 2NH_3 + SO_3 + H_2O$
Sulphation of KCl by SO ₃	(R5) $2KCl + SO_3 + H_2O \rightarrow K_2SO_4 + 2HCl$
Reduction of NO by NH ₃	(R4a) $NH_3 + OH \rightarrow NH_2 + H_2O$ (R4b) $NH_2 + NO \rightarrow N_2 + H_2O$
Oxidation of SO ₂ to SO ₃	(R6) $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$
Recombination of SO ₂ by O radicals	(R7) $SO_2 + O \rightleftharpoons SO_3$
Recombination of SO ₂ by OH radicals	(R8a) $SO_2 + OH \rightleftharpoons HOSO_2$
with HOSO ₂ as an intermediate	(R8b) $HOSO_2 + O_2 \rightleftharpoons SO_3 + HO_2$
Reduction of SO ₃ by H radicals	(R9) $SO_3 + H \rightleftharpoons SO_2 + OH$

3. Methodology

3.1 The research boiler

The paper is based on experiments carried out in two measurement campaigns, referred to as *Sulphation* and *SNCR*, in the 12 MW CFB boiler at Chalmers University of Technology [2, 8]. This boiler is mainly used for research purposes and offers the possibility to perform measurement campaigns in a full scale boiler, while maintaining control over important operation parameters such as load, air supply and composition of the fuel mix. The boiler is shown in Fig. 1 and has been described earlier in several publications including [2-4, 8].

3.2 Operating conditions and experimental procedures

The measurements during *Sulphation* were carried out during three air excess ratios ($\lambda = 1.1, 1.2$ and 1.4). The fuel properties are presented in Table 2. Selected operating conditions for each λ are presented in Table 3. The base fuel was wood chips and straw pellets were used as additional fuel, to increase the initial level of gaseous KCl to approximately 50 ppm in all tests. The fraction of straw pellets required to reach 50 ppm KCl was between 20 – 35 % of the energy input to the boiler.

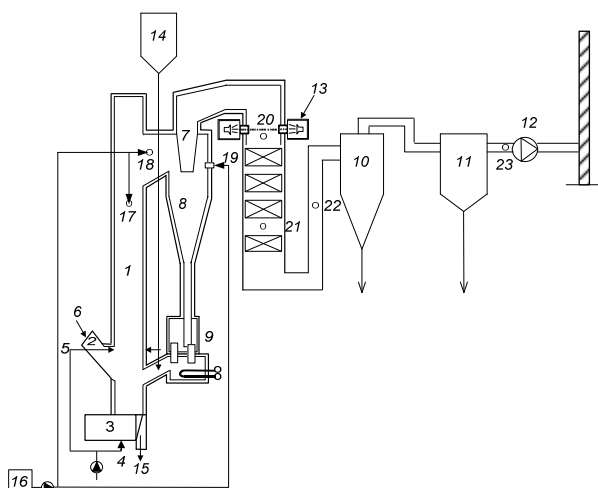


Figure 1a. The 12 MW CFB boiler. 1. furnace; 2. fuel chute; 3. air plenum; 4. primary air; 5. secondary air; 6. fuel feed and sand; 7. cyclone outlet; 8. primary cyclone; 9. particle seal; 10. secondary cyclone; 11. bag house filter; 12. flue gas fan; 13. IACM (In-situ Alkali Chloride Monitor); 14. Kaolin; 15. bed material; 16. ammonium sulphate (AS); 17-19. injection of AS and measurement positions; 17. upper part of the combustion chamber; 18 cyclone inlet; 19. in the cyclone; 20-23. measurement positions; 20. before the convection pass; 21. in the convection pass, 22. after the convection pass; 23. before the stack.

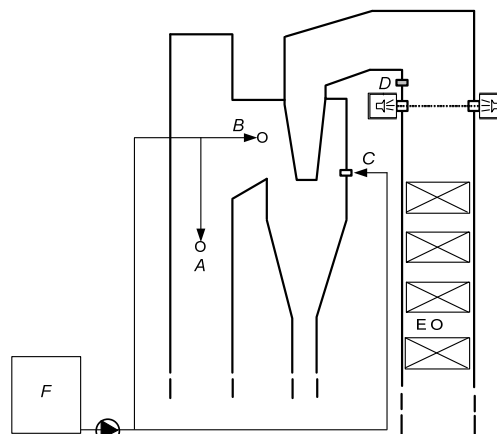


Figure 1b. Upper part of the combustion chamber, the cyclone and the convection pass. Injection of AS (A-C) and measurement positions D, E, G. A = upper part of the combustion chamber, B = the cyclone inlet, C = in the cyclone. D = before the convective pass, E = in the convective pass, F = Container with AS, G = IACM. Additive tests: B = Injection point for additives, F = reservoir for liquid ammonium sulphate, urea or ammonia.

An aqueous solution of AS (40% wt) was injected into the boiler according to two experimental procedures in test series *Sulphation* and they are described more in detail in [8]. The purpose of the first procedure was to investigate the influence of oxygen on the flue gas chemistry. AS was injected into the cyclone at three air excess ratios (λ). Each measurement was carried out for three hours and several measurement tools were applied. The measurements were performed for a reference case (Ref) and two flows of AS (low flow (amount of AS) = ASL, high flow = ASH). The corresponding molar flows and molar ratios of certain experimental parameters were presented in [8] (Table 4). The second procedure, a so-called *Transient test*, was carried out for the same air excess ratios (λ). The main purpose of the *Transient test* was to investigate the impact of the presence of combustibles (i.e. CO and unburned hydrocarbons) on the reactions of interest in Table 1. Thus the experimental strategy was to characterise more challenging conditions rather than optimising the injection of AS. Increasing amounts of AS were injected in a sequence at three positions in the boiler. The positions were in the upper part of the combustion chamber (*Comb*, 17 in Fig. 1), in the cyclone inlet (*Inlet*, 18), and in the cyclone (*Cyclone*, 19). Each sequence consisted of a reference without any injection of AS (Ref), and injection of increasing amounts of AS in AS1, AS2, AS3, AS4, AS5, AS6 and each of them was performed for 25 minutes. The results from these two experimental procedures were to large extent presented versus the molar ratios of S/Cl in [8] which is a measure to which degree a fuel mix is corrosive. Theoretically, a molar ratio S/Cl of 0.5 for added AS is sufficient for complete sulphation of K to K_2SO_4 (R5). The theoretical molar ratio for NH_3/NO is 1 in R4. However, in practise an excess is required for both R4 and R5. The results are also presented versus the molar ratio of NH_3/NO to broaden the focus to NO reduction as well. The NH_3/NO molar ratios were 1.0 (AS1), 1.5 (AS2), 2.1 (AS3), 3.1 (AS4), 4.1 (AS5), and 6.2 (AS6) during $\lambda = 1.2$.

The measurements during test series *SNCR* were carried out at operating conditions typical for a CFB boiler (Table 2 [2]) and in most tests, λ was 1.2 and the bed temperature $850^\circ C$. The base fuel was a mixture of wood pellets and wood chips, and straw pellets were used as additional fuel in some tests. The different fuel properties were presented in [2] (Table 1). The SNCR additives (AS, NH_3 , urea) were injected in the cyclone inlet (18) at a gas temperature of approximately $870^\circ C$. Two separate strategies to alter the concentration of KCl were applied in the test campaign. In the first one, straw pellets were used to raise the level of KCl and various combinations of the additives were injected. This experiment was also carried out when KCl was lowered by adding granules of S to the return leg

from the cyclone. In the second one without straw (*no straw*), PVC was instead supplied to the return leg to raise KCl and similar combinations of the additives were tested at various conditions. This means four main test cases with separate impact on the flue gas chemistry were compared.

Table 2. Fuel properties

	Straw pellets	Wood chips
Proximate analysis		
Water (wt-%, raw)	6.3	40.5
Ash (wt-%, dry)	5.1	0.9
Combustibles (wt-%, dry)	94.9	99.1
Volatiles (wt-%, daf)	80.1	81.7
Ultimate analysis (wt-%, daf)		
C	49.4	50.0
H	6.2	6.0
O	43.5	43.7
S	0.10	0.01
N	0.58	0.15
Cl	0.29	0.01
Ash analysis (g/kg dry ash)		
K	139	128
Na	3.9	6.6
Al	1.9	5.4
Si	250	31.6
Fe	1.8	4.9
Ca	65	234
Mg	14	28
P	11	15
Ti	0.1	0.3
Ba	0.7	1.7
Lower heating value (MJ/kg)		
H, daf	18.4	18.7
H, raw	16.2	10.1

Table 3. Operating parameters

Parameter	$\lambda = 1.1$	$\lambda = 1.2$	$\lambda = 1.4$
Load (MW)	6.5	5.9	5.3
Fraction of straw pellets, % of load	21.3	22.0	33.1
Bed temperature (°C)	833	838	867
Temperature, top of furnace (°C)	872	877	898
Temperature, cyclone inlet (°C)	882	878	882
Temperature, top of cyclone (°C)	888	864	828
Temperature, cyclone outlet (°C)	884	861	836
Temperature, before conv. pass (°C)	862	836	803
Temperature, after bag filter (°C)	167	165	168
Pressure drop in furnace (kPa)	6.2	6.3	6.3
Excess air ratio	1.12	1.22	1.36
Total air flow to combustor (kg/s)	2.71	2.70	2.72
Primary air flow (kg/s)	1.46	1.44	1.47
Secondary air, total flow (kg/s)	0.64	0.63	0.64
Flue gas recirculation (kg/s)	0.77	0.63	0.38
Primary air/total air flow (%)	53.8	53.3	54.2
Fluidisation velocity (m/s)	5.9	5.6	5.0
Initial NO concentration (ppm ^a)	74	96	124
Initial KCl concentration (ppm ^a)	49	55	56

daf = dry and ash free, raw = as received, a = ppm dry gas @ 6% O₂)

3.3 Measurement equipment

A so-called IACM (In-situ Alkali Chloride Monitor) located at (13) in Fig. 1 measured the alkali chlorides (KCl and NaCl) in the gas phase [21]. The result is expressed as KCl, which is the dominant gaseous alkali species at conditions prevailing in a CFB boiler during biomass combustion. IACM has been used in the present boiler in several previous projects related to alkali chloride issues in which it is described in more detail [2-4]. IACM is a part of the so-called ChlorOut concept. It consists of IACM and a sulphate-containing additive that converts alkali chlorides to less corrosive alkali sulphates [22]. The sulphate-containing additive is often ammonium sulphate, although several other sulphates are also included in the ChlorOut concept.

Flue gas was extracted through a heated probe and heated sampling lines to an FTIR (Fourier Transform Infra-Red) analyser for the determination of HCl, SO₂, H₂O, N₂O, NO, NO₂ and NH₃ on hot wet flue gases. The gas was further transported to on-line IR-VIS instruments measuring CO and SO₂ on cold dry gases and a paramagnetic analyser for O₂. A chemiluminescence analyser was used for NO and a flame ionisation detector (FID) for volatile hydrocarbons (HC_{tot}) in connection to the cold system. Methane (CH₄) was used for calibration of the FID analyser and consequently HC_{tot} is presented as ppm CH₄ equivalents. Gas concentrations were measured in locations after the convection path (22) and before the stack (23) during all test cases. Additional gas measurements were also carried out during the *Transient tests* to characterise the composition of the flue gas without injection of AS at measurement locations (17), (18), (19), (20), (22) and (23) in Fig. 1.

4. Results

4.1 Interactions between NO reduction and sulphation of KCl

The results from test series SNCR were based on primary data from [2]. The performance of the three additives was compared during the *PVC, no straw* case in Fig. 3. 45 ppm KCl was generated by a supply of PVC and the tests with urea and ammonia (NH_3) were carried out without addition of sulphur. This resulted in a simultaneous decrease of KCl with AS and unchanged level for the other additives. The reduction of NO was, nevertheless, approximately 50% at an NH_3/NO molar ratio of ~ 2 for all additives. Fig. 3 revealed a similar performance for the three additives at these test conditions. Thus it appears that the decreased KCl concentration during injection of AS (i.e. SO_3) had limited impact on the homogenous gas phase chemistry involving the reduction of NO. The impact of KCl is further investigated in Figs. 4 and 5 for urea and NH_3 respectively. Here, four different test cases with separate impact on the flue gas chemistry are compared. The major difference between test cases *PVC, no straw* and *no PVC, no straw* is that the level of KCl is increased from 3 to 45 ppm by adding PVC. The difference between test cases *straw, no S added* and *straw, S added* is that KCl was reduced from 45 to 20 ppm by adding sulphur (S) granules (molar ratio S/Cl increased from 0.4 to 3.9).

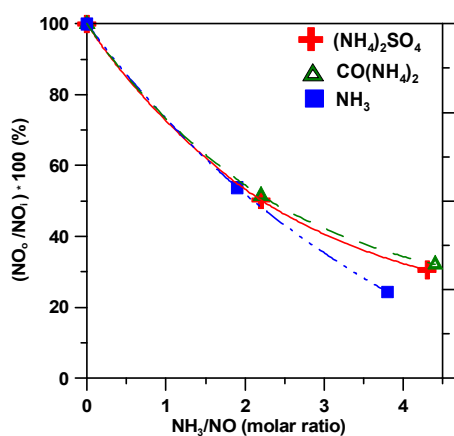


Figure 3. Reduction of NO with injection of AS, urea or NH_3 . Test case: “PVC, no straw”. $\lambda = 1.2$, gas temperature 870°C .

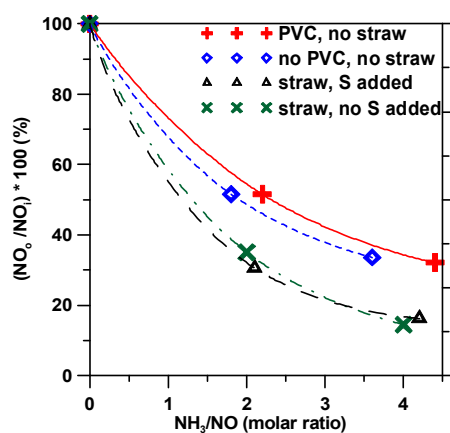


Figure 4. Reduction of NO with injection of urea. Four different test cases.

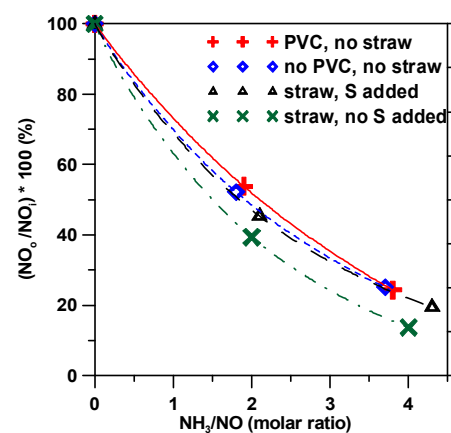


Figure 5. Reduction of NO with injection of NH_3 . Four different test cases.

The test cases in Fig. 3 (*PVC, no straw*) can be directly compared to the corresponding tests without PVC (*no PVC, no straw*) by stopping the PVC supply. It is indicated in Figs 4 and 5 that the NO reduction is somewhat improved for both urea and NH_3 when the concentration of KCl is lowered in *no PVC, no straw*. A possible explanation is that the halogens present in PVC (i.e. HCl) acted as radical inhibitors at the higher KCl concentration of 45 ppm [15]. An increased competition for OH radicals could slow down R4b. An increase in CO was also observed in Fig 6 in [2] when S was added during injection of urea. Figs 4 and 5 include the straw cases, where KCl was reduced from 45 to 20 ppm by adding S. The NO reduction was similar between the straw cases for urea in Fig. 4. A somewhat better NO reduction was obtained during the corresponding tests for NH_3 without addition of S when the level of KCl was greater. A possible explanation is that sulphation of KCl by sulphur involves oxidation of SO_2 to SO_3 (R6, R8) which means there is a competition for OH-radicals between R4 and R8. A similar interaction does not occur during injection of AS since it decomposes directly to SO_3 (R3). It needs to be further investigated whether R8 results in a less efficient NO reduction for the combination NH_3 and sulphur in comparison with AS.

It is also observed in Fig. 4 that the reduction of NO for urea was improved during the straw cases. The better performance could, however, partly be explained by a higher reference level of NO during straw, since it in general results in a greater NO reduction during SNCR. This trend is less obvious for NH_3 in the case *straw, S added* in Fig. 5. It can be explained by competition for especially OH-radicals between R7, R8 and R4a when using NH_3 . The overall impression is that urea performed somewhat better as SNCR additive than NH_3 at the conditions selected. This is revealed by the better NO reduction obtained during the test cases for “straw” (Fig. 4). The performance of AS is more similar to

NH₃ than urea since NO reduction by AS also requires OH-radicals (R4a). Further concerns during SNCR are emissions of N₂O and risk for ammonia slip and their impact was treated in [2]. Urea had the highest tendency to form N₂O. The lowest NH₃ slip was achieved for AS and the explanation was that KCl in gaseous form is sulphated into K₂SO₄. K₂SO₄ condenses into small aerosol particles which in turn can act as surfaces for decomposition of unreacted NH₃. This resulted in a lower slip using AS than during the corresponding tests with urea and NH₃ where no sulphation of KCl was achieved.

4.2 Presence of combustibles

The presence of combustibles such as CO, hydrogen (H₂), methane (CH₄), and ethene (C₂H₄) could interact on both the reduction of NO and the sulphation of KCl. Fig. 6 is adopted from [8] and shows the concentration of CO and HC_{tot} (volatile hydrocarbons) respectively at excess air ratios $\lambda = 1.1, 1.2$ and 1.4 at six measurement locations. The air excess ratio had a major impact on CO and the highest concentration was found in the upper part of the combustion chamber, *Comb*, at $\lambda = 1.1$. The concentration of CO was nevertheless above 1000 ppm during all air excess ratios in *Comb*. CO was much lower in the inlet of the cyclone despite remaining above 1000 ppm for $\lambda = 1.1$, and 1.2. The level of CO in the cyclone ranged from 50 ppm at $\lambda = 1.4$ to approximately 800 ppm at the lowest λ . The level of HC_{tot}, Fig. 6b, shows a similar pattern with the highest concentrations in *Comb*, although only 50 ppm or less remained in the cyclone. The main volatile hydrocarbons present were CH₄ and C₂H₄.

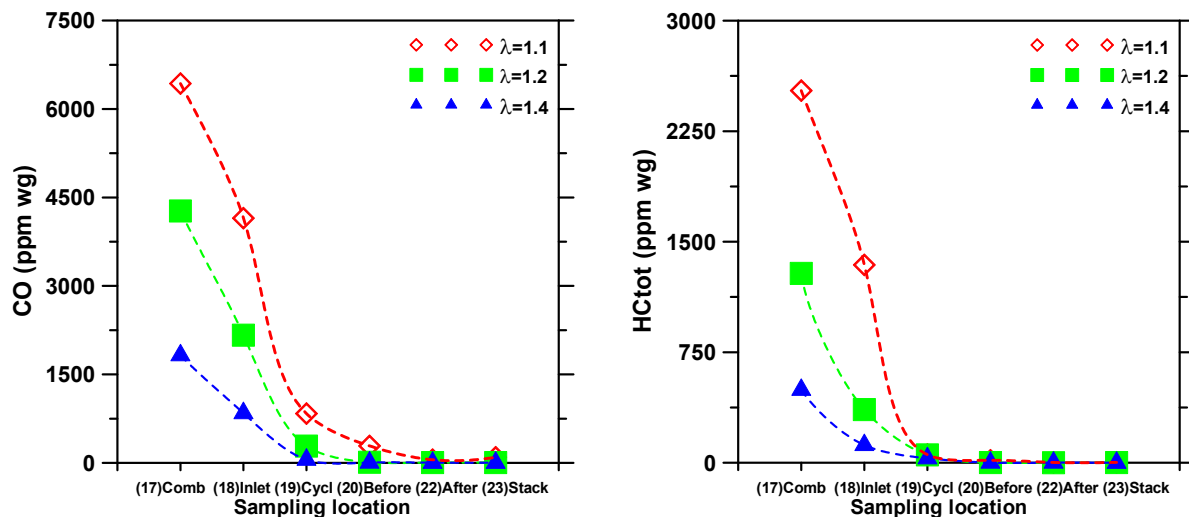


Figure 6. CO (a) and HC_{tot} (b) versus sampling location at excess air ratios $\lambda = 1.1, 1.2$ and 1.4. The sampling locations were in the upper part of the combustion chamber (17 in Fig. 1), inlet of the cyclone (18), in the cyclone (19), before the convection pass (20); after the convection pass (22), and before the stack (23).

4.3 Effect of oxygen - Air-ratio tests

There is a challenge to distinguish between interactions from oxygen (O₂) and the presence of combustibles on reduction of NO and sulphation of KCl. The strategy was to select an injection position with less influence from the presence of combustibles. Their concentration in Fig. 6 was lower in the cyclone (*Cyclone*) in comparison with the upper part of the combustion chamber and the cyclone inlet. Thus ammonium sulphate was injected *Cyclone* (19 in Fig. 1) and $\lambda = 1.1, 1.2$ and 1.4 were investigated. The operating parameters for each λ are presented in Table 3. The test cases were a reference case (Ref), and injection of low (ASL) and high (ASH) amount of AS for each λ . The molar ratios of NH₃/NO and S/Cl for Ref, ASL and ASH for the different test cases and gas concentrations of particular interest are presented in Table 4.

Injection of AS resulted in a minor increase of CO at very low levels and this effect has previously been discussed [2] and it can be explained as a competition for OH radicals between R2 and R4 [12]. The increase of CO only occurred when the initial level of CO was very low, whereas the trend was the reversed during $\lambda = 1.1$. CO was well above 100 ppm during Ref and it decreased drastically by injection of AS. The lowest level of CO was actually achieved during the lowest air excess ratio at ASH. This effect has previously been described in [23], in which AS was used both to lower NO and CO during combustion of biomass in a BFB boiler with high emissions of CO. The formation of NO

was strongly favoured by an increasing λ and the initial NO concentration for $\lambda = 1.4$ was 119 ppm which is almost twice that for $\lambda = 1.1$ during Ref. The final concentration was, nevertheless, only somewhat higher for $\lambda = 1.4$ at ASH. Fig. 7 shows the reduction of NO which was greater at higher air excess ratios. This could partly be explained by a higher initial concentration without AS.

Table 4. Gas concentrations (recalculated to ppm dry gas @ 6 % O₂).

Test case	NH ₃ /NO ^a	S/Cl ^a	O ₂ ^c , (%)	KCl ^b , ppm	NO ^d , ppm	CO ^d , ppm	HCl ^c , ppm
Ref-1.1	0.0	0.5	2.7	51	72	137	10
ASL-1.1	1.9	1.4	2.6	32	43	37	40
ASH-1.1	3.8	2.5	2.6	25	32	19	49
Ref-1.2	0.0	0.5	4.2	57	94	0	18
ASL-1.2	1.6	1.4	4.2	25	48	7	56
ASH-1.2	3.2	2.8	4.1	15	32	20	60
Ref-1.4	0.0	0.4	5.8	56	119	0	34
ASL-1.4	1.3	1.3	6.0	14	60	12	94
ASH-1.4	2.7	2.1	6.0	10	39	30	101

a = molar ratio, b = measured at (20), c = measured at (22), d = measured at (23).

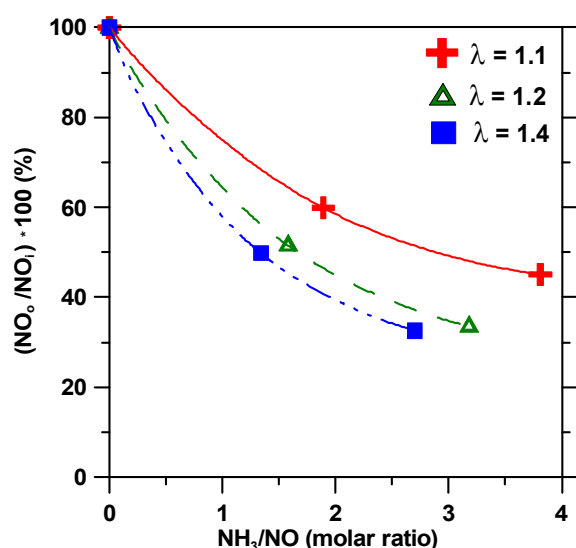


Figure 7. Reduction of NO versus molar ratio NH₃/NO during injection of AS in the cyclone at the three air excess air ratios (-- $\lambda = 1.1$, -- $\lambda = 1.2$, -- $\lambda = 1.4$).

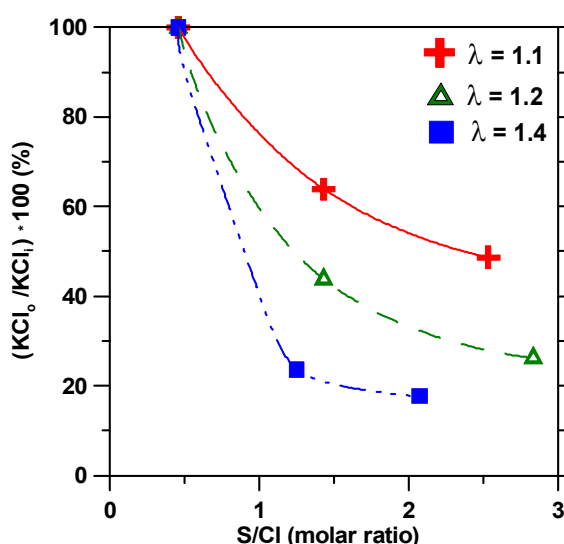


Figure 8. Reduction of KCl versus molar ratio S/Cl during injection of AS in the cyclone at the three air excess air ratios (-- $\lambda = 1.1$, -- $\lambda = 1.2$, -- $\lambda = 1.4$).

The initial concentration of gaseous KCl was set to approximately 50 ppm KCl during Ref for each λ . It required a higher fraction of straw pellets to reach 50 ppm during $\lambda = 1.4$ indicating formation of HCl was more favoured at a higher O₂. KCl was reduced to 14 ppm at a λ of 1.4 and to 25 ppm at a λ of 1.2 during test case ASL. Twice the amount of AS (ASH) was required for $\lambda = 1.1$ to obtain a reduction similar to ASL at $\lambda = 1.2$. The reduction of KCl in Figure 8 was less efficient during the lowest λ . Sulphation of gaseous KCl (R5) results in an increase of HCl which shall resemble the reduction of KCl in ppm. An increase in HCl was in all test cases noticed during injection of AS compared to Ref. The increase of HCl in ppm corresponded reasonably well with the decrease in KCl which supports that sulphation of KCl according to R5 occurred to a large extent.

The concentration of O₂ had an impact on both the reduction of NO and KCl in Figs 7 and 8 when injecting AS in the cyclone. The reduction of KCl was more affected by lowering λ than the NO

reduction. The greater impact was achieved although the initial concentrations were similar for KCl but much higher at increasing λ for NO. Reactions R2, R4 and R6-R10 depend on the O/H radical pool and thereby the level of O₂. An increased formation of SO₂ from SO₃ (R6) or the presence of H-radicals (R9) could possibly explain the less efficient sulphation during the lower air excess ratios. The presence of combustibles could also have a considerable influence on the reduction of NO and KCl. The concentration of CO in *Cyclone* ranged from 50 ppm at highest λ to approximately 800 ppm at the lowest air excess ratio. The presence of volatile hydrocarbons is shown in Fig. 6b and 50 ppm or less of HC_{tot} remained. The low levels of CO and volatile hydrocarbons in the cyclone suggest the results obtained were mainly an effect of the O₂ concentration rather than combustibles during $\lambda = 1.2$ and 1.4.

4.4 Effect of combustibles - Transient test

Ammonium sulphate (AS) was injected in three positions at excess air ratios $\lambda = 1.1, 1.2$ and 1.4 during the *Transient test*. These positions were in the upper part of the combustion chamber (*Comb*), in the inlet of the cyclone (*Inlet*), and in the cyclone (*Cyclone*). The purpose was to study how the gas composition at each injection point of AS influenced the flue gas chemistry for especially NO and KCl. Since no additional secondary air is added after (5) in Fig. 1, the oxygen concentration was similar during a specific λ . The presence of combustibles varied depending on λ and injection positions.

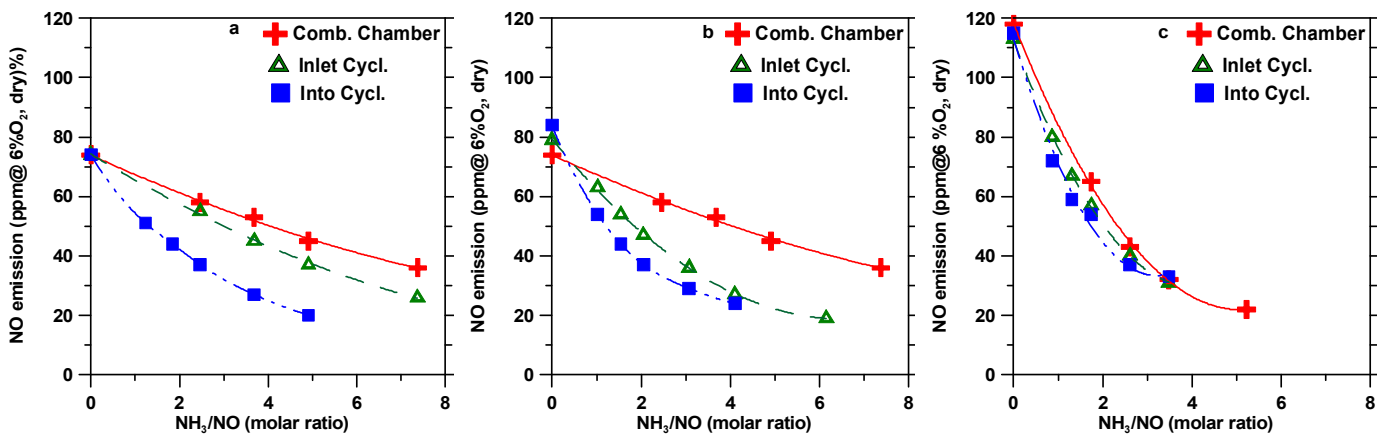


Figure 9. Concentration of NO versus molar ratio NH₃/NO during the transient test at the three different excess air ratios ($\lambda = 1.1$ (a), 1.2 (b), and 1.4 (c)). AS was injected in the upper part of the combustion chamber (Comb, 17 in Fig. 1), in the cyclone inlet (Inlet, 18), and in the cyclone (Cycl, 19).

NO in Fig. 9a was close to 75 ppm during each of the reference cases (Ref) at $\lambda = 1.1$. It was reduced to 45 ppm at a molar ratio NH₃/NO of 3.7 in *Inlet* and it required only a molar ratio of 1.8 to achieve a similar reduction in *Cyclone*. The performance of AS was more similar in *Inlet* and *Cyclone* at $\lambda = 1.2$ (Fig 9b), and significantly poorer in *Comb*. Here NO was reduced from approximately 80 ppm to less than 50 ppm at a molar ratio of 2.1 in *Inlet* and twice the amount of AS was required in *Comb* for a similar reduction. Finally, the initial level of NO was 115 ppm at $\lambda = 1.4$ and it was reduced to less than 40 ppm at a molar ratio of 2.6 in all positions. Fig. 10 shows the reduction of NO independent of inlet concentration instead. Similar trends are observed with a good reduction in *Cyclone* and significantly worse performance in the other positions at $\lambda = 1.1$. The situation was improved at $\lambda = 1.2$ and now the performance in *Inlet* resembled more of *Cyclone* rather than *Comb*. The NO reduction was similar and independent of position for $\lambda = 1.4$.

There seems to be a correlation between NO reduction and the presence of combustibles as shown in Fig 6. There are three test cases with very poor reduction and the conditions in these positions are characterised by levels of CO and HC_{tot} above 3000 and 1000 ppm respectively. The impression is that the position had a greater impact than λ on the reduction of NO. The exception is $\lambda = 1.4$ in which the reduction was similar in all cases although CO was around 800 ppm but HC_{tot} was less than 50 ppm *Comb*. This suggests that the interactions from volatile hydrocarbons are greater than those from CO for the NO reduction of AS.

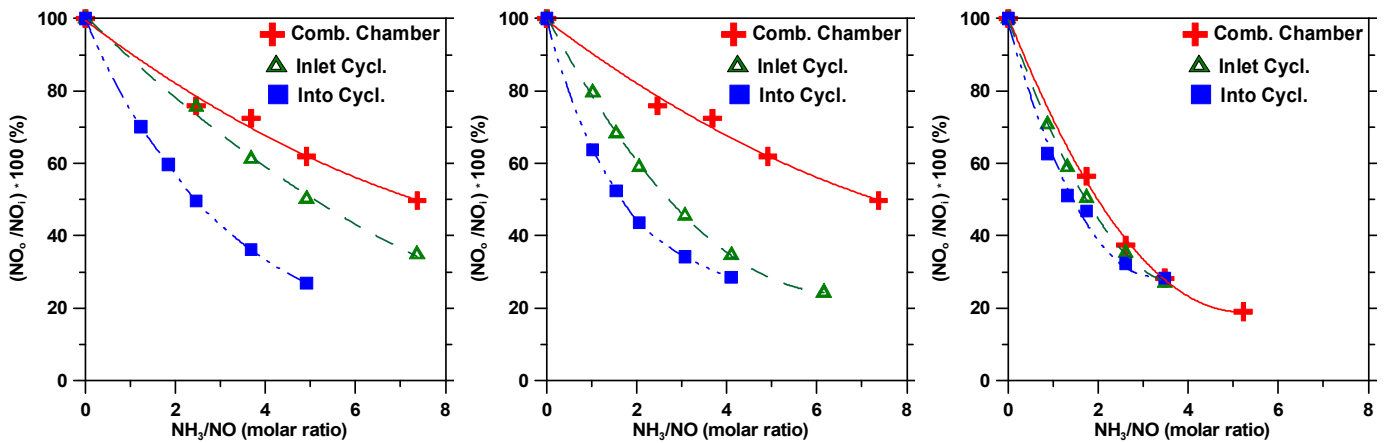


Fig. 10. Reduction of NO versus molar ratio NH_3/NO during the transient test at the three different excess air ratios ($\lambda = 1.1$ (a), 1.2 (b), and 1.4 (c). AS was injected in the upper part of the combustion chamber (Comb, 17 in Fig. 1), in the cyclone inlet (Inlet, 18), and in the cyclone (Cycl, 19).

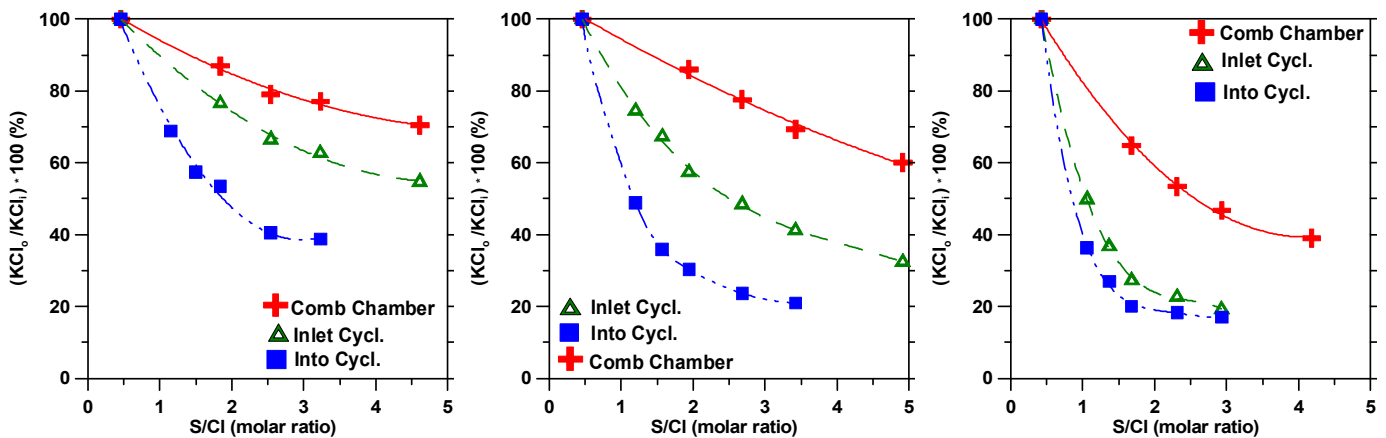


Fig. 11. Reduction of KCl versus molar ratio S/Cl during the transient test at the three different excess air ratios ($\lambda = 1.1$ (a), 1.2 (b), and 1.4 (c). AS was injected in the upper part of the combustion chamber (Comb, 17 in Fig. 1), in the cyclone inlet (Inlet, 18), and in the cyclone (Cycl, 19).

The initial concentration of gaseous KCl was approximately 50 ppm during each of the reference cases (Ref) for the three air excess ratios. Fig. 11 shows the reduction of KCl versus molar ratio S/Cl for each λ . The IACM measurements revealed that the position as well as λ had a great impact on the reduction of KCl. In general the reduction was less efficient in an earlier position, such as *Comb*, although the residence time is longer in comparison with the other positions during the same λ . The only test cases with a similar reduction of KCl for the same λ was *Inlet* and *Cyclone* during $\lambda = 1.4$. It required a molar ratio S/Cl close to 3 to obtain a reduction of KCl of 80% in those test cases as well as in *Cyclone* during $\lambda = 1.2$. The reduction during test cases *Cyclone* ($\lambda = 1.1$) and *Inlet* ($\lambda = 1.2$) also resembled each other and 40% of the initial KCl remained at a molar ratio somewhat above 3. The performance of AS in *Comb* at $\lambda = 1.4$ was somewhat poorer. The positions with the lowest reduction of KCl were *Comb* ($\lambda = 1.1, 1.2$) and *Inlet* ($\lambda = 1.1$). The *Transient test* revealed that the position had a greater impact than λ on the sulphation efficiency of AS. Especially, the position *Comb* is during the lower air excess ratios characterised by a higher level of combustibles (Fig. 6). SO_3 was thus limited by interactions from the presence of combustibles (R9) and possibly in combination with low O_2 (R6). Consequently, SO_3 was partly consumed by reactions than R5 which lowered the sulphation efficiency.

5. Summary and Conclusions

The results reveal that both the air excess ratio and the selected position had an impact on the reduction of NO as well as KCl during injection of ammonium sulphate. Fig. 12 shows the reduction of NO and KCl during six combinations of position and λ . These combinations were selected to emphasize the occurrence of interactions rather than an optimal performance of AS. Thus test cases *Cyclone* $\lambda=1.1$ and 1.2 are excluded, since they performed excellently and had a similar performance as *Inlet* $\lambda=1.4$ for both NO and KCl. The impression was that the efficiency of AS for reduction of NO and KCl in general were affected in similar ways. A less efficient reduction was achieved in earlier positions, such as *Comb*, although the residence time was longer in comparison with the other positions during the same λ . However, the burn-out of combustibles is more complete in the downstream positions, which leads to fewer interactions with the O/H radical pool.

The poorest NO reduction was achieved in positions characterised by the highest levels of CO and volatile hydrocarbons and it is also suggested the interactions from HC_{tot} were greater than those from CO for the NO reduction by AS. The main interaction is a competition for OH radicals between CO oxidation (R2) and reduction by NH_3 (R4). Similar reduction of KCl was obtained in *Comb* at $\lambda = 1.4$ *Inlet* at $\lambda = 1.2$ and in *Cyclone* at $\lambda = 1.1$. Here, the trend for NO was somewhat different with significantly better reduction in *Comb* at $\lambda = 1.4$ than in the two other positions. This is one example of a position in which the NO reduction was significantly better. This suggests the sulphation is somewhat more sensitive for interactions with the radical pool than NO reduction. The poorest sulphation occurred in *Comb* at $\lambda = 1.1$ and 1.2 which is characterised by rather low concentration of O_2 and the presence of volatile combustibles, such as CO, methane and ethene. These conditions increase the reduction of SO_3 to SO_2 (R6) from reactions with H radicals (R9). Thus the reduction of NO and KCl is influenced by the competition for OH radicals but the sulphation of KCl is also influenced by H-radicals.

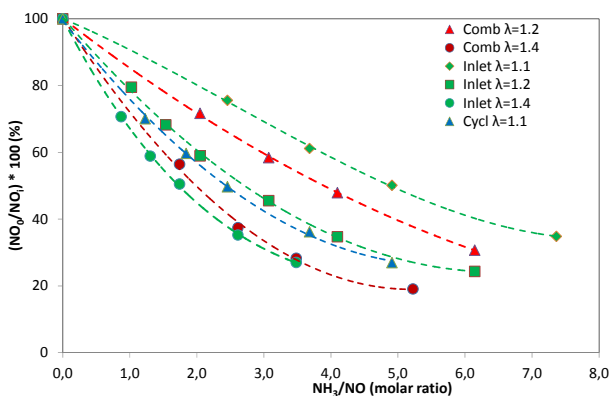


Figure 12a. Reduction of NO versus molar ratio NH_3/NO . Positions and λ for the test cases shown in the Fig.

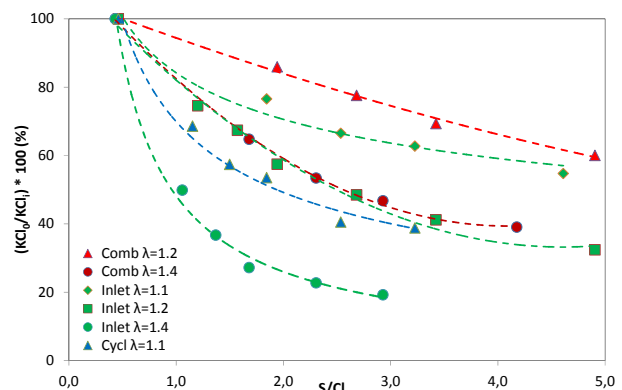


Figure 12b. Reduction of KCl versus molar ratio S/Cl . Positions and λ for the test cases shown in the Fig.

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References

- [1] Kassman, H., Broström, M., Berg, M., and Åmand, L.-E., *Measures to Reduce Chlorine in Deposits: Application in a Large-Scale Circulating Fluidised Bed Boiler Firing Biomass*. Fuel, 90, (2011). p. 1325-1334.
- [2] Kassman, H., et al. *Nitrogen containing additives for simultaneous reduction of KCl and NOx*

- during biomass combustion in a CFB boiler. in *9th International Conference on Circulating Fluidized Beds*. 2008. Hamburg, Germany.
- [3] Kassman, H., Båfver, L., and Åmand, L.-E., *The importance of SO₂ and SO₃ for sulphation of gaseous KCl – An experimental investigation in a biomass fired CFB boiler*. *Combust. Flame*, 157, (2010). p. 1649-1657.
- [4] Kassman, H., Pettersson, J., Steenari, B.-M., and Åmand, L.-E., *Two strategies to reduce gaseous KCl and chlorine in deposits during biomass combustion - injection of ammonium sulphate and co-combustion with peat*. *Fuel Process. Technol.*, 105, (2013). p. 170-180.
- [5] Wu, H., et al., *Modeling the use of sulfate additives for potassium chloride destruction in biomass combustion*. *Energy Fuels*, 28, (2014). p. 199-207.
- [6] Viklund, P., et al., *Effect of sulphur containing additives on initial corrosion of superheater tubes in waste fired boilers*. *Corrosion Engineering, Science and Technology*, 44, (2009). p. 234-240.
- [7] Aho, M., Paakinen, K., and Taipale, R., *Destruction of alkali chlorides using sulphur and ferric sulphate during grate combustion of corn stover and wood chip blends*. *Fuel*, 103, (2013). p. 562-569.
- [8] Kassman, H., Normann, F., and Åmand, L.-E., *The effect of oxygen and volatile combustibles on the sulphation of gaseous KCl*. *Combust. Flame*, 160, (2013). p. 2231-2241.
- [9] Viklund, P., Kassman, H., and Åmand, L.E., *Deposit chemistry and initial corrosion - The influence of excess O₂ and sulphate injection*. *Mater. Corros.*, (2014). p. Article in press, DOI: 10.1002/maco.201307162.
- [10] Tayyeb Javed, M., Irfan, N., and Gibbs, B.M., *Control of combustion-generated nitrogen oxides by selective non-catalytic reduction*. *Journal of Environmental Management*, 83, (2007). p. 251-289.
- [11] Mahmoudi, S., Baeyens, J., and Seville, J.P.K., *NO_x formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass*. *Biomass Bioenergy*, 34, (2010). p. 1393-1409.
- [12] Pisano, J.T., et al., *Optimization of SNCR NO_x control on a wood-fired boiler*. *Combust. Sci. Technol.*, 184, (2012). p. 1366-1379.
- [13] Zabetta, E.C., Hupa, M., and Saviharju, K., *Reducing NO_x emissions using fuel staging, air staging, and selective noncatalytic reduction in synergy*. *Ind. Eng. Chem. Res.*, 44, (2005). p. 4552-4561.
- [14] Leckner, B., et al., *Influence of additives on selective noncatalytic reduction of NO with NH₃ in circulating fluidized bed boilers*. *Ind. Eng. Chem. Res.*, 30, (1991). p. 2396-2404.
- [15] Lu, D.Y., et al., *Understanding of halogen impacts in fluidized bed combustion*. *Energy Fuels*, 15, (2001). p. 533-540.
- [16] Bae, S.W., Roh, S.A., and Kim, S.D., *NO removal by reducing agents and additives in the selective non-catalytic reduction (SNCR) process*. *Chemosphere*, 65, (2006). p. 170-175.
- [17] Zamansky, V.M., et al., *Reactions of sodium species in the promoted SNCR process*. *Combust. Flame*, 117, (1999). p. 821-831.
- [18] Glarborg, P., *Hidden interactions - Trace species governing combustion and emissions*. *Proceedings of the Combustion Institute*, 31, (2007). p. 77-98.
- [19] Hindiyarti, L., Frandsen, F., Livbjerg, H., and Glarborg, P., *Influence of potassium chloride on moist CO oxidation under reducing conditions: Experimental and kinetic modeling study*. *Fuel*, 85, (2006). p. 978-988.
- [20] Hindiyarti, L., Glarborg, P., and Marshall, P., *Reactions of SO₃ with the O/H radical pool under combustion conditions*. *J. Phys. Chem. A*, 111, (2007). p. 3984-3991.
- [21] Andersson, C., *European Patent EP 1221036*, 2006.
- [22] Andersson, C., *European Patent EP 1354167*, 2006.
- [23] Kassman, H., et al., *Decreased emissions of CO and NO_x by injection of ammonium sulphate into the combustion chamber*, in *Värmeforsk report No 908 (Summary in English)*. 2005.