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Circulating Fluidized Bed Technology 9

Joachim Werther, Wojciech Nowak, Karl-Ernst Wirth and Ernst-Ulrich Hartge (Eds.)

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NITROGEN CONTAINING ADDITIVES FOR SIMULTANEOUS REDUCTION OF KCl AND NOx DURING BIOMASS COMBUSTION IN A CFB BOILER

Håkan Kassman^{1*}, Magnus Holmgren¹, Elin Edvardsson²

Lars-Erik Åmand³, Johannes Öhlin³

¹ Vattenfall Power Consultant AB, SE-61129 Nyköping, Sweden

² Vattenfall Research and Development AB, SE-16287 Stockholm, Sweden

³ Chalmers University of Technology, Department of Energy and Environment
Division of Energy Technology, SE-41296 Gothenburg, Sweden

* corresponding author: hakan.kassman@vattenfall.com

Abstract - High levels of alkali chlorides in the flue gas can cause enhanced deposit formation and superheater corrosion during combustion of biofuels. These alkali chlorides mainly originate from potassium chloride (KCl). A challenge during combustion of biofuels is to simultaneously reduce NO_x and KCl. The ChlorOut concept has been developed by Vattenfall to minimise deposit formation and corrosion. It consists of IACM, an instrument for on-line measurements of gaseous alkali chlorides, and a sulphate-containing additive that converts alkali chlorides to less corrosive alkali sulphates. The sulphate-containing additive is often ammonium sulphate, (NH₄)₂SO₄, and, therefore, a significant NO_x reduction is also achieved. This paper presents the results from a comparison of the conventional SNCR additives (ammonia or urea) and (NH₄)₂SO₄ for reduction of NO_x and/or KCl during combustion in a CFB boiler. The fuel consisted of either a mixture of wood chips and wood pellets with added PVC or with straw pellets. Of special interest was the influence of sulphation of KCl in parallel to the reduction of NO and if these processes interact. The results show that there are rather small differences in performance concerning NO_x reduction between the additives.

INTRODUCTION

High levels of alkali chlorides in the flue gas can cause enhanced deposit formation and superheater corrosion. Alkali related problems during combustion of biofuels mainly originate from potassium chloride (KCl) which can be reduced by additives. A challenge during combustion of such fuels is to simultaneously reduce NO_x and KCl. The ChlorOut concept aims to minimise deposit formation and corrosion during combustion of biofuels. It consists of IACM [1], an instrument for on-line measurements of gaseous alkali chlorides, and a sulphate-containing additive that converts alkali chlorides to less corrosive alkali sulphates [2]. The sulphate-containing additive is often ammonium sulphate, (NH₄)₂SO₄, and, therefore, a significant NO_x reduction is also expected in parallel to the sulphation of alkali chlorides in the gas phase. The results from several different measurement campaigns with the ChlorOut concept during firing of wood or waste wood have been published including [3-4]. Improved understanding of the interaction of SNCR chemistry and the presence of gaseous sulphur (SO₂, SO₃) and chlorine (HCl, KCl) in various forms as well as aerosols is the key issue of the present paper.

THEORY

The SNCR (selective non-catalytic reaction) technology is a well established strategy to reduce NO_x, and normally ammonia (NH₃) or urea is injected into the flue gas pass at a temperature above 800°C. The use of NH₃ for reduction of NO without any catalyst goes back to a patent registered already in 1975 [5]. Since then extensive efforts have been made to improve the knowledge of combustion chemistry including species like N, S, Cl in the reaction schemes. A good review article in the area has recently been published [6] and

Table 1. Reactions of interest

Description of reaction	Reaction and number
CO is oxidised mainly by the OH radical: (Ref. 7)	(R1) $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$
Interference of alkali on CO oxidation (Ref. 7)	(R2) $\text{K} + \text{OH} + \text{M} \rightleftharpoons \text{KOH} + \text{M}$
Overall sulphation reaction of KCl (Ref. 6, 8)	(R3a) $\text{KCl} + \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{HCl}$
Oxidation of SO ₂ to SO ₃	(R3b) $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$
Sulphation of KCl from SO ₃ (Ref. 8)	(R3c) $\text{KCl} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{HCl}$
Decomposition of ammonium sulphate	(R3d) $(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O}$
Reduction of NO by NH ₃	(R4a) $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$
	(R4b) $\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$

even the influence of KCl on CO oxidation is included in [7]. It was proposed in [8] that the sulphation rate in the gas phase is limited by the presence of sulphur trioxide (SO₃). NH₃ and other NO_x reducing additives were used in the present boiler in an earlier project [9] when coal was the only fuel of interest. Reactions of particular interest for this paper are presented in Table 1.

EXPERIMENTAL

The boiler and the operating conditions

The 12 MW CFB boiler at Chalmers University of Technology (CTH) was used for the experimental runs. This research boiler has been described earlier in several publications including [9, 10]. The main focus of the present work is the exit region of the boiler, Fig. 1. The combustion chamber (1) has a square cross-section of about 2.25 m² and a height of 13.6 m. Fuel is fed from the bottom. The bed material is recirculated through the cyclone back to the combustion chamber, whereas the combustion gases enter the “convection path” (8) where the gases are cooled down to 150 °C before cleaning in a secondary cyclone and a bag filter. Gas concentrations were measured in a location just before the convection path starts (5), after the convection path and before the stack. SNCR/ChlorOut chemicals were added before the primary cyclone (3). The base fuel was a mixture of wood pellets and wood chips. Straw pellets were used as additional fuel in some tests with a constant ratio of about 20% of the energy content. Chlorine was added as PVC (norvinyl S7060 from Hydro Polymers, Sweden) in order to produce sufficient high levels of alkali chlorides in the tests without straw. The different fuel properties are given in Table 2. The chlorine content in straw pellets is 18 times higher than in wood pellets and wood chips (Table 2). The potassium (K) content on ash basis is about the same as for the two other biofuels. However, since the ash content is about 8 times higher, the loading of K increases using straw compared to wood pellets and wood chips used as base fuels. K in wood probably forms KCl with the chlorine contained in the straw and without straw, PVC addition was necessary for formation of KCl. Operating conditions typical for a CFB boiler were selected, Table 3. Silica sand (d_p=0.3 mm) was used as bed material.

Table 2. Fuel properties

	Straw pellets	Wood pellets	Wood chips
Proximate analysis			
Water (wt-%, raw)	9.0	8.5	47.4
Ash (wt-%, dry)	5.1	0.4	0.8
Combustibles (wt-%, dry)	94.9	99.6	99.2
Volatiles (wt-%, daf)	80.3	81.9	82.0
Ultimate analysis (wt-%, daf)			
C	49.3	50.5	50.8
H	6.1	6.0	5.9
O	43.7	43.4	43.2
S	0.1	0.01	0.01
N	0.5	0.1	0.1
Cl	0.27	0.02	0.01
Ash analysis (g/kg dry ash)			
K	157	138	117
Na	6.3	7.5	4.9
Al	4.0	6.7	3.7
Si	230	116	18
Fe	3.4	8.8	2.1
Ca	72.4	152	234
Mg	12	30	36
P	12	13	17
Ti	0.3	0.4	0.2
Ba	0.7	2.2	0.9
Lower heating value (MJ/kg)			
Hu, daf	18.35	19.00	18.74
Hu, raw	15.63	17.11	8.60

daf= dry and ash free, raw= as received

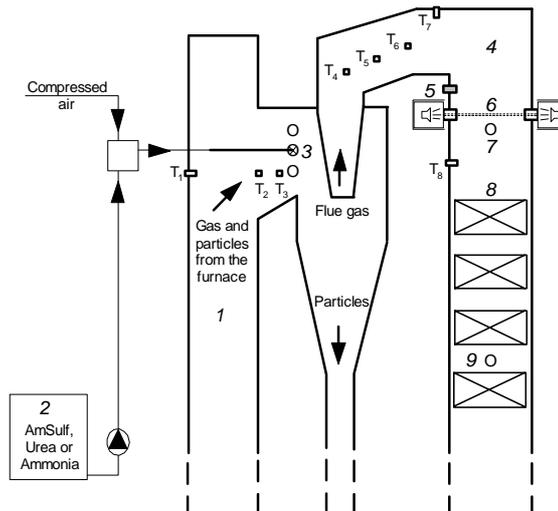


Fig. 1 The 12-MW_{th} CFB boiler: (1) combustion chamber; (2) reservoir for chemicals; (3) injection hole for SNCR/ChlorOut chemicals; (4) after burner chamber; (5) measurement hole ABC (after burner chamber); (6) IACM; (7, 9) measurement holes; (8) start of the convection section.

Table 3. Operating conditions

Operating case	"straw"	"nostraw"	"nostraw"	"nostraw"	"nostraw"
Air ratio	Normal O ₂	Normal O ₂	Normal O ₂	Low O ₂	High O ₂
Bed temperature, °C	850	850	750	850	850
Excess air ratio	1,2	1,2	1,2	1,1	1,4
Load, MW _{th}	6,0	6,1	5,9	6,6	5,3
Temp. top of combustion chamber					
average of T ₁ , T ₂ & T ₃ , °C	875	866	822	872	846
Exit temp after comb. chamber T ₄ , °C	802	791	753	814	763
Exit temp. T ₅ , °C	832	823	786	843	793
Exit temp. T ₆ , °C	833	823	786	843	793
Exit temp. T ₇ , °C	823	813	778	832	784
Temp before convection pass T ₈ , °C	808	801	769	821	773
Total riser pressure drop, kpa	5,9	5,6	6,3	5,4	5,2
S/Cl molar ratio	0.4/3.9 ⁽¹⁾ /1.8 ⁽²⁾	0.1/1.5 ⁽²⁾	0.1/1.4 ⁽²⁾	0.1/1.3 ⁽²⁾	0.1/1.3 ⁽²⁾
Cl/(K+Na) molar ratio	0,3	1,5/0,2 ⁽³⁾	1,5/0,2 ⁽³⁾	1,4/0,2 ⁽³⁾	1,7/0,2 ⁽³⁾
Ca/S molar ratio (with Ca in fuel)	5,9	10,2	10,0	9,6	10,0
Primary air flow / total air flow, %	62	63	52	62	63
Superficial flue gas velocity at top of riser U _{top} , m/s	5,1	4,9	4,8	5,1	4,6

(1)=with sulphur granules; (2)=with ammonium sulphate addition; (3)=without PVC addition.

The tests

Two reference cases (“straw” and “no straw”) were defined in the test campaign. During the “straw” case, sulphur in the form of granules was added in some cases. Sulphur was added to the return leg from the hot cyclone and various combinations of NO_x reducing agents were added at operating conditions shown in Table 3. During the “no straw” case, PVC was supplied to the return leg instead in some cases and combinations of NO_x reducing agents were tested at various

combustion temperatures and excess air ratios. The influence of PVC feed on the NO reduction was studied by separate tests where the PVC was shut off. Two key parameters, the molar ratio S/Cl and the Cl/(K+Na) require special attention. The first one (S/Cl) reflects the excess of sulphur in relation to chlorine and relates to the competition between Cl and S in reacting with K. Theoretically a molar ratio of 0.5 is sufficient to produce K_2SO_4 if K prefers S over Cl in the reaction schemes. In reality there is a competition between S and Cl and an excess of S is needed to prevent KCl from being formed. Also Ca in the fuel ash competes with K in reacting with S and therefore the molar ratios of Ca/S are given as well. In all operating cases without supply of sulphur there was an excess of lime which means that all Cl present in the fuel could react with the alkali (K+Na). The ratio Cl/(K+Na) is a measure for how much Cl that is available in relation to the alkali content of the fuel. This ratio was 0.3 in the “straw” case and 0.1 during “no straw”. This means that, there is normally a lack of Cl to form KCl when using pure wood as fuel. Adding PVC drastically increases this ratio as shown in Table 3 and increased levels of KCl are measured with IACM.

Measurements techniques

A so-called IACM (*In-situ* Alkali Chloride Monitor) located at (6) in Fig. 1 was used to measure the alkali chlorides in the gas phase. It measures the sum of the KCl and NaCl concentrations on-line but it can not distinguish between these two species. The result is expressed as KCl during biomass combustion. IACM also measures SO_2 at the same time. Light from a xenon lamp is sent across the furnace or flue gas channel. The light, which arrives at the receiver, is analysed by a spectrometer. The measurements are made by the principle of optical absorption. The detection limit at a 5 metre measuring length is 1 ppm for KCl and NaCl and 4 ppm for SO_2 . IACM has been used in the present boiler in previous projects related to alkali chloride issues [10]. Flue gas was also extracted through a heated probe and heated sampling lines to a FTIR (Fourier transform infra-red) analyser for the determination of HCl, SO_2 , N_2O , NO_2 and NH_3 on hot wet flue gases and further to on-line IR-VIS instruments measuring CO, SO_2 and N_2O on cold dry gases. A chemiluminescence analyser was used (in connection to the cold system) for the measurement of NO.

RESULTS AND DISCUSSION

Interaction of sulphation of alkali chlorides with the nitrogen chemistry

Fig. 2 shows the NO emission from co-firing with straw using the three reducing agents $(NH_4)_2SO_4$, urea and NH_3 . The starting point was a case with high level of KCl (KCl=45 ppm). NO was reduced to less than half at a NH_3/NO molar ratio of approximately 3 for $(NH_4)_2SO_4$ and KCl was simultaneously reduced from 45 ppm to 15 ppm. Testing of NH_3 and urea were performed during parallel feeding of sulphur granules in order to achieve similar conditions with respect to KCl as during $(NH_4)_2SO_4$. No clear difference between the additives was observed during addition of excess amounts and levels of NO around 10 ppm were achieved at molar ratios of NH_3/NO in the range of 4-5. Urea was more efficient than the two other additives in reducing NO at a medium range molar ratio of 2, Fig. 2. KCl was reduced from 45 ppm to 15 ppm at a S/Cl molar ratio of 1.8 during addition of $(NH_4)_2SO_4$, and to 20 ppm at a S/Cl molar ratio of 3.9 with sulphur. Sulphation of KCl was more efficient with $(NH_4)_2SO_4$ although the S/Cl molar ratio was less than half compared to sulphur. Ammonium sulphate performed better than sulphur since it is decomposed into SO_3 (reaction R3d, Table 1). The rate determining step using sulphur is instead the oxidation of SO_2 to SO_3 (R3b). This proves the presence of gaseous SO_3 is of great importance for sulphation of KCl (R3c). Similar results have for instance been observed in [3]. High KCl levels were generated by PVC supply during the “no straw” case, and the three additives were compared during these special conditions. The tests with urea or NH_3 in Fig. 3 were carried out without addition of sulphur. This resulted in decreased KCl with $(NH_4)_2SO_4$ and unchanged levels of KCl during the use of urea or NH_3 . From Fig. 3 it is evident that there are no differences in the reduction capacity of NO between the three additives. This raises the question whether a change in the concentration of KCl is important or not for the gas phase chemistry involving reduction of NO. Fig. 4 and 5 indicate that this is not the case for urea or ammonia as reducing agents. By shutting off the PVC supply, the tests shown in Fig. 3 can be directly compared to the corresponding tests without PVC and no significant difference could be obtained in the NO reduction performance. Using PVC during these tests gave an increase in KCl from 3 to 45 ppm and HCl increased as well. Fig. 4 and 5 also show the straw case, where KCl was 45 ppm without sulphur and 20 ppm by addition of sulphur granules (as shown in Fig. 2). No difference in the reduction of NO related to the level of KCl was observed for urea in the direct comparison in Fig. 4. A somewhat better reduction was obtained during the corresponding tests with NH_3 for straw if no sulphur was supplied (=high level of KCl). Urea is a better reducing agent than NH_3 which is proven by the fact that better NO reduction was measured for the “straw” case than “no straw” case (Fig. 4). The corresponding tests using NH_3 , instead gave the same levels of NO for both the “straw” case as the “no straw” case. The reproducibility in duplicates from different measurement days was high during the test campaign. It was typically a few ppm in the results presented in Fig. 3 to 6.

The transient test

An even better tool to reveal the interaction between the sulphation of KCl and the nitrogen chemistry is to perform transient tests showing the immediate response of NO, KCl, HCl, SO_2 and also including the CO as

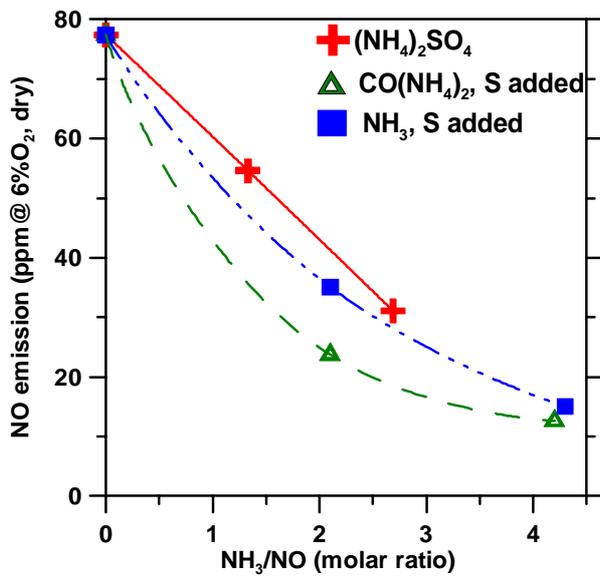


Fig. 2 Comparison of the reduction of NO with injection of $(\text{NH}_4)_2\text{SO}_4$, urea or NH_3 . Test case: "straw". S-granules added during urea or NH_3 .

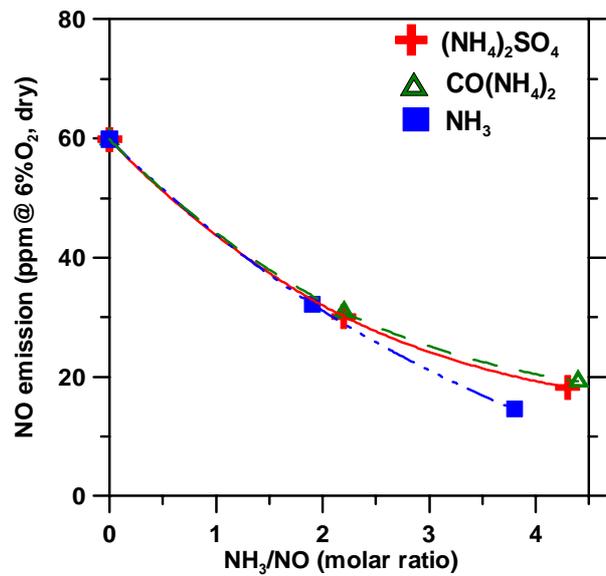


Fig. 3 Comparison of the reduction of NO with injection of $(\text{NH}_4)_2\text{SO}_4$, urea or NH_3 . Test case: "no straw" with PVC addition.

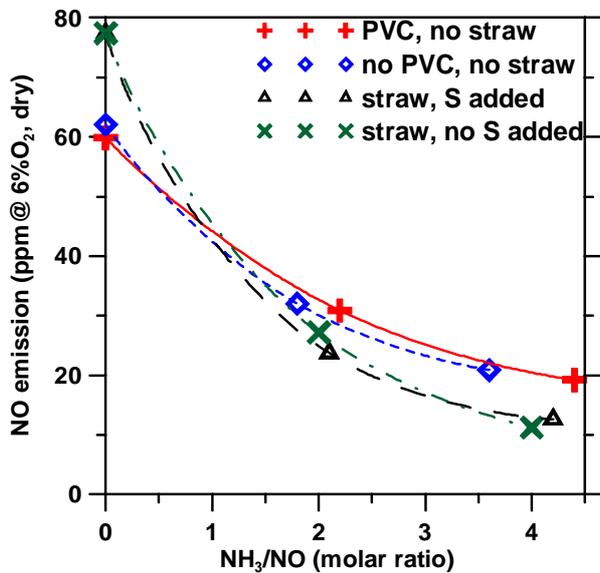


Fig. 4 Comparison of the reduction of NO with injection of urea. Test cases: "straw" or "no straw". Note the options of adding S-granules in the "straw" case or PVC in the "no straw" case.

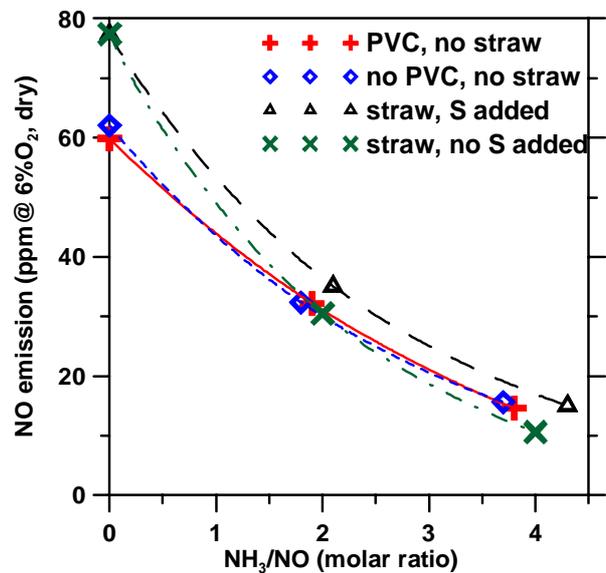


Fig. 5 Comparison of the reduction of NO with injection of NH_3 . Test cases: "straw" "no straw". Note the options of adding S-granules in the "straw" case or PVC in the "no straw" case.

a measure of oxidation performance by OH radicals. Such a test is shown in Fig. 6 and it is based on the "straw" case with addition of sulphur granules and the use of urea for NO reduction. The roman numbers represent the following operating conditions:

I. "straw" case; II. "straw" case, start of sulphur granules; III. "straw" case, sulphur added, start of urea at a molar ratio (NH_3/NO) of 4.2; IV. "straw" case, addition of urea, sulphur granules shut off.

These events resulted in changed gaseous concentrations of NO, KCl, HCl, SO_2 and CO in following way:

I Reference levels for the "straw" case were established. Note that the concentration of CO was close to zero. SO_2 was less than 15 ppm, while KCl became 45 ppm when starting the straw feed in the morning. This also caused an increased NO emission from 60 to 80 ppm (not seen in Fig. 6).

II Feeding of sulphur started at $t=20$ minutes and raised SO_2 to 225 ppm. This lowered KCl to about 20 ppm. Note the simultaneous increase of HCl proving that an immediate sulphation of KCl took place in the gas phase before the convection pass. HCl increased somewhat more in ppm than KCl decreased. This increase shall according to R3a be the same as the decrease of KCl. Part of this formation of HCl could possibly be explained by a contribution from additional heterogeneous sulphation of KCl, which has

condensed on surfaces (tubes or particles). The importance of heterogeneous and homogeneous sulphation of alkali chlorides is discussed in [7].

III Starting the urea addition at $t=65$ minutes caused a fast drop in NO to around 15 ppm. CO increased from zero to about 20 ppm. (HCl is truncated due to formation of NH_4Cl).

IV At $t=105$ minutes the sulphur granules were shut off but the urea addition continued. As expected, SO_2 dropped back to the original values and so did KCl and probably also HCl. A very interesting observation was the increase of CO from 20 to 30 ppm. This is an indication that the CO oxidation is disturbed by the presence of KCl. Support for this is given by reaction R2 in Table 1 [7]. The explanation is radical recombination on gaseous KCl leading to a lack of OH radicals needed for the CO oxidation. A minor decrease of the NO level is also indicated as CO increased. The link between CO and the nitrogen chemistry is rather complex and it is not further discussed.

Influence of air ratio and combustion temperature on the NO reduction

The influence of temperature and air ratio (O_2 concentration) on NO reduction was investigated during "no straw" with addition of PVC. The changes for various parameters are reported in Table 3 and the results are condensed into Table 4. The excess air ratio was more important for the reference level of NO before any addition of reducing agents than changing top temperature of the boiler leading to increasing NO emissions at subsequent higher excess air ratios. NO reduction was much poorer at lower excess air ratios despite the higher temperatures in the reaction zone of the SNCR chemistry.

Increase of CO during NO reduction

It is well-known that adding ammonia for NO reduction causes an increase in the CO emission if CO is not fully oxidised prior to the injection point of NH_3 . This is linked to the available amount of OH radicals needed for the final step of the oxidation of CO. Anything that competes for the OH radicals (such as radical recombination caused by high levels of KCl discussed in connection to Fig. 6) will cause an increase in CO. When using ammonia as reactant, OH radicals are consumed for the formation of NH_2 radicals. The burnout of CO is under normal operation complete at the beginning of the convection section. Low excess air ratio (1.1) or low combustion temperature (bed temperature = 750°C) increased the CO emission from zero to 10 ppm at the most. An increase in the CO emission was measured during injection of all the SNCR additives and it is shown in Table 4. The increase is minor except during the low temperature case, where the limit of proper CO oxidation was reached. This also gives the key for sorting the other tests. The high excess air ratio

Table 4. Decrease of NO or increase of CO, N_2O or NH_3 emission (in ppm) during "no straw" at a NH_3/NO molar ratio of 4

Air ratio	Normal O2	Normal O2	Low O2	High O2
Bed temperature	850°C	750°C	850°C	850°C
NO, reference	60	58	49	69
NO, urea	41	36	27	46
NO, ammonia	45	38	24	55
NO, ammonium sulphate	42	29	23	45
CO, urea	20	52	17	26
CO, ammonia	18	46	12	20
CO, ammonium sulphate	18	50	6	23
N_2O , urea	16	18	8	18
N_2O , ammonia	3	5	2	4
N_2O , ammonium sulphate	6	10	4	7
NH_3 , urea	39	25	6	58
NH_3 , ammonia	13	12	4	50
NH_3 , ammonium sulphate	15	39	1	26

Formation of N_2O and emission of ammonia slip

N_2O is formed through gas phase reactions where the NCO radical is an important intermediate. Urea can decompose into NCO which makes it especially sensitive for unwanted formation of N_2O . Urea had as expected the highest tendency to form N_2O , Table 4. This effect from urea was observed already in [12]. The formation of N_2O was, however, never higher than 20 ppm for the tests reported in Table 4.

Emission of NH_3 (NH_3 slip) is an unwanted effect during SNCR. Table 4 shows that the slip was ranging from less than 10 ppm during low excess air ratio case (highest temperature), to very high levels for the

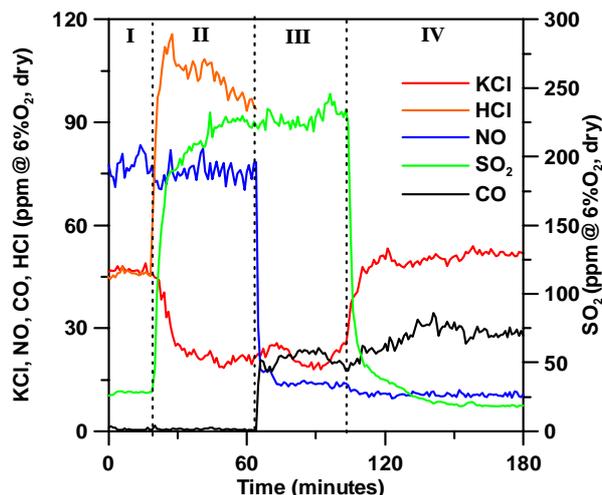


Fig. 6 Transient test of following:

I "straw" case

II "straw" case, start of S granules

III "straw" case, S added and urea ($\text{NH}_3/\text{NO}=4.2$)

IV "straw" case, no S added, urea ($\text{NH}_3/\text{NO}=4.2$)

Gas analysis in stack normalised to an O_2 concentration of 6% on dry gases.

gave a lower temperature in the reaction zone resulted in a somewhat higher emission of CO, and the opposite was true for the low oxygen case. This means that temperature is more important than the oxygen level for the CO oxidation within the range studied (excess air ratio between 1.1-1.3). These results are only relevant during low levels of CO (approx. 50 ppm or less) for ammonium sulphate. Ammonium sulphate can instead be used to simultaneously lower both NO and CO during firing of biomass in boilers with high emissions of CO [11].

opposite case with a high excess air ratio. It was also observed that the NH_3 slip is lowest when $(\text{NH}_4)_2\text{SO}_4$ is used (one exception). When using $(\text{NH}_4)_2\text{SO}_4$, KCl in gaseous form is sulphated into K_2SO_4 that condensate into small aerosol particles. These particles could act as surfaces for decomposition reactions of NH_3 . This is a possible explanation for the much lower ammonia slip in comparison with the corresponding tests with urea and NH_3 where no sulphation of KCl into K_2SO_4 was achieved.

CONCLUSIONS

Three different reducing agents for NO_x control have been tested under conditions prevailing when biomass is burned and the concentration of KCl is high. They were the conventional SNCR additives urea and ammonia (NH_3), and also ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) which is used in the ChlorOut concept. The fuel was either a mixture of wood chips and wood pellets with added PVC ("no straw") or straw pellets ("straw"). KCl was reduced by sulphur during urea and NH_3 or with $(\text{NH}_4)_2\text{SO}_4$. Conclusions from the project are:

- All three additives work well as NO reducing agents but there are some differences in their performance.
- The NO reduction was better for urea when straw was used to get a high level of KCl. No difference in NO reduction could, however, be seen between the additives during the tests with addition of PVC.
- The presence of KCl from addition of PVC / or removed by sulphur does not have any influence on the performance of NH_3 or urea with respect to the NO reduction. KCl may, however, influence the oxidation of CO leading to problems in the final burnout of CO at high KCl levels.
- A minor increase of CO was observed regardless of which of the three reducing agents that was used.
- Sulphation of KCl was more efficient with ammonium sulphate although the S/Cl molar ratio was less than half compared to sulphur. $(\text{NH}_4)_2\text{SO}_4$ reduced KCl better than sulphur since it is decomposed into SO_3 . This proves that the presence of gaseous SO_3 is of great importance for the sulphation of KCl.
- $(\text{NH}_4)_2\text{SO}_4$ made it possible to reduce both the NO emission and the concentration of KCl.

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