

## REDUCED SUPERHEATER CORROSION BY INJECTION OF AMMONIUM SULPHATE IN A BIOMASS FIRED BFB BOILER

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**Abstract** - Combustion of biomass with increased chlorine (Cl) contents can result in operational problems including increased deposit formation and superheater corrosion, because of the higher levels of alkali chlorides (KCl and NaCl) in the flue gas. Various strategies can be applied to reduce such problems and one of these is the use of on-line monitoring of alkali chlorides (IACM In-situ alkali chloride monitor) and sulphate-containing additives such as ammonium sulphate (AS). This is known as the ChlorOut concept. The sulphate additive which is sprayed into the flue gases in an appropriate position prior to the superheaters converts alkali chlorides into less corrosive alkali sulphates.

In this paper operational experiences concerning superheater corrosion during combustion of demolition wood in a Bubbling Fluidised Bed (BFB) boiler are evaluated. Parts of superheater SH2 were replaced due to corrosion after four years of operation. Injection of AS according to the ChlorOut concept was applied as a strategy to reduce the superheater corrosion in the boiler. Tube analysis after another two years of operation revealed that the superheater corrosion was significantly reduced after installation of the ChlorOut concept. These results were supported by long-term corrosion probe measurements carried out prior to installation during injection of ammonium sulphate and without any injection.

### INTRODUCTION

Combustion of biomass with increased chlorine (Cl) contents can result in operational problems. These problems include increased superheater corrosion and fouling because of the higher levels of alkali chlorides (KCl and NaCl) in the flue gas. Various strategies can be applied to reduce such problems as presented in (Henderson et al. 2006, Viklund et al. 2009, Kassman et al. 2010, Kassman et al. 2011, Kassman 2012, Kassman 2013a, Viklund et al. 2015). For example, the superheaters can be replaced at more frequent intervals, or a more corrosion resistant material like stainless steel can be used for superheaters in combination with increased soot-blowing. Another strategy is to monitor the corrosive species in the flue gas and adjust the flue gas chemistry accordingly so that the original superheater and soot-blowing conditions are maintained. In this work we investigate the latter strategy with the use of on-line monitoring of alkali chlorides (IACM In-situ alkali chloride monitor) and injection of sulphate-containing additives such as ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, AS). This is known as the ChlorOut concept (Andersson 2006a, Andersson 2006b). The sulphate containing additive which is sprayed into the flue gases in an appropriate position prior to the superheaters converts alkali chlorides (hereafter referred to as KCl) into less corrosive alkali sulphates. AS is more effective than sulphur and in addition can be used for the selective non-catalytic reduction (SNCR) of NO as shown in Kassman et al. 2008, Kassman 2010, Kassman 2015, Kassman 2017. Investigations in several boilers have shown that injection of AS reduces the content of KCl in the flue gases and also chlorine in the deposits, which both are measures for the risk for superheater corrosion (Kassman et al 2011, Kassman et al 2013a).

The objective was to evaluate the operational experiences focusing on superheater corrosion during combustion of demolition wood in a Bubbling Fluidised Bed (BFB) boiler in Jordbro, Sweden. A permanent system for injection of AS was fully implemented in regular operation after replacement of parts of the final superheater due to corrosion. Prior to the permanent installation, extensive measurement campaigns using a temporary installation were carried out. Several advanced measurement tools were applied including IACM, and probes for short-term deposit and long-term corrosion measurements. These results supported the use of the ChlorOut concept as a strategy to reduce the superheater corrosion in the boiler. The permanent installation has now been in operation for almost three years. This paper presents results from the measurement campaigns prior to the permanent installation and an evaluation after two years operation.

## CORROSION MECHANISMS AND SULPHATION OF ALKALI CHLORIDES

Both alkali metals and chlorine (or chlorides) are present in the flue gases and in deposits and can take part in the corrosion process during combustion of demolition wood. Injection of ammonium sulphate has an impact on the flue gas environment in the superheater region of a boiler. The impact involves sulphation of gaseous alkali chlorides and reduction of NO by SNCR. This is described with a wider approach in Kassman and Åmand 2017. Table 1 shows corrosion mechanisms and reactions of particular interest.

Table 1 Reactions of interest

Description of reaction	Number and reaction
Corrosion mechanisms	(R1) $\text{Fe(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_2(\text{s,g})$ (R2) $2\text{FeCl}_2(\text{g}) + 3/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{Cl}_2(\text{g})$ (R3) $\text{KCl}(\text{s,g}) + \text{H}_2\text{O} \rightarrow \text{KOH}(\text{g}) + \text{HCl}(\text{g})$
Decomposition of ammonium sulphate (AS) Sulphation of KCl by $\text{SO}_3$ Oxidation of $\text{SO}_2$ to $\text{SO}_3$ Reduction of NO by $\text{NH}_3$	(R4) $(\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O}$ (R5) $2\text{KCl} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCl}$ (R6) $\text{SO}_2 + 1/2\text{O}_2 \leftrightarrow \text{SO}_3$ (R7) $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$

The most well-known corrosion mechanism is thought to occur by the diffusion of gaseous chlorine through a defect oxide scale as described by Grabke et al 1995. Chlorine reacts with the metal, where the oxygen partial pressure is low, at the metal-oxide interface to form a metal chloride as exemplified in (R1). The volatile metal chloride then diffuses outwards through the oxide and reacts with oxygen in the outer part of the scale releasing chlorine according to (R2). The chlorine is then able to diffuse back into the scale and cause more corrosion, the so-called chlorine cycle or “active oxidation” as described in Reese and Grabke 1992 and Grabke et al 1995. Other mechanisms proposed for chlorination include diffusion of chloride ions through the oxide scale or oxide grain boundaries (Folkesson et al. 2007), a chlorine-modified non-protective oxidation process (Viklund and Pettersson 2011) and the diffusion of  $\text{HCl}(\text{g})$  (Alipour et al. 2015). In the latter case it was proposed that  $\text{HCl}$  is formed from alkali chlorides such as  $\text{KCl}$ , which once deposited, may react with water vapour forming potassium hydroxide and releasing  $\text{HCl}$  (Alipour et al. 2015), according to reaction (R3).

In addition, low melting point or liquid chloride-containing salts in the deposits increase the corrosion rate because of increased reaction kinetics and transport of ions. The salts can attack the oxide by a fluxing mechanism whereby protective oxides dissolve in the salt. Salts containing sulphates have higher melting points than their equivalent chlorides and are therefore less prone to cause corrosion problems according to Cha and Spiegel 2006.

Both gas phase and solid or liquid phase reactions have been proposed for formation of alkali sulphates from alkali chlorides found in deposits and on ash particles (Glarborg 2007). Sulphation of  $\text{KCl}$  in the gas phase is limited by the formation of  $\text{SO}_3$ , since the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is the rate-limiting step. Kassman et al. 2010 proposed AS is decomposed into  $\text{NH}_3$  and  $\text{SO}_3$  according to (R4) when injected into a boiler. The overall sulphation reaction of gaseous  $\text{KCl}$  by  $\text{SO}_3$  may be described as in (R5).  $\text{SO}_3$  is formed from oxidation of  $\text{SO}_2$  (R6) when using sulphur as an additive or during co-combustion with a sulphur containing fuel.  $\text{SO}_3$  is formed directly during injection of ammonium sulphate (R4) which also results in a reduction of NO by an SNCR reaction (R7).

## EXPERIMENTAL

### Plant description

Vattenfall's Combined Heat and Power (CHP) boiler is located in Jordbro, south of Stockholm, Sweden. The boiler in Jordbro is a Bubbling Fluidised Bed (BFB) built by Metso Wärtsilä Power and commissioned in 2010. It produces a total of 63  $\text{MW}_{\text{th}}$ , of which 20  $\text{MW}_{\text{el}}$  produced in a turbine. The boiler is designed for wood fuels as demolition (used, recycled) waste wood (DWW) and forestry residues, with a moisture content ranging from 20% to 45%, with steam data of 80 bar 470°C for 100% DWW and 495°C for 100% of forest residues. Fig. 1 shows the boiler in Jordbro with locations of importance for the present paper indicated. The fuel was DWW and its properties can vary significantly over time due to both origin and fuel supplier. Table 2 shows the fuel properties of three representative fuels which has been used in the boiler. Properties which often vary for DWW include the content of ash, nitrogen (N), alkali (Na, K), sulphur, chlorine and certain trace metals i.e. lead (Pb) and zinc (Zn). The greater amount of N and Na originates from composite board and paint (Enestam 2011). Pb and Zn mainly originates from painted wood (Enestam 2011). The molar ratio

S/Cl is a measure to which extent a fuel mix is corrosive and for the fuels in Table 2 it ranged from 0.3 to 0.8. The risk for corrosion is often considered great at a molar ratio S/Cl less than 2.0 and the content of chlorine in deposits is also a measure of the risk for corrosion. The importance of adding sulphur in the form of SO<sub>3</sub> (i.e. AS) rather than SO<sub>2</sub> (sulphur) to prevent corrosion is further discussed in Kassman et al. 2010, Kassman et al. 2013b and Kassman and Åmand 2017.

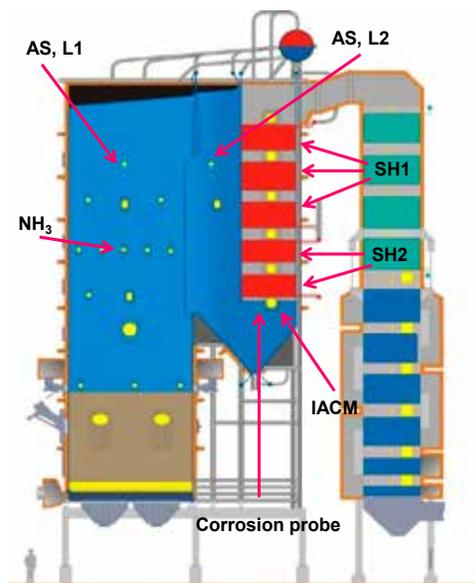


Fig. 1. The BFB boiler in Jordbro with locations for superheaters SH1 and SH2, the corrosion probe, IACM and injection points for AS and NH<sub>3</sub> indicated.

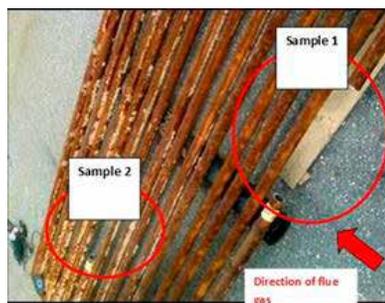


Fig. 2a. Superheater SH2 with positions for tube samples circled.

Fig. 2b. Close view of tube samples from SH2.

Table 2. Fuel properties

Fuel analysis	Fuel A	Fuel B	Fuel C
Proximate analysis			
Water (wt-%)	20.7	24.1	26.2
Ash (wt-%, ds)	3.0	3.1	2.7
Ultimate analysis			
C, Carbon, (wt-%, ds)	48.6	48.5	49.2
H, Hydrogen, (wt-%, ds)	6.0	5.9	6.3
S, Sulphur, (wt-%, ds)	0.06	0.07	0.07
N, Nitrogen, (wt-%, ds)	2.0	2.5	1.3
Cl, Chlorine, (wt-%, ds)	0.15	0.28	0.10
Lower heating value			
H, ds, (MJ/kg)	18.4	18.3	18.4
H, ar, (MJ/kg)	14.0	13.3	13.0

as = as received, ds = dry fuel

Ash analysis	Fuel A	Fuel B	Fuel C
Si, Silicon, (mg/kg ds)	4500	6400	5400
Al, Aluminium, (mg/kg ds)	800	1200	1100
Ca, Calcium, (mg/kg ds)	3400	4000	3300
Fe, Iron, (mg/kg ds)	1300	930	690
K, Potassium, (mg/kg ds)	750	900	870
Mg, Magnesium, (mg/kg ds)	530	510	450
Na, Sodium, (mg/kg ds)	840	1100	840
Pb, Lead, (mg/kg ds)	70	190	60
Zn, Zinc, (mg/kg ds)	80	150	320

The boiler was initially operated without any additives to prevent deposit formation and superheater corrosion. The superheaters are made of low alloyed carbon steel. The first section of the primary superheater SH1 is made of 16Mo3 and the remaining sections are made of 13CrMo4-5. The secondary superheater SH2 has the highest out-going steam temperature and both sections are made of 10CrMo9-10. The locations of SH1 and SH2 are indicated in Fig. 1. The expected life-time for SH2 was approximately four years at the rather corrosive conditions prevailing in the superheater region during combustion of DWW. It was found during the regular inspection in the spring of 2014 that there was extensive corrosion in the lower, hottest part of SH2. The lower parts of SH2 were replaced after four years of operation during the following revision in the fall of 2014. In order to document the extent and nature of the corrosion, two tube samples were taken for analysis from the superheaters which had been removed. The position for these tubes are within the circles in Fig. 2a. A closer view of the tube samples is shown in Fig. 2b. The superheater SH2

consist of double tubes, and four rows of tubes from the bottom up are considered to form a coil in the superheater. Sample 1 is taken from tube row 1 in the lowest coil. Sample 2 is taken from tube row 10 from the bottom up. The flue gas flows from the bottom upwards, and steam flows in the opposite direction through the tubes, so that the temperature of the material is highest in the tube where sample 1 was taken.

### **The ChlorOut installation and IACM**

The permanent ChlorOut installation was fully implemented in regular operation of the boiler during the summer of 2014. It consisted of IACM for measurement of gaseous alkali chlorides, and a dosage system for injection of ammonium sulphate. The dosage system (Fig. 3) consists of an external 40 m<sup>3</sup> storage tank (outdoors), an intermediate storage tank, pumping and control units as well as lances and nozzles. An aqueous solution of AS (40% wt) is transported from the intermediate storage tank by a pumping skid to the injection lances and nozzle. The lances are located opposite each other at two injection levels.

The injection levels for AS (L1 and L2), ammonia (NH<sub>3</sub>) and the location for IACM are indicated in Fig. 1. The injection positions for AS are in the upper part of the combustion chamber (Level L1) and in the upper part of the empty pass (Level L2). The boiler had a separate SNCR system for NH<sub>3</sub> before the injection system for AS was installed and it is still in operation. All positions for injection of AS and NH<sub>3</sub> are horizontal. The openings for IACM are located at the same position on the left and right side of the boiler.



Fig.3a. Overview dosage system and intermediate storage tank



Fig. 3b. Injection of AS in Level L2



Fig. 3c. Nozzle with opening for AS and air



Fig. 4a. The lamp side of IACM in the boiler in Jordbro.



Fig. 4b. The spectrometer side of IACM in the boiler in Jordbro.

IACM (In-situ Alkali Chloride Monitor) is a measurement device which consist of a transmitter (lamp) and a receiver (spectrometer). The lamp sends UV-light over the flue gas channel (measurement path) to a spectrometer on the opposite side of the boiler wall. Fig 4a shows the lamp side of IACM installed in Jordbro and the spectrometer side of IACM is shown in Fig 4b. The light is absorbed at characteristic wave lengths depending on the concentration of certain gaseous species such as KCl and SO<sub>2</sub>. The measuring principle is Differential Optical Absorption Spectrometry (DOAS). The result is expressed as the concentration of KCl and SO<sub>2</sub> respectively in ppm and is obtained after data evaluation of a spectrum by the IACM computer. A more detailed description of IACM can for instance be found in Andersson 2006a, Kassman et al. 2010, Kassman 2012, Leffler et al. 2016.

### **Long term corrosion measurements**

Prior to the permanent installation, extensive measurement campaigns using a temporary installation were performed. This included long term corrosion measurements both with and without injection of AS and the aim was to evaluate the ChlorOut concept. A corrosion probe was exposed prior to SH2 in the superheater region (Fig. 1). The ring material temperatures for the probe ranged from 350°C to 560°C. The temperature profiles for the probes during the two exposures were similar and temperature gradient along the probe of approximately 250°C was obtained in both cases. The temperature on the wind side of the probe was somewhat higher than the leeward side. The temperature profiles were used to estimate material temperatures for all samples rings during the evaluation of the test results. The corrosion probe had 16 sample rings and they were made of the same low alloyed material 10CrMo910 (Cr 2.3%, Mo 1%, Mn 0.6%) as in SH2.

The samples consisted of flanged rings that fit into each other and can be put together to form a tube. The sample rings were mounted on an air-cooled probe. The outer part of the probe is cooled with air, and the inner part of the probe can either be cooled with air or with water, depending on how much cooling is required. The reason for having two cooling channels is to control the temperature gradient along the probe. This is achieved by having opposite directions of the flows in the two cooling channels and adjusting the flows. There were rings with two thermocouples at each end of the probe and one at the middle. One of the thermocouples was used to regulate the cooling of the probe. The thermocouples were positioned at the wind and lee sides of the rings. The wall thickness of the sample rings was measured in 8 positions before and after exposure to determine the material loss during exposure in the boiler. The composition of the deposits was analysed by SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray analysis).

Short term deposit measurements were performed in conjunction with the corrosion measurements. The main objective of the deposit measurements was to investigate the content of chlorine and sulphur in collected deposits at the test conditions. From a corrosion point of view it is considered favourable if the deposits contain low amounts of chlorides and high amounts of sulphur in the form of sulphates. The measurements were carried out using a deposit probe placed immediately before SH2 in the same position as the corrosion probe. The deposits were collected on steel rings on a temperature controlled probe. The selected ring temperatures were 325°C, 425°C, and 500°C. The composition of the collected deposits were analysed by SEM-EDX. Three different areas on the wind and lee side of each specimen were analysed and the average composition on the wind and leeward side was calculated separately and as an average.

## **RESULTS**

Typical operating conditions and emissions for the boiler at different air excess ratios can be found in Tables 3 and 5 in Kassman and Åmand 2017. These emissions were presented both during Ref( no additive) and during injection of AS in positions L1 and L2. Experimental parameters such as the molar ratio S/Cl can be found in Table 4.

### **Corrosion probe measurements**

Table 3 shows the basic test conditions during the corrosion probe measurements. The probe exposure time in the boiler was 716 hours in the reference case and 932 hours in the ChlorOut case. When taken out from the boiler the probes were covered with a thin layer of deposits, except on the wind side where it was thicker. The material loss during long-term corrosion probe measurements with injection of ammonium sulphate (ChlorOut) and without (Reference) is shown in Fig. 5. There was significant difference in material loss between *Reference* and *ChlorOut* at greater temperatures. The use of ChlorOut reduces the material loss from extreme values, ~1700 µm/1000 hours, above material temperatures 500°C to ~100 µm/1000 hours. During Reference, a steep increase in the corrosion rate was observed at material temperatures above 460°C. The outgoing steam temperature is 470°C for SH2, which corresponded to a material temperature for the wind side of 500°C during the long-term exposure. The corrosion rate was reduced by approximately 80% at a steam temperature of 470°C. The reduction in high temperature corrosion is well in line with the purpose with injection of ammonium sulphate. Measurements of gaseous KCl by means of IACM showed that KCl was lowered from 35 ppm during *Reference* to 12 ppm during *ChlorOut*. As a consequence less chlorine was present in the deposits on the superheater tubes which leads to a reduced corrosion rate during ChlorOut.

Deposit measurement using a temporary injection system were carried out to optimise the dosage of ammonium sulphate regarding position and quantity, and also verify the effect by short-term measurements. The results obtained during short-term measurements showed that addition of AS reduced the content of KCl in the flue gases and also chlorine in the deposits. Fig. 6 shows the results from a deposit measurement

during a Reference as well as injection of AS in L1 and L2 respectively. Here the greatest content of chlorine was found during the Reference without injection of AS. These results also supported that injection of AS according to the ChlorOut concept could be applied as a strategy to reduce the corrosion rate of the superheaters in the boiler in Jordbro

Table.3: Test conditions during corrosion probe measurements.

	Flow of AS (l/h)	Injection level	Exposure time (h)	KCl <sup>a</sup> (ppm)	SO <sub>2</sub> <sup>a</sup> (ppm)
Reference	0	-	716	35	29
ChlorOut	55-65	L2	932	12	53

a = Measured before SH2 by IACM

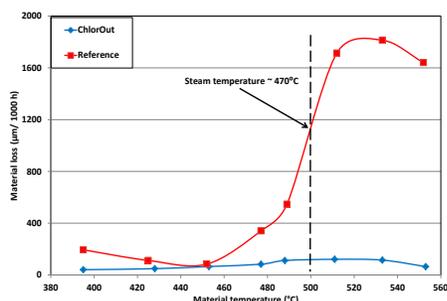


Fig. 5. Material loss during long-term corrosion probe measurements with (ChlorOut) and without (Reference) injection of ammonium sulphate.

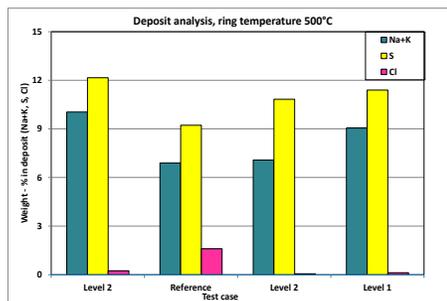


Fig. 6. Deposit analysis of Na+K, S and Cl at a ring temperature of 500°C.

### Tube analysis

Fig. 7 shows the appearance of tubes in the lower and hottest part of SH2 during a regular inspection in the spring of 2014. These tubes of low alloyed carbon steel (10CrMo9-10) were highly corroded and the oxides were loosely attached to the metal. The tubes in SH2 has an  $S_{Nom}$  of 6.3mm and the wall thickness was less than 4.0 mm in certain spot tests in the lowest row. The lower parts of SH2 were replaced after four years of operation during the following revision in the fall of 2014. Two tube samples were taken for analysis and the position for these tubes are within the circles in Fig. 2a. A closer view of the tube samples is shown in Fig. 2b and only isolated patches of the magnetite layer remained in place. The oxide on these patches was loosely attached and after being kept at room temperature for several days they became detached and fell from the tubes. These observations showed that the tubes have been subject to corrosion. This applied particularly to the lower (wind) side of sample 1, which was subject to the highest steam temperature and faced towards the incoming flue gas.

Fig. 8 shows clean-brushed surfaces on the wind side of samples 1 and 2. The tube material contains numerous small pits resulting from corrosion damage. The pits were flat-bottomed and had gentle contours. The pattern of corrosion had similarities what usually arises as a result of micromelts formed during combustion of chlorine-containing biomass fuels such as DWW. The wall thickness was measured in three rings from each tube sample. Most of the corrosion in sample 1 had taken place in the lower part of the tube which was facing the direction of the flue gas. The measurements of wall thickness are summarised as follows. The average value was 4.2 mm and the minimum 3.3 mm from a nominal value of 6,3 mm. This resulted in an average corrosion of 0.75 mm/year during operation without any additive to prevent superheater corrosion. SEM analysis were conducted on the inside of loose oxide scales. Based on the extensive corrosion a high content of chlorine and low of sulphur would be expected. However, the ratio of sulphur to chlorine was close to 4 indicating a low risk for corrosion which contradicted to the substantial corrosion which had taken place. One explanation of the favourable ratio of sulphur to chlorine was that the injection system for AS was taken into permanent operation a few months prior to the replacement of SH2.



Fig. 7. Highly corroded tubes of SH2 after nearly four years without an additive.

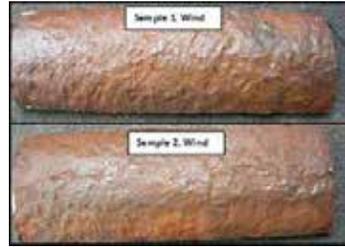


Fig. 8. Close view - Wind side of the analysed tube samples



Fig. 9. SH2 after two years with ChlorOut..



Fig. 10. Wind side of a tube in SH2.

Fig. 9 shows the appearance of tubes in the lower and hottest part of SH2 during a regular inspection in the fall of 2016 after two years of operation with injection of ammonium sulphate. Parts of the tubes were covered with a black magnetite layer ( $\text{Fe}_3\text{O}_4$ , iron oxide) which was tightly attached to the tube material. There were also a hematite layer ( $\text{Fe}_2\text{O}_3$ ) outside the magnetite and hematite is less attached to the material. There is an area in the left part of Fig. 9 with yellow corrosion products (iron chloride,  $\text{FeCl}_3$ ) on the surface. The iron chloride could have been formed under oxides during operation or after the blasting during the outage. Further to the left, there is a clean metal with smooth surface which indicate no local corrosion has occurred here. In Fig. 10 a closer view is taken of the wind side of a typical tube in the lowest row of SH2. Spot checks of the wall thickness were taken on-site during the inspection and these results might be somewhat inaccurate compared to the ones from the tube samples. The overall corrosion during the first two years of operation was less than 0.5 mm. This means the corrosion rate with injection of ammonium sulphate according to the ChlorOut concept was less than a third of it without any additive. The results from tube analysis were supported by long-term corrosion probe measurements as well as deposit probe measurements carried out prior to installation. This means these measurement tools could be applied together with IACM to predict the corrosion rate.

The flow of AS can be controlled to a specific value of KCl by IACM measurements. This value is the so-called breaking point. It can be described as the greatest allowed level of gaseous KCl for complete reduction of chlorine in the deposits. It means the minimal flow of AS for sufficient corrosion protection at a certain reference level of KCl. DWW is an inhomogeneous fuel and the reference level of KCl as well as the required flow to reach a specific value varies significantly over time. The overall appearance of the tubes resembled to a certain extent of what is observed during combustion of fuels containing low amounts of corrosive compounds rather than demolition waste wood.

## CONCLUSIONS

Results obtained from extensive measurement campaigns in the BFB boiler in Jordbro including long term corrosion measurements revealed injection of AS according to the ChlorOut concept could be applied as a strategy to reduce the corrosion rate during combustion of demolition waste wood.

The ChlorOut concept was permanently installed in the boiler in 2014 based on results from the measurement campaigns. Injection of ammonium sulphate reduced the concentration of gaseous alkali chlorides (KCl) which could be both measured on-line and controlled by IACM.

The corrosion rate was approximately 0.75 mm/year without any additive to prevent superheater corrosion and SH2 was replaced after four years of operation. Tube analysis after two years of operation with injection of ammonium sulphate revealed that the superheater corrosion was significantly reduced after the ChlorOut concept was permanently installed.

## ACKNOWLEDGEMENTS

This publication has been funded by CenBio – Norwegian Bioenergy Innovation Centre. CenBio is co-funded by the Research Council of Norway (193817/E20) under the FME scheme and the research and industry partners. The practical support from the staff at the BFB boiler in Jordbro is greatly appreciated

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