Corrosion reduction in waste- and demolition wood fired boilers by means of additives: A very corrosive case

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Test of corrosion reducing additive; ChlorOut

- ChlorOut is based on sulphate-containing solutions, developed and patented by Vattenfall

- ChlorOut converts alkali chlorides, NaCl + KCl, into less corrosive alkali sulphates

- ChlorOut is sprayed into the flue gases after combustion, but before the superheaters

- The sulphate-containing solution is normally ammonium sulphate, \((\text{NH}_4)_2\text{SO}_4\), therefore, a significant reduction of the NOx emissions is also achieved
Test plant: HKW-Mittelfeld, Kassel

CFB boiler, built 1987 by Götaverken Energy, Sweden
Capacity 36 MWth, two steam turbines: 12 MWel
Steam data: 525°C (540°C), 83 bar and flue gas temperature of 900°C
Super heater material: 10CrMo910 (2,25%Cr steel)

“No” corrosion since commissioning
Fuel change from lignite, which was the design fuel, to waste wood chips late 2008

Shortly after the fuel change, the superheaters failed due to corrosion and the superheater bundles had to be replaced
Plant sketch

Furnace (bubbling bed)
Two cyclones
Convection draft with superheaters, economizer and air preheater
Furnace is water-cooled.
No cooling of cyclones; generate high temperatures

Fluegas cleaning: Bag filters
No SNCR-system is installed
ChlorOut injections

ChlorOut solution, \((\text{NH}_4)_2\text{SO}_4\), concentration of 37% (by weight)

ChlorOut was injected;
1) before two cyclone inlets
2) after the cyclone inlets
3) a few meters before the convection pass

Cross section area of the duct is about 10m²

The temperature at the injection positions was estimated to 720 – 1000°C
Measurements and analysis

• **IACM**: Insitu Alkali Chloride Monitor, on-line measuring of NaCl + KCl. A cross-stack IACM was mounted permanently

• **OxyMap**: Oxygen measurements and temperature measurements at 8 different positions simultaneously

• **Triple temperature deposit probe** with controlled surface temperatures. Collects deposits from the flue gas at three different temperatures simultaneously (520, 565 and 600°C)

• **DOAS**: Differential Optical Absorption Spectroscopy, NH\textsubscript{3}-, NOx- and SOx-concentration measured on-line. Located after bag filters, after the flue gas fan
Analysis of the corroded superheaters
Kassel: super heater 3 (highest temperature)

Super heater tube (10CrMo910, Cr:2,25%) after less than 6 month of exposure
Analysis of corroded superheater tube

From superheater tube
Loosely sitting scale removed
Pitting corrosion on surface
Depth 0.1mm or more
SEM/EDX mapping of corroded SH-tube

Cl detected in the corrosion front
SEM/EDX mapping of scale/metal - interface

Cl enriched in the corrosion front
S detected in the outer part of scale
Point analysis of scale/metal interface

18: super heater material
11 – 14: "high S", "low Cl"
15 – 17: enriched Cl- but low S-concentration

Concentrations does not add up to 100%

<table>
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<tr>
<th>Area</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<td>95,3</td>
<td>1,2</td>
</tr>
</tbody>
</table>

Concentrations does not add up to 100%
Results from the tests and analyses
Temperature fluctuation measured at the tested injection positions

Left - Right cyclone 10 – 100°C difference
Left - 200°C difference
Deposit growth rate (deposit probe)

Deposit weight

Sample weight gain (g)

600 °C  565 °C  520 °C

Reference 1
150 l/h
Reference 2
75 l/h
Cl content in deposit (deposit probe)

Deposit composition (wt.%)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reference 1</th>
<th>150 l/h</th>
<th>Reference 2</th>
<th>75 l/h</th>
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</thead>
<tbody>
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<td>600 °C</td>
<td>8.2</td>
<td>2.6</td>
<td>0.05</td>
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<td>565 °C</td>
<td>9.6</td>
<td>0.00</td>
<td>0.07</td>
<td>0.02</td>
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<td>520 °C</td>
<td>9.8</td>
<td>0.02</td>
<td>7.8</td>
<td>0.10</td>
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</tbody>
</table>
Sulphur content in deposit (deposit probe)

**Graph:**
- **Y-axis:** Deposit composition (wt.%)
- **X-axis:** Temperatures (600 °C, 565 °C, 520 °C)
- **Legend:**
  - Reference 1
  - 150 l/h
  - Reference 2
  - 75 l/h

**Data Points:**
- **600 °C:**
  - Reference 1: ~12 wt.
  - 150 l/h: ~10 wt.
  - Reference 2: ~4 wt.
  - 75 l/h: ~2 wt.

- **565 °C:**
  - Reference 1: ~12 wt.
  - 150 l/h: ~10 wt.
  - Reference 2: ~8 wt.
  - 75 l/h: ~4 wt.

- **520 °C:**
  - Reference 1: ~10 wt.
  - 150 l/h: ~8 wt.
  - Reference 2: ~6 wt.
  - 75 l/h: ~3 wt.
Alkali chloride concentration in flue gas

ChlorOut Kassel

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Relative and absolute reduction of alkali chloride concentration in flue gas

Ex:
30MW x 1,2 = 36l/h
22MW x 1,2 = 26 l/h
NOx, SO₂, CO and O₂-concentration

NOx (blue) 175 → 65, CO-spikes (green) reduced
Low temperature deposit formation

No SNCR
Adding of NH₃
Temperature: 90 – 120°C

Indicate salmiac NH₄Cl

Drallregler vor Saugzug mit Ablagerungen
Flue gas components measured by DOAS in Kassel week 48 (wet gas)

- **NO**: 0 l/h
- **SO₂**: 32-38 l/h
- **NH₃**: 30-35 l/h

*boiler load drops*
Summary

- The corrosion attacks are due to the presence of alkali chloride in the fuel.
- The chlorine content in the deposits was reduced up to 99% during injection of ChlorOut.
- During ChlorOut injection, the alkali chloride concentration in the flue gas was reduced by up to 75% (60%).
- The NOx emissions were reduced up to 75% (60%) during ChlorOut injection.
- There are strong indications of reduced corrosion rates during ChlorOut injections.
- An increase with 200% - 350% of SO2 was measured before the flue gas cleaning during ChlorOut injection.