PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler

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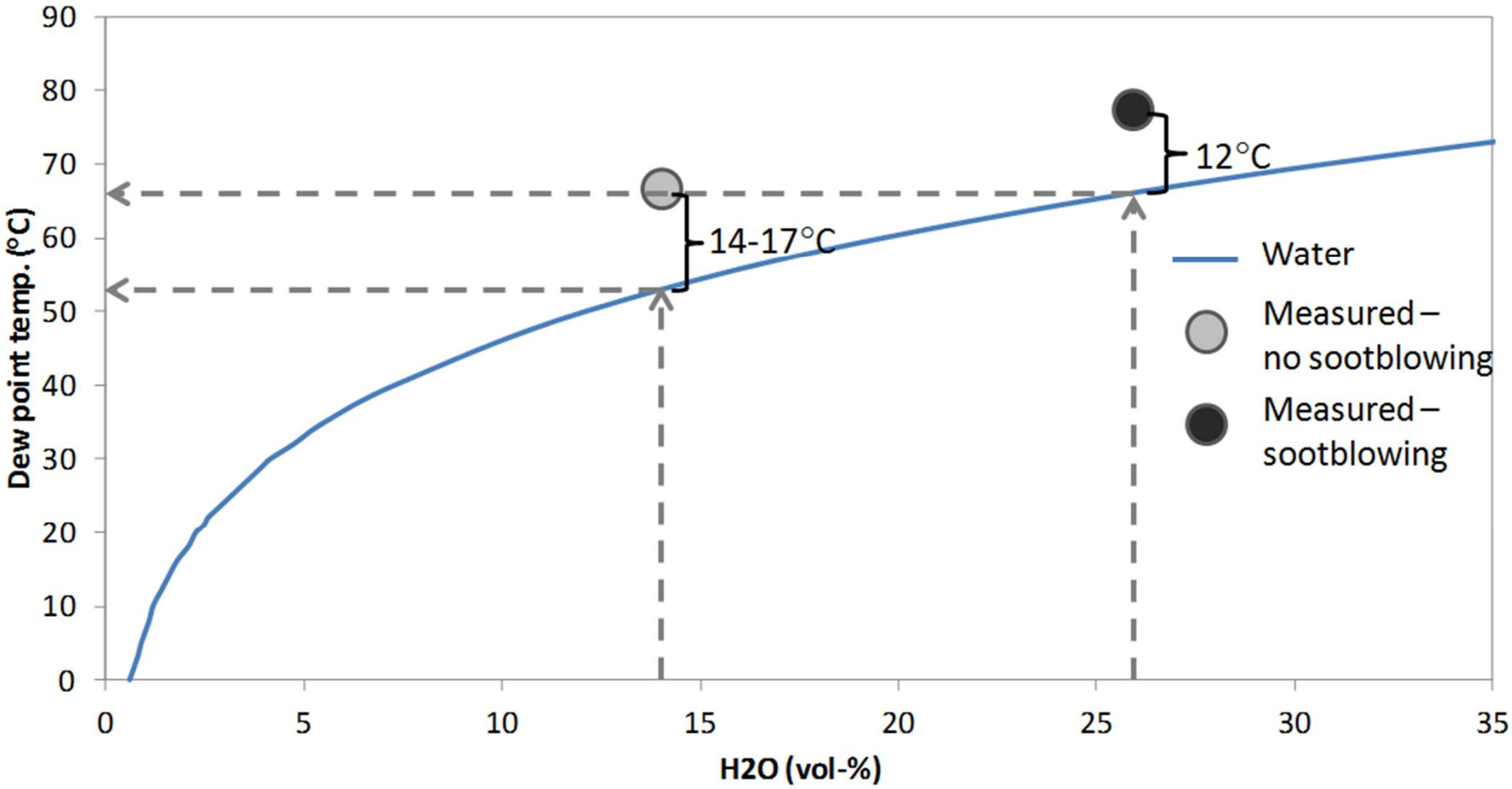
Objectives

To better understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler

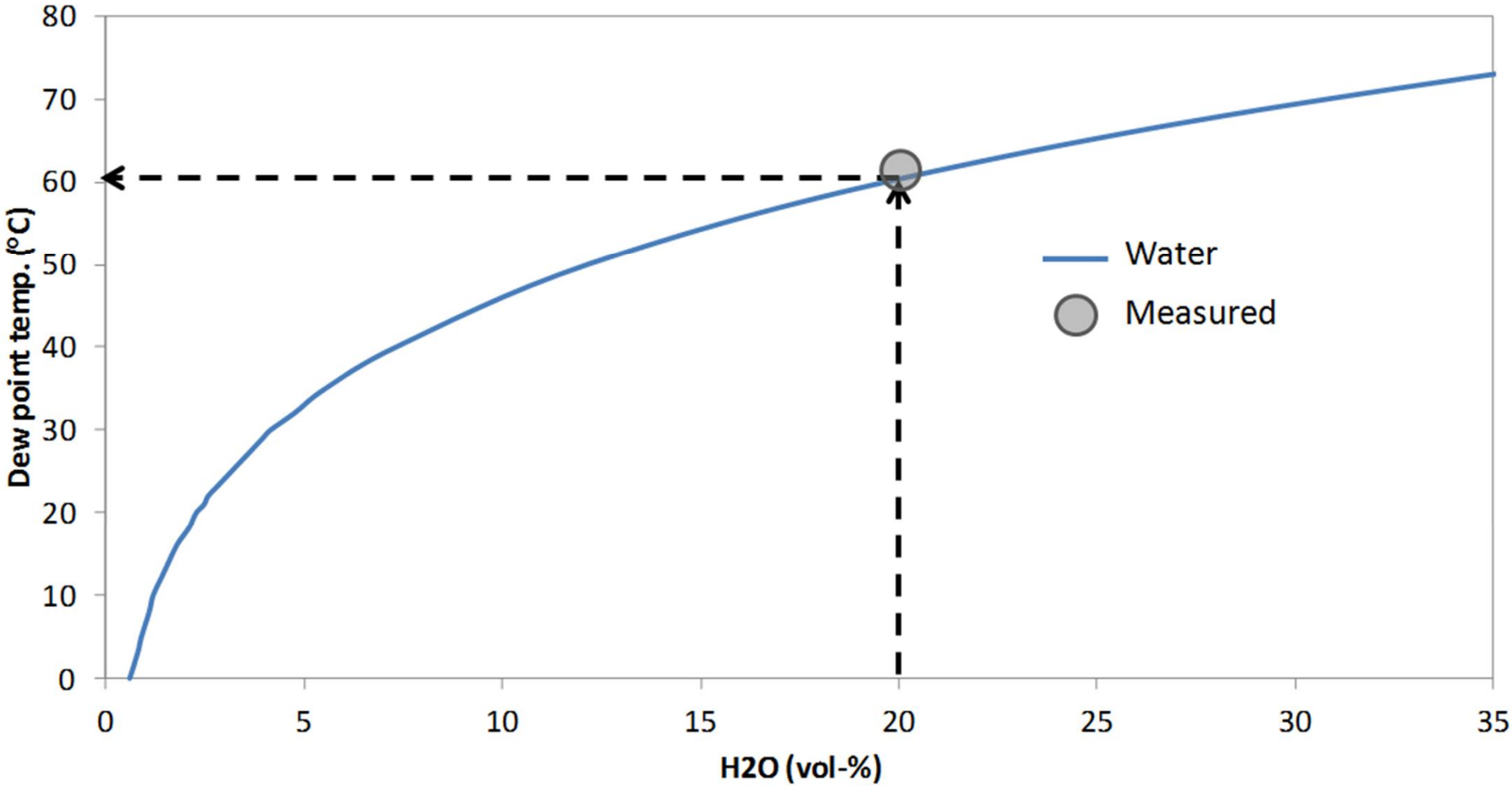
Continuation of the dew point project made in two recovery boilers.

Water dew point and measured dew point- Heinola



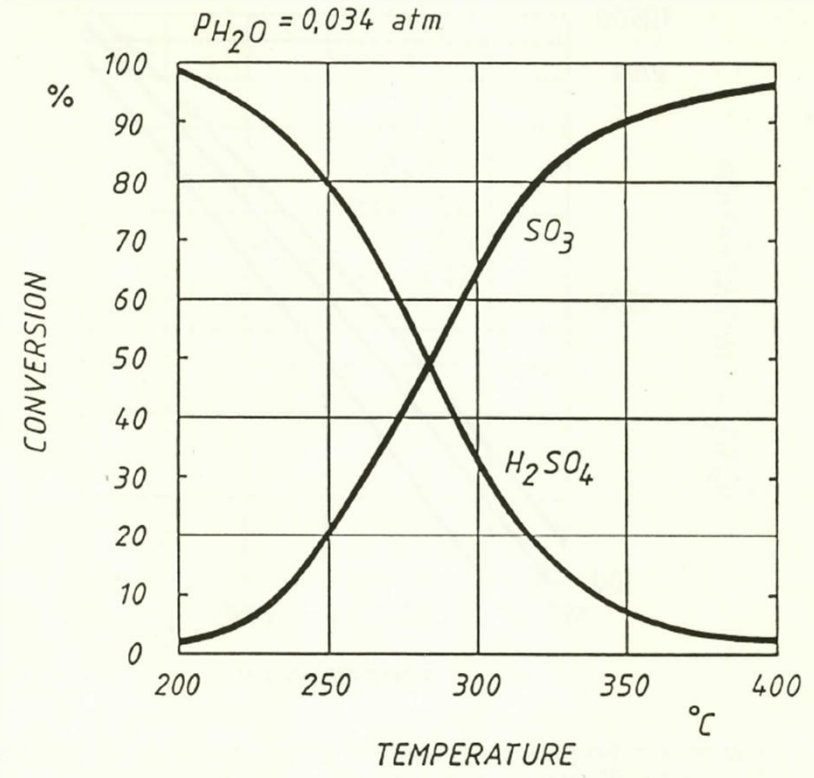
Elevated dew point due to hygroscopic salts: Na_2SO_4 (84% RH) ja $NaHSO_4$ (52% RH)

Water dew point and measured dew point - Rauma



$SO_3(g)$ and $H_2SO_4(g)$ formation

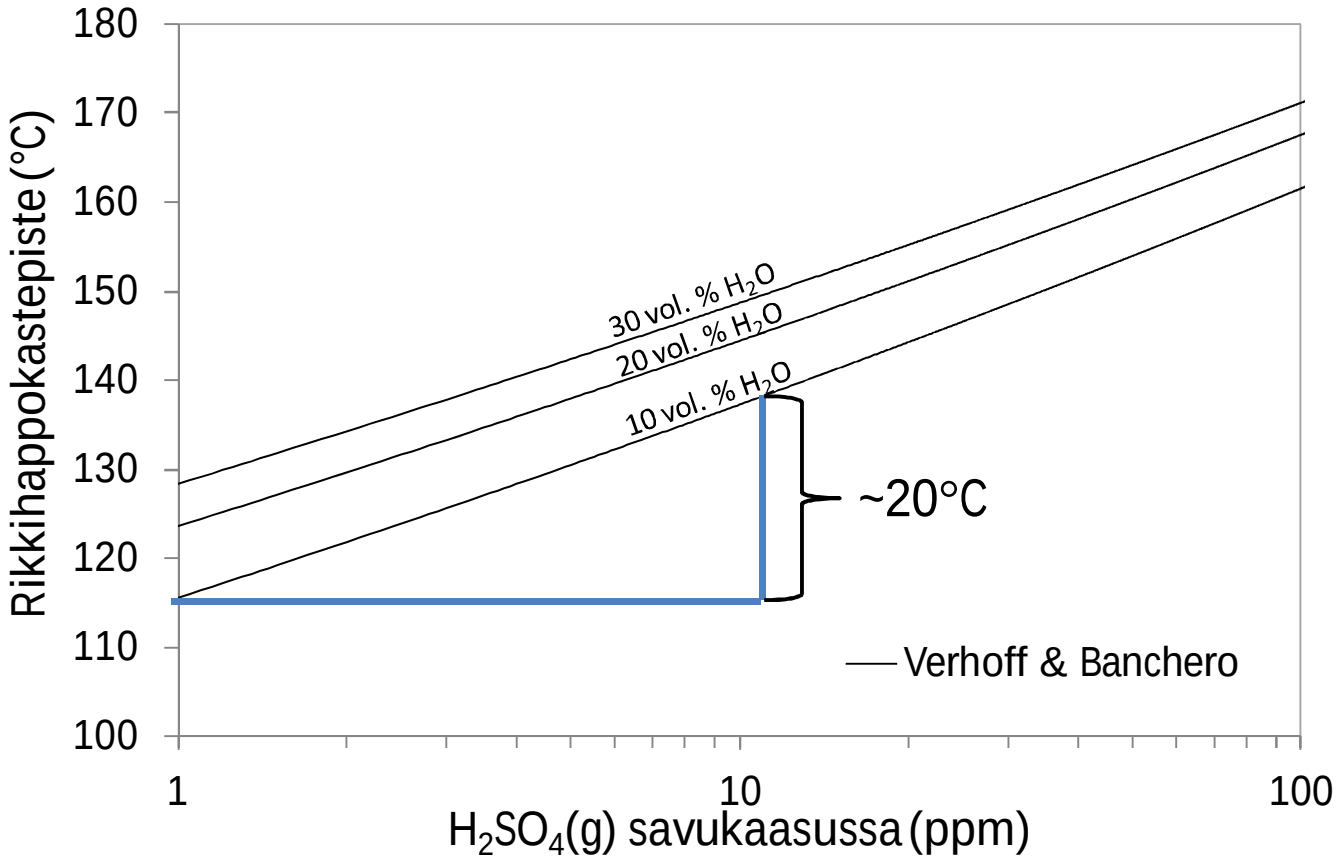
- Sulfur in fuel is oxidized to SO_2
- A fraction of the SO_2 is further oxidized to SO_3
- $SO_3(g)+H_2O(g) \rightarrow H_2SO_4(g)$
- At 200°C mostly $H_2SO_4(g)$
- Condensation of sulfuric acid may lead to severe low temp corrosion



R. Backman et al.

Sulfuric acid dew point

- When the $H_2SO_4(g)$ concentration is known the dew point temperature can be estimated

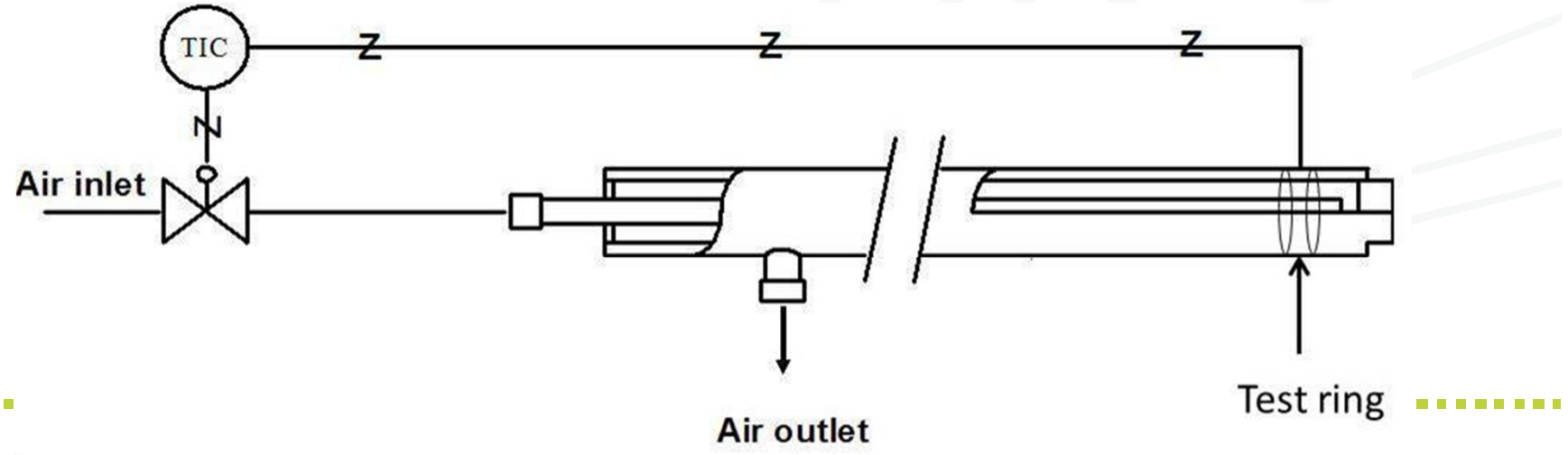


Methods

1. Corrosion measurements with a corrosion probe during:
   - -Normal operation
   - -Water wash
   - -Oil firing
2. $H_2SO_4(g)$ and SO_2 measurements during oil combustion
3. Dew point measurements (Land)

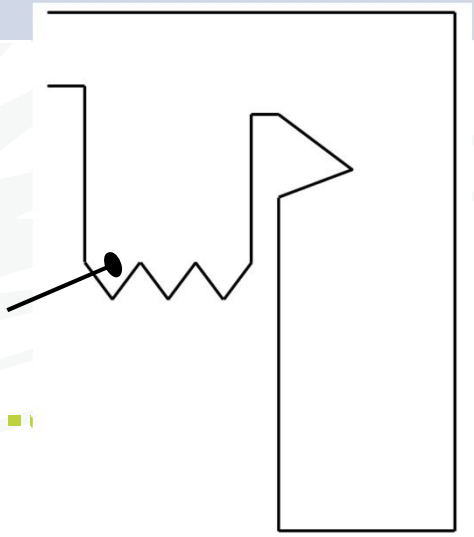
1. Corrosion test

- Corrosion probe
- Exchangable carbon steel ring in probe tip
- Ring is weighed before and after exposure
- Thermocouple located in the ring, temperature adjusted with pressurized air (PID-controller)
- 90°C was used was ring temperature



Corrosion probe tests

Date In	Date Out	Probe Temperature	Comments
31.8.2012	31.8.2012	80 °C	2h probe test
31.8.2012	31.8.2012	75 °C	2h probe test
31.8.2012	4.10.2012	90 °C	811h probe test, probe pulled before water wash
31.8.2012	17.10.2012	90 °C	1124h probe test, probe pulled after water wash, but before acid wash (oil firing)
19.10.2012	19.10.2012	90 °C	2h probe test during acid wash (oil firing)

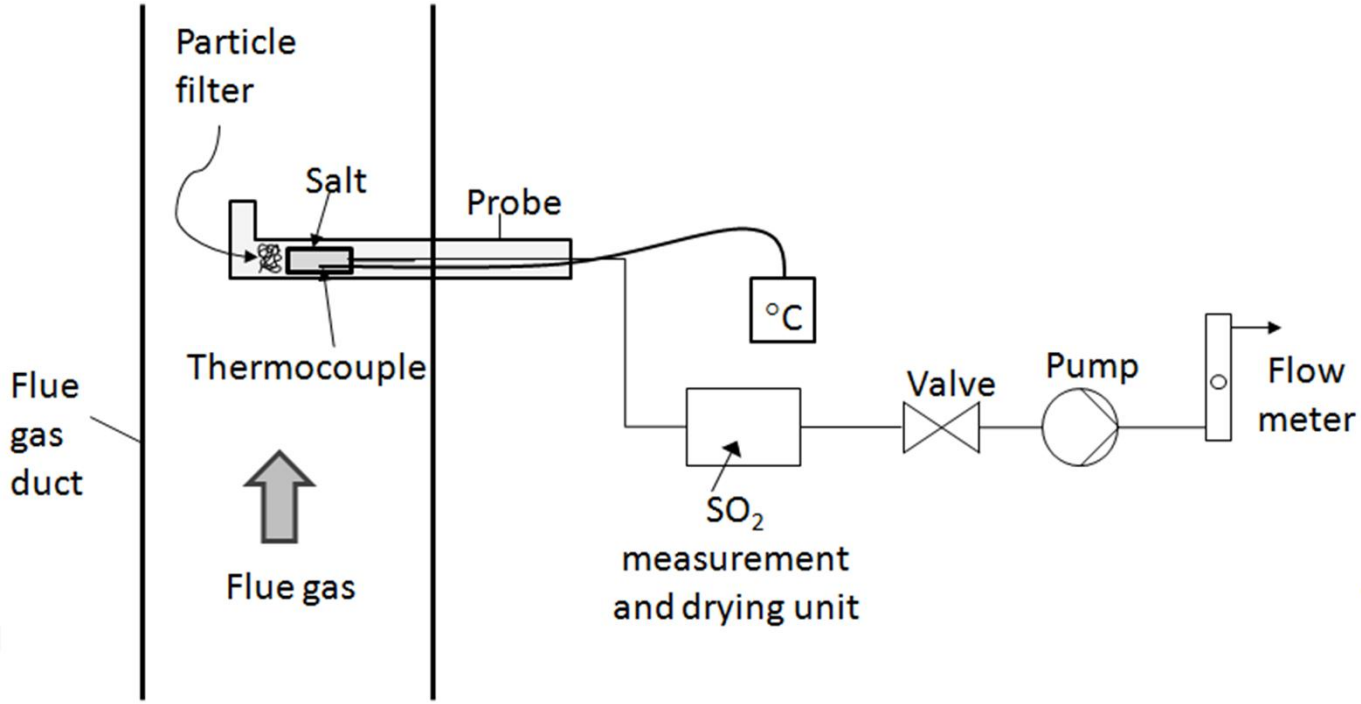


2. H_2SO_4(g) measurements

- Flue gas led through a salt (KCl)and H_2SO_4 is absorbed in the salt

$$2KCl(s) + H_2SO_4(g) \rightarrow K_2SO_4(s) + 2HCl(g)$$

- Salt dissolved in deionized distilled water and analyzed for sulfate ions with ion chromatography

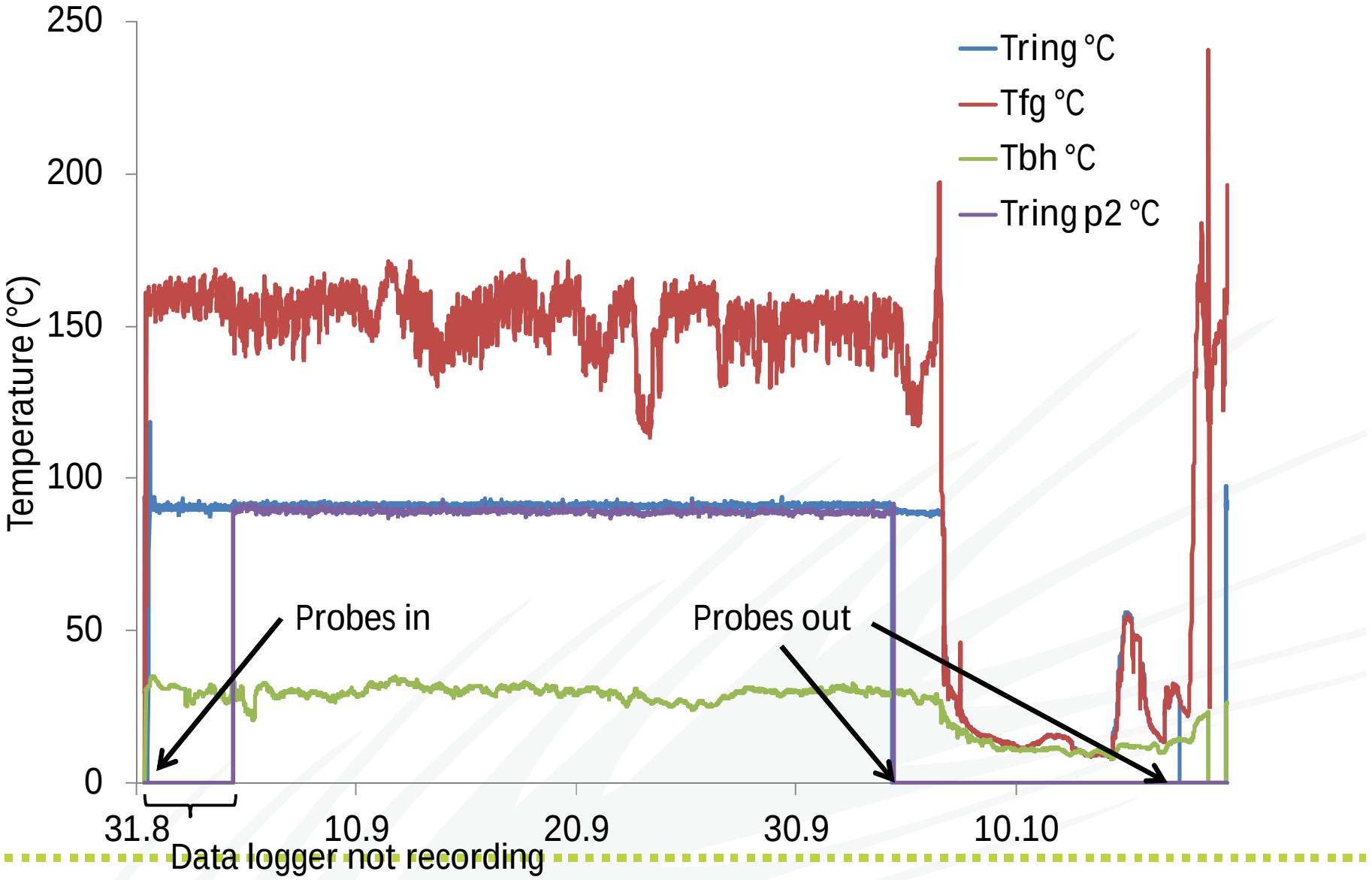


3. Dew point measurement

- Dew point probe (Land)
- Two electrodes in the probe tip
- Probe tip cooled with pressurized air
- When dew point reached, water or acid, a current is detected

Probe Study Results

Probe and Flue Gas Temperatures

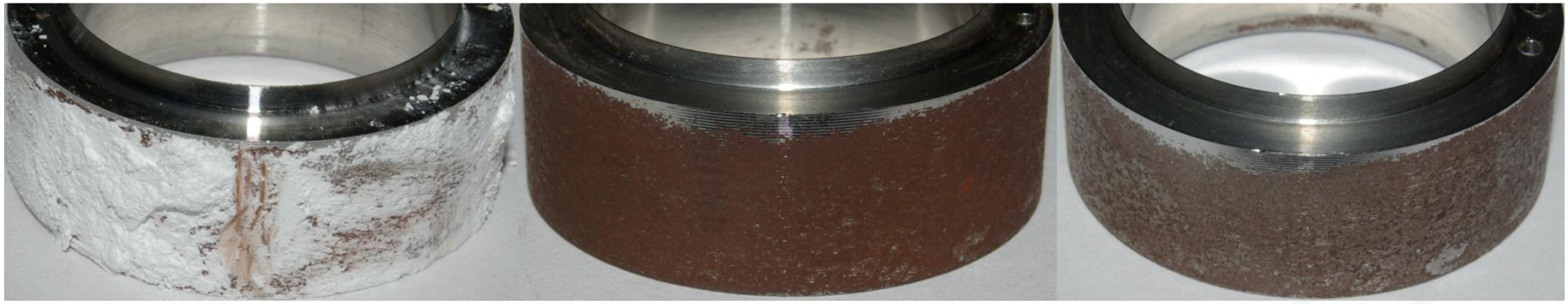


Tbh: Boiler House T

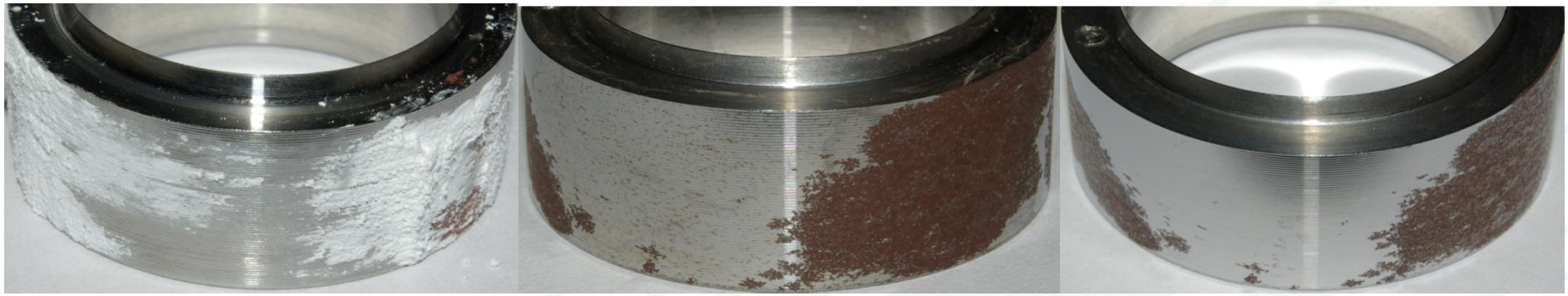
Probe After 811h of Normal Operation

Ring after 811h normal operation

up uncleaned ring water+aceton+paper 30s acid wash

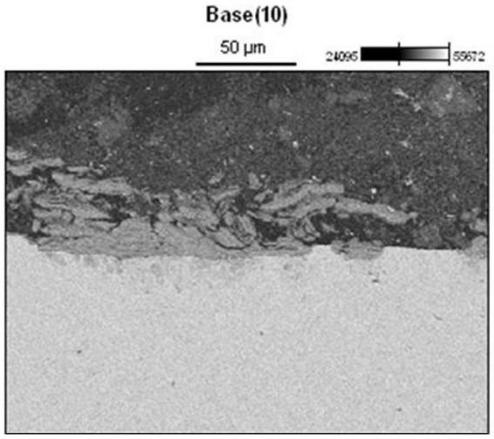


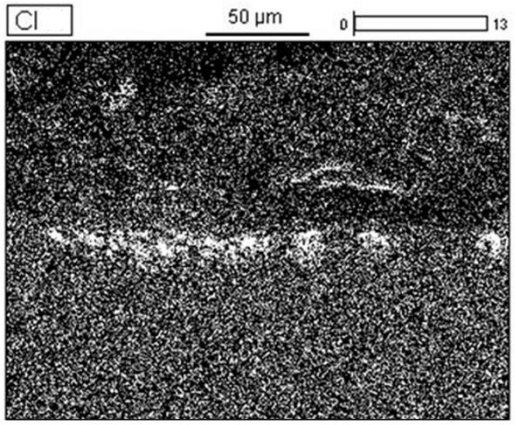
down

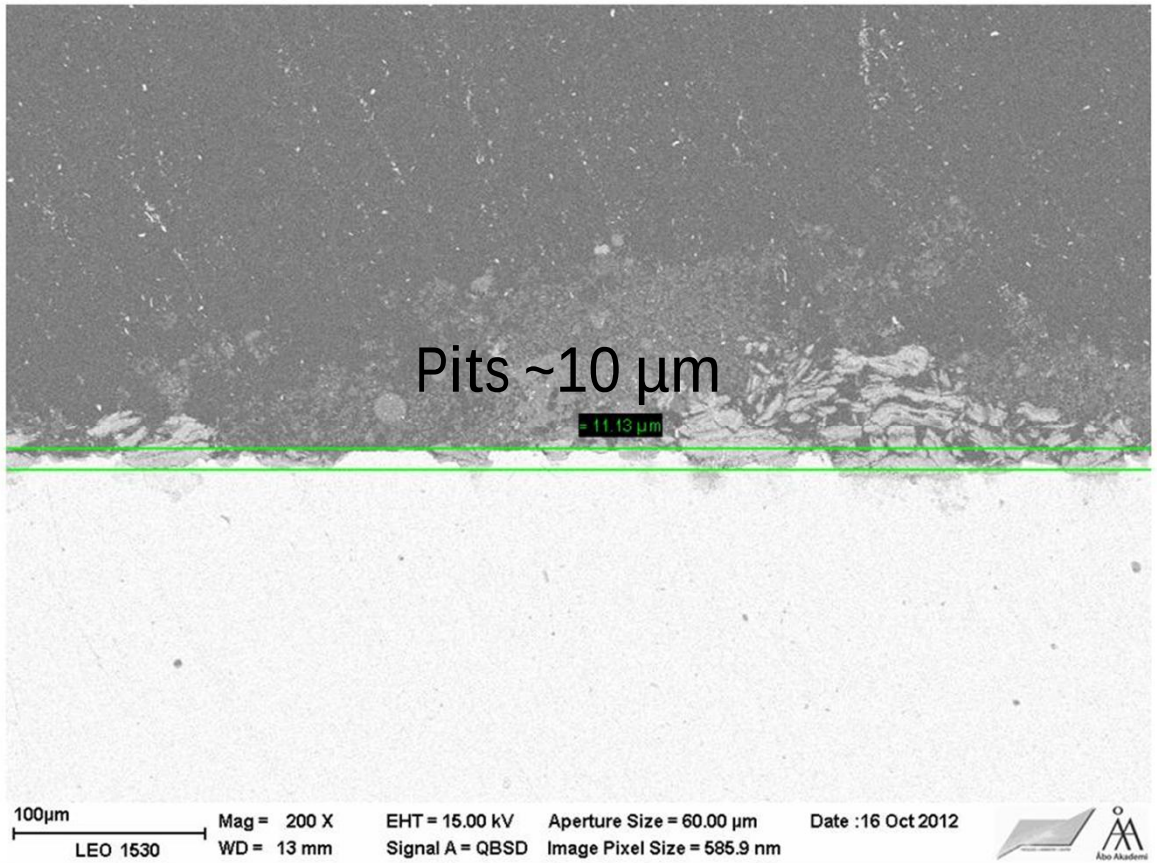


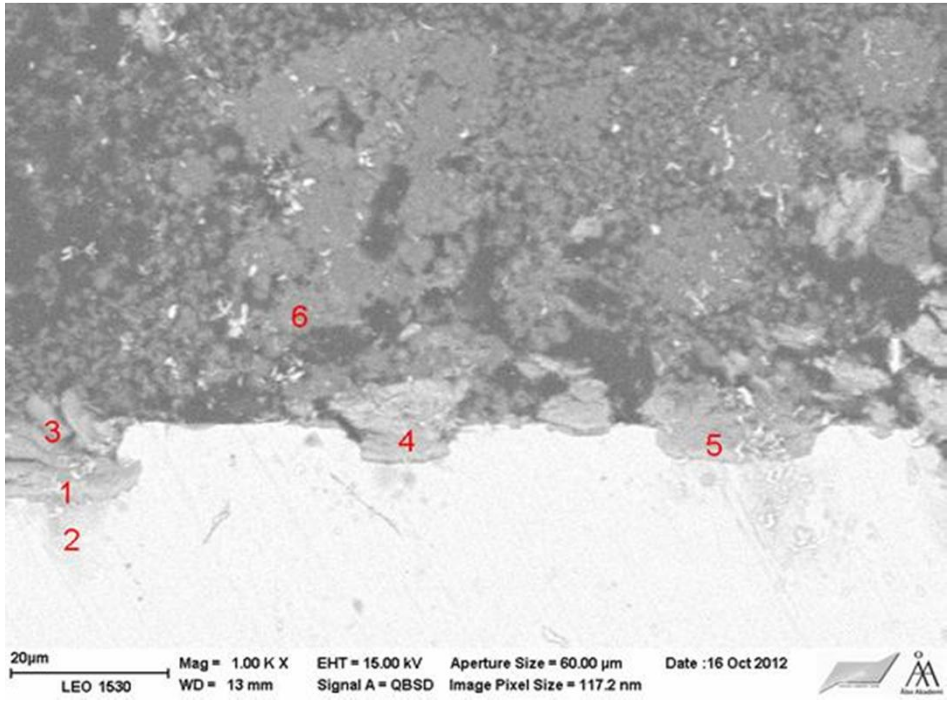
Note: Side pointing downwards (gravimetrically) -> No iron oxide

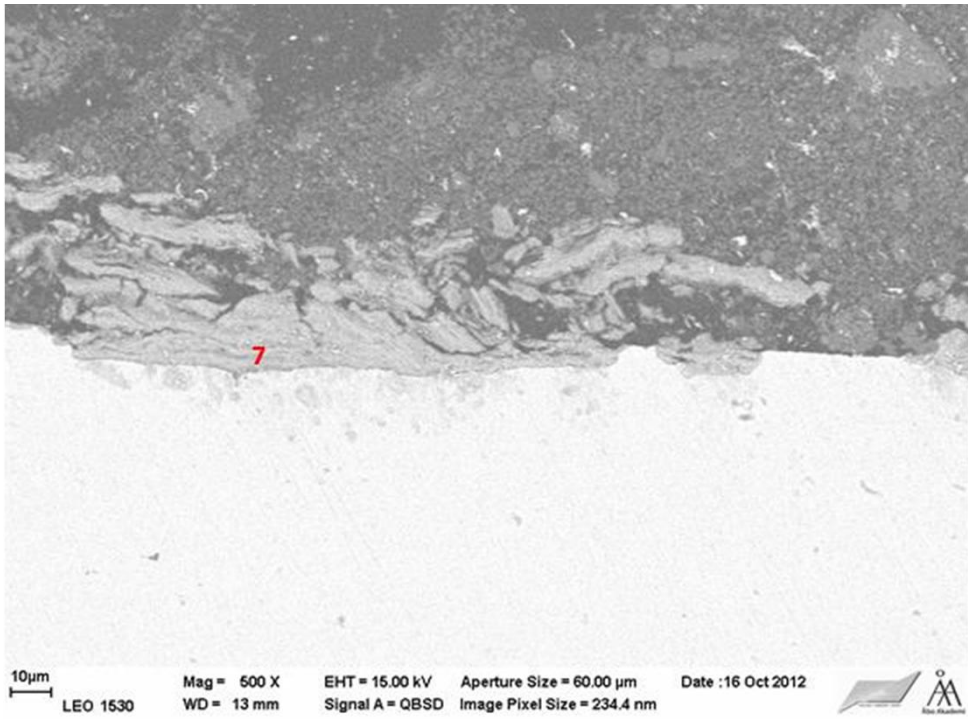
811h exposure ”normal” plant operation











atom-%

Spot	Na	Al	Si	S	Cl	K	Mn	Fe
1	1.3	0.3	0.2	0.1	0.5	0.1	0.4	38.2
2	0.0	0.3	0.2	0.0	0.6	0.0		39.3
3	3.1		0.3	1.4	0.4	1.5		34.9
4	3.7	0.3	0.2	0.6	0.7	0.3		36.4
5	1.7	0.5	0.2	0.2	1.2	0.4	0.4	37.2
6	20.5			13.5	2.3	7.3		1.1
7	0.4	0.5	0.3	0.1	2.5	0.1	0.3	37.5

Cl not balanced by Na or K

Probe after water wash - 1124h total (811h ”normal” operation + water wash)

Ring after 1124h

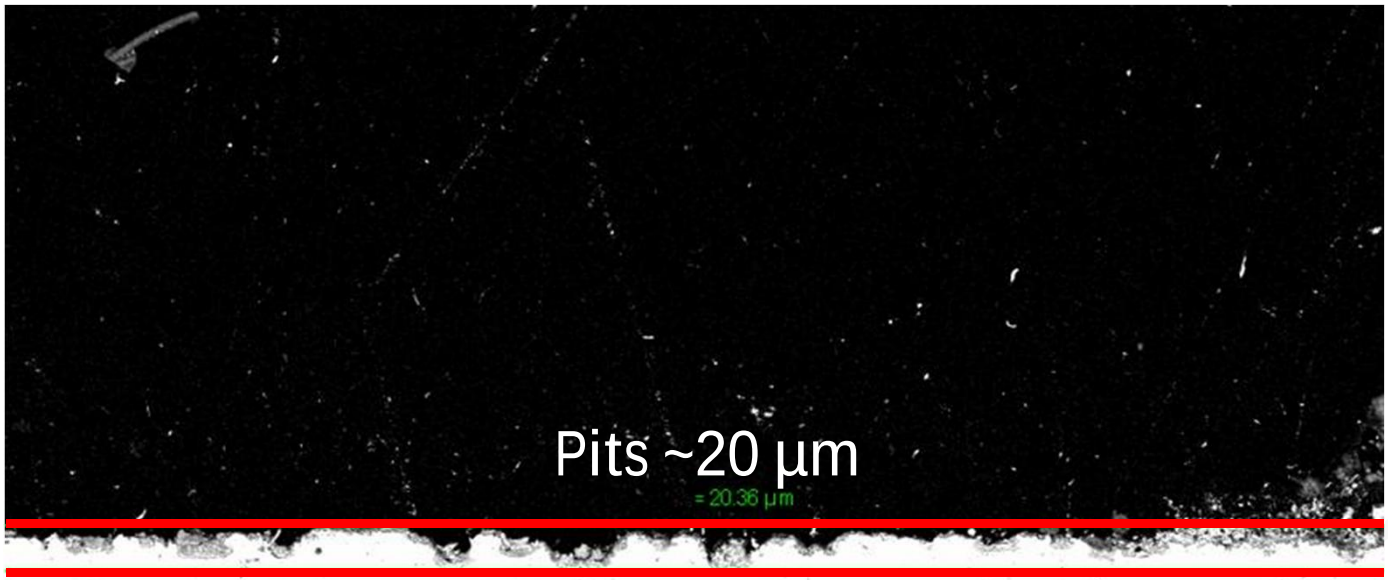
up uncleaned ring

water+aceton+paper

down

Again areas without corrosion downwards

811h exposure ”normal” plant operation
+ boiler shutdown & water wash totally
1124h



- No chlorine or sulfur found in the corrosion layer after the water wash

30µm
LEO 1530
Mag = 196 X
WD = 13 mm
EHT = 20.00 kV
Signal A = QBSD
Aperture Size = 60.00 µm
Image Pixel Size = 598.9 nm
Date :1 Nov 2012

SEM results Sample 6. Pit corrosion. No traces of chlorine in pits.

Corrosion results

Exposure time	Operation	Ring temperature	Ring Weight Loss (mg)	Avg. Corrosion Layer Thickness (µm)	Calculated Avg. Corrosion (mm/yr)
2 h	Normal	80 °C	0	0	
2 h	Normal	75 °C	0	0	
811 h	Normal	90 °C	22	2*	0.02
1124 h	Normal + water wash	90 °C	72	6**	0.05

*Pit corrosion, pits ~10 µm deep
**Pit corrosion, pits ~20 µm deep

Measurements during oil burning

- Dew point and SO_3 were measured during oil burning
- A 2h probe (90 °C) study was also made

Flue gas composition during oil burning

Date 19.10.2012

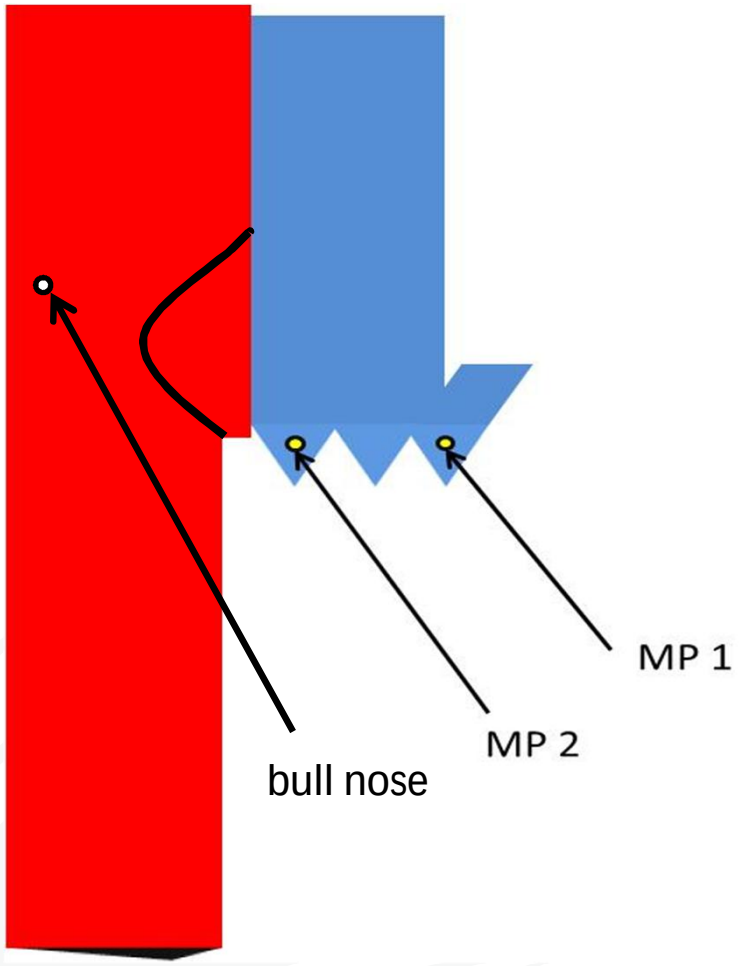
Time	Oil (t/h)	O_2 (%)	SO_2 (ppm)	SO_2 (ppm 0% O_2)	Air Ratio (λ)	Calculated Water Dewpoint (°C)
9:36	1.8	19.4	38	507	13.4	19
11:57	3.9	17.9	83	574	6.9	25

- Calculated Fuel Oil Sulfur Content 0.8% (based on flue gas analysis)

Sampling positions and SO_3 results

Date	Time	MP	SO_3 /H_2SO_4(ppm)	Temp (°C)	Oil burners
18.10	19:20-19:50	b.n.	1	240	2
19.10	10:05-10:35	1	1	150	2
	12:15-12:35	1	1	165	4
	16:27-16:37	2	3	240	4
	16:53-17:13	2	2	240	4

b.n.: bull nose



- No acid dewpoint was found in the dewpoint measurement

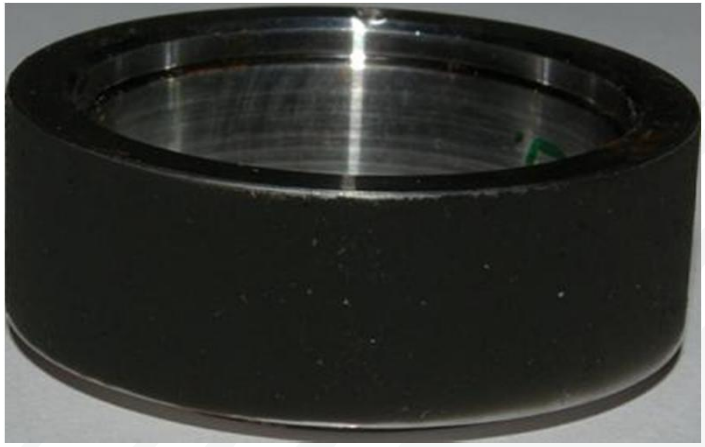
Ring after 2h exposure during oil burning

up

uncleaned ring

water+aceton+paper

down



Conclusions

- No significant corrosion seen under normal operation or after the water wash
- No acid dew point seen during oil burning
  - In part due to the extremely high dilution
- More heat can be removed from the flue gas without fear of acid dewpoint corrosion under normal operation