PROCESS CHEMISTRY CENTRE

Final Report: Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler

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4 January 2013

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Summary

Long term probe studies (~1000h) were carried out at the Rauma mill in the economizers to study corrosion in the economizers. The air cooled probes were kept at 90 °C, above the water dew point, but well below an H_2SO_4 dew point. One was pulled out after 811h of normal operation and the second was pulled out after 1124h of normal operation plus the water wash. Negligible corrosion was seen in both cases. Ring weight loss after washing off the corrosion layer gives average corrosion layers of 0.02 and 0.05 mm/year. The SEM analysis indicated pits of about 10 µm for the probe pulled out before the water wash and 20 µm in the probe pulled out after the water wash. Some chloride was seen in the pits in the corrosion layer for the probe pulled out before the water wash, indicating that the small amount of corrosion seen was chloride induced corrosion. The corrosion layer that was seen existed in the top and sides of the ring. There was a patch at the bottom of the ring where there was no corrosion. This indicated that perhaps corrosion was caused by water dripping from the soot blowers that were about 2 meters above the probe. No acid dew point corrosion was seen indicating that modern mills can recover more heat from flue gases without fear of acid dew point corrosion under normal operating conditions.

In addition, the dew point, H_2SO_4 and corrosion (2h probe study) were measured during oil burning. Conditions during oil burning were special in that a very high air-to-fuel ratio was used. While up to 3 ppm of SO_3 was measured, no acid dew point or corrosion was seen. Further work has been proposed to see if corrosion would be seen during start up of a Kraft recovery boiler on oil.

1. Introduction

The objective of this work was to better understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler. In particular this work was to clarify the conclusion of the dew point measurements at Rauma and Heinola in a previous study that indicated that there is no H_2SO_4 acid dew point, Figure 1. Figure 2 shows the impact of HCl and H_2SO_4 on dew point. Hydrochloric acid has a very small impact on acid dew point while 1 ppm of H_2SO_4 increases the dew point to over 120 °C at 20% relative humidity in the gas. Salts deposited on heat transfer surfaces are hygroscopic. They will result in absorption of water at temperatures higher than the water dew point. Sodium sulfate will absorb water about 4-5 °C above the water dew point while a salt like $NaHSO_4$ will absorb water about 14-17 °C above the water dew point. These factors were taken into account when choosing the probe temperature as described in the Method section.

The question then came up after reporting of the dew point measurements at Rauma and Heinola was why some mills see corrosion in the economizers. One subsequent hypothesis was that corrosion was promoted during the water wash. This long term probe test was designed to help clarify these earlier findings and questions.

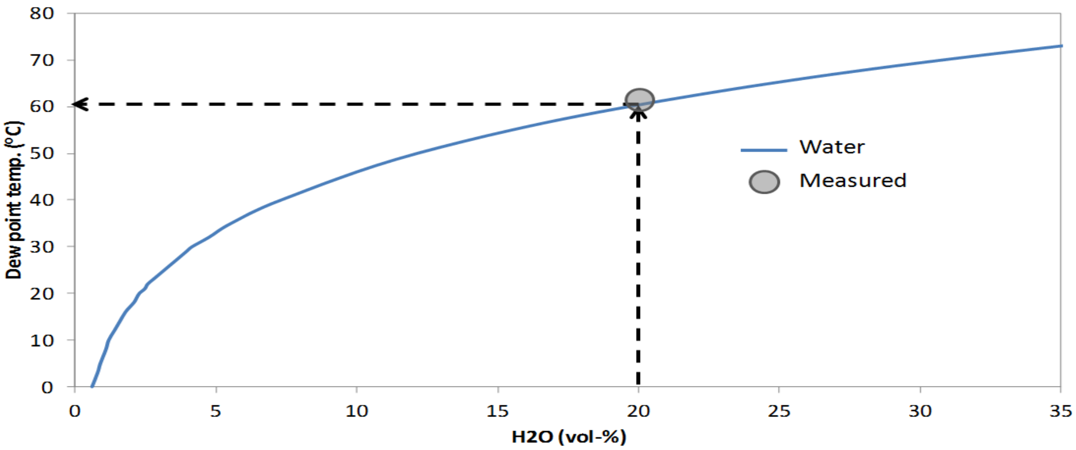


Figure 1. Water dew point temperature vs. flue gas water content. Measured dew point was for Rauma.

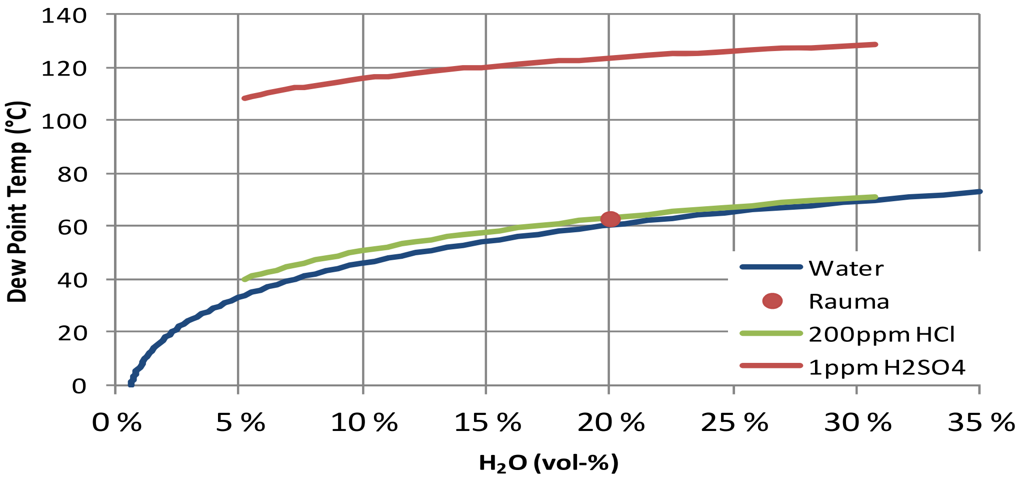


Figure 2. Water dew point and acid dew points based on 200 ppm HCl or 1 ppm H_2SO_4 as well as the measured dew point at Rauma.

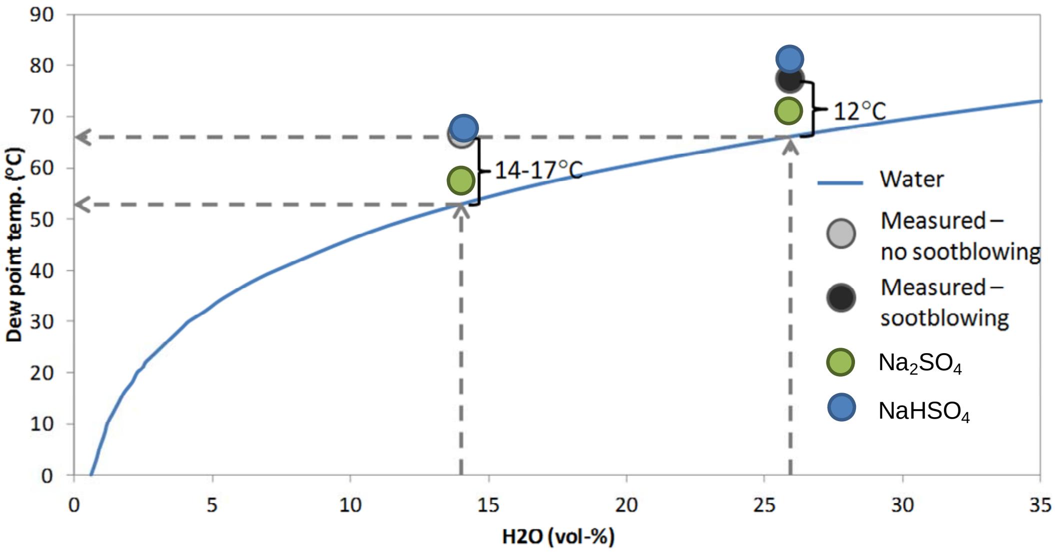


Figure 3. Effect of the salts $NaHSO_4$ and Na_2SO_4 on dew point. Dew points were measured at Heinola with and without sootblowing.

2. Method

2.1 Corrosion probe measurements

The corrosion rate experiments were conducted using an air-cooled corrosion probe, Figure 4. The probe was kept at a temperature of 90 °C. This temperature was chosen because it is well below the acid dew point but well above the water dew point or the temperature at which salts would result in the absorption of water. A fresh test ring of carbon steel is placed in the probe tip. A thermocouple is located in the test ring and the temperature in the test ring is controlled by adjusting the air flow with a PID controller. After the test the corrosion products are washed with acetone and citric acid to wash off salts and corrosion products. The weight loss was determined by weighing the ring before and after exposure. This weight loss is used to calculate an average annual corrosion rate. The corrosion probe was located below the last pass of the economizers before the ESP, Figure 5 (MP 1). The H_2SO_4 measurements were taken at MP1, MP2 and at the bull nose. The schedule for the probe studies are given in Table I.

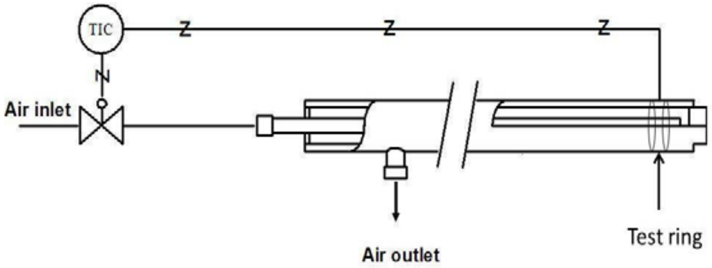


Figure 4. Air-cooled corrosion probe with temperature regulation.

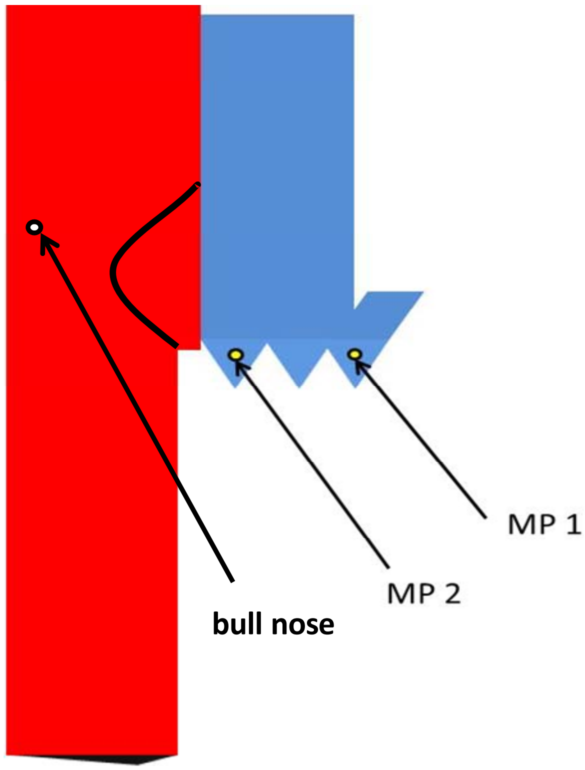


Figure 5. Measurement points for the SO_3 measurements. MP1 was the location for all corrosion probe studies.

Table I. Schedule for the probe studies.

Date In	**Date Out**	**Probe Temp.**	**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 oil firing
19.10.2012	19.10.2012	90 °C	2h probe test during oil firing

2.2 H_2SO_4 measurement

The concentration of H_2SO_4 was measured in the flue gas during oil firing in the recovery boiler. The oil firing was carried out under very special circumstances in which very high air-to-fuel ratios resulting in a flue gas with comparatively low SO_2 and low levels of H_2O. A salt method was used for measuring the concentration of H_2SO_4 in the flue gas.

The salt method is a lesser known method, and was found in a Värmeforsk report on different H_2SO_4 measurement techniques (Cooper et al., 1994). The method has been tested and refined at ÅAU. In this method the H_2SO_4 is absorbed into a salt, e.g. potassium chloride (KCl):

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

The measurement setup used for the salt method is shown in Figure 5. The salt is heated to about 200°C, to avoid condensation in the salt. The salt is then dissolved in water and analyzed for sulfate ions by ion chromatography.

Potassium chloride (KCl) was used instead of NaCl in the field measurements, to be able to detect any contamination from Na_2SO_4 from the fly ash. A 99.999% pure KCl salt was used, to avoid impurities.

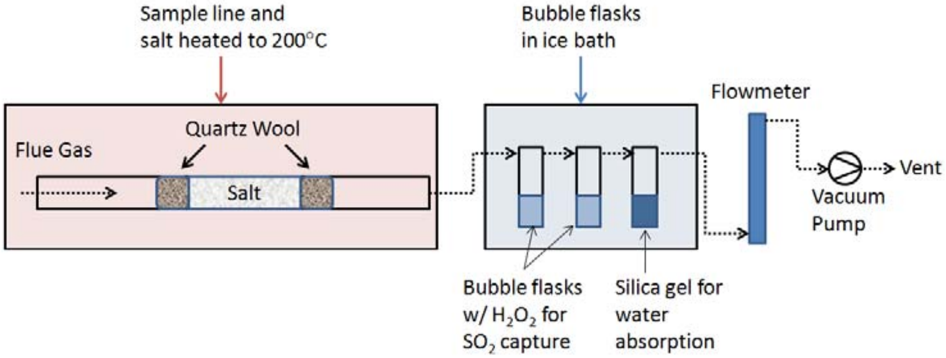


Figure 6. Schematic picture of the salt method.

2.3 Acid dew point measurement

The acid dew-point temperature was measured in the flue gas duct by an acid dew-point probe from Land. The probe has a sensor in the tip consisting of two platinum electrodes insulated from each other with a Pyrex glass. The surface temperature of the sensor is controlled by adjusting the air flow. After the surface temperature reaches the flue gas temperature the temperature can slowly be decreased. As soon as condensation on the sensor takes place the glass surface between the electrodes becomes conductive and an electric current signal can be registered by the instrument. As noted in the results, the probe was not sensitive enough to measure the dew point given the low concentrations of both H_2O and H_2SO_4 during oil firing.

3. Results

The flue gas temperature in the economizers was about 150 °C and did not drop below about 110 °C during normal operation, Figure 7. The probes were isothermal at 90 °C. The data logger did not record the temperature for one of the probes for the first few days, but the conditions were the same for both probes. The feed water temperature to the economizers was just over 110 °C, Figure 8. Corrosion at the feed water entrance to the economizers is nominal. This is another indication that acid dew point corrosion does not occur in the Rauma boiler. If it did, there should be corrosion here as 110 °C is below the calculated acid dew point temperature for 1 ppm H_2SO_4 and 20% relative humidity, Figure 2.

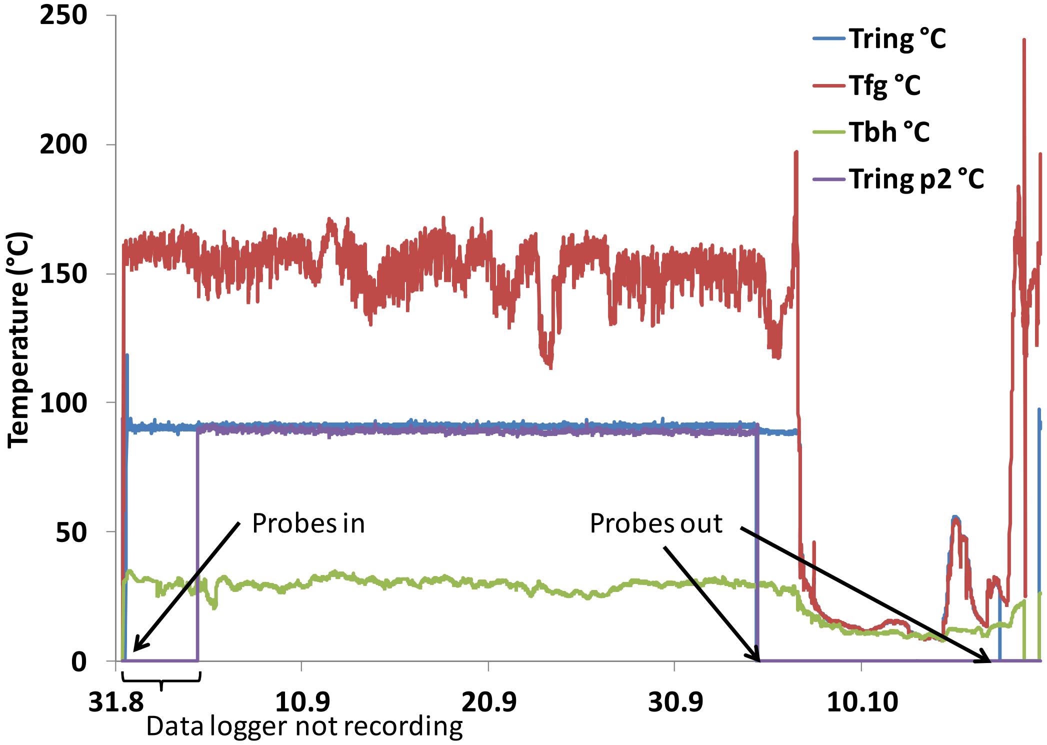


Figure 7. Temperatures of the probes (Tring and Tring p2), flue gas (Tfg) and boiler house (Tbh).

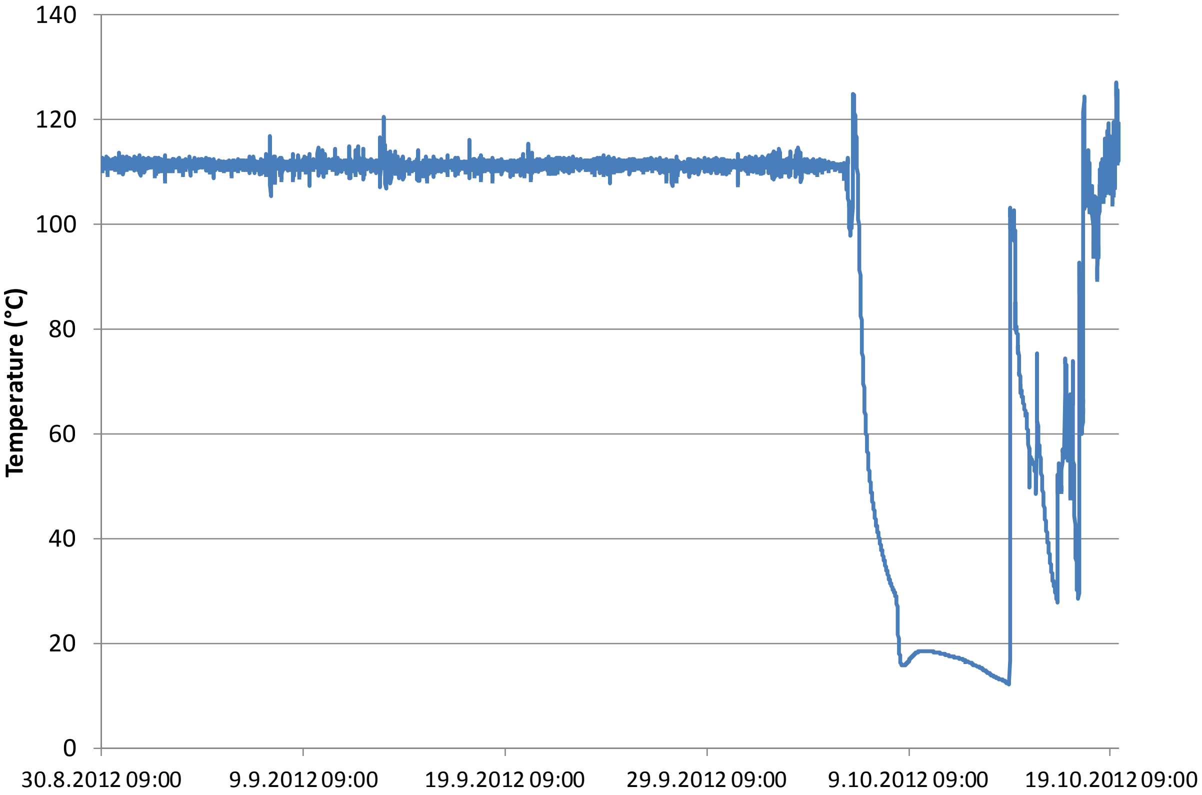


Figure 8. Feed water temperature to the economizers.

After 811h of normal operation the probe was covered in ash, Figure 9. There was virtually no corrosion on the probe, Figure 10. What little corrosion occurred was found on the top of the probe, but not on the bottom-most edge of the probe. The probe was placed in one of the lower turns in the economizers and it is not clear which were the windward and leeward sides of the probe. The corrosion layer was pitting up to approximately 10 µm, Figure 11. In some spots of the corrosion layer, the chloride was not balanced by alkali indicating iron chloride and chloride induced corrosion. One explanation for the combined observations of corrosion being present on the top but not bottom and the presence of chloride in the corrosion layer is that a small amount of water is dropping on the probe from the sootblowers. This would dissolve NaCl in the salt resulting in a chloride containing solution until the water evaporates.

The probe that was pulled out after the water wash, Figure 12, had more corrosion than the probe pulled out before the water wash, but it was still a low level of corrosion, Figure 13. Again, the bottommost edge was not corroded. Based on the weight loss of the ring after the corrosion products were washed from the ring using acetone and acetic acid, the calculated average corrosion for the two probes on an annual basis was 0.02 and 0.05 mm/year for the probes pulled out before and after the water wash respectively, Table II.

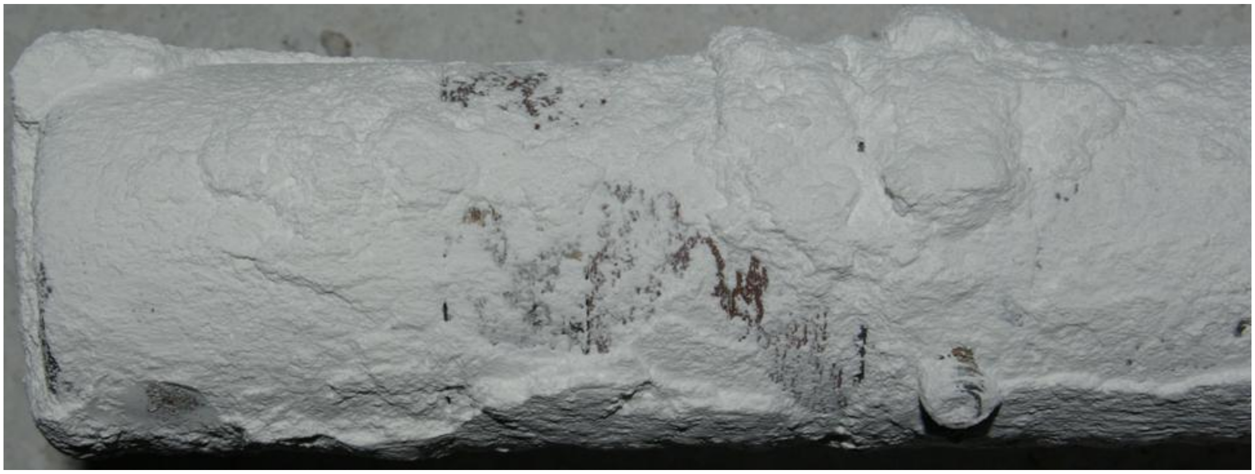


Figure 9. Probe after 811h of Normal Operation

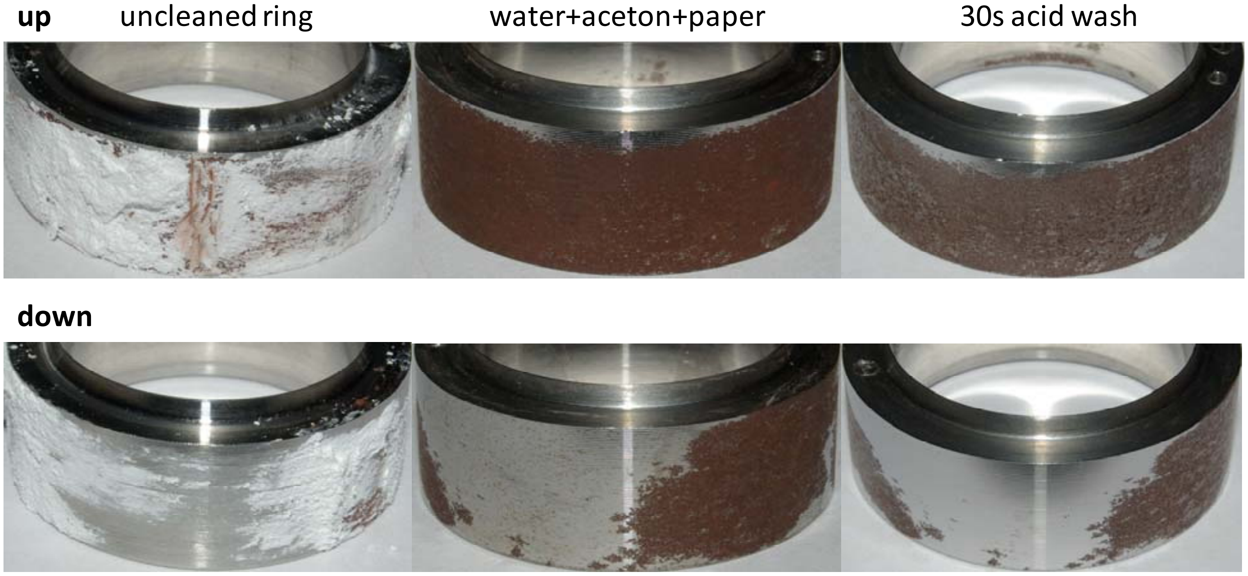
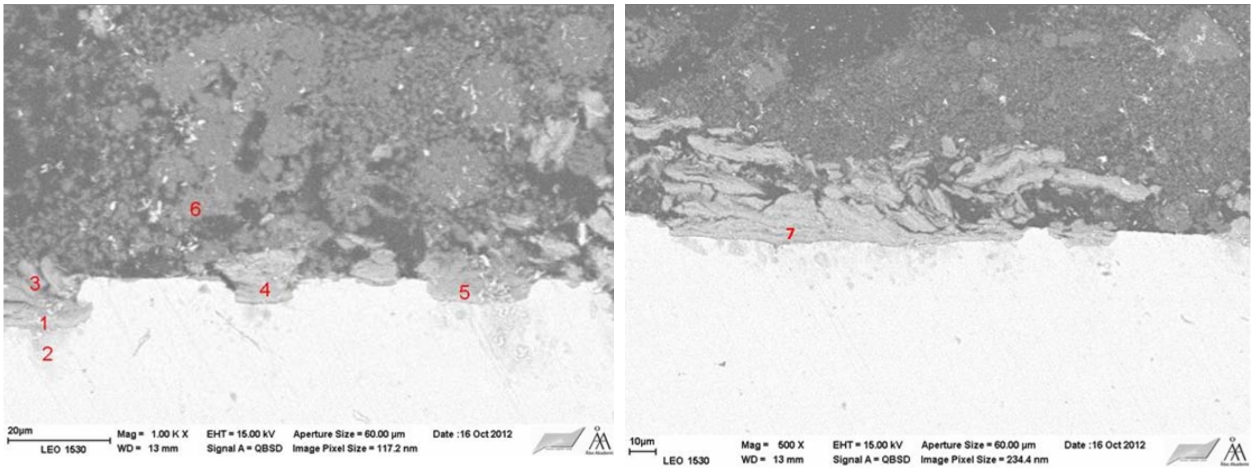


Figure 10. Ring after 811h normal operation. No iron oxide was found on the bottom edge of the probe.



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

Figure 11. Spot analysis of corrosion layer from probe pulled out after 811 hours of normal operation (before water wash). In spots 2 and 7, the Cl is not balanced by Na or K.

Figure 12. Probe after water wash - 1124h total (811h ”normal” operation + water wash)

Figure 13. Ring after 1124h. Not that there are some areas without corrosion downwards on the bottom edge of the ring.

Table II. Corrosion layer thicknesses for the rings in the different probe studies. [a]Weight loss after washing with acetone and acetic acid to remove corrosion products. *Pit corrosion, pits ~10 µm deep. **Pit corrosion, pits ~20 µm deep.

Probe Time	**Probe Temperature**	**Ring Weight Loss (mg)** [a]	**Avg. Corrosion Layer Thickness (µm)**	**Calculated Avg. Corrosion (mm/yr)**
2 h	80 °C	0	0	
2 h	75 °C	0	0	
811 h	90 °C	22	2*	0.02
1124 h	90 °C	72	6**	0.05
2 h	90 °C (oil)	0	0	

After the water wash and after acid washing the inside of the tubes, oil was burned in the boiler to put an oxide layer on the inside of the tubes. The air ratio used was extremely high, resulting in a flue gas with a high oxygen content and low H_2O and SO_2 content due to the high level of dilution, Table III. Dew point and H_2SO_4 were measured during oil burning at three different points: the bull nose and two different points in the economizer, Figure 5. The Land dew point analyzer was not sufficiently sensitive to measure a dewpoint given the very low concentrations of H_2SO_4 and H_2O. The highest H_2SO_4 level measured was about 3 ppm when four burners were firing oil, Table IV.

A 2h probe (90 °C) study was also made in the economizers. The probe study was carried out at the same time the measured SO_3 level was highest, but no corrosion was seen on the rings, Figure 14. Had there been an acid dew point above 90 °C, corrosion should have occurred during the two hour probe study.

Table III. Flue gas composition during oil burning. Date 19.10.2012. Calculated Fuel Oil Sulfur Content 0.8% (based on flue gas analysis). No acid dewpoint was found in the dewpoint measurement.

Time	**O_2 (%)**	**SO_2 (ppm)**	**SO_2 (ppm 0% O_2)**	**Air Ratio (λ)**	**Calculated Dewpoint (°C)**
9:36	19.4	38	507	13.4	19
11:57	17.9	83	574	6.9	25

Table IV. Sampling positions and SO_3 results. b.n.: bull nose.

Date	**Time**	**MP**	**SO_3 (ppm)**	**Temp (°C)**	**# of 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
	13:10-13:20	1	3	165	4
	16:27-16:37	2	3	240	4
	16:53-17:13	2	2	240	4

Figure 14. Ring after 2h exposure during oil burning.

4. **Conclusions**

Based on the corrosion results from the long term probe studies, annual corrosion rates were calculated to be 0.02 and 0.05 mm/yr for the probe pulled before the water wash and the probe pulled after the water wash respectively. Pitting was observed with pit depths of approximately 10 and 20 µm for the two probes. The presences of chloride in some of the pits that was not balanced by alkali indicated chloride induced pitting. On the rings from both of the probes, there was a patch at the gravimetric bottom of the ring where there was not corrosion. It seems probable that some water dripped down from the soot blowers that were about 2 m above the probe. This would have resulted in a chloride containing solution, even if for a short time before the water evaporates.

It was clear that there was no acid dew point corrosion during normal operation. This is also supported by the fact that there is not acid dewpoint corrosion seen where the feed water to the economizer comes into the boiler. The feed water temperature is between about 110 °C and 115 °C. This temperature is sufficiently low that if H_2SO_4 is present, acid dewpoint corrosion would be seen. From this study we can conclude mills can take more energy out of the flue gas without dew point corrosion under normal operational conditions.

There was also no dew point corrosion seen during the oil firing. This may be due to the high air ratios used in this instance. A follow up study during start-up on oil could clarify if during start-up acid dew point corrosion can be seen if the probe temperature is 90 °C.

5. Reference

Cooper, D.; Ferm, M. Jämförelse av mätmetoder för bestämning av SO_3 koncentrationer i rökgaser. *Värmeforsk, Institutet för Vatten- och Luftvårdsforskning Göteborg* 1994, Report 937