APPENDIX 1

Project budget and schedule 14.12.2012



SKYREC



SKYREC Budget 14.12.2012

- Projects paid: 788 171 €
- Projects to be invoiced: 14 900,00 €
- Sum (projects ordered): 803 071 €
- Funding from TEKES (350 000 €) is OK
- Project budget total: 805 000 €
- 805 000 €- 803 071 €= 1 929 €left

Projects to be invoiced

Company, Project name	will be invoiced
ÅA: Probe Study of Corrosion in the Economizers of a Kraft	14 900 €
Recovery Boiler	
Budget left	16 829 €
Sum	1 929 €

SUOMEN SOODAKATTILAYHDISTYS FINNISH RECOVERY BOILER COMMITTEE

Things to be done: meeting 19.12.2012

- Accepting final report:
 - furnace material tests, VTT
- Results from last project:
 - Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler, ÅA
- Commenting final report

APPENDIX 2

ÅA, Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler Corrosion – presentation 19.12.2012 PROCESS CHEMISTRY CENTRE



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

Tor Laurén <u>Emil Vainio</u> Nikolai DeMartini Mikko Hupa

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 - Rauma



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

- Sulfur in fuel is oxidized to SO₂
- A fraction of the SO₂ is further oxidized to SO₃
- $SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g)$
- At 200°C mostly H₂SO₄(g)
- Condensation of sulfuric acid may lead to severe low temp corrosion



Sulfuric acid dew point

 When the H₂SO₄(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. H₂SO₄(g) and SO₂ 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	3° 08	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. H₂SO₄(g) measurements

 Flue gas led through a salt (KCI) and H₂SO₄ is absorbed in the salt

 $2\mathsf{KCI}(\mathsf{s}) + \mathsf{H}_2\mathsf{SO}_4(\mathsf{g}) \rightarrow \mathsf{K}_2\mathsf{SO}_4(\mathsf{s}) + 2\mathsf{HCI}(\mathsf{g})$

 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



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	CI	K	Mn	Fe
	1	1.3	0.3	0.2	0.1	0.5	0.1	0.4	38.2
Γ	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
ſ	7	0.4	0.5	0.3	0.1	2.5	0.1	0.3	37.5
<u> </u>									

CI not balanced by Na or K

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



Ring after 1124h



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



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

Æ

 30μm
 Mag = 196 X
 EHT = 20.00 kV
 Aperture Size = 60.00 μm
 Date :1 Nov 2012

 LE0 1530
 WD = 13 mm
 Signal A = QBSD
 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	3° 08	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 SO₃ 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 SO₃ results

Date	Time	MP	SO ₃ /H ₂ SO 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	8 8
	12:15- 12:35	1	1	165	4	
	16:27- 16:37	2	3	240	4	MP 1
	16:53- 17:13	2	2	240	4	bull nose
b.	n.: bull nos	е				

• No acid dewpoint was found in the dewpoint measurement

Ring after 2h exposure during oil burning



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

APPENDIX 3

ÅA, Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler Corrosion – draft report 16.12.2012





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

Nikolai DeMartini, Tor Laurén, Emil Vainio, Mikko Hupa

Åbo Akademi University

17 December 2012

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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. No acid dew point corrosion was seen indicating that modern mills can recover more heat from flue gases.

In addition, the dew point, SO_3 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 4 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.

The question then came up, 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.

2. Method

Two probes were inserted into the economizer section at Rauma at the same time. Both probes were kept at 90 °C by air cooling. One was pulled just prior to the planned recovery boiler shutdown and the second was pulled after the water wash. A temperature of 90 °C was chosen because it is well above the water dewpoint, even in the presence of HCl and salt, but below a H₂SO₄ dewpoint, Figure 2. It is also well above the temperature water is absorbed by the salt due to the hygroscopic nature of salts such as Na₂SO₄, Figure 3. The hygroscopic nature of salt is shown for both Na₂SO₄ and NaHSO₄ in Figure 3, but only NaHSO₄ is not present in the dust in Rauma. The presence of Na₂SO₄ is expected to result condensation at temperatures a few degrees °C above the water dew point. The choice of 90 °C was confirmed by two 2h probe studies, one at 80 °C and one at 75 °C. The schedule for the probe studies are given in Table I.



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.

Additionally, SO_2 and SO_3 were measured in the flue gas and short term probe corrosion tests 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 .

		Probe	
Date In	Date Out	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

Table I. Schedule for the probe studies.

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 4. 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.



Figure 4. Temperatures of the probes (Tring and Tring p2), flue gas (Tfg) and boiler house (Tbh).

After 811h of normal operation the probe was covered in ash, Figure 5. There was virtually no corrosion on the probe, Figure 6. What little corrosion occured 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 μ m, Figure 7. 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 negligible amount of corrosion seen along with the lack of sulfur in the corrosion layer indicated clearly that there is no acid dew point corrosion.

The probe that was pulled out after the water wash, Figure 8, had more corrosion than the probe pulled out before the water wash, but there was still virtually no corrosion, Figure 9. Again, the bottommost

edge was not corroded. The average corrosion for the two probes estimated on an annual basis was 0.02 and 0.06 mm/year for the probes pulled out before and after the water wash respectively, Table II.



Figure 5. Probe after 811h of Normal Operation



Figure 6. Ring after 811h normal operation. No iron oxide was found on the bottom edge of the probe.



atom-%								
Spot	Na	Al	Si	S	Cl	К	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 7. 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 8. Probe after water wash - 1124h total (811h "normal" operation + water wash)

uncleaned ring up water+aceton+paper down



Figure 9. 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. *Pit corro	sion, pits '	~10
μm deep. **Pit corrosion, pits ~20 μm deep.		

Probe	Probe	Ring Weight	Avg. Corrosion Layer	Calculated Avg.
Time	Temperature	Loss (mg)	Thickness (μm)	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. 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 SO_3 were measured during oil burning at three different points, the bull nose and two different points in the economizer, Figure 10. No acid dew point was measured. The highest SO_3 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 11. There was clearly no acid dew point, but it is not clear why no acid dew point was seen even when SO_3 neared 3 ppm. Had there been an acid dew point, corrosion would have been expected in 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	O2 (%)	SO₂ (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



Figure 10. Measurement points for the SO_3 measurements.

Date	Time	MP	SO₃ (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
	13:10-20	1	3	165	4
	16:27-16:37	2	3	240	4
	16:53-17:13	2	2	240	4

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

Figure 11. Ring after 2h exposure during oil burning.

up uncleaned ring water+aceton+paper

down



4. Conclusions

No significant corrosion seen under normal operation or after the water wash for the probes held at 90 °C. It was clear that there was no acid dew point corrosion due to H_2SO_4 formation during normal operation and 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, but the results clearly show no acid dew point corrosion during normal operation of a modern Kraft recovery boiler. A follow up study during start-up on oil could clarify if during start-up an acid dew point can be seen.

APPENDIX 4

VTT, Analysis of the furnace material test samples – presentation 19.12.2012



Characterisation of probe test samples exposed to BLRB lower furnace environments

SKYREC JR 19.12.2012 Pekka Pohjanne, VTT

VTT TECHNICAL RESEARCH CENTRE OF FINLAND

19/12/2012

VII

Test materials

Material	%C	%Mn	%Si	%Cr	%Ni	%Mo	%Fe	%Cu	Other
Carbon steel									
P265GH	≤0.2	0.80 -	≤0.40	≤0.30	≤0.30	≤ 0.08	bal.	≤0.30	
		1.40							
Austenitic stainless steels									
3R12	≤0.02	1.3	0.4	18.5	10.5		bal.		
[304L]									
3RE28 ^{A)}	0.023	1.77	0.39	25.6	21.0	0.06	bal.	0.06	
[310]									
3xRE28 A)	0.012	1.63	0.35	25.2	21.3	0.25	bal.	0.14	
High nickel alloys									
Sanicro 28	≤0.02	≤2.0	≤0.6	27	31	3.5	bal.	1.0	
[UNS N08028]									
Sanicro 38	≤0.03	0.8	≤0.5	20	38.5	2.6	bal.	1.7	Ti: 0.8
[mod. 825]									
HR11N	0.03	2.0	0.6	27.0	38	0.5 -	bal.		N: 0.1
						1.5			
Nickel base alloys									
Sanicro 67	0.02	≤0.5	≤0.5	30	60		bal.		Co: <0,05
[Alloy 690]									
Super 625	0.1	≤0.5	≤0.5	20 - 23	bal.		≤5.0		W: 3.15-4.15
									Al: 0.4
									$Co \le 1.0$
	1		1	1	1	1		1	

A) Tube samples analysed by VTT

- A. Wall thickness measurements before and after testing (corrosion rate)
 - Thickness profiles at a function of circumference from three locations (axial direction)
 → average & maximum WT losses
- B. Characterisation and corrosion mechanism
 - SEM/EDS from metallographic cross sections after/before the profile measurements
 - Few analysis also from unexposed reference samples
- Tests No.1...3 Materials tested in as received condition
- ✓ Tests No.4 and 5 The outer and inner surfaces machined and hand grinded/polished



VTT TECHNICAL RESEARCH CENTRE OF FINLAND

19/12/2012

4

Corrosion resistance evaluation – Procedures



Probe No. 2 – Specimens tested in as received condition















VIT

Test matrix

Test No.	Test materials	Test duration, hours		Effective temperature
		Total	Effective ^{A)}	
1	3R12(AISI 304L), 3RE28(AISI 310S), Sanicro28, Sanicro38	1000	906 (pressure over 9 bar)	ca. 440°C
2	3R12(AISI 304L), 3XRE28, HR11N, Sanicro67,	1000	744 (pressure over 8 bar)	ca. 440°C
3	3R12(AISI 304L), HR11N, Sanicro38, Super625	1000	750 (pressure over 7 bar)	ca. 430°C
4	3R12(AISI 304L), carbon steel (P265GH), Sanicro67, Super625	2700	2154 (pressure over 9 bar)	ca. 440°C
5	3R12(AISI 304L), Sanicro28, HR11N, Sanicro38	2630	2157 (pressure over 9 bar)	ca. 440°C

A)Used in corrosion rate calculations

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19/12/2012



Results – Probe test No. 1

Probe No.1 after the test





Probe No.1 after the test




Results – 3R12 (304L)



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Results - 3R12 (304L)





VIT

Results – 3RE28



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19/12/2012

Results – 3RE28





VIT



VT

Probe test No. 1 – Average corrosion rates



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Probe test No. 1 – Maximum corrosion rates





Probe test No. 1 – Metallography





a) 3R12



c) Sanicro 28

contenting Voltage/Spot Size/Magnification/Detector/ 10C1382 20 VV 4 500 x BSE ______50 um___

d) Sanicro 38

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Probe test No. 1 – EDS analysis



19/12/2012



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Results – Probe test No. 2

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Probe No. 2 after the test



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Probe No. 2 after the test



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Probe test No. 2 – Average corrosion rates







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Probe test No. 2 – Metallography



d) Sanicro 67

VII





Probe test No. 2 – EDS analysis

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Results – Probe test No. 3





Probe No. 3 after the test









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Probe test No. 3 – Maximum corrosion rates



√vπ







Probe test No. 3 – Metallography

c) Sanicro 38

d) Super 625

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Probe test No. 3 – EDS analysis



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Results – Probe test No. 4

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Probe No. 4 after the test



Probe No. 4 after the test



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19/12/2012

Probe test No. 4 – Average corrosion rates





VVII

VII



Probe test No. 4 – Maximum corrosion rates

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c) Sanicro 67

d) Super 625



VIT





Probe test No. 4 – EDS analysis

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19/12/2012



Results – Probe test No. 5

V

Probe No. 5 after the test





Probe No. 5 after the test







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19/12/2012

VT

Probe test No. 5 – Maximum corrosion rates







c) HRIIN

d) Sanicro 38

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19/12/2012

VIT

Probe test No. 5 – EDS analysis





VIT

Summary

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19/12/2012

Summary

19/12/2012

Summary



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19/12/2012



Summary

- Corrosion resistance in lower furnace conditions is improved by alloying, especially by chromium.
- According to the wall thickness measurements the test materials can be put in following order based on increased resistance:

C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67

- Carbon steel corroded at extremely high rate (>4 mm/a) at the temperature of 440 °C.
- 3R12 (AISI 304L) corrodes in such high rate (>0.6 mm/a) at 440 °C that it can't be safely used in the lower furnace in the future high pressure recovery boilers,

19/12/2012

√vπ

Summary

- Performance of the Sanicro 38 and HR11N was satisfactory in long term test at 440 °C (CR_{max} ~ 0.1...0.2 mm/a), but it is recommended to verify their performance also at lower temperature (400 °C).
- The new material group which looks promising is the high chromium alloys 3RE28/3XRE28 and Sanicro 28, but their long term performance should be verified in the future.
- If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers, since its corrosion rate was lowest from the studied alloys.
- Based on the long term test the Super 625 is the second best choice for the future high pressure boiler, but because of its relatively high corrosion rate in short term test more and longer tests are needed to verify its performance.



Summary

- In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test.
 - Some error to the measurement results; especially to the maximum corrosion rates
 - Most significant when samples had surface scratches and dents.
- Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing.
- Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.



VTT creates business from technology

APPENDIX 5

VTT, Analysis of the furnace material test samples – draft report 26.11.2012

RESEARCH REPORT



Characterisation of probe test samples exposed to BLRB lower furnace environments

Author:

Pekka Pohjanne

Confidentiality:

Confidential





Report's title				
Characterisation of probe test samples exposed to BLRB lower furnace environments				
Customer, contact person, address	Order reference			
Soodakattilayhdistys ry.				
Project name	Project number/Short name			
SKYREC Sondi	33189			
Author(s)	Pages			
Pekka Pohjanne	70/			
Keywords	Report identification code			
	VTT-R- <i>DRAFT</i>			

Abstract

Current trend to increase electricity generation of recovery boilers possess new demands for the tube materials, when the material temperatures are increased due to higher steam values. Operational experiences from current boilers have shown that the AISI 304 L compound tubes suffer from accelerated corrosion in furnace wall, when the material temperatures are increased from normal values due to the internal surfaces scales. This indicates that the AISI 304L might be unsuitable cladding material for the future high pressure boilers.

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours.

The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. According to the wall thickness measurements the test materials can be put in following order based on increased resistance: C-steel << $3R12 < HR11N \sim Sanicro 38$ (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67.

Confidentiality	{Public, Restricted, Confidential}				
{Add city} 26.11.2012 Written by	Reviewed by	Accepted by			
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1 Introduction

Increasing boiler pressure induces a corresponding increase in tube temperature in steam generator. Operational experiences from current boilers indicate that AISI 304L (3R12), which has been the most commonly used cladding material, suffers from accelerated corrosion at higher than normal operation temperatures, which are sometimes encountered when internal surfaces in furnace wall tubes are covered with thick scale. These temperatures would be normal at high pressure boilers, and thus AISI 304L appears non-suitable cladding material for high pressure boilers. Currently few alternative materials are used, such as Sanicro38 (mod. UNS N08825) and HR11N, but their corrosion resistance at high temperatures has not been thoroughly studied and operational experiences are still limited. Also other highly alloyed materials are available, but data on their corrosion resistance are lacking.

2 Goal

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT.

3 Experimental

3.1 Test materials, specimens and evaluation procedures

The test materials were carbon steel (P265GH), three austenitic stainless steels 3R12 (AISI 304L), 3RE28 (AISI 310) and 3XRE28, three austenitic high nickel alloys Sanicro 28 (UNS N08028), Sanicro 38 (mod. UNS N08825) and HR11N and two austenitic nickel base alloys Sanicro 67 (UNS N06690) and Super 625. Chemical compositions of the test materials are shown in Table 1.

After exposure the material performance was assessed with wall thickness measurements and metallographic analysis. Before measurements, after cutting from the probe, the samples were thoroughly washed under water with nylon brush and rinsed with ethanol to remove deposits. The wall thickness profiles of the test samples were measured before and after testing with coordinate measurement machine as a function of circumference from three axial locations (Z = 15, 25 and 32 mm) so that from each location 100 points were measured, Figure 1.

In tests No.1 - 3 the 3R12, 3RE28, 3XRE28, Sanicro 28, Sanicro 38 and Sanicro 67 specimens were cut from composite tubes and tested in as received condition, whereas the HR11N and Super 625 specimens were machined from lager solid pieces and tested in as machined condition. In tests No.4 and 5 the outer and inner surfaces of all specimens were machined and hand grinded/polished prior assembly to the probe (Figure 2) to improve the accuracy of wall thickness measurements. The average corrosion rates were calculated on the basis of



average wall thickness loss at the specimen apex (ca. 35...50 points/ $30...45^{\circ}$ angle at apex). The maximum corrosion rates were calculated from the wall thinning curved derived from the wall thickness measurements.

For metallographic analysis one cross-section per sample (Z = 15 mm) was prepared and analysed with scanning electron microscope (SEM). The composition of oxide layers and deposits was determined with energy dispersive spectroscopy (EDS).

Material	%C	%Mn	%Si	%Cr	%Ni	%Mo	%Fe	%Cu	Other
Carbon steel									
P265GH	≤0.2	0.80 -	≤0.40	≤0.30	≤0.30	≤0.08	bal.	≤0.30	
		1.40							
Austenitic stainles	ss steels								
3R12 [304L]	≤0.02	1.3	0.4	18.5	10.5		bal.		
3RE28 ^{A)}	0.023	1.77	0.39	25.6	21.0	0.06	bal.	0.06	
[310]									
3xRE28 ^{A)}	0.012	1.63	0.35	25.2	21.3	0.25	bal.	0.14	
High nickel alloys									
Sanicro 28	≤0.02	≤2.0	≤0.6	27	31	3.5	bal.	1.0	
[UNS N08028]									
Sanicro 38	≤0.03	0.8	≤0.5	20	38.5	2.6	bal.	1.7	Ti: 0.8
[mod. 825]									
HR11N	0.03	2.0	0.6	27.0	38	0.5 - 1.5	bal.		N: 0.1
Nickel base alloys									
Sanicro 67	0.02	≤0.5	≤0.5	30	60		bal.		Co: <0,05
[Alloy 690]									
Super 625	0.1	≤0.5	≤0.5	20 -	bal.		≤5.0		W: 3.15-4.15
				23					Al: 0.4
									$Co \le 1.0$

Table 1. Nominal composition of the test materials if not otherwise mentioned.

A) Tube samples analysed by VTT





a)

b)

Figure 1. The wall thickness profiles were measured before and after testing with coordinate measurement machine a) as a function of circumference b) from three axial locations (Z = 15, 25 and 32 mm).



Figure 2. Examples of sample surfaces prior exposure: a) in as received condition for the probe No. 2 and b) after machining and hand grinding for the probe No. 7.



3.2 Test conditions

The probe tests were conducted in Metsä Fibre Joutseno mill by Boildec Oy. The test matrix and test conditions are summarised in Table 2 and Table 3, more detailed information from the test set-up and parameters can be obtained from the probe test reports /1...5/. Maximum cladding temperatures in a high pressure boiler are about 400°C, when internal surfaces are clean. With scaling, cladding temperatures may become higher and, consequently, the test temperature was selected to be 440°C. The exposure durations varied from 1006 to 2700 hours so that target duration of 1000 h was applied in the first three tests and it was extended to above 2000 h in the last two tests to ensure the validity of the results.

Test No.	Materials	Total test duration
1	3R12, 3RE28, Sanicro 28, Sanicro38	1006
2	3R12, 3XRE28, HR11N, Sanicro 67	1023
3	3R12, HR11N, Sanicro 38, Super 625	1250
4	3R12, carbon steel, Sanicro 67, Super 625	2700
5	3R12, Sanicro 28, HR11N, Sanicro 38	2630

Table 2. Test matrix.

Table 3. Summary of the test conditions during exposure tests.

Test No.	Te	Effective	
	Total	Effective ^{A)}	temperature [°C]
1	1006	906 (pressure over 9 bar)	~440
2	1023	744 (pressure over 8 bar)	~440
3	1250	750 (pressure over 7 bar)	~430
4	2700	2154 (pressure over 9 bar)	~440
5	2630	2157 (pressure over 9 bar)	ca. 440°C

^{A)}Used in corrosion rate calculations



4 Results

4.1 Probe test No.1

Total test duration of the test No. 1 was 1006 hours from which 906 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3RE28, Sanicro 28 and Sanicro 38, Figure 3. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.





Figure 3. Macrographs taken from the probe No. 1 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.



4.1.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 4...11. The results showed that marked wall thinning had taken place on the 3R12 specimen. For the other materials the data was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that tube wall thicknesses varied a lot as a function of circumference.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate, order of 0.7 mm/a, was measured for the 3R12 material. Corrosion rate was next highest in the Sanicro 38, for which a maximum corrosion rate of ca. 0.2 mm/a was determined. The maximum corrosion rates of Sanicro 28 and 3RE28 materials were in the order of 0.1 mm/a and they were best performing materials in this test.

The reason to the negative values in average corrosion rates is that the washing and brushing with nylon brush was not effective enough to remove all deposits from the surfaces prior wall thickness measurements, indicating that average corrosion rates may give too optimistic result. Respectively the maximum corrosion rates may give too conservative results, if there are some problems in specimen alignment during WT measurements; this is a specific concern of samples with scratches or dents.









Figure 4. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 5. Circumferential wall thinning curves from 3R12 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 6. Circumferential wall thickness profiles from 3RE28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 7. Circumferential wall thinning curves from 3RE28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.






Figure 8. Circumferential wall thickness profiles from Sanicro 28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 9. Circumferential wall thinning curves from Sanicro 28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 10. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 11. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 12. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after after 906 h exposure in lower furnace at 440 °C (Probe test No. 1).



4.1.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed, Figure 13. According to the EDS (Figure 14) analysis the thin layers (thickness ca. 5 μ m) on 3RE28 and Sanicro 28 were depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. Whereas the composition of thin layer on 3R12 was similar to the base material and no sulphur was detected.



Figure 13. Cross sections from a) 3R12, b) 3RE28, c) Sanicro 28 and d) Sanicro 38 after 906 h exposure in lower furnace at 440 °C (Probe test No. 1)





Figure 14. Results from the EDS analysis performed for the 3R12, 3RE28 and Sanicro 28 specimens after 906 h exposure in lower furnace at 440 °C (Probe test No. 1). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.



4.2 Probe test No.2

Total test duration of the test No. 2 was 1023 hours from which 744 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3XRE28, HR11N and Sanicro 67, Figure 15. According to visual inspection the inner surfaces of the specimens were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed. The outer surfaces of the specimens appeared to be in good condition but the thin dark and white deposits on the surfaces hindered accurate examinations.





b)

Figure 15. Macrographs taken from the probe No. 2 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.



4.2.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 16...23. The results showed that marked wall thinning had taken place on the 3R12 specimen and lesser degree also on the HR11N specimen. The data of the 3XRE28 and Sanicro 67 materials was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that the wall thickness variations were smaller in the machined HR11N specimen than in the other specimens tested in as received condition. The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate in the order of 0.6 mm/a was measured for the 3R12 material. The corrosion resistance of the 3XRE28, HR11N and Sanicro 67 was practically at the same level.











a)



Figure 17. Circumferential wall thinning curves from 3R12 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 18. Circumferential wall thickness profiles from 3XRE28 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 19. Circumferential wall thinning curves from 3XRE28 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 20. Circumferential wall thickness profiles from HR11N specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.











Figure 21. Circumferential wall thinning curves from HR11N specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 22. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 23. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 24. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 744 h exposure in lower furnace at 440 °C (Probe test No. 2).



4.2.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 25. According to the EDS analysis (Figure 26) the thin, a few μ m thick layer, observed on 3XRE28 was depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. The similar thin layer on Sanicro 67 contained high amounts of sulphur and was depleted in nickel and iron whereas chromium content was at the same level than in the base material.



Figure 25. Cross sections from a) 3R12, b) 3XRE28, c) HR11N and d) Sanicro 67 after 744 h exposure in lower furnace at 440 °C (Probe test No. 2)





Figure 26. Results from the EDS analysis performed for the 3XRE28 and Sanicro 67 specimens after 744 h exposure in lower furnace at 440 °C (Probe test No. 2). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.



4.3 Probe test No. 3

Total test duration of the test No. 3 was 1250 hours from which 750 hours at the target temperature of 430 °C. The test materials in this exposure were 3R12, HR11N, Sanicro 38 and Super 625, Figure 27.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. Some deposits were observed on the inner surfaces but based on their appearance they originate from the probe cutting conducted after the probe has been removed from the boiler. The outer surfaces of the specimens were covered with dark and brown deposits but appeared to be in good condition.



a)



Figure 27. Macrographs taken from the probe No. 3 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.



4.3.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 28...35. The results showed that marked wall thinning had taken place only on the 3R12 specimen. Some wall thinning was observed also on the Super 625 specimen. The data of the HR11N and Sanicro 38 was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. In addition the data in this test was more scattered than in the previous test indicating that all deposits were not removed from the surfaces in washing performed for the specimens' prior measurements.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 36. In this test the corrosion rate of 3R12 was in the order 0.4 mm/a, i.e. about 0.2 mm/a lower than in the first two tests, most probably due the lower probe temperature. The corrosion rate of the Super 625 was unexpectedly high ca. 0.3...0.4mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.1 mm/a, and they were best performing materials in this test.









Figure 28. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



35 (69)





Figure 29. Circumferential wall thinning curves from 3R12 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 30. Circumferential wall thickness profiles from HR11N specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 31. Circumferential wall thinning curves from HR11N specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 32. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 33. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 34. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 35. Circumferential wall thinning curves from Super 625 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 36. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)



4.3.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning. The layers formed on 3R12, HR11N and Sanicro 38 were thin ca.5 μ m in thickness. Whereas on the Super 625 ca. 10...20 μ m thick peeling like scale was observed.

According to the EDS analysis (Figure 38) the layers on 3R12, HR11N and Sanicro 38 were depleted in iron and nickel and enriched in chromium and contained also sulphur. The layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur. Reference analysis made from unexposed reference samples showed that the depleted/enriched layers are formed during exposure and do not originate from the specimen manufacturing process.



Figure 37. Cross sections from a) 3R12, b) HR11N, c) Sanicro 38 and d) Super 625 after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)





Figure 38. Results from the EDS analysis performed for the 3R12, HR11N, Sanicro 38 and Super 625 specimens after 750 h exposure in lower furnace at 430 °C (Probe test No. 3). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.



4.4 Probe test No. 4

Total test duration of the test No. 4 was 2700 hours from which 2154 hours at the target temperature of 440 °C. The test materials in this exposure 3R12, carbon steel, Sanicro 67 and Super 625, Figure 39.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. The outer surfaces of the 3R12, Sanicro 67 and Super 625 specimens were covered with thin dark deposits but appeared to be in good condition. The carbon steel specimen was heavily corroded.





Figure 39. Macrographs taken from the probe No. 4 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the side surface of carbon steel specimen is clearly visible on inner surface.



4.4.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 40...47. The results showed that intense wall thinning had taken place on carbon steel specimen. Marked wall thinning was also observed on the 3R12 specimen and lesser degree also on the Super 625 specimen. The data of the Sanicro 67 specimen was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. The results showed also that surface polishing prior testing together with longer exposure time reduced data scatter and thus improved accuracy.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. Highest corrosion rates, ca. 4 mm/a, were measured for the carbon steel as expected. The 3R12 had the second highest corrosion rates, order of 0.6 mm/a. Maximum corrosion rate of the Super 625 was in the order 0.1 mm/a in this test, i.e. significantly lower than in the test No.3, where a maximum corrosion rate of 0.2...0.3 mm/a was observed. The best material in this test was Sanicro 67, its maximum corrosion rate was only about 0.02 mm/a.









Figure 40. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 41. Circumferential wall thinning curves from 3R12 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.






Figure 42. Circumferential wall thickness profiles from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 43. Circumferential wall thinning curves from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 44. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 45. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 46. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 47. Circumferential wall thinning curves from Super 625 specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 48. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2154 h exposure in lower furnace at 440 $^{\circ}C$ (Probe test No. 4).



4.4.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning, Figure 49. The carbon steel showed scale thickness of about 25 μ m after 2700 h exposure. The layers formed on 3R12 and Sanicro 67 were thin ca.5 μ m in thickness. Whereas on the Super 625 ca. 10...20 μ m thick peeling like scale was observed.

According to the EDS analysis (Figure 50) the layer on 3R12 was depleted in iron and nickel and enriched in chromium and contained also sulphur. The layer on Sanicro 67 contained sulphur and was depleted in iron and nickel, but the chromium content was at the same level than in the base material. The outermost layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur.



Figure 49. Cross sections from a) carbon steel b) 3R12, c) Sanicro 67 and d) Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4).





Figure 50. Results from the EDS analysis performed for the carbon steel, 3R12, Sanicro 67 and Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.



4.5 Probe test No. 5

Total test duration of the test No. 5 was 2630 hours from which 2157 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, Sanicro 28, HR11N and Sanicro 38, Figure 51. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.





b)

Figure 51. Macrographs taken from the probe No. 5 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the middle of Sanicro28 specimen, that hindered WT measurements after exposure, is clearly visible on inner surface.



4.5.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them for 3R12, HR11N and Sanicro 38 are presented in Figures 52...57. The results showed that marked wall thinning had taken on the 3R12 specimen. Some wall thinning was observed also on the Sanicro 38 specimen and locally also on the HR11N specimen. The WT profile measurements for the Sanicro 28 sample after the test failed due to the thermocouple that was soldered on the inner surface of the specimen (Figure 51b).

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. In this test the corrosion rate of the 3R12 was in the order 0.8 mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.15 mm/a, i.e. at the same range than in the previous tests.





Figure 52. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.





a)



Figure 53. Circumferential wall thinning curves from 3R12 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 54. Circumferential wall thickness profiles from HR11N specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.









Figure 55. Circumferential wall thinning curves from HR11N specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 56. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 5): a) axial location Z = 15 mm and b) axial location Z = 25 mm.











Figure 57. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.







Figure 58. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2157 h exposure in lower furnace at 440 $^{\circ}C$ (Probe test No. 5).



4.5.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 49. The layers found on 3R12, Sanicro 28, HR11N and Sanicro 38 were very thin ca. 2 μ m in thickness. EDS analysis showed that iron and nickel depletion and chromium enrichment had taken place in some locations in all materials and that in these locations sulphur was also detected (Figure 50).



Figure 59. Cross sections from a) 3R12, b) Sanicro 28, c) HR11N and d) Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5).

67 (69)



Figure 60. Results from the EDS analysis performed for the 3R12, Sanicro 28, HR11N and Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.



5 Conclusions

The coordinate measurement machine proved its applicability to determine wall thickness profiles from difficult shapes. In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test. This caused some error to the measurement results; especially to the maximum corrosion rates calculated from the tests No. 1-3, where the materials were tested in as received condition i.e. when the samples had surface scratches and dents. Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing. Their adverse effect was clearly seen as negative average corrosion rate values in most resistant alloys.

Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.

In current tests highest corrosion rate, ca. 4 mm/a, was measured for the carbon steel as expected. The traditional composite tube material 3R12 had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C (Figure 61). Based on the results of 3R12 the reproducibility of the probe tests was so good that different probe tests can be used to compare different materials to each other.

In current tests no marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were in the order of 0.15...0.2 mm/a in the long term (>2000 h) test, i.e. about four times lower than that of the 3R12 (Figure 61).

In short term (<1000 h) tests the corrosion resistance of the 3RE28, 3XRE28 and Sanicro 28 were as good as or even slightly better than that of the Sanicro 38 or HR11N (Figure 62). Because the 3RE28 and 3XRE28 were not included in the long term tests and no results were obtained for the Sanicro 28 from the long term test No. 5, due to the misplaced thermocouple, it is recommended to verify their promising performance with long term tests in the future.

The results for the Super 625 were inconsistent. In short term 750 h test at 430 °C it's corrosion resistance was only slightly better than that of the 3R12, but in the long term 2154 h test at 440 °C it's resistance was even better that of the Sanicro 38 and HR11N (Figure 62). Similar kind of behaviour was observed in Sanicro 67. In short term 744 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion rate was only 1/10 of that of the Sanicro 38 and HR11N and 1/5 of the Super 625.





Figure 61. Calculated maximum corrosion rates for the 3R12, HR11N, Sanicro 38, Super 625 and Sanicro 67 materials from the probe test No. 1 - 5.



Figure 62. Calculated maximum corrosion rates for the 3RE28, 3XRE28, HR11N and Sanicro 38 from the probe test No. 1-3 and 5.



6 Summary

The aim of this study was to evaluate different potential cladding materials for compound tubes in actual recovery boiler lower furnace conditions. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours.

The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. Corrosion resistance in lower furnace conditions is improved by alloying, especially by chromium. According to the wall thickness measurements the test materials can be put in following order based on increased resistance:

C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67

The carbon steel corroded at extremely high rate (>4 mm/a) at the temperature of 440 °C. Also the 3R12 (AISI 304L) corrodes in such high rate (>0.6 mm/a) at 440 °C that it can't be safely used in the lower furnace in the future high pressure recovery boilers, where material temperatures are expected to rise to level of 400...440 °C. The performance of the Sanicro 38 and HR11N was satisfactory in long term test at 440 °C (CR_{max} ~ 0.1...0.2 mm/a), but it is recommended to verify their performance also at lower temperature (400 °C). The new material group which looks promising is the high chromium alloys 3RE28/3XRE28 and Sanicro 28, but their long term performance should be verified in the future. If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers, since its corrosion rate was lowest from the studied alloys. Based on the long term test the Super 625 in the second best choice for the future high pressure boiler, but because of its relatively high corrosion rate in short term test more and longer tests are needed to verify its performance.

APPENDIX 6

Summary report 19.12.2012

19.12.2012

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FOREWORD

The main driving force of the project has been the increase the electricity generating potential and energy efficiency of recovery boilers. This is in line with the Finnish Government's long-term climate and energy strategy and the aims of the European Union and its objectives. This Finnish Recovery Boiler Committee project has had important role in the recovery island research in Finland. Project has given valuable information to the recovery boilers users and manufacturers. Project gives insight into future recovery boiler technology

SKYREC-project was coordinated by a directing committee consisting of committee chairman Matti Tikka UPM-Kymmene Oyj, Kuusankoski, and as members Kaj Nordbäck Finnish Recovery Boiler Committee, Lasse Koivisto Andritz Oy, Varkaus, Martti Korkiakoski TEKES, Timo Peltola Sandvik Materials Technology, Helsinki, Mika Paju Oy Metsä-Botnia Ab, Joutseno, Kalle Salmi Metso Power Oy, Tampere, Keijo Salmenoja Andritz Oy, Helsinki, Timo-Pekka Veijonen Stora Enso Oyj, Imatra, sekä Hidenori Ogawa Sumitomo Metal Industries Ltd.

In addition the directing committee was assisted by **Olli Talaslahti** Oy Metsä-Botnia Ab, Rauma, (chairman of the liquor subcommittee), **Reijo Hukkanen** Stora Enso Oyj, Oulu (chairman of the incident sub-committee), project coordinator **Esa Vakkilainen** Lappeenrannan University of Technology and as secretary **Markus Nieminen** Pöyry Finland Oy, Vantaa.

Finnish Recovery Boiler Committee

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GENERAL

SKYREC-project was preceded by SoTuII- research program "Recovery boiler of the future II – possibilities to increase power production 1.4.2003 - 30.10.2006" which results are utilized in this project.

The rise of oil world market price and EU CO_2 emission trade scheme has paid attention to CO_2 free bioenergy. The increase in the average cost of electricity has also paid attention to recovery boiler electricity production. For pulp mills the significance of electricity generation from recovery boiler has been secondary. The most important factor in recovery boiler process and steam cycle has been high availability. Increasing electricity production means changes in recovery boiler parameters, typically main steam pressure and temperature. This means increases in material temperatures. This means increases corrosion if no changes are made.

In 2008 the Finnish forest industry's consumption of electricity was about 25 billion kWh. This was about 60% of industries and 30% of Finland's total electricity consumption. In 2008 pulp mills produced energy 150 000 TJ from black liquor. Black liquor's share of biofuels used to produce heat and power is over 50%. Recovery boiler produced electricity has substantial impact on Finland's bioenergy strategy to reach EU targets.

In 2010 almost 7 million tons of chemical pulp was produced in Finland. Electricity production from black liquor was about 6 billion kWh which is 850 kWh/ton of pulp. Production could be even 1500 kWh/ton of pulp; recovery boiler electricity production potential is substantial. Increase of bioelectricity could be 4 billion kWh or about 4% of Finland's electricity production.

2 SUMMARY OF THE PROJECT

SKYREC- research program "Possibilities to increase recovery boiler power production into a new level 1.1.2008 – 30.6.2011" was divided into several sub-programs. The program was part of TEKES (Finnish Funding Agency for Technology and Innovation) funded activities. It received 50 % public support. Without this funding the project could have not been started.

2.1 Project

Project time frame was 3.5 years (1.1.2008 - 30.6.2011). The length was rather long, but as the project had lots of measurement activities at operating recovery boilers, all time was needed. The project had to apply for 12 months extension. The reason was the economic turndown in 2009 which caused temporary shutdowns to pulp mills and measurement projects in operating recovery boilers could not be completed as planned.

The original budget for the project was 700 000 \in (of which TEKES 350 000 \in). When Sumitomo joined the project autumn 2008, budget increased to 805 000 \in The project was coordinated and the funding administrated by the Finnish Recovery Boiler Committee. Almost all of the funding was spent by various universities and research organizations.

Finnish Recovery Boiler Committee was one of the project cost share partners that formed a directing committee. The participating companies consisted of major material manufacturers, recovery boiler manufacturers and users in Finland.

2.2 Background

2.2.1 Basis for project

The rise of oil world market price and EU CO_2 emission trade scheme has paid attention to CO_2 free bioenergy. The increase in the average cost of electricity has also paid attention to recovery boiler electricity production. For pulp mills the significance of electricity generation from recovery boiler has been secondary. The most important factor in recovery boiler process and steam cycle has been high availability. Increasing electricity production means changes in recovery boiler parameters, typically main steam pressure and temperature. This means increases in material temperatures and increases corrosion if no changes are made. In practice the main limiting factors to gain a higher power-to-heat ratio are sulfidation and hot corrosion.

2.2.2 What we knew

Before the project started we knew reliable and proven methods to increase electricity production are increase of black liquor dry solids over 80%, air preheating to 190 °C, feedwater preheating to 160 °C and main steam parameters to 490 °C and 90 bar. Sootblowing steam taken from turbine outlet instead of superheater/boiler also increases electricity generation.

In earlier project (SOTU II) studied resistance/behaviour of the chosen boiler steam/superheater tube materials under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in an ambient atmosphere, but resistance/behaviour of tube materials in reducing conditions was needed.

We knew that the most important factor is the corrosion rate in deposits. Corrosion rate increases when T_0 (FMT) is exceeded. Especially the amount of potassium and chloride in black liquor (and therefore in deposits) affects the corrosion rate. Similarly the fact that presence of sulfides in deposits increases corrosion was known.

Material composition affects the corrosion rate. Chrome improves the resistance to oxidation and sulfidation. Similarly nickel increases the resistance to chloride corrosion. It was known that that the conventional 3R12 (AISI 304L) composite tube material can't be safely used in the future high pressure recovery boilers. We knew from refractory materials that silicon based ceramics resistance in lower furnace oxidizing-reducing atmosphere is unsatisfactory, aluminum based ceramics react with sodium and magnesium based don't endure the effect of water vapour.

2.2.3 Things we wanted to know

One interest was to study the future recovery boiler concepts, especially once-through recovery boiler concept. Other project objective was to determine if mixing other biofuels in with black liquor would alter the combustion characteristics of the black liquor and study possibilities for extracting gases from the lower part of a recovery boiler, to be used in the lime kiln instead of oil and natural gas.

We wanted to know the resistance/behaviour of the superheater tube materials under reducing conditions and to study the corrosion performance of various superheater tube materials for recovery boilers at high material temperatures. We wanted also test different potential furnace materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers.

There is a need for updating and standardizing the recovery boiler water treatment and water chemistry guidelines since the boiler pressure has increased in new and future boilers, the capacities of the old plants, have been increased, the usage of the new chemicals has increased, and the monitoring of the water chemistry is largely done by on-line measurements.

2.2.4 Aims

The steering committee for SKYREC-project listed the following aims:

- Increasing electricity production from recovery boiler and changing the appropriate main parameters and process connections.
- Performance of tube materials for recovery boilers at high material temperatures
- Update the water treatment and water chemistry guidelines for future recovery boilers

2.2.5 Steering committee

SKYREC-project was coordinated by a directing committee consisting of committee chairman Matti Tikka UPM-Kymmene Oyj, Kuusankoski, and as members Kaj Nordbäck Finnish Recovery Boiler Committee, Lasse Koivisto Andritz Oy, Varkaus, Martti Korkiakoski TEKES, Timo Peltola Sandvik Materials Technology, Helsinki, Mika Paju Oy Metsä-Botnia Ab, Joutseno, Kalle Salmi Metso Power Oy, Tampere, Keijo Salmenoja Andritz Oy, Helsinki, Timo-Pekka Veijonen Stora Enso Oyj, Imatra, sekä Hidenori Ogawa Sumitomo Metal Industries Ltd.

In addition the directing committee was assisted by **Olli Talaslahti** Oy Metsä-Botnia Ab, Rauma, (chairman of the liquor subcommittee), **Reijo Hukkanen** Stora Enso Oyj, Oulu (chairman of the incident sub-committee), project coordinator **Esa Vakkilainen** Lappeenrannan University of Technology and as secretary **Markus Nieminen** Pöyry Finland Oy, Vantaa.

2.2.6 Work Packages

The SKYREC-project consisted of the following work packages (WP):

WP1 New recovery boiler concepts

- WP2 Increasing superheated steam temperature
- WP3 Increasing recovery boiler pressure
- WP4 Ensuring boiler and feedwater quality

Work packages consisted of the following subprojects:

WP1: New recovery boiler concepts

- Once-through and reheater recovery boiler concept studies (LUT)
- Co-firing black liquor and biomass (ÅA)
- Pulp mill optimal steam pressure levels (LUT)
- Utilization of pyrolysis gases from the recovery boiler Preliminary studies (ÅA)
- Dew point measurements in Rauma and Heinola mill (ÅA)
- Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler

WP2: Increasing superheated steam temperature

- Corrosion tests of superheater materials in reducing conditions (ÅA)
- Full scale material exposure in Joutseno (VTT)

WP3: Increasing recovery boiler pressure

- Phenomena of transformation in recovery boiler char bed (LUT)
- Refractory material/ceramics in recovery boiler furnace (UO)
- Field tests of furnace materials (Boildec/VTT)

WP4: Ensuring boiler and feedwater quality

- Organic amines and natural organic matter in steam water cycle (VTT)
- Effect of organic amines to magnetite layer formation (VTT)
- TOC balances (Teollisuuden Vesi Oy)
- TOC removal methods and their applicability in make-up water treatment (Teollisuuden Vesi Oy)
- Reduction of TOC from recovery boiler make-up water (UO)
- Activated carbon and UV-treatment field tests (UO/Cewic/JP-analysis)
- Comparison study of active carbon grades (UO/Cewic/JP-analysis)
- Water quality and water treatment guidelines (Teollisuuden Vesi Oy)

2.2.7 Experiences from SKYREC

SKYREC-project was a large endeavor to the whole Finnish recovery Boiler Committee. Both the amount of research carries and need for financing have been large compared to normal, routine work for the committee. Project budget for SKYREC was several times the normal yearly budget.



Coordinating the project could be done within the organization of Recovery Boiler Committee. So the capability of doing "large" projects exists. Division of responsibilities and daily routines between the working groups and the steering committee needs sharpening especially coordination and information sharing.

The project management could be done easier and simpler. But the work done is a good base to continue. Internal reporting had time lags that can be straightened out in the future.

2.2.8 What was accomplished?

Project produces vast amounts of solid research. Several new hypotheses were confirmed. Especially new information about recovery boiler water treatment and water chemistry were obtained which is expected to utilize by fewer incidents in recovery boiler water side. Also several tube material field tests were carried out successfully.

International interest toward Finnish Recovery Boiler Committee did intensify. This kind of large research is not commonly done by other associations. These kinds of projects offer unlimited co-operation possibilities. Expansion of committee activities to outside Finland is a direct result.

In spite of all work done, some unfinished business remains. New recovery boiler concepts were studied but it will need more work to utilize these ideas. As we have successfully completed this phase, we should continue and utilize the lessons learned.

These kinds of projects increase significantly the know-how and expertise of recovery boiler users. This kind of research that benefits all should be conducted under one roof. Finnish Research Agency TEKES needs to be thanked for its part. This kind of project cannot happen without its financial support.

3 **REPORTS**

Several reports were published during SKYREC-project and project results were presented in many different forums. Summary of each sub-project report is presented in Chapter 5.

3.1 Sub-project reports

Sub-projects reports listed by author:

VTT (Technical Research Centre of Finland) reports:

- Organic amines and natural organic matter in steam water cycle Jouko Hildén, Pekka Pohjanne. Report 27.4.2009.
- <u>Effect of organic amines to magnetite layer formation</u> Mikko Vepsäläinen, Petri Kinnunen, Timo Saario, Pekka Pohjanne, Stella Rovio. Report 29.6.2010.
- <u>Full scale material exposure in Joutseno</u>
 Martti Mäkipää, Janne Kärki, Markku Orjala. Report 21.4.2011
- <u>Characterisation of probe test samples exposed to BLRB lower furnace</u> <u>environments</u> Pekka Pohjanne. Report 26.11.2012

Teollisuuden Vesi Oy reports:

- <u>TOC balance of Stora Enso Laminating Papers mill</u> Jani Vuorinen. Report 26.5.2009
- <u>TOC removal methods and their applicability in make-up water treatment</u> Jani Vuorinen, Maija Vidqvist. Report 20.1.2010
- <u>Water quality and water treatment guidelines</u> Maija Vidqvist, Jani Vuorinen 2011

Boildec Oy reports:

- <u>Field tests of furnace materials test No 1</u> Timo Karjunen. Report 27.4.2010.
- Field tests of furnace materials test No 2 Timo Karjunen. Report 6.7.2010.
- Field tests of furnace materials test No 3 Timo Karjunen. Report 17.9.2010.
- <u>Field tests of furnace materials test No 4</u> Jussi Vänskä. Report 7.6.2011
- Field tests of furnace materials test No 5



Jussi Vänskä. Report 22.12.2011

Åbo Akademi (ÅA) reports:

- <u>Co-firing black liquor and biomass</u> Nikolai DeMartini, Esperanza Monedero, Patrik Yrjas, Mikko Hupa. Report 24.8.2009
- <u>Corrosion tests of superheater materials in reducing conditions Part 1</u> Patrik Yrjas, Dorota Bankiewicz. Report June 2010
- <u>Utilization of Pyrolysis Gases from the Recovery Boiler Preliminary studies</u> Mikko Hupa, Nikolai DeMartini, Anders Brink, and Markus Engblom. Report 15.12.2010
- <u>Co-firing black liquor and biomass, Phase 2 report</u> Nikolai DeMartini, Niklas Vähä-Savo, Mikko Hupa, Report 19.4.2011.
- <u>Corrosion tests of superheater materials in reducing conditions Part 2</u> Patrik Yrjas, Dorota Bankiewicz. Report February 2012.
- <u>Dew Point Measurements in Rauma and Heinola mill</u>
 Nikolai DeMartini, Emil Vainio, Tor Lauren, Mikko Hupa. Report December 2011.
- Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler Tor Lauren, Emil Vainio, Nikolai DeMartini, Mikko Hupa. Report December 2012.

Lappeenranta University of Technology (LUT) reports:

- <u>Phenomena of transformation in recovery boiler char bed</u> Tanja Pentinsaari. Report 5.11.2009.
- <u>Once-through and reheater recovery boiler concept studies</u>
 Vakkilainen Esa, Kaikko Juha, Hamaguchi Marcelo. Report 15.2.2010.
- Pulp mill optimal steam pressure levels
 Aapo Hiltunen, Esa Vakkilainen, Report 26.7.2011.

Oulu University (OU) / CEWIC reports:

- <u>Reduction of TOC from recovery boiler make-up water</u> Tero Luukkonen. Report 18.4.2010.
- <u>Recractory materials/ceramics in recovery boiler furnace</u> Riku Mattila. Report 2.5.2011.
- <u>Activated carbon and UV-treatment in TOC removal- field tests</u> Tero Luukkonen, (JP-Analysis) Jaakko Pellinen (JP-analysis), Jaakko Rämö (OU), Ulla Lassi (OU). Report February 2011
- <u>Comparison study of active carbon grades</u>

Emma Tolonen (OU), Jaakko Pellinen (JP-analysis), Tero Luukkonen (Pacs), Hanna Runtti (OU), Ulla Lassi (OU), Jaakko Rämö (OU). Report June 2012

3.2 Final seminar

Final seminar was held on 20.10.2011 at Sokos Hotel President Helsinki. The following presentations were held:

- Project summary
 Esa Vakkilainen, Lappeenranta University of Technology
- Co-firing black liquor and biomass laboratory tests
 Nikolai DeMartini, Åbo Akademi
- Dew point measurements in Rauma and Heinola
 Nikolai DeMartini, Åbo Akademi
- Improving heat recovery in biomass-fired boilers project presentation Doug Singbeil, FPInnovations
- Full scale material exposures in Joutseno recovery boiler Martti Mäkipää/Markku Orjala, VTT
- Corrosion tests of superheater materials in reducing conditions
 Dorota Bankiewicz, Åbo Akademi
- Field tests of furnace materials
 Timo Karjunen, Boildec Oy / Pekka Pohjanne, VTT
- Refractory materials/ceramics in recovery boiler furnace
 Riku Mattila, Oulu University
- TOC removal methods and water quality guidelines
 Maija Vidqvist, Teollisuuden Vesi Oy
- Activated carbon and UV-treatment in TOC removal- field tests
 Tero Luukkonen, JP-Analysis / Oulu University

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3.3 International co-operation

SKYREC project was presented the following papers/seminars.

- Finska Sodahusföreningens verksamhet 2009, Markus Nieminen, Sodahuskonferensen 2009, Stockholm, October 2009.
- SKYREC-project review, Esa Vakkilainen, Keijo Salmenoja, Improved Heat Recovery in Biomass-Fired Boilers - Kick-off Meeting, Oak Ridge, December 2009
- Finnish Recovery Boiler Committee 2009 review, Markus Nieminen, Inspecta Skog 2010, Sundsvall, March 2010.
- Co-firing black liquor and biomass in a laboratory single droplet reactor effects on emissions and combustion characteristics, Nikolai DeMartini, Esperanza Monedero, Patrik Yrjas, Mikko Hupa, International Chemical Recovery Conference 2010, Williamsburg, Virginia, March 2010
- Co-firing black liquor and biomass in a laboratory single droplet reactor effects on emissions and combustion characteristics, Nikolai DeMartini, Esperanza Monedero, Patrik Yrjas, Mikko Hupa, Tappi Journal, September 2010
- Finska Sodahusföreningens verksamhet 2010, Markus Nieminen, Sodahuskonferensen 2010, Stockholm, October 2010.
- SKYREC-project review, Esa Vakkilainen, Keijo Salmenoja, Improved Heat Recovery in Biomass-Fired Boilers - Annual review meeting, Tampa, January 2011
- Finnish Recovery Boiler Committee 2010 review, Markus Nieminen, Inspecta Skog 2011, Sundsvall, March 2011.
- Reduction of total organic carbon in recovery boiler make-up water with active carbon filtration, Tero Luukkonen, Reijo Hukkanen, Jaakko Pellinen, Jaakko Rämö, Ulla Lassi, Powerplant Chemistry, 2/2012



SKYREC FINAL REPORT

4 **PROJECT BACKGROUND**

Recovery boiler size keeps increasing, FIGURE 4-1. The recovery boiler size doubles about every 20 years. Boilers with over 200 square meter bottom area are typical for the largest new greenfield mills. The largest recent proposals have been for a 7000 tds/d boiler. Average boiler size has typically been about half of the largest boiler bought. The recovery boiler is now challenging circulating fluidized bed boilers for the title of largest bio-fuel fired boiler. Recovery boiler furnace size is about the size of the largest natural circulation coal fired boilers. This means that the existing mechanical and commercial limits of furnace size for natural circulation units have now been reached. These challenges mean further research.



FIGURE 4-1. Size of the recovery boiler as a function of purchase year.

Black liquor dry solids has always been limited by the ability of available evaporation technology to handle highly viscous liquor. As technology has evolved so has the final black liquor dry solids. The virgin black liquor dry solids of recovery boilers is shown in FIGURE 4-2 as a function of purchase year of that boiler.

On average the virgin black liquor dry solids content has increased. This is especially true for latest very large recovery boilers. Design dry solids for the new green field mills and new recovery islands have been either 80 or 85 % dry solids. In Asia and
South America 80 % (earlier 75 %) dry solids is in use. In Europe 85 % (earlier 80 %) dry solids is in use.



FIGURE 4-2. Virgin black liquor dry solids as a function of purchase year of the recovery boiler.

The main steam temperature of recent recovery boilers is shown in FIGURE 4-3 as a function of MCR capacity of that boiler. The average steam temperature increases with size. Small boilers tend to have lower pressures to reduce specific cost. There are many boilers with main steam parameters higher than 500 °C. Recovery boiler market share development is shown in FIGURE 4-4.





FIGURE 4-3. Main steam temperature as a function of recovery boiler capacity.



FIGURE 4-4. Recovery boiler market share

4.1 Objectives

The primary interest was to increase recovery boiler electric efficiency to a new level. In preceding SoTu II- research program methods for laboratory and in situ tests were developed which results were utilized in this project. Project aim wasn't to resolve single company research and development issues, but to gain general knowledge for number of companies to utilize.

Emphasis was in situ tests which would provide practical information to increase the recovery boiler power-to-heat ratio material and maximize electricity production. Recovery boilers usually have high demand for make-up water compared to utility boilers. This calls for care to be taken to eliminate organic matter in water treatment when increasing main steam pressure and temperature. The aim was to update the water treatment and water chemistry guidelines to correspond future recovery boilers and study effect and behavior of water chemicals in elevated temperature and pressure.

There have been other projects (TULIKOR, SOMA, and SOTU2) that have objective to increase recovery boiler electric efficiency. In these projects the emphasis has been in the material technology and aim to provide knowledge for current recovery boilers. Boiler manufacturers have had also own projects to increase recovery boiler power to heat ratio. SKYREC project concentrated issues that have not studied before.

4.2 Ways

Ways to achieve the project objectives were defined in the project planning phase:

- Literary research
- Laboratory tests
- In situ tests
- Writing guidelines and distributing information

4.3 Organisation

Project manager was Finnish Recovery Boiler Committee chairman and steering committee was established to manage the project economics and scientific orientation. Every cost sharing partner had member in the steering committee. FRBC's sub-committees, mostly durability sub-committee and black liquor sub-committee participated by directing the sub-projects. Project organization is presented in FIGURE 4-5.

SUOMEN SOODAKATTILAYHDISTYS FINNISH RECOVERY BOILER COMMITTEE



*Sumitomo joined the project autumn 2008

FIGURE 4-5. Project organisation and coordination.

4.4 Budget

The original project budget was 700 000 \in (of which TEKES 350 000 \in). When Sumitomo joined the project autumn 2008, budget increased to 805 000 \in , TABLE 4-1.

Partner	Share	2008	2009	2010	lotal
Andritz Oy	7 %	25 000 €	20 000 €	5 000 €	50 000 €
Metsä-Botnia Oy	7 %	25 000 €	20 000 €	5 000 €	50 000 €
Metso Power Oy	7 %	25 000 €	20 000 €	5 000 €	50 000 €
Stora-Enso Oy	7 %	25 000 €	20 000 €	5 000 €	50 000 €
Sandvik	7 %	25 000 €	20 000 €	5 000 €	50 000 €
UPM-Kymmene Oy	7 %	25 000 €	20 000 €	5 000 €	50 000 €
FRBC	7 %	25 000 €	20 000 €	5 000 €	50 000 €
Tekes	50 %	175 000 €	140 000 €	35 000 €	350 000 €
Total	100 %	350 000 €	280 000 €	70 000 €	700 000 €
Sumitomo		35 000 €	35 000 €	35 000 €	105 000 €
Total		385 000 €	315 000 €	105 000€	805 000 €

TABLE 4-1 SKYREC-budget

4.5 Schedule

The planned schedule was 2.5 years (1.1.2008 - 30.6.2010) The project had to apply for 12 months extension. The reason was the economic turndown in 2009 which caused temporary shutdowns to pulp mills and measurement projects in operating recovery boilers could not be completed as planned.



THE PROJECT

The SKYREC-project was divided into four work packages:

WP1	New recovery boiler concepts
WP2	Increasing superheated steam temperature
WP3	Increasing recovery boiler pressure
WP4	Ensuring boiler and feedwater quality

5.1 NEW RECOVERY BOILER CONCEPTS (WP1)

The work package 1 (WP1) studied the new recovery boiler concepts to increase the electricity generating potential and energy efficiency of recovery boilers. Most of the concepts weren't studied previously.

One objective of the work package was to determine if mixing other biofuels in with black liquor would alter the combustion characteristics of the black liquor. Other subproject concentrated to get reliable information of the dew point and low temperature corrosion conditions in recovery boiler flue gas ducts and flue gases coolers. Aim is to maximize the heat that can be utilized from the flue gases through the use of heat recuperators. One sub-project studied possibilities for extracting gases from the lower part of a recovery boiler, to be used in the lime kiln instead of fossil fuels.

5.1.1 Once-through and reheater recovery boiler – concept studies

In this study several recovery boiler concepts were compared with the whole pulp mill energy balance being considered. Steam and electricity generation for each recovery boiler case was calculated to study how this might increase the electrical efficiency, TABLE 5-1.

The studied concepts were:

- A. Natural circulation 82 %, 490 °C, 9.0 MPa (10 year old, reference Joutseno)
- B. Natural circulation 85 %, 505 °C, 10.2 MPa (new, reference Kymi)
- C. Natural circulation 85 %, 515 °C, 12.0 MPa (high steam values, reference Yonago)
- D. Assisted circulation 85 %, 540 °C, 16.0 MPa (reference SoTu)
- E. Natural circulation 85 %, 515/400 °C, 12.0/3.4 MPa (SkyRec)
- F. Once-through 85 %, 540/460 °C, 26.0/5.4 MPa (SkyRec+)

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		Joutseno	Kymi	Yonago	SoTu	SkyRec	SkyRec+
Case		Α	в	С	D	E	F
Capacity	tds/d	5500	5500	5500	5500	5500	5500
capacity (virgin)	tds/d	5005	5005	5005	5005	5005	5005
Dry solids	%	82.0	85.0	85.0	85.0	85.0	85.0
Main steam pressure RB	bar(a)	94.0	104.0	124.0	164.0	124.0	264.0
Main steam temp. RB	°C	490.0	505.0	515.0	540.0	515.0	540.0
Steam generation							
Steam flow RB	kg/s	215.0	226.4	233.6	232.0	224.0	218.5
Change in steam flow	%	0.0	5.3	8.6	7.9	4.1	1.6
Electricity							
Pulping usage total	MW	87.6	88.1	88.9	90.2	88.2	93.2
Mill total usage	MW	91.1	91.7	92.4	93.8	91.8	96.8
Electricity production	MW	149.3	153.9	161.8	175.6	162.3	177.9
Surplus electricity	MW	58.2	62.2	69.4	81.7	70.5	81.1
Efficiency to electricity	%	20.4	20.4	21.4	23.2	21.5	23.5
Change in electricty	MW	0.0	4.0	11.2	23.6	12.3	22.9
	%	0.0	6.8	19.3	40.5	21.1	39.4
Cost							
Cost difference	M€	9.2	0.0	6.5	17.1	24.3	27.0
Electricity difference	MWe	-4.0	0.0	7.3	19.6	8.3	19.0
Cost for additional	k€/MWe	-2310	0	890	875	2921	1422
Price of extra power	€/MWh	-57.8	0.0	22.2	21.9	73.0	35.6

TABLE 5-1. Steam and electricity generation for each case

Conclusions:

- The increase in electricity generation seems very profitable up to case C.
- Modern recovery boiler (Case C) does produce about 20 % more electricity than roughly ten years ago, (Case A).
- From cost of additional power, going to assisted circulation concept of 540 °C steam (Case D) seems desirable. ~40% electricity increase.
- Reheater boiler concept (Case E) seems not at all profitable. The additional electricity generation was only marginal.
- Once-through recovery boiler (Case F) did produce as much additional electricity (~40%) than the assisted circulation (Case D), but higher cost.
- The pulping electricity usage is not constant. The main parameter that changes is the recovery boiler feedwater pump power requirement
- One of the most successful ways to increase electricity generation form recovery boilers has been the implementation of different preheating schemes

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5.1.2 Co-firing black liquor and biomass

The objective of this work was to determine if mixing other biofuels in with black liquor would alter the combustion characteristics of the black liquor. The four biofuels mixed with black liquor were bark, wood chips, peat and biosludge. The specific variables followed were swelling, carbon evolution (CO 2 + CO), and NO formation tendency. There were changes in all of these, but not for all mixtures and that the level of added fuel made a difference.

The largest changes in swelling were seen for peat and bio-sludge addition. The cause of these changes is not clear as 13,2 % and 25,5 wt % peat addition resulted in higher and lower swelling respectively when compared to the black liquor. Similarly, the 0,8 % biosludge mixture resulted in more swelling, while the swelling of the 1,8 % biosludge mixture had swelling similar to the black liquor.

The char burning stage is on average increased only slightly by the addition of bark, wood chips and biosludge, but more significantly by peat, especially the 25,5 wt% peat mixture FIGURE 5-1. This was caused in part by the significantly lower swelling of this mixture. Peat also had a significant impact on NO formation, resulting in an increase in NO formed during both the devolatilization and char burning stages. The other fuels did not result in a significant change in the NO formed.



FIGURE 5-1. Times of the combustion stages (drying, devolatilization, and char burning) for the fuel mixtures

Wood, bark and peat all resulted in more cyanate, with peat resulting in the largest increase. This is consistent with the nitrogen content of the mixtures, with the peat-BL mixture having the highest nitrogen content.

Increasing wood generally resulted in longer char burning and total combustion times while devolatilization times were about the same for all wood addition levels, FIGURE 5-2. There was no sharp transition as there had been with 26% peat, though the 50 wt-% d.s. wood appeared to result in a significant increase in combustion time and therefore 35 wt-% wood was also studied. Combustion times for the 26% and 35% wood mixtures were similar and longer than for 13%, but shorter than for 50%.



FIGURE 5-2. Devolatilization, char burning and total combustion times for 4 different addition levels of dry wood with black liquor.

5.1.3 Utilization of Pyrolysis Gases from the Recovery Boiler - Preliminary studies

This work was carried out to study possibilities for extracting gases from the lower part of a recovery boiler, to be used in the lime kiln. The extracted amount should be such that it would cover the need of a lime kiln with 30 MW thermal input, typical at a $500\ 000 - 550\ 000$ ADt pulp mill.

FIGURE 5-3 presents the heating value of the gas as air factor corresponding to the composition (chemical equilibrium at 900°C). The amount of gas to be extracted to cover 30 MW is indicated for two cases. The sensible enthalpy is excluded in calculation of the amount of gas needed. In addition to the heating value, the gas

would contain some energy because of its temperature. Taking zero degrees Celsius as the reference temperature, in the case of 10kg/s extracted, the gas would contain 30 MW as heating value and about 9 MW as sensible enthalpy; the sensible enthalpy being 30% compared to the heating value of the gas. In the case of 3 kg/s extracted, there would be about 3 MW sensible enthalpy, which is 10% compared to the heating value. Results from existing CFD simulations of two recovery furnaces were analyzed for the local gas composition in the lower furnace.



FIGURE 5-3. Gas heating value as function of air factor, from equilibrium calculations at 900°C. Region of air factors which would result in adiabatic temperatures below 900°C also indicated

The following conclusions are made:

- Extraction of gas with a heating value of 3 MJ/kg could be feasible with normal recovery boiler operation.
- Existence of suitable location for gas extraction depends on recovery boiler operation. A high fuel-to-air ratio, for example, close to a furnace wall would be desirable.
- Dust load is estimated to be in the range $30-80 \text{ g/Nm}^3$
- Factors not included in this study, but which could be relevant to consider include: modifications to recovery boiler operation to maximize gas heating value; gas extraction; and removal of dust from the extracted gas

5.1.4 Pulp mill optimal pressure levels

Pulp mills are trying to increase their profitability by improving energy effectiveness and intensifying production in mills. One way to improve electricity production in mills is to lower steam pressures in pulping processes. In that case steam can be expanded to lower pressure in turbine. However, lowering the steam pressures increases also investment costs of mill because of bigger pipe sizes and heat transfer areas.

In this work is specified the economically optimal steam pressures for Finnish pulp mill types producing 600,000 tons of pulp per year. In the work for different pulp mill types used in Finland were formed energy balances and investment estimations in accordance with steam pressure levels. Energy balance calculations were done with Millflow-calculation application. The optimal steam pressure levels were determined on the bases of energy balances and cost estimations. The investment costs accordant with low pressure steam level were calculated for the part of piping, pulp dryer and evaporator.

On the bases of the results it is economically profitable to choose the lowest possible steam pressure levels defined by pulping processes and equipment's, FIGURE 5-4.



FIGURE 5-4. Electricity price and steam pressure level effect to sale income in traditional pulp mill

In addition in the work was estimated the effect of lowering the middle pressure steam and sootblowing steam pressures for electricity production in pulp mills. In the work was also examined profitability of building own middle or low pressure steamlines for some pulping processes. For this master's thesis was also gathered information about steam pressures used in Finnish pulp mills and about the reasons of choosing the pressure levels.

5.1.5 Dew Point Measurements in Rauma and Heinola mills

During combustion of black liquor some SO_2 is formed. The concentration of SO_2 varies between zero and several hundred ppm depending on a number of boiler operating conditions such as liquor dry solids content and air distribution. A small part of this SO_2 oxidizes further to form sulfur trioxide (SO_3). As the flue gas temperature drops in the convective pass SO_3 reacts with water vapor to form sulfuric acid (H_2SO_4):

SO 3 (g) + H 2 O(g) \rightarrow H 2 SO 4 (g)

The gaseous sulfuric acid starts to form an acid mist below the acid dew point or condensate on cold surfaces. The sulfuric acid dew point temperature at different H_2SO_4 (g) concentrations is shown in FIGURE 5-5. Below 100°C practically no gaseous H_2SO_4 is found in the flue gas.



FIGURE 5-5. Sulfuric acid dew point temperature in a flue gas with 15 and 25 vol-% H₂O

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Severe low-temperature corrosion may occur on cold surfaces, e.g., the air-pre-heaters or flue gas duct if their material temperature is below the acid dew point. This kind of corrosion can be avoided by keeping all cold end surfaces above the acid dew point.

There is an increased interest in efficient use of the flue gas energy even down to temperatures lower than today and clearly below the normal acid due point temperatures (< 120°C). However, very little information is available for the corrosion tendency in recovery boiler flue gases at these lower temperatures. The objective of this study was to get reliable information of the dew point in recovery boiler flue gas ducts and of corrosion tendencies of surfaces having these low temperatures 70-110°C. Dew point measurements were made with a commercial instrument ("Land") and corrosion measurements with air-cooled probes and samples analyzed with SEM-EDS.

At the Rauma Kraft mill the dew point measured was equal to the water dew point, 62-64°C, FIGURE 5-6. Neither SO₂ nor H_2SO_4 was found in the flue gas. Corrosion started below 65°C, i.e. below the dew point of water.



At the Heinola sulfite mill a somewhat elevated dew point of water was found. This can be the high amount of and the hydroscopic nature of Na_2SO_4 . The concentration of SO_2 was between 1200-1600 ppmv, in dry gas, before the scrubber. The measured H_2SO_4 was below 1 ppmv measured with the salt method and 1-4 ppmv measured with controlled condensation method. This implies that there is a reaction between



H₂SO₄ with Na₂SO₄ to form acidic NaHSO₄. At 80°C significant corrosion was observed.

The study would indicate that corrosion should not occur to any significant extent in the economizers under normal operating conditions due to acid dew point corrosion. One hypothesis is that the corrosion is caused by acidic condensates during shutdowns and water washes.

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

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. The question then came up, 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.

Two probes were inserted into the economizer section at Rauma at the same time. Both probes were kept at 90 °C by air cooling. One was pulled just prior to the planned recovery boiler shutdown and the second was pulled after the water wash. A temperature of 90°C was chosen because it is well above the water dewpoint, even in the presence of HCl and salt, but below a H₂SO₄ dewpoint, FIGURE 5-7.



FIGURE 5-7. Water dew point and acid dew points based on 200 ppm HCl or 1 ppm H₂SO₄ as well as the measured dew point at Rauma.

It is also well above the temperature water is absorbed by the salt due to the hygroscopic nature of salts such as Na_2SO_4 or $NaHSO_4$, but only $NaHSO_4$ is not present in the dust in Rauma. The presence of Na_2SO_4 is expected to result condensation at temperatures a few degrees C° above the water dew point. The choice of 90 °C was confirmed by two 2h probe studies, one at 80 °C and one at 75 °C. The flue gas temperature in the economizers was about 150 °C and did not drop below about 110 °C during normal operation.

The first probe was pulled out after 811h of normal operation and the probe was covered in ash. There was virtually no corrosion on the probe, FIGURE 5-8. 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.



FIGURE 5-8 Ring after 811h normal operation. No iron oxide was found on the bottom edge of the probe.

The corrosion layer was pitting up to approximately 10 μ m. 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 negligible amount of corrosion seen along with the lack of sulfur in the corrosion layer indicated clearly that there is no acid dew point corrosion.

The second probe that was pulled out after the water wash and annual shutdown had more corrosion than the probe pulled out before the water wash, but there was still virtually no corrosion. Again, the bottommost edge was not corroded. The average corrosion for the two probes estimated on an annual basis was 0.02 and 0.06 mm/year for the probes pulled out before and after the water wash respectively.

After the water wash and after acid washing the inside of the tubes, oil was burned in the boiler. 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. Dew point and SO_3 were measured during oil burning at three different points, the bull nose and two different points in the economizer. No acid dew point was measured. The highest SO_3 level measured was about 3 ppm when four burners were firing oil, TABLE 5-2.

TABLE 5-2 Sampling positions and SO₃ results. b.n.:bull nose.

Date	Time	MP	SO ₃ (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
	13:10-20	1	3	165	4
	16:27-16:37	2	3	240	4
-1	16:53-17:13	2	2	240	4

Conclusions:

No significant corrosion seen under normal operation or after the water wash for the probes held at 90°C. It was clear that there was no acid dew point corrosion due to H_2 SO₄ formation during normal operation and 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, but the results clearly show no acid dew point corrosion during normal operation of a modern Kraft recovery boiler.

5.2 INCREASING SUPERHEATED STEAM TEMPERATURE (WP2)

During the combustion process in the recovery boilers, the carryover particles convey often unburned C which increases risk of fireside corrosion. Based on earlier investigation the influence of reducing conditions remained unclear.

One goal of work package 2 (WP2) was to estimate the resistance/behaviour of the chosen boiler steam/superheater tube under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in a reducing atmosphere.

Other objective of the work package was to study the corrosion performance of various superheater tube materials in recovery boilers at high material temperatures.

5.2.1 Corrosion tests of superheater materials in reducing conditions, part 1&2

Part 1

Sub-project objective was to estimate the resistance/behaviour of the chosen boiler steam/superheater tube under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in a reducing atmosphere. The tests were performed using a laboratory method for studying high temperature corrosion developed at Åbo Akademi. The method is based on the estimation of the oxide/corrosion layer thickness or/and depth of the material degradation. The recognition of the oxide/corrosion layer composition is also included.

The material samples were exposed to high temperature in a horizontal tube furnace for 168 h (7 days), at 450°C - 600°C. The furnace was equipped with a tightly closed glass reactor. The composition of the gas flowing through the reactor during the tests was 5% CO, 95% N₂ with a flow of 2.0 l/min. After the corrosion test, the specimens were allowed to cool down to room temperature inside furnace with a continuous flow of the gas mixture through the reactor. The samples were then ready to be analyzed with SEM/EDX in order to identify various chemical elements. The corrosion products were identified using x-ray images. The corrosion layer thickness was determined using scanning electron microscope back-scatter images.

The materials can be classified as two low alloy steels: ferritic (10CrMo9-10) and martensitic (T91), high nickel austenitic stainless steel (S28) and nickel based austenitic stainless steel (HR11N). Synthetic ashes salt 5, salt 8, salt 9 and salt 10 are

introduced with respect to previous project dealing with the same salts and are used for comparison and recognition purposes. The chemical compositions of the synthetic ashes used in the experiments are shown in FIGURE 5-9.

Broadly speaking, the chosen composition of the tested salts could be explained as follows:

- Salt 5 reference salt only potassium sulfate containing black liquor does not exist
- Salts 8 and 10 "represent" black liquors with low and low/medium Cl content
- Salt 9 no potassium unlikely for the black liquor. Prepared in order to check what is the role of K.





For the salts where no potassium was added and just 0.3 wt% of CI⁻ (Salts 5 and 9) only low corrosion rates were observed. The exception was 10CrMo with Salt 5 at 600°C where the corrosion rate was slightly increased as with the HR11N nickel based austenitic stainless steel with Salt 9 at 600°C. An explanation based on the temperature sensitivity of the sulfate reduction is proposed.

The results showed that salts containing both potassium and chlorine in the salt mixture (when comparing four tested salts) induced corrosion:

- at reducing conditions for all steels \geq 550°C

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at ambient conditions for low grade steels especially ≥ 500°C, for all steels ≥ 550°C
 (T₀ of the K containing salts slightly above 500°C)

In reducing conditions and high temperature (600°C):

- Low grade steels were destroyed mainly by grain boundary corrosion
- Austenitic steels underwent heavy depletion of Cr from the surface

Sulfur was often found on the corrosion front beneath the depleted surface of the bulk material suggesting formation of metal sulfides. This was typically but not exclusively observed in the cases of high alloy steels, S28 and HR11N.

In a previous project (SOTU2) the same salts have been used for corrosion tests in ambient atmosphere. A comparison of these results for Salts 5, 8, 9, and 10 in ambient and reducing atmosphere is presented below on separate graphs (FIGURE 5-10).



FIGURE 5-10. The mean oxide layer/corrosion product thickness of the tested materials in ambient (green bars - oxy) and reducing atmosphere (red bars- red). The corrosion tests duration 168h.

Reducing conditions induced mainly internal attack of the steel and in ambient conditions growth of the oxide layer was promoted. Ambient atmosphere appeared to be more harmful than reducing. Thermodynamic calculations in combination with the results and the literature give indications that no significant reduction of sulfate to sulfide occurred below 600°C and even at 600°C this reaction was limited. In combination with the corrosion results this also further suggests that the corrosion in reducing conditions is strongly dependent on Na_2S formation in combination with a melt being present.

Part 2

In the part 1 of the project it was concluded that only a low reduction level of sulfate to sulfide was achieved with the test setup used. Thus, in Part 2 black liquor (BL) char and Na₂S (simulating reduced Na₂SO₄) were added to the previously tested salts (5 and 10). Same four materials (10CrMo9-10, T91, Sanicro 28 and HR11N) were tested in reducing atmosphere ($95N_2$ -5CO vol%) at 525°C and 565°C.

The chemical composition of the synthetic ashes used in the experiments is shown in TABLE 5-3. The difference between Salts 5 and 10 and 5r 10r in a fact that in salts 5r and 10r part of Na_2SO_4 (10 mol%, 50 mol% or 90 mol%) was replaced with Na_2S and additionally 5 wt-% of BL-char was added to each mixture. The numbers 10, 50 or 80 (mol%) after "r" stands for the amount of Na_2S instead of Na_2SO_4 in the salt mixtures.

Salt	Na ₂ SO ₄	Na ₂ S	K2SO4	KCI	BL char	T0, °C
	1	mol	6		wt%	
5	100					886
5r10	90	10	0	0	5	585*
5r50	50	50	0	0	5	583*
5r80	20	80	0	0	5	571*
10	78		17	5		
10r10	70	8	17	5	5	494
10r50	39	39	17	5	5	498
10r80	15	62	17	5	5	513

TABLE 5-3. The detailed compositions of the salts and their first calculated melting points, T₀.(Part 2)

The exposures to Salt 5r10, Salt 5r50 and Salt 5r80 resulted in high corrosion of the low alloy materials, 10CrMo9-10 and T91, FIGURE 5-11. The corrosion products were very brittle, voluminous and had a form of curled flakes. The flakes composed of Fe, O and high amounts of C. The high alloy materials, Sanicro 28 and HR11N,



performed well under the tested conditions. The corrosion measured on those materials did not exceed $10 \,\mu$ m.



FIGURE 5-11. The mean corrosion layer thickness of the tested materials with Salts 5r10, 5r50 and 5r80 in reducing atmosphere at 525°C and 565°C. The corrosion tests duration 168 h.

The exposures to Salt 10r10, Salt 10r50 and Salt 10r80 resulted in an extreme corrosion of low alloy materials, 10CrMo9-10 and T91, FIGURE 5-12. The corrosion product thickness was measuring a few hundred μ m. The morphology and the composition of the corrosion products was similar to the one observed after exposures with salts 5r. Also significant corrosion was measured on the HR11N in most of the tests. Some exposures indicated slightly better resistance, but since no clear trend could be observed in this case, no finite conclusions can be drawn. The Sanicro 28 performed best out of tested material, however, a clear corrosion was observed at 565°C with the highest amount of Na₂S in the salt.



FIGURE 5-12. The mean corrosion layer thickness of the tested materials with Salts 10r10, 10r50 and 10r80 in reducing atmosphere at 525°C and 565°C. The corrosion tests duration 168 h.

The results from tests with two salts 5r10 and 10r10 (both at 565°C) in reducing conditions were compared with results from oxidizing conditions (at 600°C) with corresponding salts 5 and 10, FIGUREs 5-13 and 5-14.



FIGURE 5-13. The mean corrosion layer thickness with Salt 5r10 at 565°C in reducing atmosphere and Salt 5 at 600°C in oxidising atmosphere



FIGURE 5-14. The mean corrosion layer thickness with Salt 10r10 at 565°C in reducing atmosphere, Salt 10 at 600°C in oxidising

The comparison of the results showed that reducing conditions and reduced salts were more aggressive to the tested materials, especially to the low alloy steels 10CrMo9-10 and T91, although the comparison was made to results obtained at a higher

temperature. The corrosion layer thickness on austenitic stainless steels was measurable but $<10 \ \mu m$ under reducing conditions in tests with Salt 5r10 while in tests oxidizing conditions with Salt 5 no corrosion was detected. The results for HR11N with Salt 10r10 under reducing conditions at 565°C were comparable to the results obtained from tests under oxidizing conditions with Salt 10 at 600°C while Sanicro 28 performed better in a reducing environment with Salt 10rX.

5.2.2 Full scale material exposure in Joutseno

Objective of the sub-project was to study the corrosion performance of various superheater tube materials for recovery boilers at high material temperatures. Full scale material exposures were carried out in Joutseno recovery boiler by September-October 2010. Materials selected for the study were 347H, AISI 310, HR11N, SAN 28, Super 625 and SAN 69. Two identical cooled probes with 6 material samples in each were exposed in the boiler for a time of one month. Nominal material temperatures on the exposed side of each probe were 530 °C and 570 °C. The boiler operated at 80% dry solids firing mode using softwood liquor with some 0.1 chlorine as fuel.

The surface temperatures of the probes vary depending on the direction of the flue gas flow. The windward temperature is maintained constant by adjusting the cooling rate and the temperatures on other sides change when deposits are formed. The terminology of different measuring directions is presented in Figure 5-15 and the experimental setup in Figure 5-16.



FIGURE 5-15. The terminology of different measuring directions on the probe referring the flue gas flow is presented above.





FIGURE 5-16. Probe ready for insertion through an inlet located about one meter below the sootblower at level 10¹/₂, between 2nd and 3rd superheater.

Corrosion conditions were found to be highly variable depending on the flue gas flow direction and the temperature exposure history. Maximum metal loss was typically observed to occur on the leeward side of the probe. The extent of metallic corrosion at locations was, however, related to the presence of chloride. Corrosion morphologies noticed are known as typical of each material tested in terms of oxide scale growth, grain boundary attack and internal penetration.

The materials ranking according to the maximum total metal loss typically found on the leeward side of the probe for each material tested was considered to be as: SAN 28 < 347H < AISI 310 < HR11N < SAN 69 ~ Super 625 (best). Predictive calculations referring to deposit conditions with about 0.5 % chloride, 5 % potassium and certain amount of carbonate resulted to a similar ranking considered to be as: SAN 28 < 347H<AISI 310 < HR11N < Super 625 ~ SAN 69 (best).

Performance of the six materials tested is considered as unsatisfactory, Super 625 and possibly SAN 69 excluded, in the actual test conditions; i.e., at such conditions where the probes were exposed to steam blowing from a close vertical distance and at average tube material temperatures of about 570 and 540 °C, peaking for short time up to 590°C. There exist, however, no major quantitative or qualitative differences

between the results of the present study and recent full scale recovery boiler and laboratory test data available in the literature taking in regard the temperature sensitivity of the corrosion phenomena in question and the statistical nature of the extent of localized corrosion in place and time, FIGURE 5-17.



FIGURE 5-17. Schematic presentation of extrapolated corrosion data applied from two different sources. Experimental exposure time in RB superheater area in each case is as follows. This study: 600 h; Keiser et al [2010]: 1000 h.

5.3 INCREASING RECOVERY BOILER PRESSURE (WP3)

Increasing boiler pressure induces a corresponding increase in tube temperature in steam generator. Operational experiences from current boilers indicate that AISI 304L (3R12), which has been the most commonly used furnace material, suffers from accelerated corrosion at than normal operation temperatures, which are sometimes encountered when internal surfaces in furnace wall tubes are covered with thick scale. Maximum material temperatures in a high pressure boiler are about 400°C, when internal surfaces are clean. With scaling, material temperatures may become higher even 440°C. These temperatures would be normal at high pressure boilers, and thus AISI 304L appears non-suitable cladding material for high pressure boilers. Currently few alternative materials are used, such as Sanicro38 and HR11N, but their corrosion resistance at high temperatures has not been thoroughly studied and operational experiences are still limited. Also other highly alloyed materials are available, but data on their corrosion resistance are lacking.

The objective of this work package was to test different potential furnace and refractory materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. Also the phenomena of transformation in char bed which affect to structure and thermal properties of the char bed have studied in this work package.

5.3.1 Phenomena of transformation in recovery boiler char bed

The phenomena of transformation in char bed which affect to structure and thermal properties of the char bed have studied in this work. Also those factors, which caused these phenomena, have studied. These factors are internal thermal and physical changes (temperature differences, associated stress, structure and density change) in the char bed and the outside factors (large ash chunk falling from the superheaters, boiler load and liquor spraying change), which are caused by the changes in recovery boiler driving situation.

The overall shape and composition of char bed is well defined. Recovery boiler char bed consists mostly of combustion residue. It contains unreacted carbon, sodium carbonate, sodium sulfate, sodium sulfide and sodium chloride with smaller amounts of similar potassium compounds. The structure is partly porous, but contains rocklike sintered sections. Both passive and active parts of the char bed are relatively porous and light. The heat capacity per volume is much less than e.g. rocks. Thermal conductivity of char bed is close to insulating materials. The heat stored in the char bed is about 4200MJ/m 2 and the heat stored in smelt is 340MJ/m². At full capacity new heat is brought at about 3MJ/s. The char bed contains considerable amount of heat.

Cooling of the char bed has been problematic especially when the boiler has been stopped though emergency shutdown. Then it can happen that the char bed is large and contain molten smelt. One must prevent smelt water contact. This can bet be done so that the char bed is disturbed as little as possible. The char bed is let to cool and all smelt is let to solidify before the water wash is started to minimize the possibility of explosion. During emergency stoppage the fuel flow is closed and most of the water in the boiler is drained. The char bed top surface cools by convection and the bottom tubes are operated at temperature corresponding to the boiler pressure. These outside changes are fast compared to char bed cooling time. The bed has been with sodiumbicarbonate (NaHCO₃), which is a solid powder like chemical. Another tried cooling chemical has been liquid carbondioxide (CO₂), which in storage pressure to atmospheric pressure causing cooling. The cooling increase from additional cooling remains unproven.

Cooling model was created by using 1-dimensional ADL-model in experimental part of this work, FIGURE 5-18. The model is based on Stora Enso Oulu recovery boiler char bed measuring report. Cooling diagram was made by a function of temperature and depth by using the ADL-model. The results agreed with the measuring results.

Bed height [m]	Cooling time [h]
0.1	2.5
0.2	6.5
0.4	19
0.6	39
0,8	69
1	108
1.2	154
1.4	202
1.6	255
1.8	313
2	382

FIGURE 5-18. Total required time to cool charbed to less than 500°C.



5.3.2 Refractory materials/ceramics in recovery boiler furnace

Refractory materials are widely used in recovery boiler lining and the significance will increase in high pressure recovery boilers. Current, the most commonly used, materials performance won't probably fulfill future high pressure recovery boilers criteria.

The aim of the study was to determine what refractory materials have better performance than traditionally used materials. In situ tests were done at Stora Enso Oulu mill in 16.2–2.3.2010 and 4.4.2011–18.4.2011. The first test of different refractory materials was for two weeks in the recovery boiler liquor gun holes (both sides of the boiler). The appearance of the test materials after the two weeks indicated that wear off was quite similar in different sides of the furnace, castables need to be stronger (some broke off during steel frame take out) but fewer sement and dense materials were quite good, FIGURE 5-19.



FIGURE 5-19. Refractory materials after test

Because of this performance, the decision was to find harder ZrO_2 castable and improve spinel and other castables bonding to be more chemically resistant by nanospinel. Result was that there is no harder ZrO_2 castable in the market and

nanospinel manufacturing failed due to laboratory accident. For the 2nd test it was decided to use best from 1st test and Hassle B1800 castable.

Second field test data also indicated that mechanically weak materials won't last; although they are chemically stable against black liquor char and dense material wear off by thermal shock and cracks easily. So wear off numbers are a bit misleading, TABLE 5-4.

Findings of the study were that best material is Hassle D39A castable which is already in use. ZrO_2 and full spinel castables could have the potential but lacking of manufacturers. More tests need to be made before final conclusion can be made for MgO*Cr2O3 potential against Hassle D39A castable.

Frame position	Test material	Wear off
1	Dense Al2O3	0-0 mm
2	MgO-iron brick	5-13 mm
3	Hassle B1800 castable	+5-10 mm
4	Hassle D39A castable	10-20 mm
5	Al2O3*MgO spinel castable	30-48 mm
A1	Dense Al2O3	25-32 mm
A2	MgO-iron brick	10-18 mm
A3	Hassle B1800 castable, lost in funace	-
A4	Hassle D39A castable	2-5 mm
A5	Al2O3*MgO forming castable	10-19 mm

FABLE 5-4.	Second to	est wear-off	results
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5.3.3 Field tests of furnace materials

The goal of this work was to test different potential furnace materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. Maximum cladding temperatures in a high pressure boiler are about 400°C, when internal surfaces are clean. With scaling, cladding temperatures may become higher and, consequently, the test temperature was selected to be 440°C.

The setup consists of natural circulation circuit which includes steam generator in which the test materials are placed, FIGURE 5-20. The steam generator is installed into liquor gun opening so that the front wall, consisting of the test materials, is at same level with furnace wall tubes. The natural circulation circuit is cooled by air. Air flow is controlled so that the circuit pressure is kept constant. The set point for circuit pressure is selected so that the heat transfer liquid saturation temperature is 40°C higher than water saturation temperature at 169 bar pressure. This yields cladding temperatures 40°C higher than at 169 bar pressure, i.e. about 440°C. The heat transfer liquid used in the experiments is diphenyl oxide, which allows the circuit operation at moderate pressure.



FIGURE 5-20. Steam generator front wall with tested materials and experimental setup before installation into liquor gun

The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test matrix is shown in TABLE 5-5. After the tests the material performance was assessed with thickness measurements and

metallographic analysis. The wall thickness profiles of the test samples were measured before and after testing with coordinate measurement machine, as a function of circumference from three axial locations (Z = 15, 25 and 32 mm) so that from each location 100 points were measured, FIGURE 5-21.





After exposure, before the measurements the samples were thoroughly washed under water with nylon brush and rinsed with ethanol to remove deposits. In tests No.1-3 (test time 1000 hour) the materials were tested in as received condition, whereas in tests No.4 and 5 (test time 2700 hours) the outer and inner surfaces were machined and hand grinded/polished prior assembly to the probe. The grinding and polishing was performed to improve the accuracy of wall thickness measurements. For metallographic analysis one cross-section per sample (Z = 15 mm) was prepared and analysed with scanning electron microscope (SEM). The composition of oxide layers and deposits was determined with energy dispersive spectroscopy (EDS).

The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. Tests were done in Oy Metsä-Botnia Ab Joutseno recovery boiler.

Test 1:	Test 2:	Test 3:	Test 4:	Test 5:
Mar 2 - Apr 15, 2010	May 15 - Jun 20, 2010	Jul 16 - Sep 6, 2010	Feb 2 - Jun 6, 2011	Jul 26 - Dec 19, 2011
1006h	1023h	1250h	2700h	2630h
AISI 304L (reference	AISI 304L (reference	AISI 304L (reference	AISI 304L (reference	AISI 304L (reference
material)	material)	material)	material)	material)
A ISI 310S (3RE28)	Sanicro 67	Super 625	Carbon steel	HR11N
		(Sumitomo "N")		(Sumitomo "R")
Sanicro 38	HR11N	HR11N	Sanicro 67	Sanicro 38
	(Sumitomo "R")	(Sumitomo "R")		
Sanicro 28	A ISI 310S (3xRE28)	Sanicro 38	Super 625	Sanicro 28
			(Sumitomo "N")	

 TABLE 5-5. Test schedule and chosen materials

Results

The coordinate measurement machine proved its applicability to determine wall thickness profiles from difficult shapes. In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test. This caused some error to the measurement results; especially to the maximum corrosion rates calculated from the tests No. 1-3, where the materials were tested in as received condition i.e. when the samples had surface scratches and dents. Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing. Their adverse effect was clearly seen as negative average corrosion rate values in most resistant alloys.

Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.

In current tests highest corrosion rate, ca. 4 mm/a, was measured for the carbon steel as expected. The traditional composite tube material 3R12 had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C. Based on the results of 3R12 the reproducibility of the probe tests was so good that different probe tests can be used to compare different materials to each other.

In current tests no marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were in the order of 0.15...0.2 mm/a in the long term (>2000 h) test, i.e. about four times lower than that of the 3R12 (FIGURE 5-22).

46 (69)



FIGURE 5-22. Calculated maximum corrosion rates for the 3R12, HR11N, Sanicro 38, Super 625 and Sanicro 67 materials from the probe test No. 1 - 5.

In short term (<1000 h) tests the corrosion resistance of the 3RE28, 3XRE28 and Sanicro 28 were as good as or even slightly better than that of the Sanicro 38 or HR11N (FIGURE 5-19). Because the 3RE28 and 3XRE28 were not included in the long term tests and no results were obtained for the Sanicro 28 from the long term test No. 5, due to the misplaced thermocouple, it is recommended to verify their promising performance with long term tests in the future.

The results for the Super 625 were inconsistent. In short term 750 h test at 430 °C it's corrosion resistance was only slightly better than that of the 3R12, but in the long term 2154 h test at 440 °C it's resistance was even better that of the Sanicro 38 and HR11N (Figure 5-23). Similar kind of behaviour was observed in Sanicro 67. In short term 744 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion rate was only 1/10 of that of the Sanicro 38 and HR11N and 1/5 of the Super 625.

47 (69)



FIGURE 5-23. Calculated maximum corrosion rates for the 3RE28, 3XRE28, HR11N and Sanicro 38 from the probe test No. 1-3 and 5.

5.4 ENSURING BOILER AND FEEDWATER QUALITY (WP4)

There are two primary sources of carbon-based molecules in a recovery boiler or in the steam it produces: compounds that enter with makeup water and organic treatment chemicals. Organic compounds in the make-up water originate from raw water (mainly natural organic matter, NOM), organic internal water treatment chemicals and impurities (lubricants, oils, degraded ion exchange resins etc.). Organic compounds decompose at high temperatures and pressures of the water-steam cycle. The higher the temperature and the pressure, the greater the decomposition of organic compounds that occurs. Therefore TOC removal efficiency has a link to energy efficiency. End products are low molecular weight organic acids (mainly formic and acetic acid), ammonia and carbon dioxide. Organic acids and carbon dioxide are related to corrosion in a water-steam cycle although there is some controversy on their relevance.

Recovery boilers which supply steam to many separate processes, resulting in incomplete recovery and losses of condensate, are often integrated as part of a large factory complex. Therefore large quantities of make-up water are needed and even relatively very small amounts of impurities (e.g. organic compounds) present in the make-up water can have dramatic negative effects on the operation of a water-steam cycle. So, organic compounds in the cycle are one of the most important challenges in water-steam cycle chemistry.

Work package 4 (WP4) objectives was to study the characteristic of carbon-based molecules and their effect on water-steam cycle corrosion. One aim was to study effect and behavior of water chemicals degradation products in elevated temperature and pressure. Other aim was to investigate the removal of organics from recovery boiler make-up water with different methods and to update the water treatment and water chemistry guidelines to correspond future recovery boilers.

5.4.1 Organic amines and natural organic matter in steam water cycle

The first sub-project of the work package was literature survey to organic amines and natural organic matter in steam water cycle. Aim was to get information about properties of organic alkalizing amines used in Finland, estimate effect on condensate quality based on current data and degradation products, estimate effect of amines on air heater corrosion and make brief review of the role of natural organic matter ingress.

The literature is rich with documentation of the methods' mechanisms and results as well as the products into which treatment chemicals break down as they are exposed to the temperatures and pressures of the steam cycle. For years, the vast majority of fossil-fueled and nuclear plants have treated their boiler water with carbon-based chemicals—amines. The positive effect of these chemicals on pH and corrosion prevention is well known. However, effect of these chemicals on high pressure and temperature steam drum boilers is not clear and both sides debating whether organics do more harm than good to boilers can trot out data to support their position.

Limit values for organics difficult to set:

- No conclusive evidence that breakdown products of TOC are harmful to materials of construction
- Type of TOC must be taken into account
- Type of cycle chemistry has an impact of breakdown of TOC

However VGB R450 L (2004) states dissolved organic carbon (DOC) content in make-up water should not exceed 0.2 ppm. It is recommended to strive for less than 0.1 mg/l. (the knowledge of the type of organics is very important and not the sum parameter DOC). Even the lowest value might be too high in special cases, depending on the nature of organic matter and make-up water demand. As general rule high make-up rates require a minimization of the DOC content but the limit shall be determined plant specific.

By literature survey and air heater corrosion cases it is estimated that the failures are caused by two-phase FAC (flow accelerated corrosion)

- Failures occur on temperature range 140 180 °C
- Failures occur on two-phase zone
- Failures occur on areas where equipment geometry promotes turbulent flow
- Environment and failure mode are similar compared to air cooled condensers and low pressure feed water heaters in fossil boilers

Prevention of FAC:

- For air cooled condensers the current approach is to operate with higher pH in the range of 9.6 to 9.8 or even above.
- Dimensioning or structural means to reduce turbulence
- Use of chromium alloyed construction materials (minimum 1,25 % recommended)
- If two phase FAC exists chromium alloyed steel is probably most cost effective solution in utility boilers and HRSG's – (this will of course just address FAC locally and not the root cause of the problem)
- Local pH adjustment for example feeding amine to air heater steam line.

5.4.2 Effect of organic amines to magnetite layer formation

When organic compounds enter the boiler they are exposed to extreme temperature and pressure. If the compound is volatile, it is carried over into the superheater tubing. Under these conditions, most organic compounds break down. Amines and nitrogencontaining oxygen scavengers produce ammonia, and carbon molecules form CO2 and a host of carboxylic acids such as formic, acetic, butyric, propionic, and glycolic acid.

Aim was to study the effect of alkaline chemicals on the protective oxide layer (magnetite) on the inner surface of the recovery boiler in 340 °C. The rate of thermal degradation and concentration of decomposition products alkaline were also studied. Chosen amines were: cyclohexylamine, 2-amino-2-methyl-1-propanol, morpholine and ammonia as reference. These compounds are generally used as boiler water chemicals.

During the tests degradation of chemicals where monitored with on-line pHmeasurement and concentration of amines with capillary electrophoresis (ppb level). Magnetite layer formation to polished and pre-oxidized samples was monitored by EIS (Electrochemical Impedance Spectroscopy). Test arrangement is shown in FIGURE 5-24.



FIGURE 5-24. Test arrangement

From studied amines morpholine had the best thermal resistance (340 °C) and 2amino-2-methyl-1-propanol the weakest, FIGURE 5-25. Concentration of decomposition products was minimal, in low-oxygen water degradation products are mainly low molecular weight amines and alcohols, not organic acids. Accurate analysis of low concentration degradation products needs qualitative methods.



FIGURE 5-25 Change in hydroxyl ion concentration during test (~ 340 °C)

After 12 hours the magnetite layer had been developed on the surface of polished samples, FIGURE 5-26. Potential was on the thermodynamic stability zone of magnetite. Alkaline amines had effect on magnetite layer properties of polished and pre-oxidated samples. Ammonia and morpholine had more large oxide particles on the



sample surface. According to mass transfer resistance there was no significant difference in corrosion rate between the tested amines.



FIGURE 5-26. Change in potential (funktion on time) of polished carbon steel sample (\approx 340 °C)

5.4.3 TOC balances

Aim of the sub-project was to study the organic compound levels between boilers that use and don't use volatile organic water treatment chemicals and compare different make-up water sources and water treatment effect on the amount of organic matter make-up water. Total organic carbon (TOC) and anion concentrations were measured.

Measurements from water-steam cycle were done between 30-31.3.2009. Mill uses the Kymi-river as raw water source, demineralization is done by ion exchange and water chemistry is so-called inorganic. Chemical treatment consists of trisodium phosphate, Na_3PO_4 (pH adjustment), hydrazine, N_2H_4 (to scavenge the oxygen) and ammonia NH_3 (alkalinity control). TOC-balances are presented with and without organic water treatment chemicals.

Normal water chemistry balance, FIGURE 5-27:

- TOC content in make-up water doesn't exceed 0,2 mg TOC/l.
- Balance figures are logical
- Make-up water MB (mixed bed) doesn't remove organic matter coming from ion exchange
- steam quality fulfills guidelines value (< 0,1 mg TOC/l)
- TOC-load of water chemicals is negligible



FIGURE 5-27. TOC-balance, normal water chemistry

TOC-balance without volatile organic water treatment chemicals was also measured, FIGURE 5-28. Balance was made after chemical dosing pumps were stopped and when condensate direct conductivity and cation conductivity before mixed bed exchanger was almost same. The process was without volatile chemicals over 10 hours.

Balance without volatile chemicals

- TOC content in make-up water exceeds 0,2 mg TOC/l in the end ion exchange cycle.
- despite increased TOC content steam quality fulfills guidelines value (< 0,1 mg TOC/l)



FIGURE 5-28. TOC-balance without volatile organic water treatment chemicals

5.4.4 TOC-removal methods and their applicability in make-up water treatment

This literature study aim was to clarify different water treatment methods and their TOC removal efficiency. As conclusion the conventional way (chemical precipitation + ion exchange) has long been recognized as a technology capable of removing many dissolved compounds from water that cause water quality problems but in the future there will be other methods as well. Summary of different water treatment methods is presented in TABLE 5-6.

Over 90 % of organic compounds are typically removed with the combination of conventional chemical water treatment and demineralization processes. There are how-ever electrically neutral fractions (e.g. polysaccharides, proteins and low molecular weight compounds) present in surface waters that remain in the produced make-up water. As a result, conventional demineralization performed by ion exchange cannot remove these fractions effectively.

In boiler water treatment granular activated carbon (AC) filters are conventionally used as a last step before demineralization whilst powdered AC can also be used after the coagulation phase in a water treatment process. AC can effectively remove organic compounds (especially high molecular weight species) by adsorption and by operating as a bioreactor. The biological mechanism requires certain levels of nutrients in the water before accumulation of microorganisms is sufficient. However the question of microorganisms contaminating treated water often arises if the water to be treated is very pure.

The 185 nm wavelength UV-treatment is used to TOC reduction, however these systems are only moderately effective to remove TOC. But UV can also be used for TOC reduction as part of an Advanced Oxidation Process (AOP). In general, AOP refers to the process of using UV photolysis of ozone (O_3) and/or hydrogen peroxide (H_2O_2) to create hydroxyls which increases TOC reduction.

Nanofiltration uses less energy than reverse osmosis since the membrane elements have larger pores and have lower feed pressure requirements. Reverse Osmosis (RO) membrane treatment is an effective treatment process for water systems with brackish water supplies. Nanofiltration was developed on the same principles as RO, but can effectively remove contaminants from raw water with total dissolved solids lower than 1,000 mg/L.

Reverse Osmosis is one of the best technologies removing TOC from waters. RO is a membrane treatment technology and can achieve up to 90% removal of low-molecular-weight organic compounds and organic acids. Nanofiltration (NF) efficiency to remove these low-molecular-weight organic compounds is lower, but in some cases nanofiltration is feasible. Nanofiltration uses less energy than reverse osmosis since the membrane elements have larger pores and have lower feed pressure requirements.

A new magnetic ion exchange resin (MIEX) has been developed in Australia for use in a continuous ion exchange process that overcomes many of the problems associated with conventional ion exchange systems. The MIEX resin has been specifically designed for the removal of dissolved organic carbon (DOC) from drinking water supplies. MIEX resin is not limited to only DOC removal and will remove other negatively charged ions (anions) from water such as sulfates, sulfides and arsenate.



Removal method	Principle	TOC- reduction rate	Comments and notes
UV-AOP	Destroys neutral organic molecules with the help of OH- radicals. Decomposition products are carbon dioxide and organic acids, which can be removed with ion exchange.	30 % > 30 % when combined with ion exchange	Efficiency depends on the inlet TOC and actual organic components present in the water. Could be installed also before ion exchange, but preferably after strong anion before mixed bed filter. Some units installed to achieve TOC guarantee level of 0,2 mg/l.
UV- 185 nm	Destroys smaller organic non-ionic components to CO_2 .	2070 %	The system is used in ultrapure water units. Not competitive, if TOC concentration > 0,1 mg/l
Reverse osmosis	Removes efficiently TOC. Cut-off value for non-ionic compounds > 100 g/mol.	> 95 %	The best available technology to remove biopolymers and unharged organic molecules.
Nanofiltration	Removes efficiently both organics and ionic compounds. Cut-off value for non-ionic compunds is > 300500 g/mol.	8090 %	Alternative treatment for chemical treatment with simultaneous salt removal (6080 %). Colour removal units in operation e.g. in Norway for waters with high TOC values.
Activated Carbon	Based on adsorption. Capacity dependent on water quality and TOC components. Efficiency may be very high with the new filters.	2080%, 50% for biological filters with high retention times.	Is used within drinking water treatment units to remove taste and odour. After first operation period the efficiency in TOC removal retains.

TABLE 5-6. Summary of the different water treatment methods and TOC removal

5.4.5 Reduction of TOC from recovery boiler make-up water

The first part of this experimental work was to determine the TOC removal efficiency of an existing water treatment process (plant A) and to compare that with two other water treatment processes (plants B and C) using the same raw water source (the Oulu River). Second task was to evaluate whether activated carbon (AC) can be used to treat demineralized water in order to reduce the residual TOC level without posing a risk of contaminating the water with, for example, microorganisms.

Plant C supplies potable water while plants A and B produce demineralized process water. The main differences in the processes are the coagulation-flocculation chemicals employed and the use of an ozone-AC combination at plant C. A comparison of the results of the three water treatment processes is shown in FIGURE 5-29. The comparison is based on three series of samples collected over the period 24.09.2009 - 20.10.2009.



FIGURE 5-29. Comparison of TOC levels after each process stage for all three water treatment plants using the Oulu River as a raw water source.

As expected, raw water at all three plants had practically the same TOC level $(11.7-11.9 \text{ mg L}^{-1})$ during the sampling period. There is a remarkable seasonal TOC variation in the Oulu River, in 2009 TOC level varied between $10 - 20 \text{ mg L}^{-1}$. Plant C has a more efficient coagulation-flocculation-flotation stage (78 % TOC reduction) than plants A and B (71 % reduction). One possible reason for this is the ferric sulphate coagulation chemical used at plant C since ferric-based coagulants generally removes NOM better than aluminium-based chemicals. AC filtration at plant C only reduced the TOC level by 17.4 %, which was due to long operation cycles. The AC filter had already been in use for 4.5 years at the time of sampling. The ion exchange series at plants A and B removed a substantial part of the remaining TOC.

As expected anion exchangers removed most of the TOC since electrically charged NOM is usually anionic because of carboxyl groups. Finally the MB exchangers acted as polishing filters and removed 69 % of the remaining TOC present at plant B and 5.2 % present at plant A. It is possible that anion exchangers were not working efficiently at plant B during the sampling.

Removal of organics from recovery boiler make-up water with (AC) was investigated in pilot scale experiment. One pilot scale AC filter unit was installed inside a stream at plant A and monitored over the period 19.12.2009–27.2.2010. The ACs used in the experiment was acid washed low ash content AQUACARB 607C 14X40. The results of TOC measurements are presented in FIGURE 5-30.



FIGURE 5-30. TOC measurement results of pilot AC filter test

Overall, the AC filter removed about 60 % of TOC and there was no difference between water flows 1-3,5 l/min. However, the reduction decreased in the end of experiment. This might be due to moving the filter (noncontinuos flow), filtering hot condensates or lye which is used to regenerate of the anion resin.

As a conclusion, AC filtration is a potential technology for TOC removal from demineralized water.

5.4.6 Activated carbon and UV-treatment - field tests

In this project activated carbon (AC) experiments was continued both in pilot and full scale. In addition removal of organics from recovery boiler make-up water with ultra violet (UV) treatment in pilot scale was investigated. Total organic carbon (TOC), conductivity, silica concentration and composition of organic compounds were monitored during the experiments.

AC was used in a novel way to remove organic compounds from demineralized water. AC is conventionally used before demineralization, but when implemented later in the process the lifetime of AC can be extended. Demineralized water was treated further with an AC filter followed by a mixed-bed ion exchanger (MB). In pilot scale tests there was also a subsequent AC filter after the MB unit, FIGURE 5-31. TOC reductions were monitored for 11 months and 3 months in pilot scale filters and full scale AC filters, respectively.



FIGURE 5-31. Testing scheme of pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB).

Other task of the project was to evaluate whether UV treatment can be used to treat demineralized water in order to reduce the residual TOC level. Also contact time and use of oxidizing chemicals effect to removal rate was studied. Experimental setup of pilot scale UV treatment is presented in FIGURE 5-32.



FIGURE 5-32. Experimental setup of pilot scale UV treatment.

As result UV treatment was able to remove up to 30 % of residual TOC but removal efficiency did not improve with increased number of UV chambers (contact time), wave length (more energy), H_2O_2 (oxidant) and TiO₂ (catalyst).

One possible reason for this result is that demineralized water TOC content is too high for UV treatment. Water should be pretreated with e.g. RO which is normal procedure in microelectronic or pharmaceutical industry water treatment. Reason for negligible effect of TiO₂ catalyst might due to type of catalyst porous net. Experimental set-up with H^2O^2 oxidant failed because plastic piping released organic compounds. Medium pressure lamp (wavelength peaks at 254 nm and 185 nm) was much better (30 % TOC removal) than low pressures lamp (wavelength peak sharply at 185 nm) which effect was negligible.

The results of TOC measurements during the pilot scale AC filter tests are presented in FIGURE 5-33a. Overall, the first AC filter removed 38–70 % of TOC, the MB unit up to 12 % and the second AC filter up to 13 %. Furthermore, the MB unit and especially the second AC filter occasionally increased the TOC level.





FIGURE 5-33. TOC measurement results of pilot (a) and full scale AC filter tests (b)

The role of the second AC filter after the MB unit seems to be insignificant in terms of TOC reduction, however dissolved organic carbon (DOC) levels measured with the LC-OCD method showed that the second AC filter removed a substantial part of residual DOC (TABLE 5-7). The role of the MB unit is important since conductivity increases extensively in an AC filter. The MB unit removes ionized inorganic material which is released from the AC bed. However, the identity of this ionized material remains unclear.

TABLE 5-7. Composition of organic compounds in different parts of the water treatment process. Samples were collected on 22.9.2011. All concentrations are stated in μ g L⁻¹

	DOC	Hydrophobic	Hydrophilic				
			Biopolymers	Humic substances	Building blocks	LMW neutrals	LMW acids
Raw water	7 832	635	155	4 758	1 267	976	41
Chemically treated water	3 136	541	56	803	1 038	698	n.d.
Demineralized water	155	29	22	n.d.	26	72	5
AC1 filtered water	62	2	18	n.d.	9	31	3
After pilot MB	125	n.d.	32	n.d.	30	49	14
AC2 filtered water	37	n.d.	14	n.d.	5	17	2

TOC reductions measured in the full scale AC filter are shown in FIGURE 5-33b. The TOC reductions were between 40–65 % and were slightly higher than those measured with the pilot scale filters. The conductivity of filtered water increased similarly as with the pilot scale filters and so a subsequent MB unit was needed to reduce conductivity.

It was hypothesized that if an AC filter could operate biologically, then the conductivity increase would be due to the conversion of organic carbon to carbonate. However, colony forming unit (CFU) counts of the AC filtered water showed that there was no or insignificant biological activity. Furthermore the nutrient content of

demineralized water is too low to allow microorganisms to accumulate. This is actually beneficial as microbial activity in the AC bed could possibly endanger the water quality.

Organic fractions removed with AC were mainly decomposition products of humic substances (so-called building blocks) and low molecular weight neutral organic compounds. These fractions are characterized by an electrically neutral structure, which is the reason why ion exchange cannot remove them effectively.

As conclusion, activated carbon filtration with acid washed AC is a suitable method for the reduction of residual TOC in demineralized water both in pilot and full scale. Based on the experiments UV treatment is non-competitive technology for TOC removal from recovery boiler demineralized water due to high energy consumption and investment costs.

5.4.7 Comparison study of active carbon grades

This project in follow-up for the activated carbon (AC) field tests project. The aim was to study open issues from previous project such as active carbon operation mechanism, conductivity increase and AC grade differences. Understanding active carbon operation model would help to optimize the AC filter operation. One task of the project was to evaluate the effectiveness of impregnated active carbon versus non-impregnated active carbon in the removal of TOC. Also effectiveness of oxidation (ozone and hydrogen peroxide) before AC filter was tested.

Comparison between active carbon grades was carried out in pilot scale; test arrangement is presented in FIGURE 5-34. Totally four grades were chosen, three acid washed active carbons (AQUACARB 607C, CPG-LF, GAC 1240 PLUS) and one non-acid washed active carbon (GCN 1240). Technical data of active carbon grades are presented in TABLE 5-8.

	GAC 1240 PLUS	CPG-LF	AQUACARB 607C	GCN 1240
Acid Wash	Yes	Yes	Yes	No
Material	Coal	Coal	Coconut shell	Coconut shell
Particle size	0,425 - 2 mm	1,2 - 1,4 mm	0,425 - 1,4 mm	0,425 - 1,7 mm
lodine number	> 950 mg/g	> 950 mg/g	1100 mg	> 1100 mg/g
Ash content	Not Indicated	< 0,5 %	<1%	Not indicated

TABLE 5-8. Technical data of tested active carbon grades



FIGURE 5-34. Test arragement comparing different active carbon grades

Adsorption of organic molecules from demineralized water on active carbon material is depending on the characteristics of the organic molecules and the active carbon and the solution chemistry. The specific mechanisms by which the adsorption of many compounds, especially organic compounds, takes place on this adsorbent are still ambiguous.

There were no differences between active carbon grades regarding TOC removal efficiency. TOC removal efficiency was about ~40%. This is in line with previous active carbon studies. Non-acid washed was as effective as acid washed active carbon. Dissolved organic carbon (DOC) level and composition of organic compounds (ppb) measured with the LC-OCD method are presented in Figure 5-35. All active carbon grades removed the hydrophobic compounds, part of neutral organic compounds and decomposition products.

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FIGURE 5-35. Composition of organic compounds in deminaralized water and after AC filter (ppb).

The term impregnation is defined as the fine distribution of chemicals and metal particles in the pores of AC. It is known that AC absorption capability or reactivity towards certain molecules can be enhanced by impregnation with metals such as silver, copper, nickel, aluminum and iron. In this study TOC removing efficiency of silver impregnated AC, Fe(III) impregnated AC and Fe(IV) impregnated AC TOC removing efficiency from demineralized water was tested in pilot scale. The measured TOC removal efficiency was about ~40% which is the same efficiency as active carbon without any impregnation

Oxidation before active carbon filter can used to increase the removal of organic compounds. Ozone is a powerful oxidant which reacts with organic matter in water through two different ways, the so-called direct and indirect reactions. Ozone/AC system could eliminate organic micropollutants of low reactivity with ozone by enhancing ozone transformation process into OH radicals and/or adsorption on the surface of activated carbon. Ozone (54,73 mg O₃/min) and hydrogen peroxide (1 ppm) was applied in a vessel (45 l) filled with deminarized water with a residence time of 40 minutes. Oxidized demineralized water was passed through the active carbon filter (CPG-LF, capacity 5 l) and mixed-bed ion exchanger (Purolite MB400, capacity 5 l) with flow rate 0,8 l/min. Ozone and hydrogen peroxide was tested separately and together. Either ozone or hydrogen peroxide did not lower the TOC, so the role of the oxidation before the AC filter unit seems to be insignificant in terms of TOC reduction.

5.4.8 Water quality and water treatment guidelines

Water treatment and water chemistry are essential to the safe operation of black liquor recovery boilers. The guidelines presently used in the plants are based on old norms, on the values given by boiler or by chemical suppliers, and on best practices based on plants' own experiences. There has been a need for updating and standardizing the guidelines for some time since the boiler pressure has increased in new boilers, the capacities of the old plants have been increased, the usage of the new chemicals has increased, and the monitoring of the water chemistry is largely done by on-line measurements.

Guidelines will show the present state of the water chemistry and they are applied to the recovery boilers within the pressure range from 6.0 to 16.0 MPa. VGB, EPRI and Värmeforsk water chemistry guide lines and recommendations are used as a reference point. The guidelines do not comment the measures how make up water is processed to the desired quality. It is assumed that from any kind of raw water source it is possible to produce make-up water with the required quality but both the technique and the cost will vary. When writing the guidelines, both the safe and the economical production have been thought.



The report has been structured in a way it is both the guide book and the water chemistry work book. The guidelines have been shown in the separate tables and FIGUREs, for example condensate quality requirements, TABLE 5-7 and operation area of phosphate chemistry, FIGURE 5-27.

TABLE 5-9. Condensate quality (minimum requirement)

Condensate					
		Ammonia	Ammonia and organic amine		
pН		8.5	- 10.0		
Cation conductivity	mS/m	< 0.05	<0.08		
Direct conductivity	mS/m	<	1.0		
SiO ₂	µg/kg	< 20			
Na	µg/kg	< 20			
тос	µg/kg	<200	<600		
O ₂	µg/kg	≤ 20			
Fe	µg/kg	≤ 10			
Cu	µg/kg	≤ 5			
Hardness	dH	< 0.01			



Compared to the heat and power boilers, recovery boilers have special features not found in the other power plants. They are the high heat flux in the boilers, the steam usage in the air pre-heaters, the probable contamination of the process condensates, the great portion of the make-up water in the feed water and the increasing usage of the organic conditioning chemicals.

One of the main objectives of this work is the increase of the control of the steamwater cycle in the situations when there is a high concentration of the organic substances in the feed water, when there are possible leakages to the condensates and when the feed water consists 30...40 % of make-up water. Different action levels and responsible person are presented in TABLE 5-8.

Action level or range	Characterisation	Responsibility for action	Action during operation	Action during start-up
0	Normal operation value. Water chemistry related problems are eliminated.	Operator	The maintenance of chemical control through the monitoring of key parameters.	
0 -AL1	Acceptable range. Water chemistry related problems and increase of costs unlikely.	Water Chemist	Identify the possibilities for optimisation. Justify the cost of improvement.	
AL1				
AL1 – AL2	Loss of chemical control possibly leading to long term damage.	Operator	Find and eliminate the cause within one week of operation. Further actions to minimise possible damage.	Action level 1 for key parameters should be achieved in 24 hours after turbine start-up.
AL2				
AL2 – AL3	Loss of chemical control possiblly leading to short and long term damage.	Operator	Find and eliminate the cause withing one day.Further actions to minimise damage.	AL2 for steam parameters until turbine is brought into service.
AL3				
AL3 Outside	Chemistry out of control connected with immediate damage	Operation manager or supervisor	The unit is recommended to be shut down within 1 hour using normal shut down procedures if one of the key parameters is outside AL3.	Boiler blow- down or condensate drain until AL3 is attained for the key parameters.

TABLE 5-10. Action levels and responsible persons

The second important part of the guidelines is to give instructions how to control and follow water chemistry. It emphasizes the use of most comprehensive and reliable on line analyzers combined with the manual sampling and the laboratory analysis. The alternatives for the extensive and time consuming measuring routines have been found from the other standards, e.g. ASME and EPRI. The objective has been to find the

required minimum number of the measurements by putting the emphasis on the quality of the measurements instead of quantity. Quality recommendation for 16 MPa drum boiler, inorganic chemistry with no Cu-metals is presented in FIGURE 5-28.



Kuva 5-37. Water quality recommendation for 16 MPa drum boiler, inorganic chemistry

In addition to the actual guidelines and to the monitoring instructions estimations on the benefits achieved by the better quality water are explained. They include efficiency improvement, decrease in the corrosion rate and minimization of the deposit formation both in the boiler and in the turbine. In case of being below or over the limits the included tables describe the possible reasons, explain the seriousness of the abnormalities with action limits and give instructions for checks and procedures.

The condensate polishing and the selected technology e.g. mixed bed and softening ion exchange are fundamentally connected to the recovery boiler processes due to occasionally poor quality condensates and due to the use of the organic conditioning chemicals making them demanding processes to run and follow up. Thus, the quality of condensates, the applicability and the functionality of the condensate polishing have been considered as its own entity.