Finnish Recovery Boiler Committee

# SKYREC STEERING COMMITTEE MEETING 1/2012

TIME April 12th, 2012 10.00 – 15.00

PLACE Pöyry Finland Oy, Vantaa

PARTICIPANTS

| | |
|---|---|
| Matti Tikka | UPM-Kymmene Oyj, Kymi, chairman |
| Lasse Koivisto | Andritz Oy, Varkaus |
| Hidenori Ogawa | Sumitomometal Industries,Ltd. |
| Timo Peltola | Sandvik, Helsinki |
| Mika Paju | Oy Metsä-Botnia Ab, Joutseno |
| Keijo Salmenoja | Andritz Oyj, Helsinki |
| Timo-Pekka Veijonen | Chairman of Finnish Recovery Boiler Association |

Group members without a right to vote:

| | |
|---|---|
| Esa Vakkilainen | LUT, project coordinator |
| Markus Nieminen | Finnish Recovery Boiler Association, secretary |

Other:

| | |
|---|---|
| Pekka Pohjanne | VTT (part time) |
| Dorota Bankiewicz | Äbo Akademi (part time) |

APPENDICES

1 Summary of the appendices
2 Project budget and schedule 12.4.2012
3 ÅA, Dew point measurements – final report 7.12.2011
4 ÅA, Corrosion tests in reducing conditions, PART II – presentation 12.4.2012
5 ÅA, Corrosion tests in reducing conditions, PART II – final report 15.2.2012
6 VTT, composition analyses of 3RE28 and 3xRE28 materials
7 Boildec Oy, Field tests of furnace materials – test report No.5 22.12.2011
8 VTT, Analysis of the furnace test materials – presentation 12.4.2012
9 Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment – final report 28.2.2012
10 Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment – PPChem article 2/2012

DISTRIBUTION
Steering committee and their substitutes
Durability Sub Committee, Black Liquor Sub Committee
Board of the FRBC
MNN, PLA

# 1 CALLING MEETING TO ORDER

## 1.1 Absences

| | |
|---|---|
| Martti Korkiakoski | Tekes |
| Kalle Salmi | Metso Power Oy, Tampere |
| Reijo Hukkanen | Stora Enso Oyj |
| | |
| | |

## 1.2 Agenda

Åbo Akademi project: corrosion tests in reducing conditions – PART II was discussed first.

## 1.3 MEMO of the previous meeting (3/2011)

The memo of the previous meeting was accepted.

# 2 MEETING DECISIONS

PROJECTS:
Åbo Akademi, Dew point measurements
- Final report was accepted

Åbo Akademi, Corrosion tests in reducing conditions – PART II
- Final report was accepted

Boildec Oy, Field testing of furnace materials
- Report from test No. 5 was accepted

VTT, Analysis of the furnace test materials
- VTT will do the re-analyses and then write final report before the summer holidays.

Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment
- Final report was accepted

PROJECT IDEAS:
- Dew point, part 2 offer will be inquired from Åbo Akademi
- Last projects will decided by e-mail

OTHER ISSUES
- Writing the final report in English is on-going

# 3 BUDGET

Budget (situation 12.4.2012) is presented in APPENDIX 1

Ordered work sum is currently 764 258,37 €, from which 748 908,37 € is already paid. Project budget is 805 000 € so we have 40 741 € left.

TEKES refund is complete (350 000 eur), last part was paid in February.

## 4 TIME SCHEDULE

Schedule (situation 12.4.2012) is presented in APPENDIX 1.

One project is still ongoing:
- VTT: Analysis of the furnace test materials

Last furnace test (No. 5) was completed in December 2012, but analyses of test materials are still ongoing. Final report from the analyses will be completed before the summer holidays.

Writing the final report in English is ongoing. Secretary will send the final report for comments when it is ready.

## 5 FINISHED PROJECTS

You can download all the memos, reports, presentations, videos that has been published so far from the download system:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/ListOfDownloadableFiles?Openview

## 6 ONGOING PROJECTS

### 6.1.1 Åbo Akademi, Dew point measurements

**Objective:**
Make dew point measurements, SO3 measurements and corrosion measurements in two boilers: one Kraft boiler with the possibility of operating with low and high SO2 and O2; and Heinola’s NSSC boiler with extremely high SO2 Measurements would be taken behind the ESP, before any scrubber.

The purpose is to get reliable information of the low temperature corrosion conditions in recovery boiler flue gases being cooled further.

All material about this project can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/982c9bb8c552f1e2c225784500511608?OpenDocument

**Status and schedule:**
Results were presented in previous meeting (3/2011) and final report was received in December 2011, APPENDIX 2.

Conclusions:

- Dewpoint
  - Acid dewpoint was not found at either mill
  - Water dewpoint was measured in Rauma
  - Elevated dewpoint found at Heinola, but not acid dewpoint
- H2SO4
  - Isopropanol method was not applicable
  - Salt method appears to work well
  - H2SO4/SO3 theory needs further clarification
- Corrosion
  - At Rauma corrosion started below 65 °C (dewpoint was 62-64 °C)
  - At Heinola, corrosion started at 80-90 °C (slightly higher than the dewpoint)

**Decision:**
Final report was accepted.

**Comments:**
- HCl dew point would be also interesting to measure, it is close to water dew point
- Not only concentrate to SO3, also other sulphur species?
- One week dew point measurement with high SO2 in Rauma seems difficult in environmental and boiler fouling point of view.
- Temperature for maximum corrosion about 20 C lower than the dew point
- If $H_2SO_4$ and $SO_2$ is not detected -> below detection limit
- Could we have HCl in the fuel gas?

**Questions and answers:**

**Question 1:** How good were measuring/determing dew point in recovery boilers
**Answer 1:** Our dew point meter is measuring the conductivity between two mirror electrodes at the probe tip. The temperature of the probe tip is controlled. When the probe tip reaches the dew point temperature a current between the electrodes is recorded.

**Question 2:** Does carbon steel corrode when close to the dew point. How long SO2/SO3-periods cause considerable corrosion
**Answers 2:** I need to come back to you on this.

**Question 3:** In Rauma you can adjust the SO2 level with oil burner, is this adjustablity that you looking for?
**Answer 3:** How long periods are they willing to burn oil? Wouldn't it be quite costly to do that for 4-5 days? Adjustability is not as important as steady conditions. We want one normal test run with no SOx and one with higher SOx. What is a level of SO2 the mill can live with for 4-5 days. I assume emission limits are also an issue. We have not set suggested levels of SO2 yet, but high SO2 should be high for the mill.

**Question 4:** Dew point measurements (can you measure pH of the condensing gas)
**Answer 4:** No pH measurement in the dew point meter, but if we come up with a method of collecting condensate then we could measure pH.

**Question 5:** Flue gas samples SO3 (Do you have hydrogen peroxide wash and filter?)
**Answer 5:** SO2/SO3 measurements with impinger bottles filled with isopropyl alcohol (for SO3) and hydrogen peroxide solutions (for SO2)

## 6.2 Åbo Akademi, Corrosion tests in reducing conditions – PART II

**Objective:**
The goal of the project is to estimate the resistance/behaviour of the chosen boiler steam/superheater tube materials (10CrMo9-10, T91, S28, HR11N) under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in a reducing atmosphere.

Part 1 tests were done in a gas containing CO and N2 and additionally active carbon were placed on the synthetic salts. The analysis of the results indicated that no or only a small reduction (at 600 °C) of the sulphate to sulfide was achieved with the test setup used.

In part 2 tests are done with the same base salts as earlier, but with black liquor char and some of the sulphur replaced and added as Na2S. Test temperatures were chosen 565°C and 525°C.

All material about this project can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/c34e7ba7b0495d93c22578450050d90b?OpenDocument

**Status and schedule:**
Dorota Bankiewicz presented the results, APPENDIX 3.

Conclusions:
- The exposures to salts 5r resulted in a high corrosion of low alloy materials (10CrMo9-10 and T91)
- Corrosion products were voluminous, brittle and composed of Fe, O, some Na and high amount of C
- S28 and HR11N showed quite good resistance to salts 5r – corrosion < 10 µm
- The exposures to salts 10r caused extreme degradation of low alloy materials (10CrMo9-10 and T91) and also significant degradation of HR11N
- The morphology of the corrosion products on low alloys materials was similar to the one observed after the exposures with salts 5r
- S28 performed best out of tested materials, however increased corrosion was measured after the exposures to salt 10r80 at 565 °C

**Decicion:**
Final report, APPENDIX 4, was accepted.

**Comments:**

- Åbo Akademi decided to use 5% BL char, because in the preliminary tests 10% didn’t increase oxide layer considerably more. Manufacturing BL char is also time consuming
- The specimens were allowed to cool down to room temperature inside furnace with a continuous flow of the gas mixture through the reactor
- With this test procedure we don’t know how much of the original metal layer is disappeared, also we don’t know the density of the corrosion layer. Density affects to the thickness of the layer
- Different corrosion mechanism between low and high alloy steels: with low alloy steels there is no chlorine in corrosion products
- No iron sulphide formed with low alloy steels
- With high alloy steels there is sodium chromium formation
- Corrosion difference between Sanicro 28 and HR11N could be explained with Sanicro’s molybdenum content. Molybdenum increases corrosion resistance in reducing conditions

## 6.3 Boildec Oy, Field testing of furnace materials

**Objective:**
Corrosion field tests of furnace materials are made with Boildec’s probe in the Joutseno recovery boiler.

**Current schedule and materials:**

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

VTT has made composition analyse, APPENDIX 5 to the Sandvik4C54 material (test 2) and the composition is almost same as AISI 301S, so unfortunately no welded 25% Cr material is tested.

All material about this project can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/7f412bc439a50026c225779e0022ff99?OpenDocument

**Status and schedule:**

All five test are done, test 5 was completed 19th December, totalling 2630 of which 2154 were effective (probe pressure over 8 bar), test report APPENDIX 6.

**Decision:**
Report from test No. 5 was accepted.

**Comments:**

- One thermocouple added inside the probe, showing heating oil temperature
- All samples should be machined to provide more accurate thickness measurements.
- Same material, different thickness -> can we repeat 304L test behaviour, tests 1, 2 and 3 had temperature difference
- Temperature is at maximum, test period can be extended to get some corrosion
- Corrosion mechanism seems to be dissolution -> VTT would like have reference sample if possible

## 6.4 VTT, Analysis of the furnace test materials

**Objective:**
Preparation and analyses (corrosion rate, surface characterisation) of Boildec Oy furnace test materials.

**Status and schedule**
Pekka Pohjanne, VTT presented the preliminary analyse results from test No 5, APPENDIX 7.

Conclusions:

- Carbon steel corrodes at extremely high rate (4 mm/a) at the temperature of 440 °C.
- The 3R12 (AISI 304L) composite tube material corrodes in such high rate (average ca. 0.5-0.6 mm/a and maximum ca. 0.8 mm/a) that it can’t be safely used in the lower furnace
- Sanicro 38 (mod. UNS N08825) and HR11N are ca. 3-4 times better than the 3R12 (AISI 304L). HR11N long term sample needs to be re-analysed (Probe No. 5)
- Sanicro 28? - Long term sample needs to be re-analysed (Probe No. 5)

VTT will do the re-analyses and then write final report before the summer holidays.

All material about this project can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/59c6c1175b09c7cdc22577f2004d3fe6?OpenDocument

**Comments:**

- Test No.3 San38 results (material thickness increased during test) could change if sample is washed.
- Test No.5 San28 results are problem because thermocouple was welded to the inner side
- Test No. 5 HR11N inner side has deposits from unknown source (oil, other specimens?)
- One reason different corrosion between tube sides might that probe is not in the center of the boiler -> more radiation to the other tube side
- Is there any problems Sanicro 28 in lower furnace, thermal expansion? Typically San 38 is used, not San 28
- Measurement scale (wall thickness measurements) in the presentations should always be same, easier to compare
- Could there be summary slide for all materials
- Issues for the future tests
  - test material preparation (grinding, polishing equally)
  - how materials are welded to the probe
  - drilling the thermocouple

## 6.5 Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment

**Objective:**
The idea is to carry out field tests with activated carbon and UV-treatment. Project includes monitoring industrial size activated carbon test and the Hanovia UV-treatment tests. Investment costs and operating costs are evaluated.

**Status:**
All tests are done, final report, APPENDIX 8. An article about the project results are published in the Power Plant Chemistry journal, APPENDIX 9.

Conclusions:

- Active carbon can remove up to 40 - 60 % of residual organic material (TOC)
- AC bed lifetime before regeneration is at least 10 months
- Subsequent MB is needed to remove elevated conductivity and silica
- AC works fine in full scale
- UV treatment was able to remove up to 30 % of residual TOC
- Removal efficiency did not improve with:
  - Lower wave lenght (more energy)
  - $H_2O_2$ (oxidant)
  - $TiO_2$ (catalyst)
  - Number of UV chambers (contact time)

All material about this project can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/3f2d98f53d8f033ec225784500514a60?OpenDocument

The durability committee continues the project with Committee funding, the project aim is to test different active carbons and does impregnation of catalyst and ozone increase TOC-reduction.

**Decicion:**
Final report was accepted

## 7 PROPOSALS

Project has about 40 000 eur left and steering group will decide which projects will be ordered by e-mail.

### 7.1 Teollisuuden Vesi, Advantages of improving recovery boiler make-up water quality - investment and operation costs

Teollisuuden Vesi Oy offers a work where the investment costs and operating costs of different TOC removal methods (reverse osmosis, UV-treatment, nanofiltering, active carbon filtering) are calculated. Calculations are made for new and existing pulp mills. Also some information regarding the selection of the method and designing are studied. Total price 17 600 eur. Price: 17 600 eur.

**Decicion:**
By e-mail

### 7.2 VTT, Effect of water quality and different chemicals on magnetite layer properties

**Objective:**
Increase of recovery boiler steam temperature and pressure will have effect on water chemical degradation and magnetite layer properties. Degradation of alkaline chemicals in over 300 °C has not been studied and effect on magnetite layer in 340 °C is not known. Price: 68 000 eur.

Part 1: Decomposition of alkaline amines by hydrolysis
- Static autoclave
- Chemical concentration higher than previous test, for example 50 mg/l
- Qualitative and quantitative analyses of the chemical decomposition products in water and steam 2 hours after chemical addition -> HPLC-MS (Liquid chromatography-mass spectrometry) technique
- Concentration of decomposition products from water and steam with capillary electrophoresis (ppb level)

Part 2: Decomposition of alkaline amines by oxidation
- Water circulation unit, temperature 340 °C
- Normal chemical concentration
- Concentration of organic acids with capillary electrophoresis (ppb level)
- Samples 0h, 12h, 24, 48h after chemical addition

Part 3: The effect of chemicals and decomposition products on magnetite layer formation and properties

- Circulating water circuit
- Autoclave volume smaller than circulating water tank volume -> chemicals decomposition is minimal during the test
- Magnetite layer formation is monitored by EIS (Electrochemical. Impedance Spectroscopy) during 24h test
- After the test magnetite layer is examined with SEM/EDS.

VTT's suggestion for amines:

- Morpholine: in previous tests morpholine had the best thermal resistance. New test arragement will provide more information about effect on magnetite layer.
- 5-aminopentanol: EPRI has studied it's applicability for PWR reactors secondary circulation. According to literature this amine has good base strength, partition coefficient and thermal resistance. It is also environmentally safe.
- Dimethylamine: This amine has positive effect on magnetite presipitation. But it is extremely volatile. Other options could be dodecylamine or dietylaminoetanol.

**Decision:**
By e-mail

### 7.3 Other proposals

## 8 PROJECT IDEAS

### 8.1 Dew point, part 2

Keijo Salmenoja, Andritz will send inquiry to the Åbo Akademi about the project. The aim is to understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler.

The dewpoint 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 acidic condensates during shutdowns and water washes. In the project probe tests are carried out during normal operation and shutdown.

## 9 OTHER ISSUES

### 9.1 Final report

Writing the final report in English is on-going. Secretary will send the final report for comments when it is ready.

### 9.1.1 Northern America

ORNL project “Improving heat recovery in biomass-fired boilers” had project review meeting in Oak Ridge on November 2011. Presentation can be downloaded:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/b5935265c0ebb8b3c225788e00437cb8?OpenDocument

## 9.2 Changes in steering committee

New chairman of Finnish Recovery Boiler Committee Timo-Pekka Veijonen, Stora Enso will replace Kaj Nordbäck. Reijo Hukkanen will be the Stora Enso member of steering committee.

Steering committee:

Members:

| | |
|---|---|
| Lasse Koivisto | Andritz Oy, Varkaus |
| Hidenori Ogawa | Sumitomometal Industries,Ltd. |
| Timo Peltola | Sandvik, Helsinki |
| Mika Paju | Oy Metsä-Botnia Ab, Joutseno |
| Keijo Salmenoja | Andritz Oyj |
| Timo-Pekka Veijonen | Chairman of Finnish Recovery Boiler Association |
| Matti Tikka | UPM-Kymmene Oyj, Kymi, chairman |
| Martti Korkiakoski | Tekes |
| Reijo Hukkanen | Stora Enso Oyj |
| Kalle Salmi | Metso Power Oy, Tampere |

Non voting members:

| | |
|---|---|
| Esa Vakkilainen | LUT, project coordinator |
| Markus Nieminen | Secretary of Finnish Recovery Boiler Committee |

## 9.3 Translating project reports into English

Translation of report is done:

- Sulfidation tests
  Mustala, Sanni, Pohjanne, Pekka, Heikinheimo, Liisa, Pankakoski, Pekka and Kinnunen, Tuomo, VTT 10.3.2006.

- Field test of furnace materials and heat flux measurements – summary
  Karjunen Timo, Boildec Oy

- Corrosion chemistry of recovery boiler flue gas side – laboratory tests
  Mikko Hupa, Bengt-Johan Skrifvars ja Linus Silvander. Åbo Akademi 31.10.2005.

# 10 NEXT MEETING

Last meeting of the SKYREC-project will be held in autumn 2012; exactly date will be decided later when last projects schedule is known.

In last meeting there should summary of the sub-projects results, each project accomplishment in few lines.

Markus Nieminen

# APPENDIX 1
# APPENDIX SUMMARY

**APPENDIX 2**
**Project budget and schedule 12.4.2012**

**APPENDIX 3**
**Åbo Akademi, Dew point measurements**
**final report 7.12.2011**

**APPENDIX 4**
**Åbo Akademi, Corrosion tests in reducing conditions, PART II**
**presentation 12.4.2012**

**APPENDIX 5**
**Åbo Akademi, Corrosion tests in reducing conditions, PART II**
**final report 15.2.2012**

**APPENDIX 6**
**VTT, composition analyses of 3RE28 and 3xRE28 materials**

**APPENDIX 7**
**Boildec Oy, Field tests of furnace materials**
**test report No.5 22.12.2011**

**APPENDIX 8**
**VTT, Analysis of the furnace test materials**
**presentation 12.4.2012**

**APPENDIX 9**
**Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment**
**final report 28.2.2012**

**APPENDIX 10**
**Cewic, Reduction of TOC in recovery boiler makeup water**
**article Powerplant Chemistry 2/2012**

# APPENDIX 2
# SUMMARY
# Project budget and schedule 12.4.2012

# SKYREC Budget 12.4.2012

- Projects paid: 748 908,37 €
- Projects to be invoiced: 15 350,00 €
- Sum (projects ordered): 764 258,37 €

- Funding from TEKES (350 000 €) is OK
- Project budget total: 805 000 €
- 805 000 € - 764 258 € = 40 741 € left

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# Projects to be invoiced

| Company, Project name | will be invoiced (total cost) |
|---|---|
| ÅA: Corrosion tests in reducing conditions – PART II A&B | 15 350 €<br>(30 700 €) |
| Sum | 15 350 € |
| Budget left | 40 741 € |
| Sum | 56 091 € |

# Projects paid (1/4)

| **WP1: New recovery boiler concepts** | |
|---|---|
| ÅA: Co-combustion of mixed fuels, part 1 | 7 500 € |
| ÅA: Corrosion tests in reducing conditions – PART II A | 15 350 € |
| ÅA: Co-combustion of mixed fuels, part 2, Wood + lean BL | 16 500 € |
| ÅA: Co-combustion of mixed fuels, part 2, Biosludge | 7 100 € |
| ÅA: Utilization of Pyrolysis Gases from the Recovery Boiler | 8 500 € |
| LUT: Pulp mill optimal steam pressure levels | 16 000 € |
| LUT: Recovery boiler as once-through boiler | 33 800 € |
| ÅA: Dew point measurements | 30 000 € |
| Sum | 119 400 € |

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# Projects paid (2/4)

| **WP2: Increasing superheated steam temperature** | |
|---|---|
| ÅA: Corrosion tests in reducing conditions – PART I | 37 000 € |
| ÅA: Corrosion tests in reducing conditions – PART II | 15 350 € |
| VTT: Corrosion study of recovery boiler superheater materials | 104 000 € |
| Sum | 156 350 € |

# Projects paid (3/4)

| **WP3: Increasing recovery boiler pressure** | |
|---|---|
| Boildec: Material testing in furnace, tests 1-4 | 100 264 € |
| VTT: Analyzes for Boildec tests 1-4 | 35 800 € |
| Boildec: Material testing in furnace, test 5 | 20 000 € |
| Boildec Oy: Material testing in furnace test 5 continuation | 8 075 € |
| VTT: Analyzes for Boildec test 5 | 11 500 € |
| Oulun Yliopisto: Ceramic structural materials | 15 000 € |
| LUT: Dynamic char bed | 14 800 € |
| Sum | 205 439 € |

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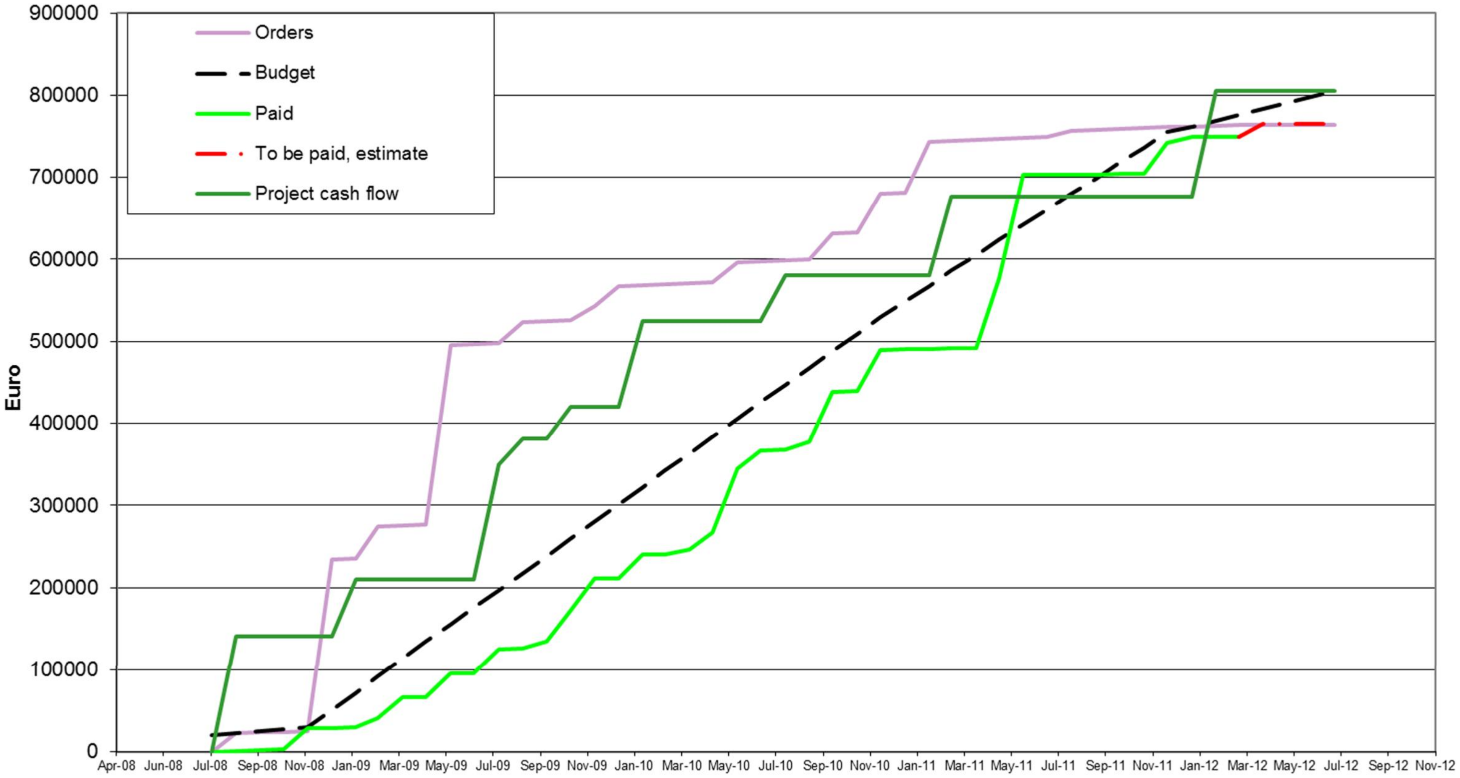
# Projects paid (4/4)

| **WP4: Ensuring boiler and feedwater quality** | |
|---|---|
| Teollisuuden vesi: Effect of water quality to airheater corrosion, TOC-balance | 24 600 € |
| Teollisuuden vesi: TOC removal methods and their applicability in make-up water treatment | 45 000 € |
| Teollisuuden Vesi: FRBC’s Water quality recommendation | 31 500 € |
| VTT: Literature study amines | 17 700 € |
| VTT: Magnetite formation | 65 000 € |
| OY: Reduction of TOC from recovery boiler make-up water | 10 000 € |
| Cewic: Activated carbon and UV-treatment - field test, part 1 | 15 500 € |
| Cewic: Activated carbon and UV-treatment – field test, part 2 | 18 942 € |
| Sum | 228 242 € |



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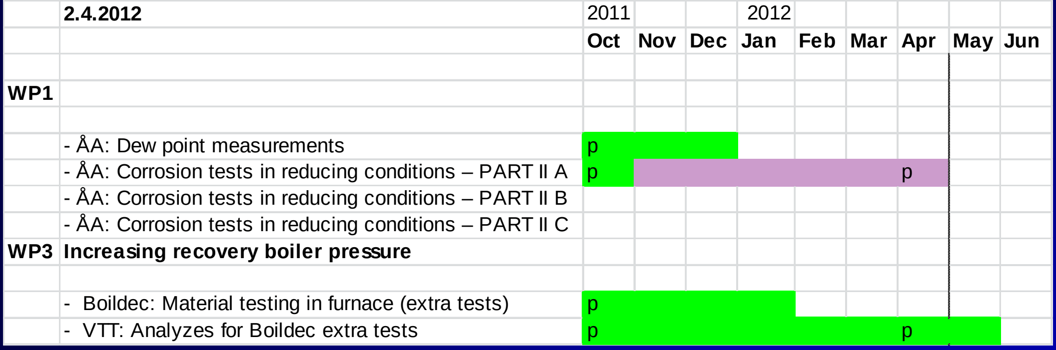
# Things to be done

- Ordering last projects
- Monitoring last projects
- Final report in english

# Schedule



| | 2.4.2012 | 2011 | | | 2012 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **Oct** | **Nov** | **Dec** | **Jan** | **Feb** | **Mar** | **Apr** | **May** | **Jun** |
| | | | | | | | | | | |
| **WP1** | | | | | | | | | | |
| | | | | | | | | | | |
| | - ÅA: Dew point measurements | 🟩 p | 🟩 | 🟩 | | | | | | |
| | - ÅA: Corrosion tests in reducing conditions – PART II A | 🟩 p | 🟪 | 🟪 | 🟪 | 🟪 | 🟪 | 🟪 p | | |
| | - ÅA: Corrosion tests in reducing conditions – PART II B | | | | | | | | | |
| | - ÅA: Corrosion tests in reducing conditions – PART II C | | | | | | | | | |
| **WP3** | **Increasing recovery boiler pressure** | | | | | | | | | |
| | | | | | | | | | | |
| | - Boildec: Material testing in furnace (extra tests) | 🟩 p | 🟩 | 🟩 | 🟩 | | | | | |
| | - VTT: Analyzes for Boildec extra tests | 🟩 p | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 p | 🟩 | |

- Furnace material test analyse report ready
- Final report in english ready

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# Changes in steering committee

- New chairman of Finnish Recovery Boiler Committee Timo-Pekka Veijonen, Stora Enso
- Reijo Hukkanen will be the Stora Enso member of steering committee

# New steering committee

| | |
|---|---|
| Members: | |
| Lasse Koivisto | Andritz Oy, Varkaus |
| Hidenori Ogawa | Sumitomometal Industries,Ltd. |
| Timo Peltola | Sandvik, Helsinki |
| Mika Paju | Oy Metsä-Botnia Ab, Joutseno |
| Keijo Salmenoja | Andritz Oyj |
| Timo-Pekka Veijonen | Chairman of Finnish Recovery Boiler Association |
| Matti Tikka | UPM-Kymmene Oyj, Kymi, chairman |
| Martti Korkiakoski | Tekes |
| Reijo Hukkanen | Stora Enso Oyj |
| Kalle Salmi | Metso Power Oy, Tampere |
| Non voting members: | |
| Esa Vakkilainen | LUT, project coordinator |
| Markus Nieminen | Secretary of Finnish Recovery Boiler Committee |

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# English translation SOTU2

- Sulfidation tests
  - Mustala, Sanni, Pohjanne, Pekka, Heikinheimo, Liisa, Pankakoski, Pekka and Kinnunen, Tuomo, VTT 10.3.2006.
- Field test of furnace materials and heat flux measurements – summary
  - Karjunen Timo, Boildec Oy
- Corrosion chemistry of recovery boiler flue gas side – laboratory tests in oxidicing conditions
  - Mikko Hupa, Bengt-Johan Skrifvars ja Linus Silvander. Åbo Akademi 31.10.2005.

# APPENDIX 3
# SUMMARY
# Åbo Akademi, Dew point measurements
final report 7.12.2011

# Report: Dew Point Measurements at the Recovery Boilers in Rauma and Heinola

Emil Vainio, Tor Laurén, Nikolai DeMartini, Mikko Hupa

Åbo Akademi University

7 December 2011

*Contents:*

## 4. Summary

At the Rauma Kraft mill the dew point measured was equal to the water dew point, 62-64°C. Neither $SO_2$ 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 explained by the high amount of fly ash 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 $H_2SO_4$ with $Na_2SO_4$ to form acidic $NaHSO_4$. At 80°C significant corrosion was observed.

The flue gases of the two boilers appear not to cause sulfuric acid induced low-temperature corrosion.

## 5. Literature

1. Haase, R. och Borgmann, H. W., VGB 76, pp 16-19, 1962.

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

3. http://www.epa.gov/ttn/emc/promgate/m-08.pdf

4. Yen Hsiung Kiang, "Predicting Dewpoints of Gases", Chemical Engineering 88 (3): 127 (1981).

# APPENDIX 4
SUMMARY
Åbo Akademi, Corrosion tests in reducing conditions, PART II
presentation 12.4.2012

PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI
UNIVERSITY

# Skyrec II

Steering committee meeting 1/2012

April 12th, 2012

---

## Selection of new salts – TGA tests

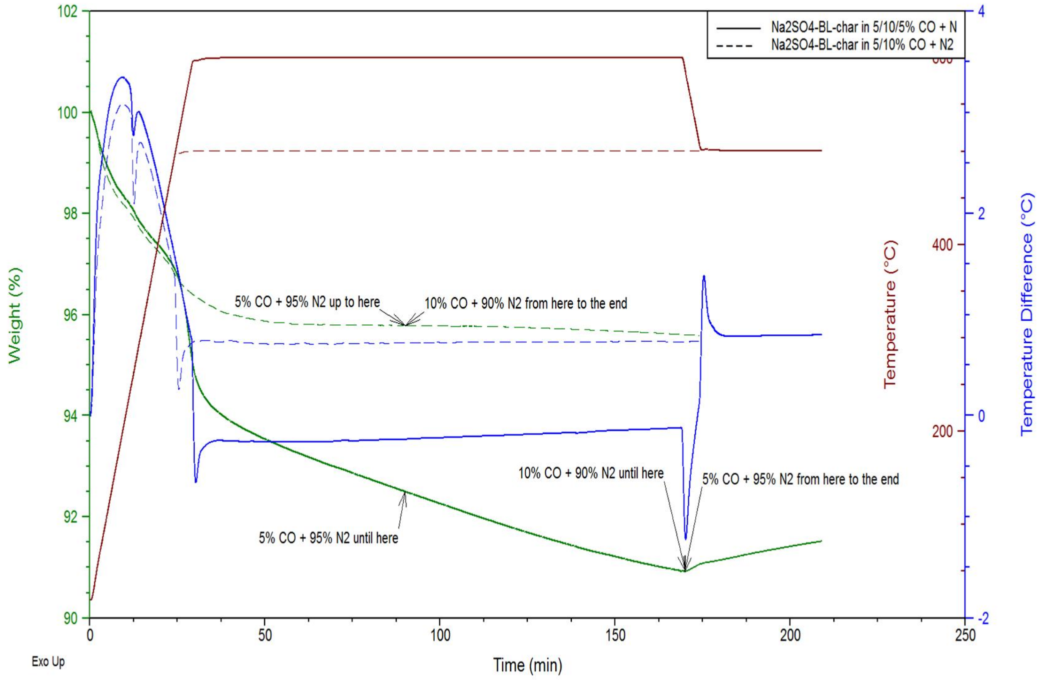
Pure $Na_2SO_4$ and the mixture of $Na_2SO_4$ + BL char was tested in TGA in $N_2$ and in $N_2$ + 5% CO gas mixture and heated up to 1000 °C:

- in $N_2$
$Na_2SO_4$ - negligible weight loss was observed
$Na_2SO_4$ + BL char - weight loss 20%

- in $N_2$ + CO
$Na_2SO_4$ - negligible weight loss was observed
$Na_2SO_4$ + BL char - weight loss 46% (C available from BL char + from CO) - best reduction level

Reduction of $Na_2SO_4$ to $Na_2S$ occurred in both cases with BL char but above 730 °C (above the corrosion test temperature)

# Selection of new salts – TGA tests



The mix of $Na_2SO_4$-BL char was heated up to 500 and 600 °C in $N_2$ and $N_2$ + CO

---

# Selection of new salts – TGA tests

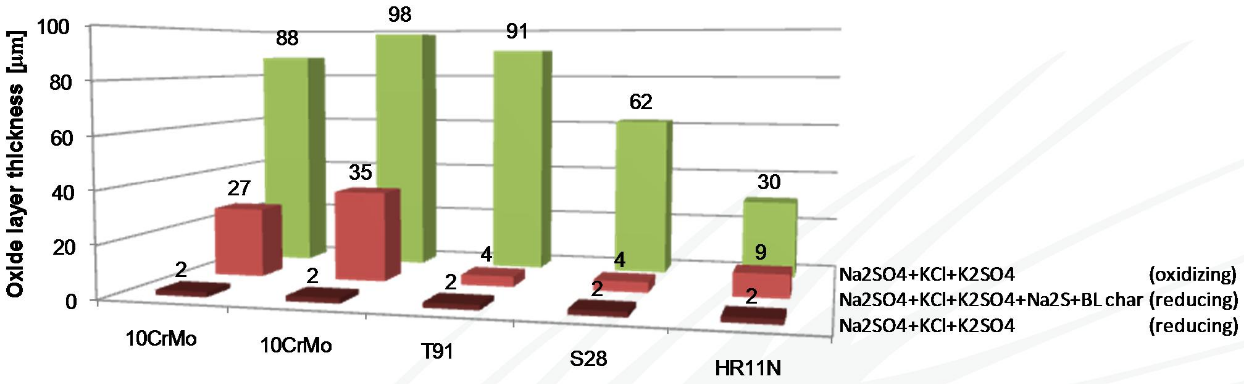
- At 500 °C the reduction of $Na_2SO_4$ to $Na_2S$ was negligible
- At 600 °C <10 wt-% mass loss was observed (including water evaporation)

Since the reduction at 600 °C also proceeded quite slowly it was decided to prepared a salt mixture which already contains certain level of reduced $Na_2SO_4$ ($Na_2S$). The half (mol%) of $Na_2SO_4$ form the previously used Salt 10 was exchanged with $Na_2S$. Additionally, to stimulate reduction 30 wt-% of BL char was added to the salt mixture

| | $Na_2SO_4$ | $Na_2S$ | KCl | $K_2SO_4$ | BL char (wt-%) |
|---|---|---|---|---|---|
| Salt 10 (mol%) | 78 | - | 5 | 17 | - |
| Salt 10r (mol%) | 36 | 39 | 5 | 18 | 30 |

# Skyrec II - trial test

Reducing vs. Oxidising conditions at 550 ºC.
Exposures with Salt 10 and 10r50+BL char



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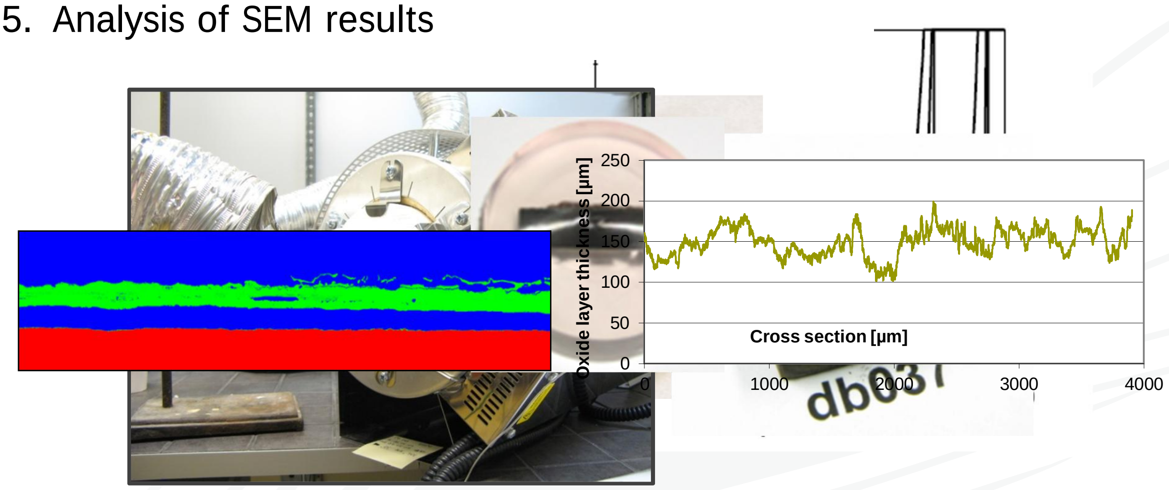
# Laboratory method for HT corrosion tests

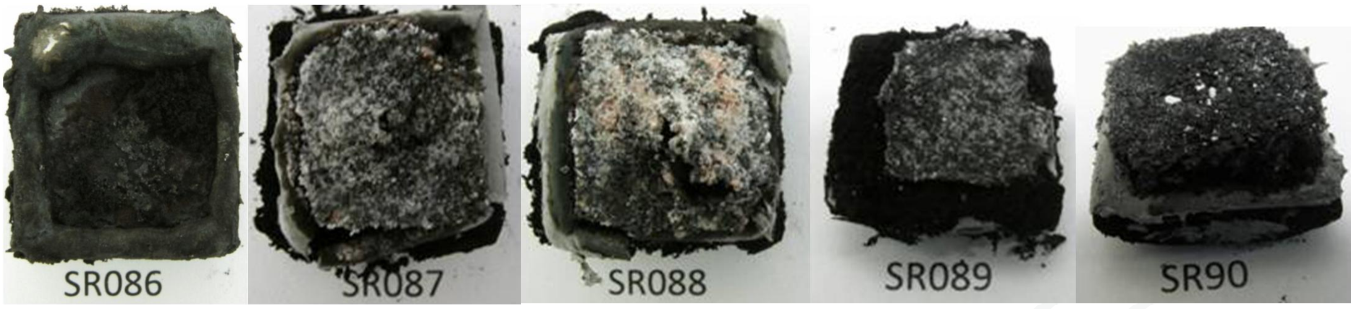
1. Preparation of salts
2. Preparation of steel samples for the experiment
3. Tube furnace tests
4. Preparation of samples for SEM/EDXA
5. Analysis of SEM results



# Skyrec II - Testing of wood char effect

- 5 samples of 10CrMo were tested
- 10r50 mixture ($Na_2S + Na_2SO_4 + K_2SO_4 + KCl$) was used
- 0, 5, 5, 10 and 30 % of BL char was added to the synthetic ash respectively and mixtures were placed on the samples
- tests were done in reducing atmosphere at 565 °C for 168 h

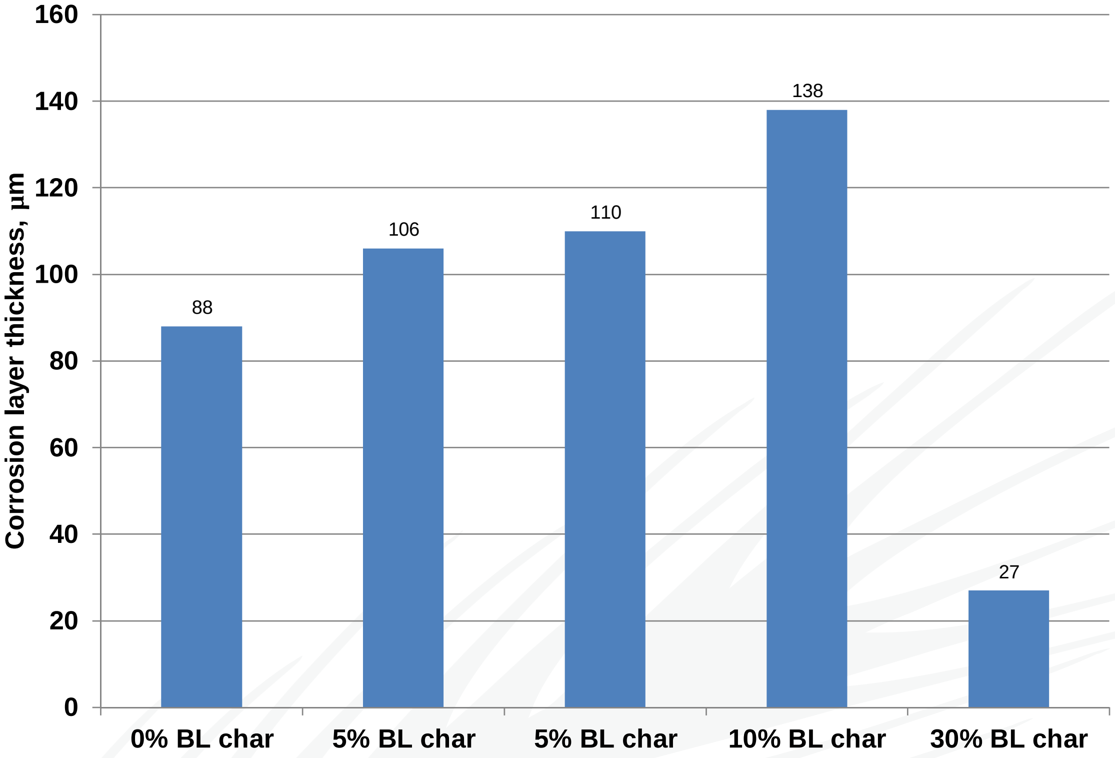
# Results – digital pics of the samples after test



0% BL char 5% 5% 10% 30%

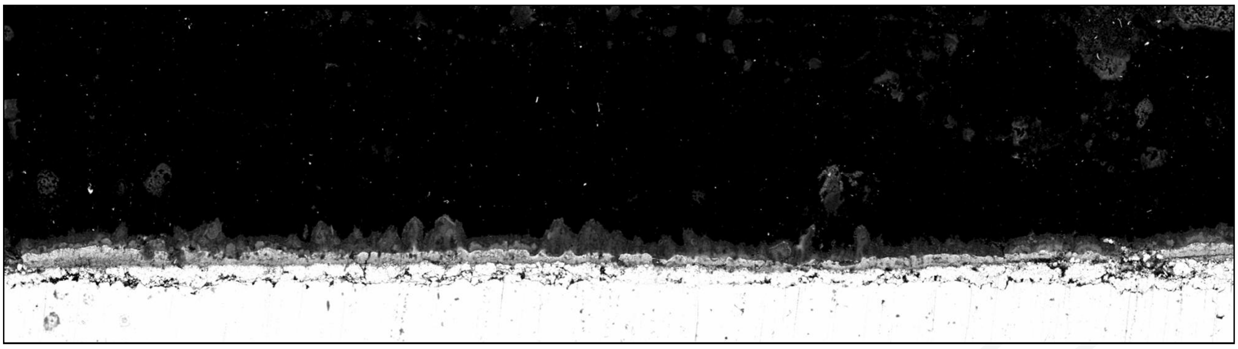
After the test, the salt containing BL char was swollen and very brittle.
Surrounding of the sample was full of black, soot-like powder.

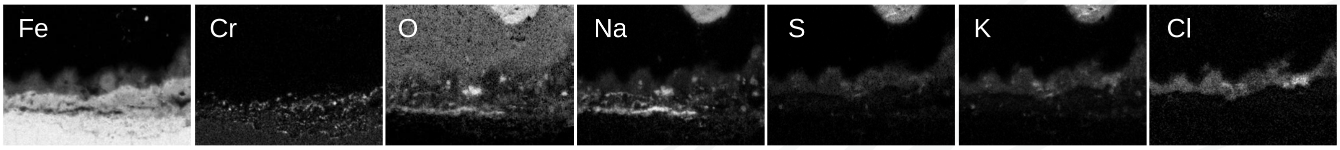
# Results - BL char effect - oxide layer thickness



# Results – x-ray maps

**($Na_2S+Na_2SO_4+K_2SO_4+KCl$, 30-wt% BL char)**





Not much of the corrosion products were found on the surface of the sample exposed to salt containing 30% BL char. The surface was, however, visibly damaged.

The sample was swollen and it was difficult to retain all the products present on the surface exactly as they were (this was the case for all the samples containing BL char)

# Remarks

- in all cases the corrosion rates were significant

- when no BL char was added to the salt mixture, the surface of the steel was mainly internally degraded

- BL char additions (5 and 10%) caused increased material degradation with visibly consumed material. Internal oxide + material degradation occurred

- addition of 5% of BL char seems to be enough

- reasonably low corrosion rate was measured when 30% BL char was added - too big dilution of the salt

- BL char addition seems to influence (decrease slightly) $T_0$ of the salt mixture

I. When no BL char was added, the separate salt particles were visible

II. When BL char was added, the salt looked more molten like on the SEM pics, also the salt cake was heavily swollen and brittle after taking out from the oven, surrounded with black soot like powder

# Skyrec II - project

1. High temperature behaviour of steels under alkali- sulfates/sulfides and chlorides containing synthetic ashes in reducing atmosphere

Temperatures: 525ºC, 565ºC

Salts:

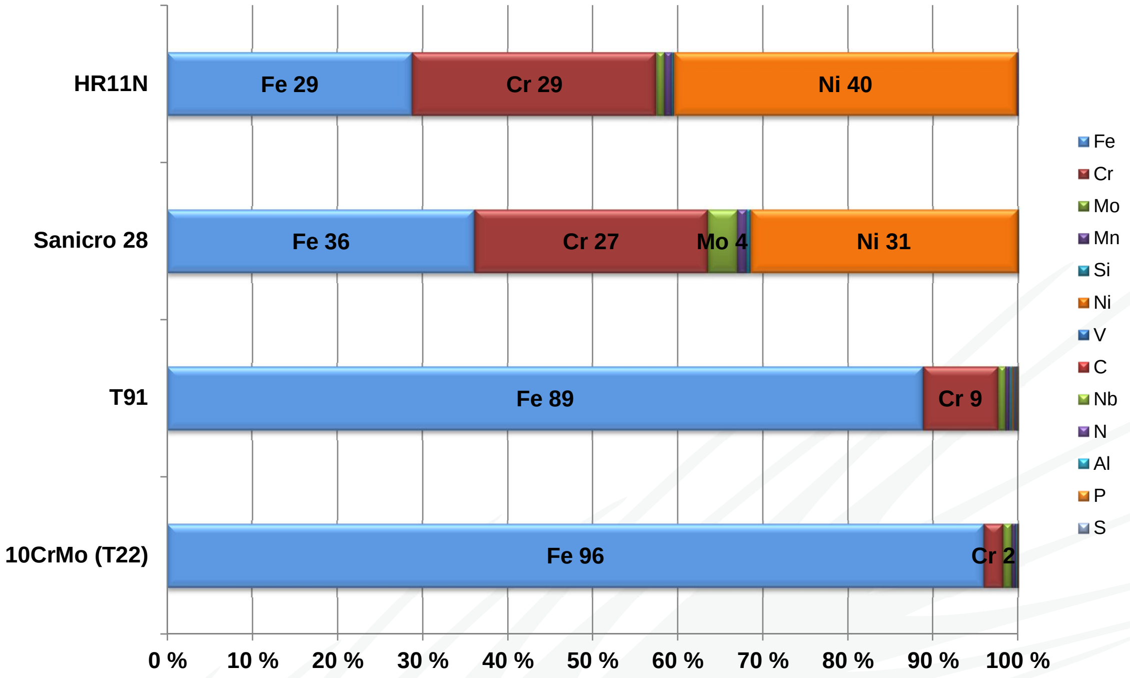
| mol% | $Na_2SO_4$ | $Na_2S$ | $K_2SO_4$ | KCl | BL char wt% | T0, °C |
|---|---|---|---|---|---|---|
| 5 | 100 | | | | | 886 |
| 5r10 | 90 | 10 | 0 | 0 | 5 | 585* |
| 5r50 | 50 | 50 | 0 | 0 | 5 | 583* |
| 5r80 | 20 | 80 | 0 | 0 | 5 | 571* |
| 10 | 78 | | 17 | 5 | | 522 |
| 10r10 | 70 | 8 | 17 | 5 | 5 | 496 |
| 10r50 | 39 | 39 | 17 | 5 | 5 | 504 |
| 10r80 | 15 | 62 | 17 | 5 | 5 | 510 |

* very little melt, a lot starts to form at 730 °C

Steels: 10CrMo9-10, T91, S28, HR11N

Atmosphere: reducing (5% CO + 95% $N_2$ – 2 l/min)

# Skyrec II - tested steels composition



# Skyrec II – performed tests

| Temp, °C | Salt | Steel | Mean corr layer thickness, µm |
|---|---|---|---|
| 525 | 5r80+5% Blchar | 10CrMo | 18 |
| 525 | 5r80+5% Blchar | T91 | 72 |
| 525 | 5r80+5% Blchar | Sanicro 28 | 12 |
| 525 | 5r80+5% Blchar | HR11N | 2 |
| 565 | 5r10+5% Blchar | 10CrMo | 53 |
| 565 | 5r10+5% Blchar | T91 | 92 |
| 565 | 5r10+5% Blchar | Sanicro 28 | 8 |
| 565 | 5r10+5% Blchar | HR11N | 6 |
| 565 | 5r50+5% Blchar | 10CrMo | 120 |
| 565 | 5r50+5% Blchar | T91 | 151 |
| 565 | 5r50+5% Blchar | Sanicro 28 | 5 |
| 565 | 5r50+5% Blchar | HR11N | 3 |
| 565 | 5r80+5% Blchar | 10CrMo | 192 |
| 565 | 5r80+5% Blchar | T91 | 170 |
| 565 | 5r80+5% Blchar | Sanicro 28 | 42 |
| 565 | 5r80+5% Blchar | HR11N | 6 |

duplicates

| | | | |
|---|---|---|---|
| 525 | 5r80+5% Blchar | Sanicro 28 | 2 |
| 565 | 5r10+5% Blchar | 10CrMo | 15 |
| 565 | 5r50+5% Blchar | HR11N | 2 |
| 565 | 5r80+5% Blchar | T91 | 118 |

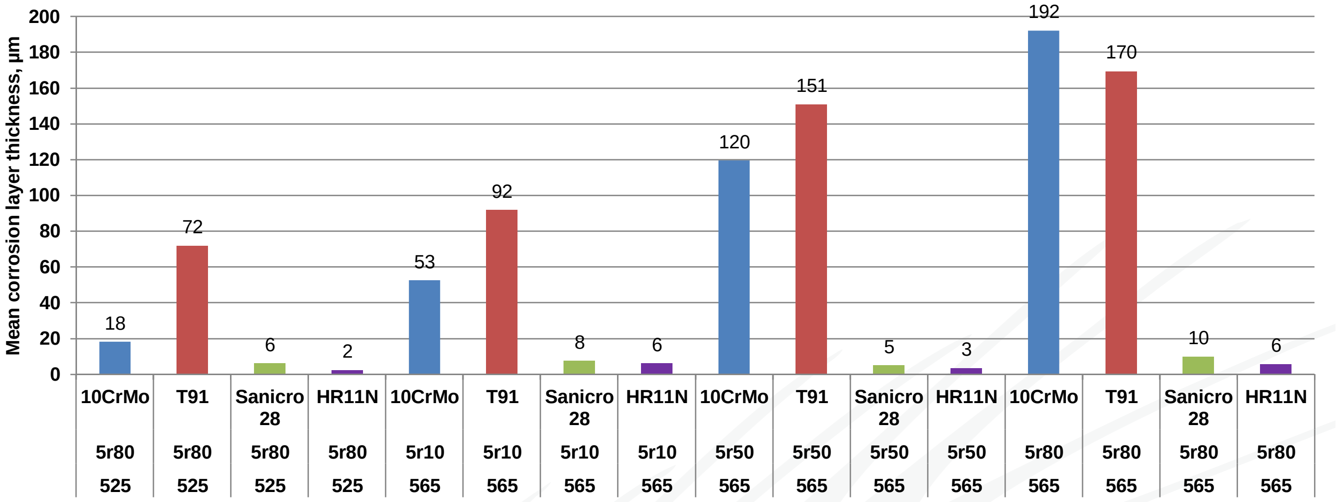
| Temp, °C | Salt | Steel | Mean corr layer thickness, µm |
|---|---|---|---|
| 525 | 10r10+5% Blchar | 10CrMo | 11 |
| 525 | 10r10+5% Blchar | T91 | 12 |
| 525 | 10r10+5% Blchar | Sanicro 28 | 17 |
| 525 | 10r10+5% Blchar | HR11N | 55 |
| 525 | 10r80+5% Blchar | 10CrMo | 180 |
| 525 | 10r80+5% Blchar | T91 | 189 |
| 525 | 10r80+5% Blchar | Sanicro 28 | 6 |
| 525 | 10r80+5% Blchar | HR11N | 14 |
| 565 | 10r10+5% Blchar | 10CrMo | 274 |
| 565 | 10r10+5% Blchar | T91 | 735 |
| 565 | 10r10+5% Blchar | Sanicro 28 | 9 |
| 565 | 10r10+5% Blchar | HR11N | 51 |
| 565 | 10r50+5% Blchar | 10CrMo | 562 |
| 565 | 10r50+5% Blchar | T91 | 467 |
| 565 | 10r50+5% Blchar | Sanicro 28 | 18 |
| 565 | 10r50+5% Blchar | HR11N | 80 |
| 565 | 10r80+5% Blchar | 10CrMo | 490 |
| 565 | 10r80+5% Blchar | T91 | 316 |
| 565 | 10r80+5% Blchar | Sanicro 28 | 26 |
| 565 | 10r80+5% Blchar | HR11N | 19 |

duplicates

| | | | |
|---|---|---|---|
| 525 | 10r10+5% Blchar | HR11N | 32 |
| 525 | 10r80+5% Blchar | Sanicro 28 | 4 |
| 565 | 10r10+5% Blchar | 10CrMo | 185 |
| 565 | 10r50+5% Blchar | HR11N | 38 |
| 565 | 10r80+5% Blchar | T91 | 90 |

# Skyrec II

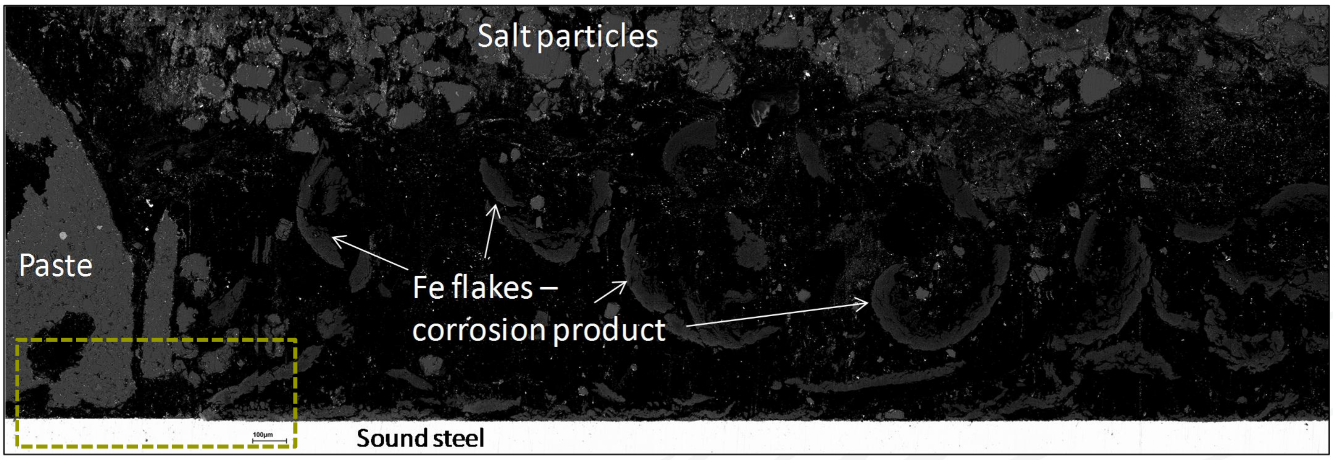
## results with Salts 5r ($Na_2SO_4$) + $Na_2S$ + BL char at 525 °C and 565 °C

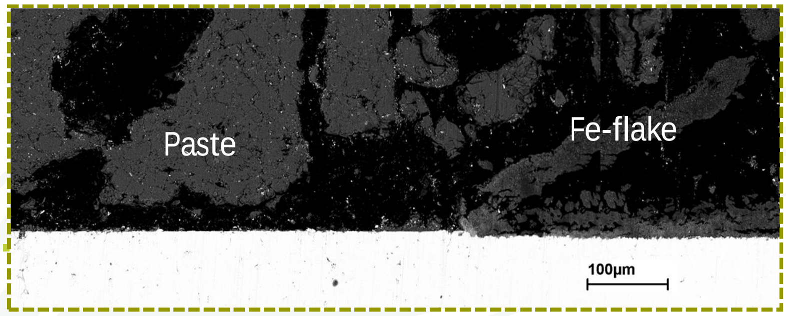


All the salts mixtures contained 5 wt-% BL char

# Skyrec II

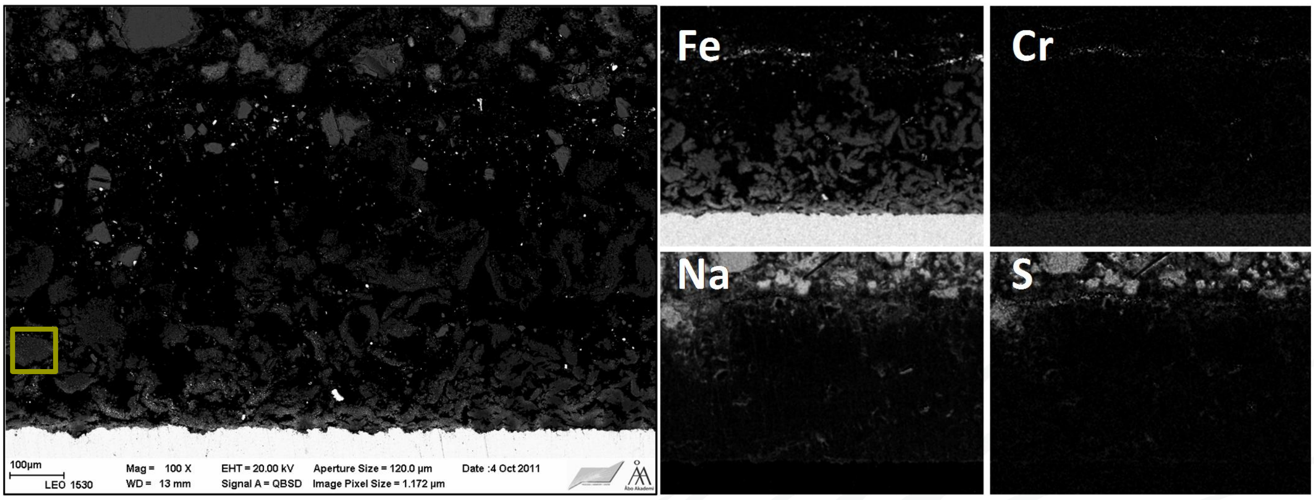
## T91 exposed to Salts 5r50 at 565 °C





# Skyrec II

## 10CrMo9-10 exposed to Salts 5r80 at 565 °C



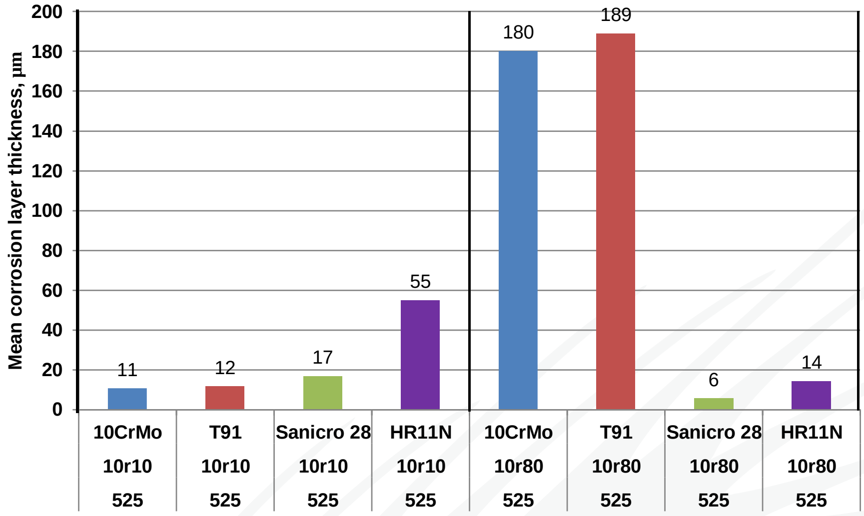
The SEM analysis of the corrosion product (flakes)

| Element | Wt.% | At.% |
|---|---|---|
| C | 64.89 | 82.89 |
| O | 9.64 | 9.25 |
| Na | 1.63 | 1.09 |
| Fe | 22.33 | 6.14 |

---

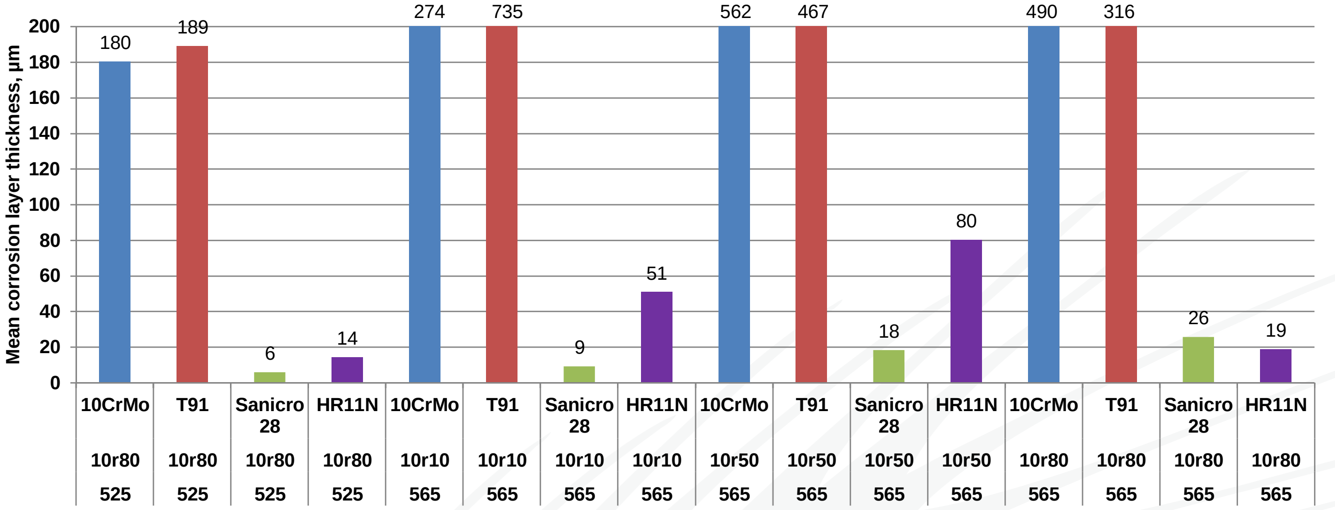
# Skyrec II

## results with Salts 10r10 and 10r80 ($Na_2SO_4$/$K_2SO_4$/KCl) + $Na_2S$ + BL char at 525 °C



# Skyrec II

## results with Salts 10r ($Na_2SO_4$/$K_2SO_4$/KCl) + $Na_2S$ + BL char at 525 °C and 565 °C



All the salts mixtures contained 5 wt-% BL char

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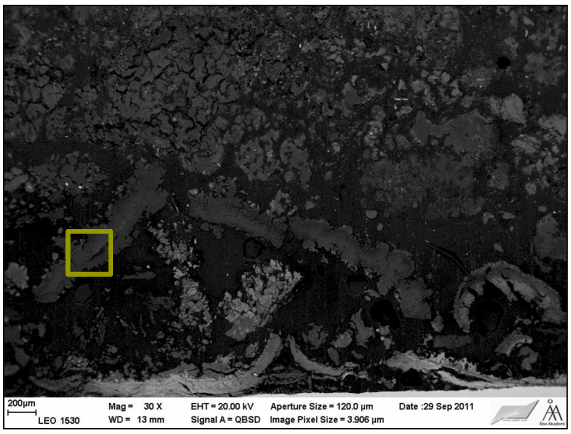
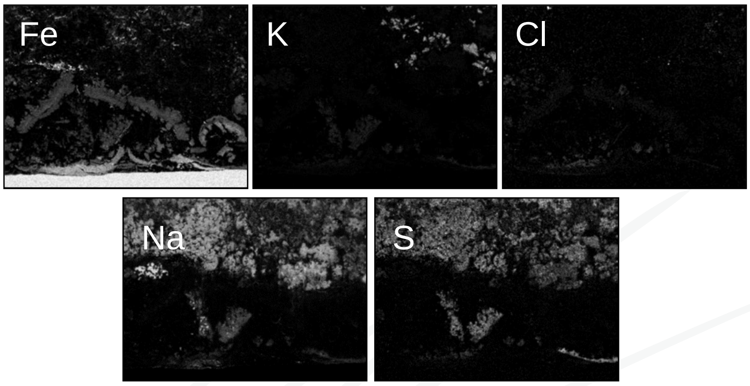
# Skyrec II

## 10CrMo9-10 exposed to Salts 10r50 at 565 °C



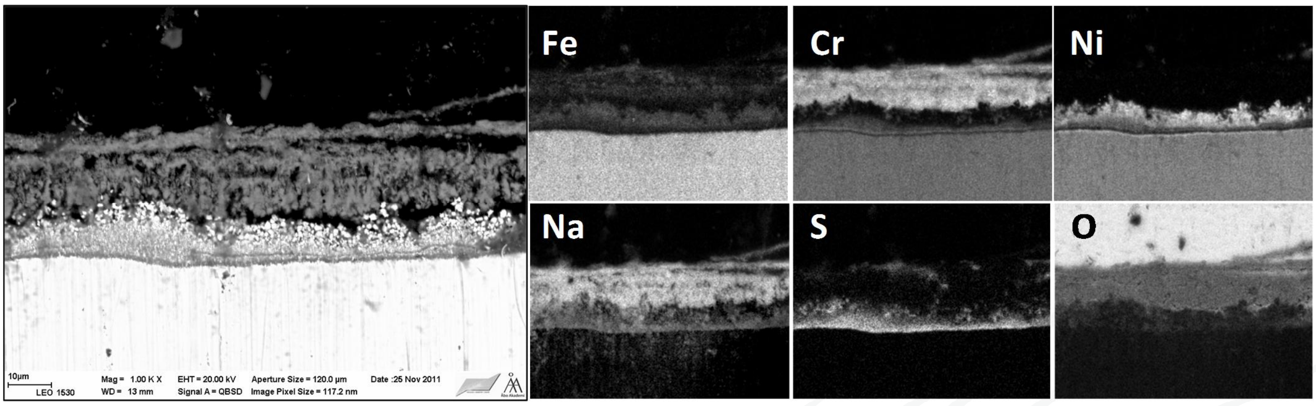


The SEM analysis of the corrosion product (flakes)

| Element | Wt.% | At.% |
|---|---|---|
| C | 64.35 | 82.15 |
| O | 9.94 | 9.53 |
| Na | 2.12 | 1.42 |
| Fe | 19.76 | 5.43 |

# Skyrec II

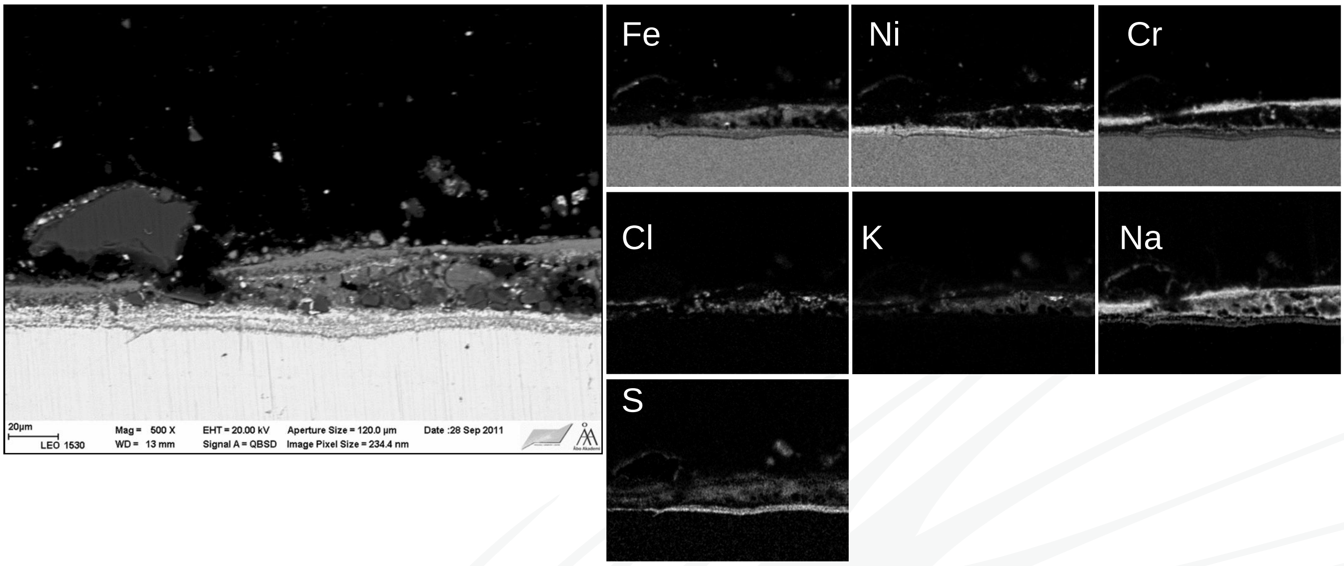
## HR11N exposed to Salts 10r10 at 525 °C



The degradation of the austenitic materials (S28 and HR11N) was different from the one observed on low alloy steels – no flakes

# Skyrec II

## S28 exposed to Salts 10r80 at 565 °C



# Skyrec II – conclusions

- the exposures to salts 5r resulted in a high corrosion of low alloy materials (10CrMo9-10 and T91)

- corrosion products were voluminous, brittle and composed of Fe, O, some Na and high amount of C

- S28 and HR11N showed quite good resistance to salts 5r – corrosion < 10 µm

- the exposures to salts 10r caused extreme degradation of low alloy materials (10CrMo9-10 and T91) and also significant degradation of HR11N

- the morphology of the corrosion products on low alloys materials was similar to the one observed after the exposures with salts 5r

- S28 performed best out of tested materials, however increased corrosion was measured after the exposures to salt 10r80 at 565 °C

# APPENDIX 5
# SUMMARY
# Åbo Akademi, Corrosion tests in reducing conditions, PART II
final report 15.2.2012

# Skyrec II

## Final report

## Confidential

***Dorota Bankiewicz, Patrik Yrjas***

Report written at the Laboratory of Inorganic Chemistry/ÅA
lead by prof. Mikko Hupa

**February 2012**

# Preface

Skyrec II is a continuation of the previous project Skyrec. This report is based on the results obtained from laboratory tests performed at Åbo Akademi University by the Laboratory of Inorganic Chemistry. The experiments were carried out during 2011 in agreement with Suomen Soodakattilayhdistys – Finnish Recovery Boiler Committee. The analyses of the samples were finalized in the beginning of 2012. The first results from Skyrec II were presented on a Skyrec internal meeting at Pöyry October, 5 2011 in Vantaa and also on the Skyrec Seminar October, 20 2011 in Helsinki. This report presents a summary of all tests performed in the project. Due to the high number of SEM and X-ray pictures, only chosen samples with identified corrosion will be presented also in the form of pictures. However, all the results (SEM/EDX) will be delivered together with the report on DVD:s.

In the first part of the Skyrec project it was concluded that only a low reduction level of sulfate to sulfide was achieved with the test setup used. Thus, in Skyrec II Black Liquor (BL) char and $Na_2S$ (simulating reduced $Na_2SO_4$) were added to the previously tested salts (5 and 10). The goal of the project was to estimate the resistance/behavior of the chosen boiler steam/superheater tube materials under alkali- sulfates/sulfides and 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 laboratory work was carried out by Jaana Paananen and Jan-Erik Eriksson. The SEM/EDX analyses were done by Linus Silvander. TGA tests were carried out by Peter Backman. The analyses of the results, meeting materials and final report have been written by Dorota Bankiewicz in co-operation with, reviewed and commented by Patrik Yrjas.

1 Attachment: 3 DVD's with SEM/EDX results from all performed tests

The content of the report is confidential and is the property of:

*Suomen Soodakattilayhdistys – Finnish Recovery Boiler Committee.*

## *Authors*

*Åbo Akademi University,*

*February 2012*

# Table of Contents

# 5. Conclusions

The presented results should be taken as indicative. The precision of the received results may differ due to the fact that the handling of the samples, especially of the low alloy materials which corroded to a high degree, after the heat treatment was extremely difficult. The corrosion products were brittle, powdery and swollen. Even the gentlest movement of the sample was causing replacement of the corrosion products. The samples were, however, treated with the highest caution.

Test exposures were carried out with Salt 5r10, Salt 5r50 and Salt 5r80 which were mixtures of $Na_2SO_4$ and $Na_2S$, and Salt 10r10, Salt 10r50 and Salt 10r80, which in turn were mixtures of $Na_2SO_4$, $K_2SO_4$, KCl and $Na_2S$. To all salt mixtures 5wt-% of Black Liquor char was added. The tests were performed in a reducing atmosphere at 525°C and 565°C.

The exposures to Salt 5r10, Salt 5r50 and Salt 5r80 resulted in high corrosion of the low alloy materials, 10CrMo9-10 and T91. 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 µm.

The exposures to Salt 10r10, Salt 10r50 and Salt 10r80 resulted in an extreme corrosion of low alloy materials, 10CrMo9-10 and T91. The corrosion product thickness was measuring a few hundred µm. 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 $Na_2S$ in the salt.

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. 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 µm under reducing conditions in tests with Salt 5r10 while in tests under 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 S28 performed better in a reducing environment with Salt 10rX.

# References

[1] Westén-Karlsson, M. *Assessment of a Laboratory Method for Studying High Temperature Corrosion Caused by Alkali Salts*. Lic. Thesis, Åbo Akademi University, Åbo, Finland 2008, ISBN 978-952-12-2116-3

[2] Bankiewicz, D., Yrjas, P., Hupa, M. *High temperature corrosion of steam tube materials exposed to zinc salts*. Energy&Fuels 23 (7), 3469-3474 (2009)

[3] Bankiewicz, D., Yrjas, P., Hupa, M. Skyrec Final report, February 2010.

# APPENDIX 6
# SUMMARY
# VTT, composition analyses of 3RE28 and 3xRE28 materials

VTT EXPERT SERVICES OY

VTT Expert Services Oy
PL 1001, 02044 VTT
(Kemistintie 3, 02150 Espoo)
Puh. 020 722 111, Fax 020 722 7010

# ANALYYSITODISTUS

Optinen emissiospektrometri, Spectrolab S
Kantokaasumenetelmä, Leco TC-136
(sisäiset menetelmät T001-021, T001-022, T001-023)

N:o

Liite

Sivuja 1/1

Tilaaja: VTT Pekka Pohjanne

Tilaus:

Saapumispäivä: 9.11.2011

Analysointipäivä: 10.11.2011

| Näyte | Koostumus % | | | | | | | | | | | | | | | | Anal. n:o. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | S | P | Cr | Ni | Mo | Cu | Al | W | V | Ti | Co | | | |
| 3RE28 | 0,023 | 0,39 | 1,77 | 0,002 | 0,015 | 25,6 | 21,0 | 0,06 | 0,06 | 0,030 | 0,01 | 0,06 | 0,01 | 0,06 | | | 445/11 |
| 3xRE28 | 0,012 | 0,35 | 1,63 | 0,002 | 0,026 | 25,2 | 21,3 | 0,25 | 0,14 | 0,035 | 0,04 | 0,07 | 0,01 | 0,07 | | | 446/11 |
| | | | | | | | | | | | | | | | | | |
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FINAS
Finnish Accreditation Service
T001 (EN ISO/IEC 17025)

Espoo, 18.11.2011
VTT Expert Services Oy

Tulos pätee vain analysoiduille näytteille.
Mittausepävarmuustaulukko toimitetaan pyydettäessä.

Erikoistutkija Tomas Törnkvist

# APPENDIX 7
# SUMMARY
# Boildec Oy, Field tests of furnace materials
# test report No.5 22.12.2011

Prepared by: Jussi Vänskä
Date: 22.12.2011
Subscriber: Finnish Recovery Boiler Committee

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**FURNACE TUBE TEST PROBE**

The aim of this test was to expose selected materials to recovery boiler furnace conditions for about 2720 hours, i.e. the same time as used in previous test, so that the average material temperatures on furnace side surface is 440°C ± 10°C. Materials tested were 3R12 (304L), Sanicro28, Sanicro38 and HR11N.

The test was started by installing the test probe in place on 26nd of July 2011. Set value for system pressure was set at 9,4 bar(a). The test began when pressure exceeded 8,0 bar(a) at 8:36 am. The saturation temperature of heat transfer oil exceeded then 370°C according to thermocouple readings (and was about 20°C more than water saturation temperature at 170 bar pressure).

The test was completed on 19th of December 2011 at 10:30 am when the probe had been exposed to recovery boiler furnace conditions for 2630 hours, i.e. close to the target time.

**Instrumentation of the test device**

The test probe was equipped with four thermocouples, two of which installed vertically and horizontally in the middle of the top (3R12) and the lowest (HR11N) test pieces. Other two thermocouples were installed inside the tip, one measuring the cooling oil temperature and the other one inside surface temperature. The set value for system pressure was selected on the basis of the thermocouple readings and the data from previous tests. The pressure was adjusted with a cooling fan regulated by PI controller.

The probe was also equipped with two electric heating elements to make sure that the system pressure would not drop too low when the tip of the probe is sprayed by black liquor (the probe was installed in an empty liquor gun opening, i.e. close to operating liquor guns). The electric heating elements were automatically turned on/off when temperature of the test device dropped below/increased above the set point. The set point was selected so that the system pressure would remain above 3 bar(a) (with cooling oil saturation temperature more than 315°C) all the time the probe is installed.

## Inner side surface temperature, cooling oil temperature and system pressure during the test

In figure 1 are shown the temperature on the inner side surface, cooling oil saturation temperature and system pressure during the test.

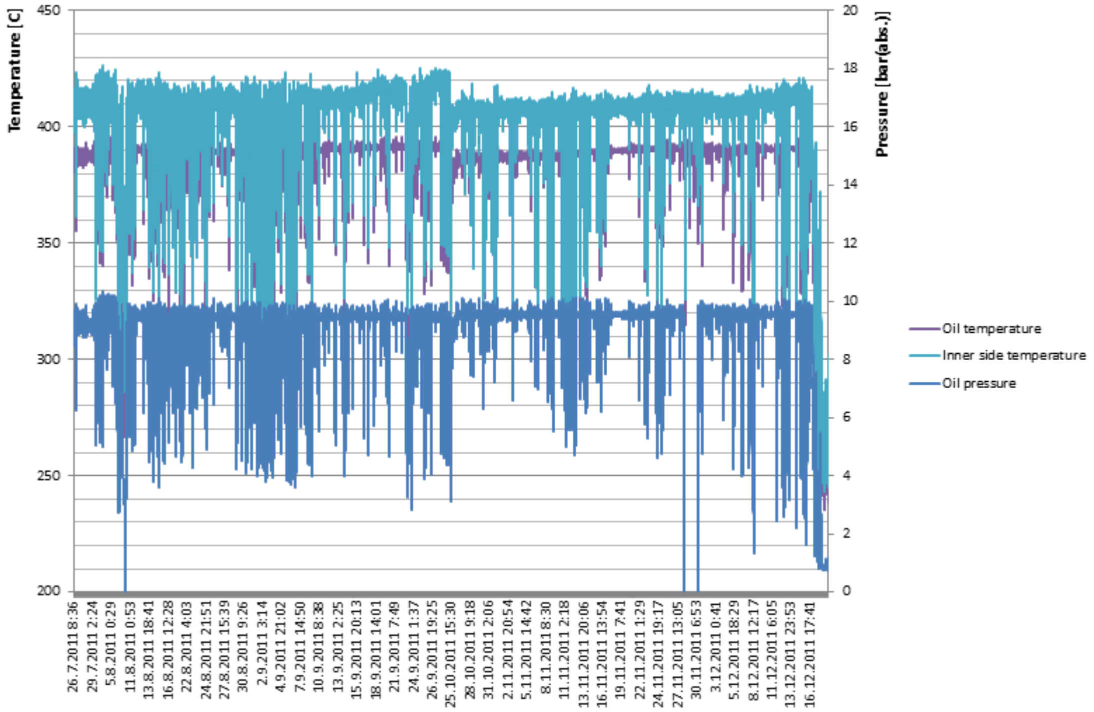


**Figure 1.** Inner side surface temperature, cooling oil saturation temperature and system pressure during the test.

During the test there was found small leakages in the test probe cooling oil system and the probe had to be drawn out of the liquor gun opening two times and cooled down for repairing the leakages.

During the test period the recovery boiler in question was also shut down for annual outage for about 30 days. After the outage the cooling oil was replaced and the cooling oil system was rinsed with a solvent to clean the system. That than be seen in a slight drop in probe inner side temperature roughly in the middle of the test period.

During the whole 2630 hour test period the system pressure stayed above 8 bar(a) 2157 hours (2154 hours in previous test).

**Material temperatures**

The two thermocouples inside the test pieces broke down almost immediately after installing the probe into liquor gun opening. Due to this the calculated heat fluxes from the previous test will be referred in estimating the temperatures on test pieces on furnace side surfaces. The probe geometry and operation were the same in both tests.

In previous test the average heat flux across the top test piece was calculated to be 142 kW/m$^2$ and 173 kW/m$^2$ across the lowest test piece. Average inner side temperature was now 410,8 °C, which is close to what it was in previous test 411,6 °C. Heat fluxes across the test pieces can now be estimated to be roughly the same as in previous test and can be used in estimating the test piece surface temperatures.

Heat transfer coefficient for 3R12 material (top test piece) at 400 °C is 22 W/m°C, 45,3 W/m°C for carbon steel at 400 °C and cladding thicknesses 1,65 mm for 3R12 material and 4,88 mm for carbon steel. Heat transfer coefficient for HR11N material (lowest test piece) 400 °C is 18,5 W/m°C and material thickness 3,64 mm.

Now the estimates of material temperatures on probe furnace side surface can be calculated by using above mentioned material properties, measured inner side temperature and estimated average heat fluxes obtained from the previous test. In figure 2 are shown the temperature distributions on upper and lower test pieces during the test.

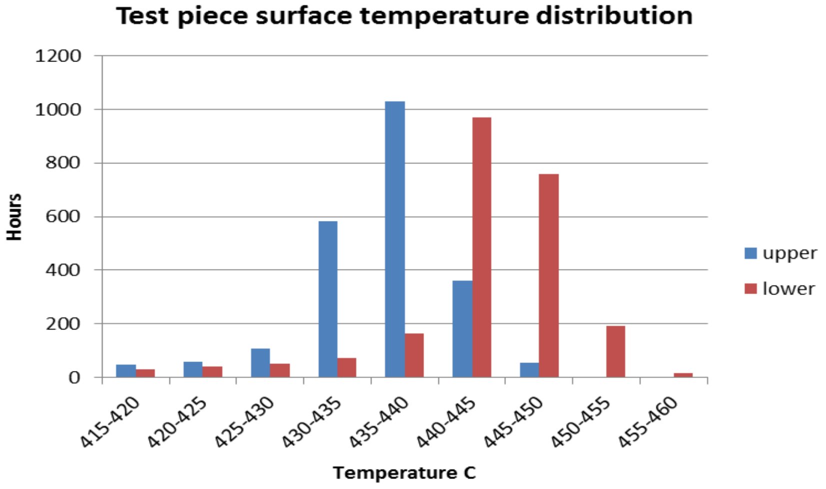


**Figure 2.** Temperature distribution on upper and lower test piece on furnace side surfaces during the test.

Prepared by: Jussi Vänskä
Date: 22.12.2011
Subscriber: Finnish Recovery Boiler Committee

## Summary

Test material average temperatures were estimated to be close to what they were in previous test according to probe inner side temperature measurements (410,8 °C vs. 411,6 °C). The estimate of the average temperature on the surface of the top test piece (3R12) was now 437°C and 445°C on the surface of the lowest test piece (HR11N). The total exposure time was 2630 hours of which the pressure stayed above 8 bar(a) 2157 hours, i.e. 82 % of the time.

The temperatures in other two test pieces were not measured, but there is no reason to believe that they would have been markedly different from those of the upper test piece.

As the estimated surface temperatures in all test pieces were reasonable close to the target value of 440 ± 10°C for a significant portion of the test duration and there were no uncontrolled excursion of material temperatures, the test was carried out successfully.

# APPENDIX 8
# SUMMARY
# VTT, Analysis of the furnace test materials presentation 12.4.2012

Business from technology

# FIELD TESTS OF FURNACE MATERIALS - Results from probe test No. 5

SKYREC JR 12.04.2012

Pekka Pohjanne, VTT

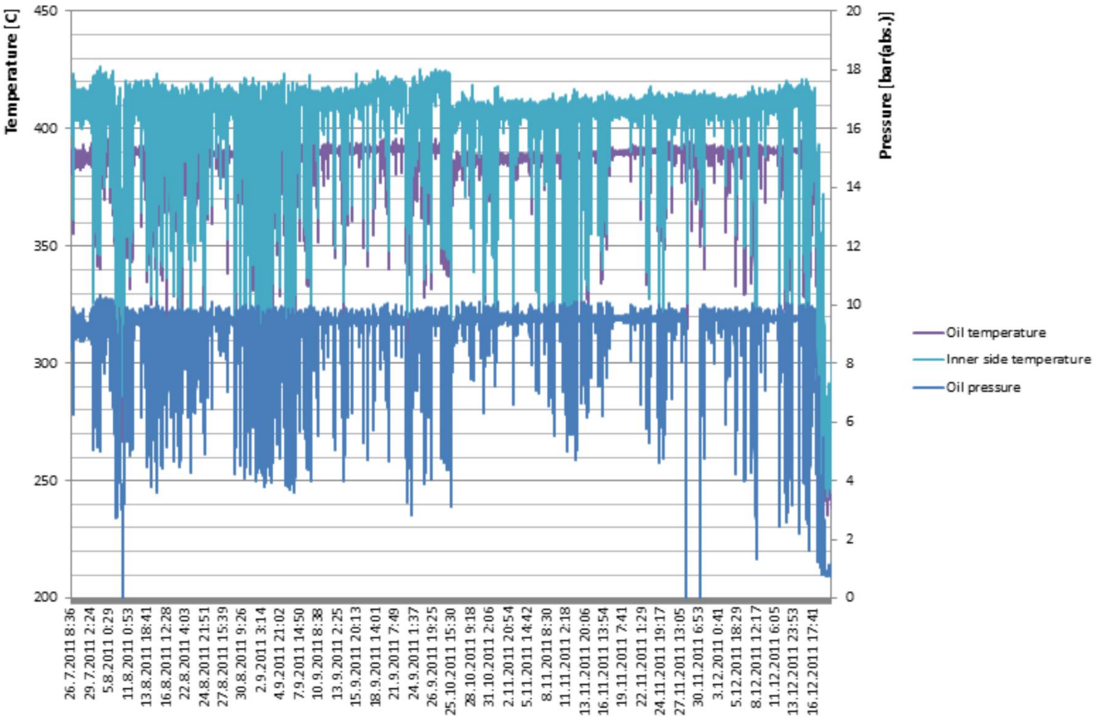
---

# TEST MATRIX

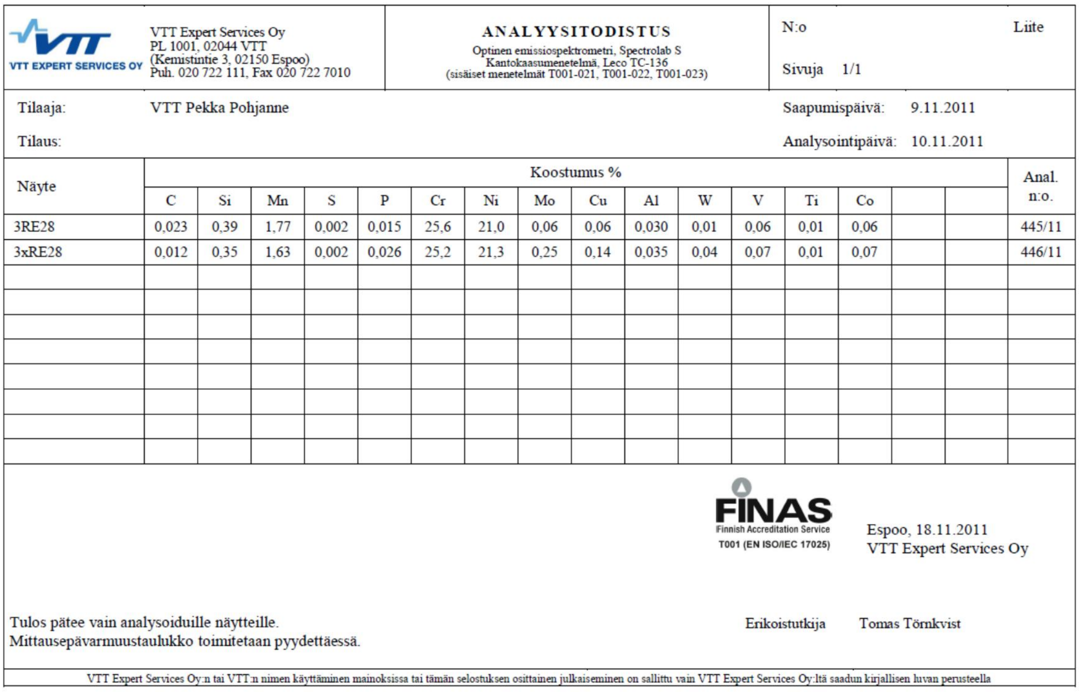
| Test No. | Test materials | Test duration, hours | | Effective temperature |
|---|---|---|---|---|
| | | Total | Effective$^{A)}$ | |
| 1 | 3R12(AISI 304L), 3RE28(AISI 310S), Sanicro28, Sanicro38 | 1000 | 906<br>(pressure over 9 bar) | ca. 440°C |
| 2 | 3R12(AISI 304L), 3XRE28, HR11N, Sanicro67, |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

$^{A)}$Used in corrosion rate calculations

# Temperature and circuit pressure in the test No. 5



# Chemical compositions of the 3RE28 and 3XRE28



VTT EXPERT SERVICES OY

VTT Expert Services Oy
PL 1001, 02044 VTT
(Kemistintie 3, 02150 Espoo)
Puh. 020 722 111, Fax 020 722 7010

**ANALYYSITODISTUS**

Optinen emissiospektrometri, Spectrolab S
Kantokaasumenetelmä, Leco TC-136
(sisäiset menetelmät T001-021, T001-022, T001-023)

N:o

Liite

Sivuja 1/1

Tilaaja: VTT Pekka Pohjanne

Tilaus:

Saapumispäivä: 9.11.2011

Analysointipäivä: 10.11.2011

| Näyte | Koostumus % | | | | | | | | | | | | | | | | Anal. n:o. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | S | P | Cr | Ni | Mo | Cu | Al | W | V | Ti | Co | | | |
| 3RE28 | 0,023 | 0,39 | 1,77 | 0,002 | 0,015 | 25,6 | 21,0 | 0,06 | 0,06 | 0,030 | 0,01 | 0,06 | 0,01 | 0,06 | | | 445/11 |
| 3xRE28 | 0,012 | 0,35 | 1,63 | 0,002 | 0,026 | 25,2 | 21,3 | 0,25 | 0,14 | 0,035 | 0,04 | 0,07 | 0,01 | 0,07 | | | 446/11 |
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FINAS
Finnish Accreditation Service
T001 (EN ISO/IEC 17025)

Espoo, 18.11.2011
VTT Expert Services Oy

Tulos pätee vain analysoiduille näytteille.
Mittausepävarmuustaulukko toimitetaan pyydettäessä.

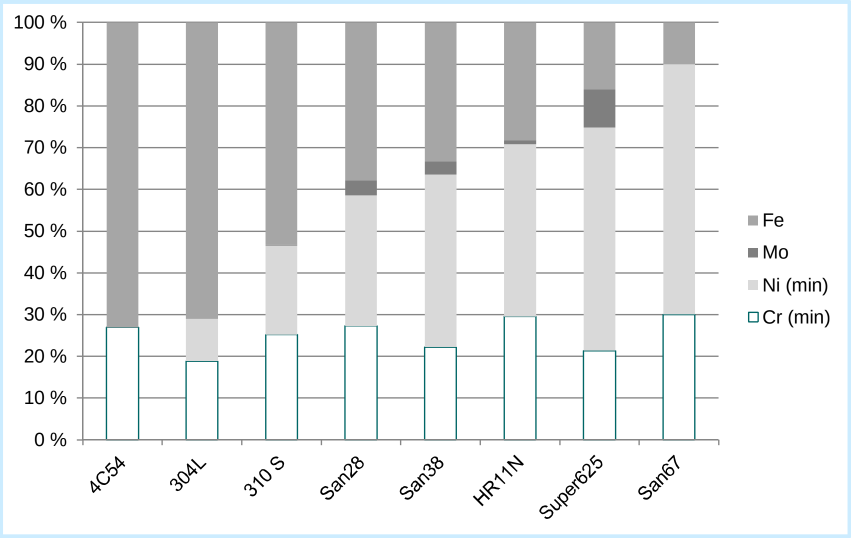
Erikoistutkija Tomas Törnkvist

VTT Expert Services Oy:n tai VTT:n nimen käyttäminen mainoksissa tai tämän selostuksen osittainen julkaiseminen on sallittu vain VTT Expert Services Oy:ltä saadun kirjallisen luvan perusteella

# TEST MATERIALS

**Selected by SKYREC Steering committee**

- Carbon steel (P265GH), 3R12 (AISI 304L), 3RE28 (AISI 310S), 3XRE28 (AISI 310/310S)), Sanicro 28, Sanicro 38 (mod. UNSN08825), Sanicro 67 (Alloy 690), HR11N and Super 625.



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# Results – Corrosion rates

# Corrosion resistance evaluation – Procedures

**A. Wall thickness measurements before and after testing (corrosion rate)**

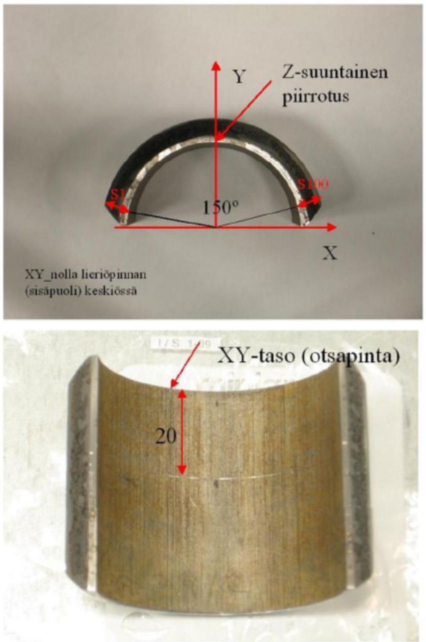
- Thickness profiles at a function of circumference from three locations (axial direction)
  → average & maximum WT loseses

**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



*Measurements with coordinate measurement machine*

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# Probe No.5 after the test

# Probe No.5 after the test

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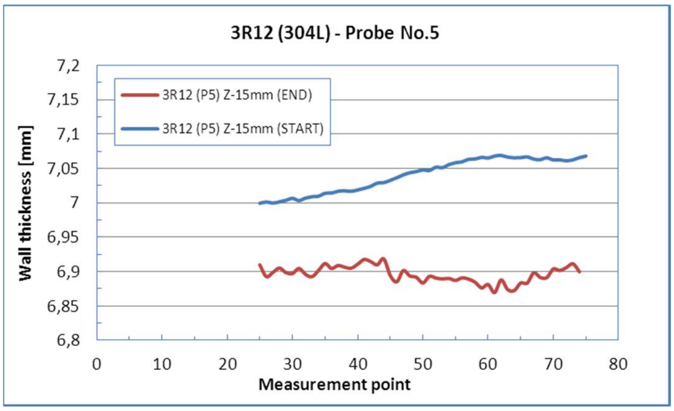
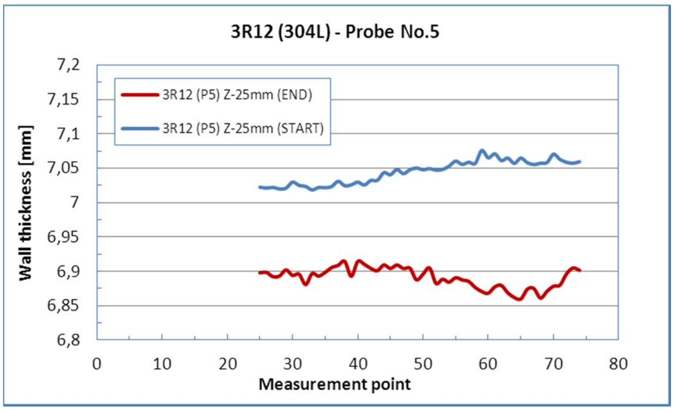
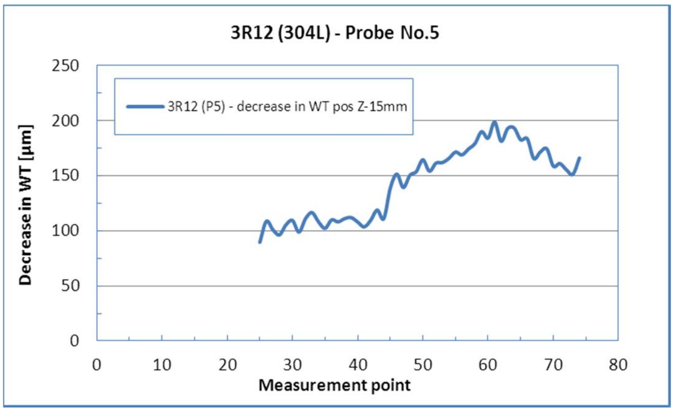
# Results – 3R12 (304L)

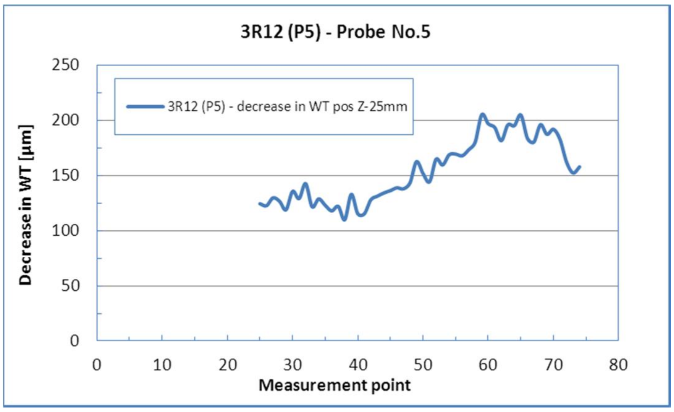
# 3R12 (AISI 304L) – Examples of WT profiles



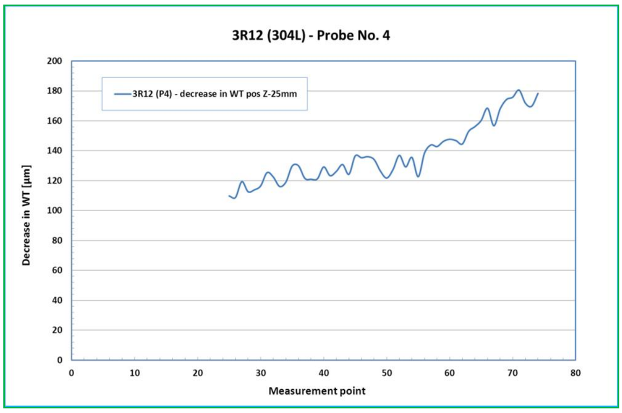


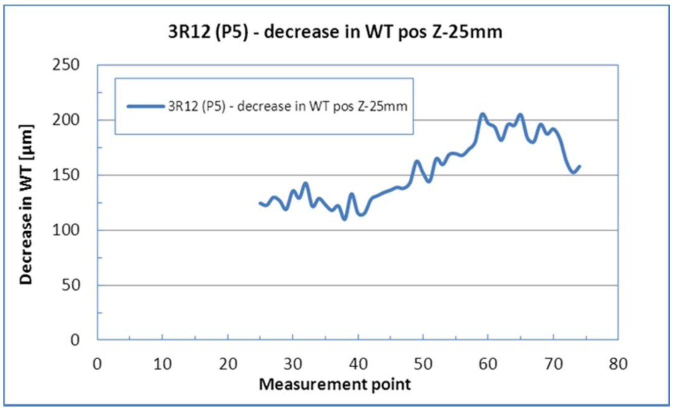
# 3R12 (AISI 304L) - Examples of WT thinning





# 3R12 (AISI 304L) – Comparison btw. test No.4 & 5





- *Probe No.4 – Effective test duration 2154 h & temperature 440°C*
- *Probe No.5 – Effective test duration 2157 h & temperature 440°C*

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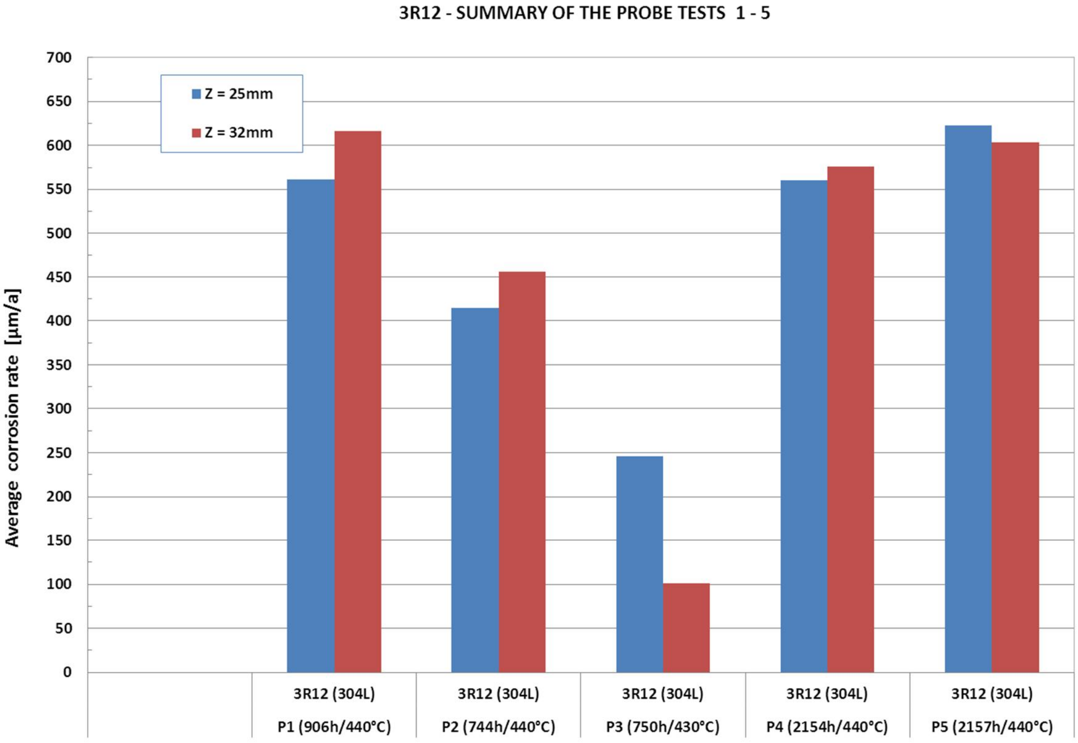
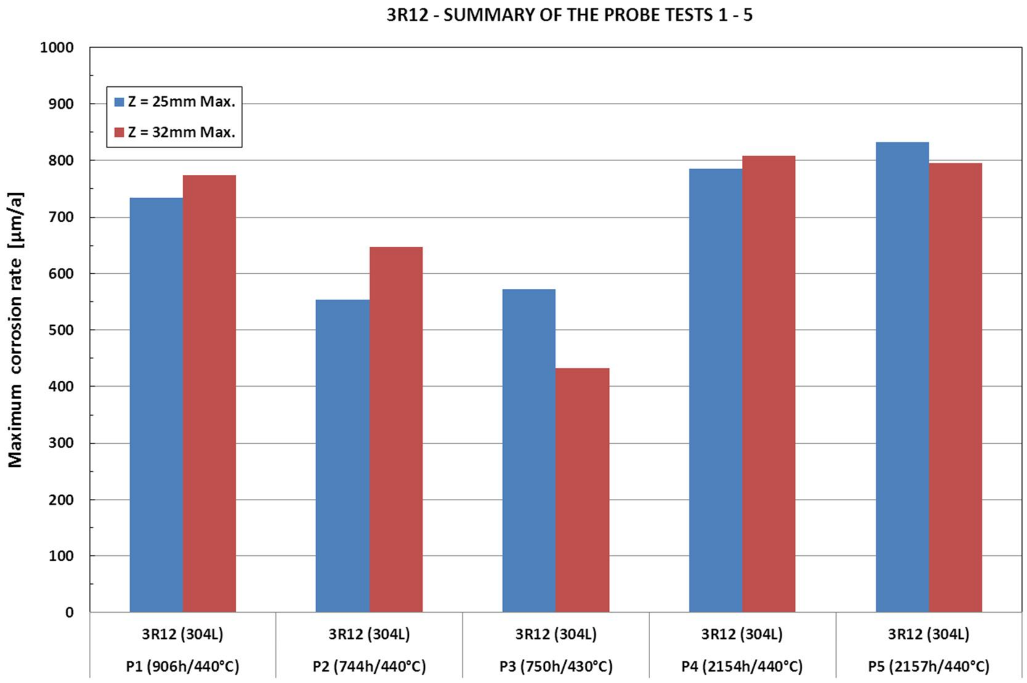
# 3R12 (AISI 304L) – Average corrosion rates



# 3R12 (AISI 304L) – Maximum corrosion rates



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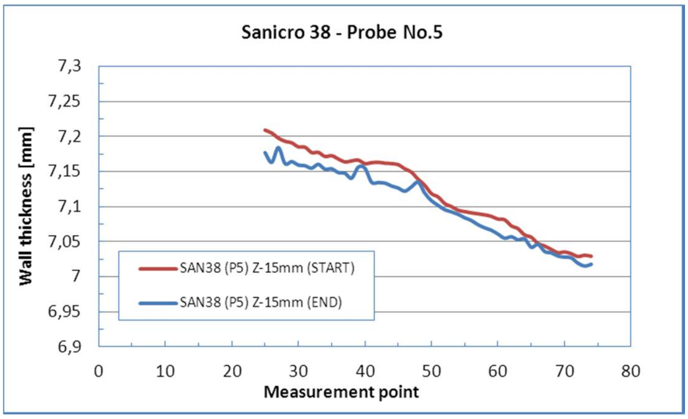
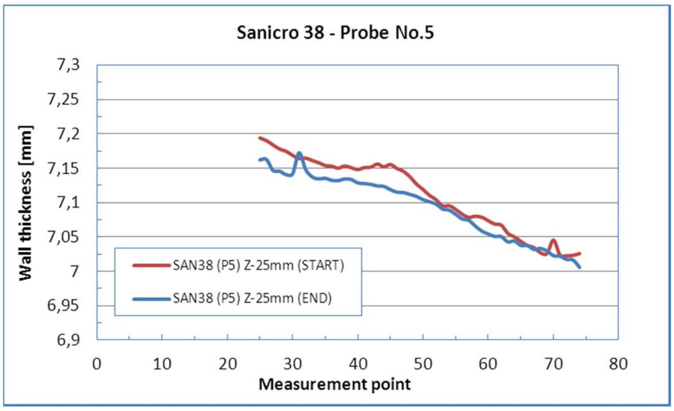
# Results – Sanicro 38

# Sanicro 38 – Examples of WT profiles





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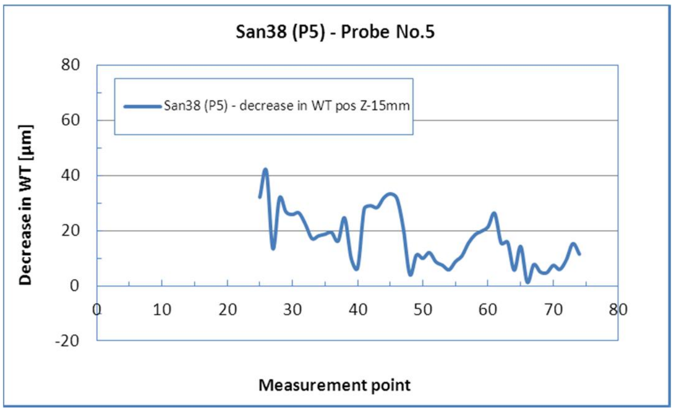
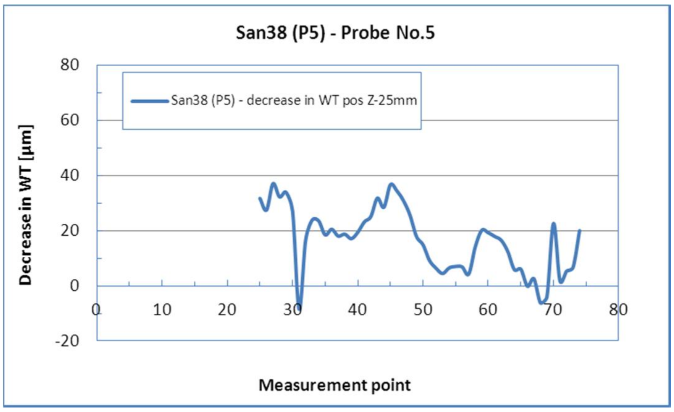
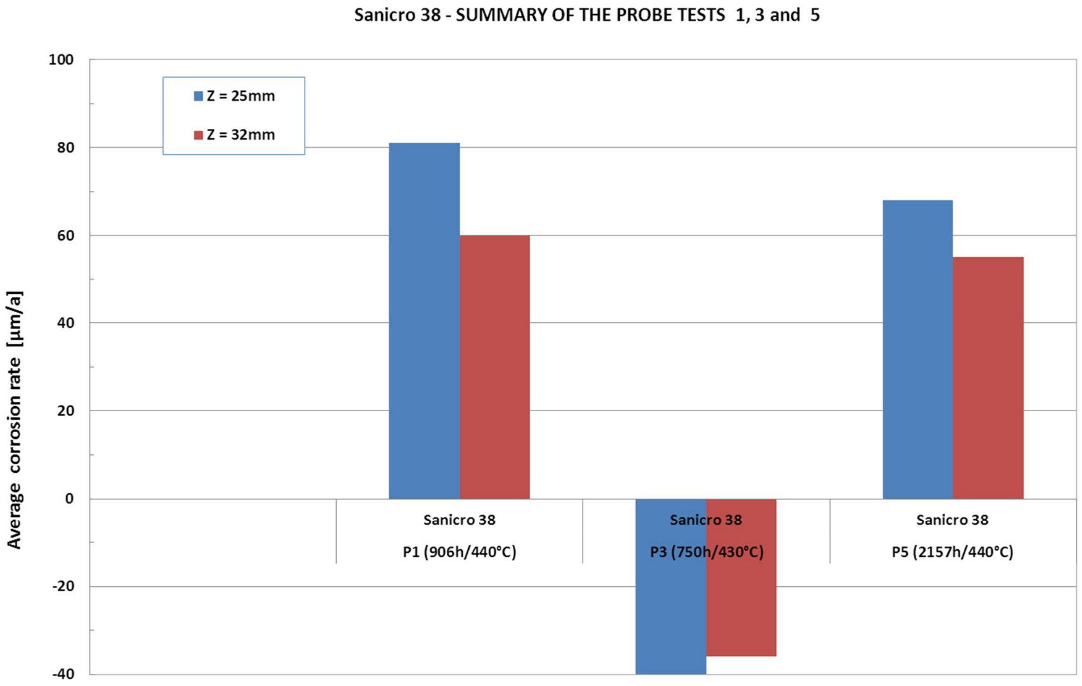
# Sanicro 38 - Examples of WT thinning





# Sanicro 38 – Average corrosion rates



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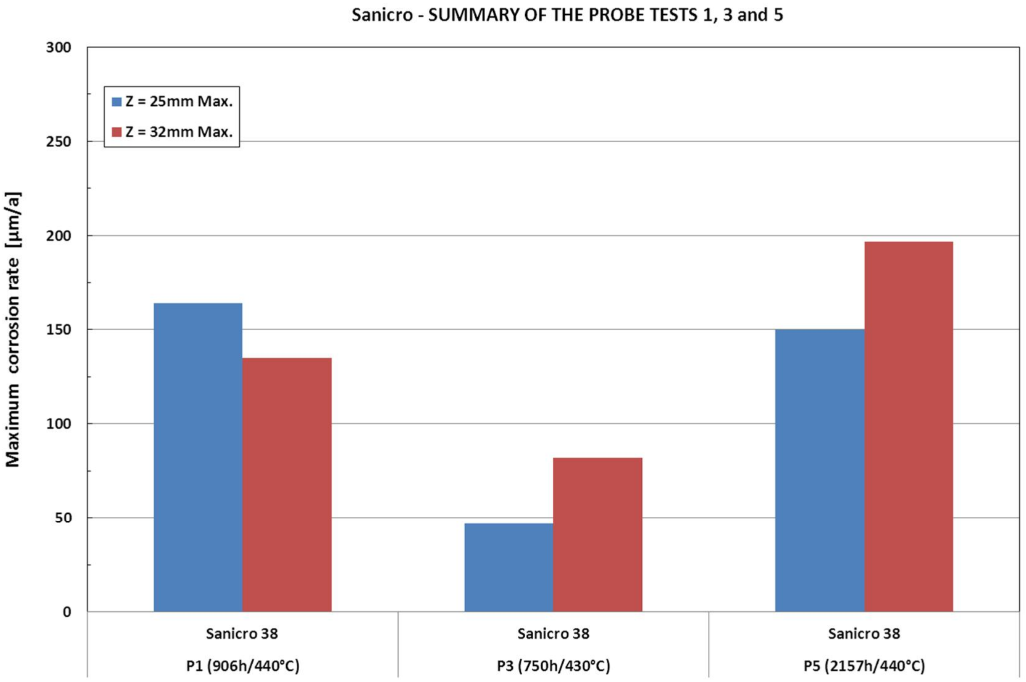
# Sanicro 38 – Maximum corrosion rates



# Results – Sanicro 28

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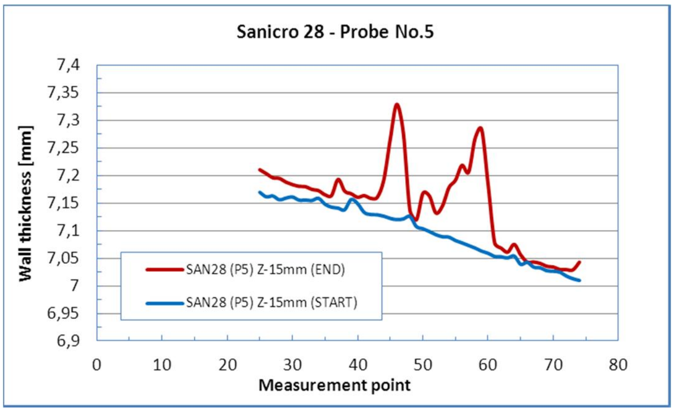
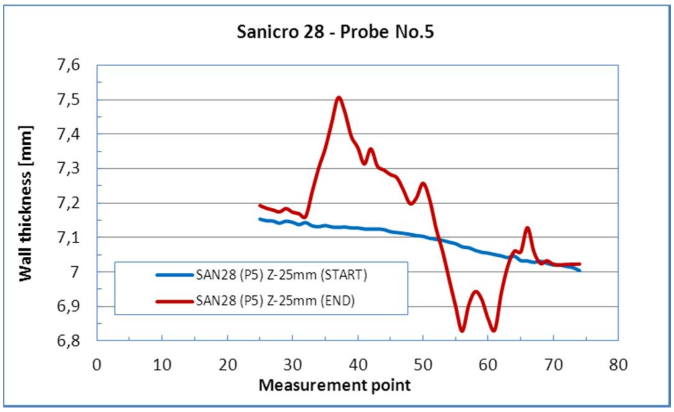
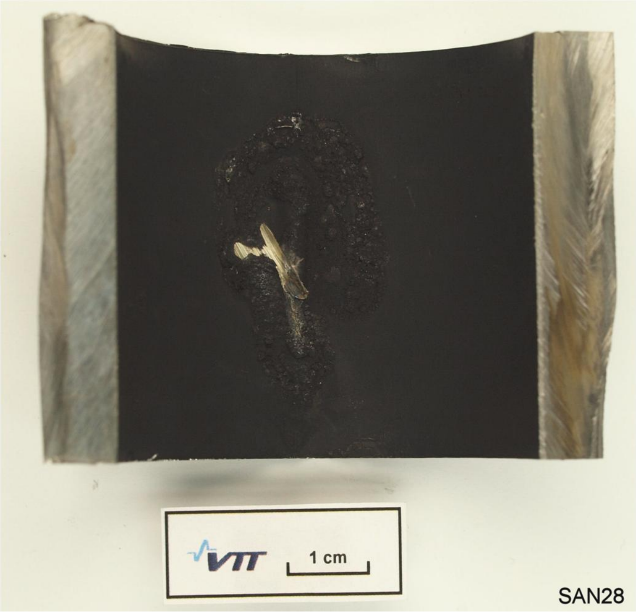
# Sanicro 28 – Examples of WT profiles



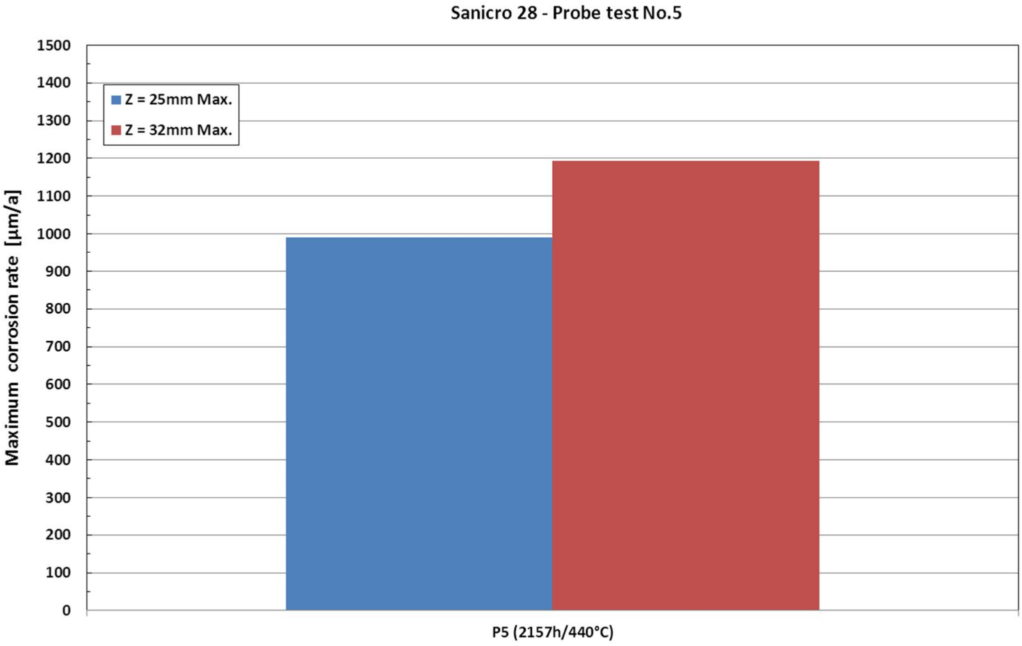


# Results – Sanicro 28 after the test No.5



- Thermocouple was welded to inner surface so that thickness measurements are difficult !!!

# Sanicro 28 – Maximum corrosion rates



- Needs to be cleaned and measured again

# Results – HR11N

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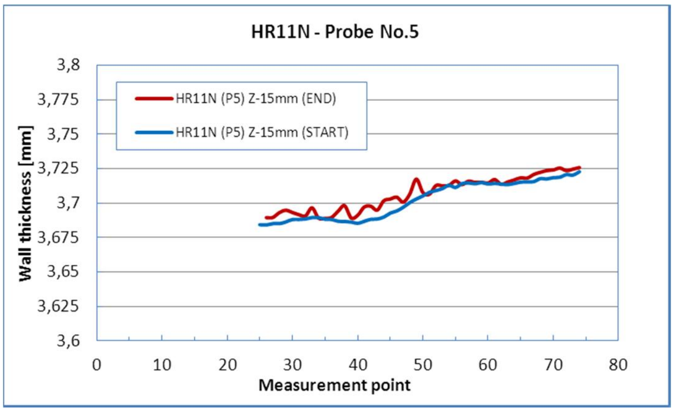
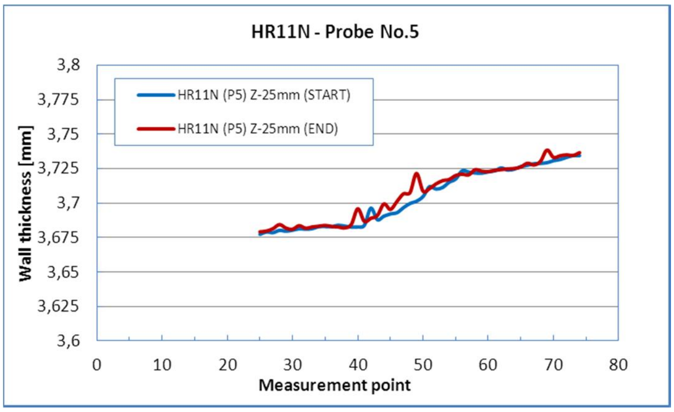
# HR11N – Examples of WT profiles





# Results – HR11N after the test No.5

- Deposits on the inner surface → needs additional cleaning & new measurements

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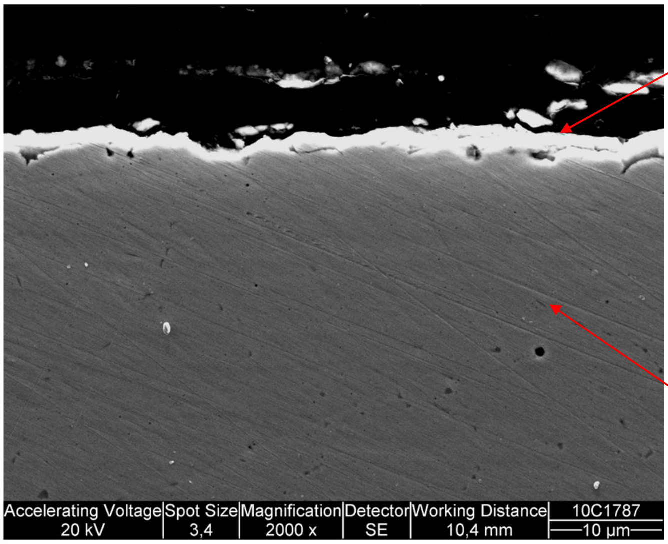
# Results – Characterisation

# First results/observations from last year Dec. 2010



***Thin white outer layer***

| *Element* | *Weight %* | *Weight % Error* |
|---|---|---|
| *O* | 14.26 | +/- 0.27 |
| *Na* | 1.24 | +/- 0.11 |
| *Al* | 0.46 | +/- 0.06 |
| *Si* | 1.01 | +/- 0.06 |
| *S* | 7.16 | +/- 0.26 |
| *Cl* | 0.47 | +/- 0.07 |
| *K* | 1.00 | +/- 0.06 |
| *Ti* | 0.12 | +/- 0.03 |
| *Cr* | 29.57 | +/- 0.20 |
| *Mn* | 0.10 | +/- 0.10 |
| *Fe* | 7.84 | +/- 0.19 |
| *Ni* | 35.45 | +/- 0.38 |
| *Mo* | 1.33 | +/- 0.56 |
| *Total* | 100.00 | |

***Bulk material***

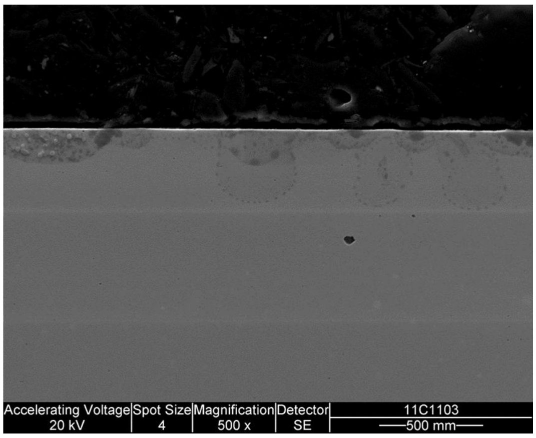
| *Element* | *Weight %* | *Weight % Error* |
|---|---|---|
| *Al* | 0.15 | +/- 0.03 |
| *Si* | 0.43 | +/- 0.03 |
| *Ti* | 0.21 | +/- 0.03 |
| *Cr* | 30.66 | +/- 0.14 |
| *Mn* | 0.20 | +/- 0.09 |
| *Fe* | 10.42 | +/- 0.19 |
| *Ni* | 57.93 | +/- 0.41 |
| *Total* | 100.00 | |

**What happens?**

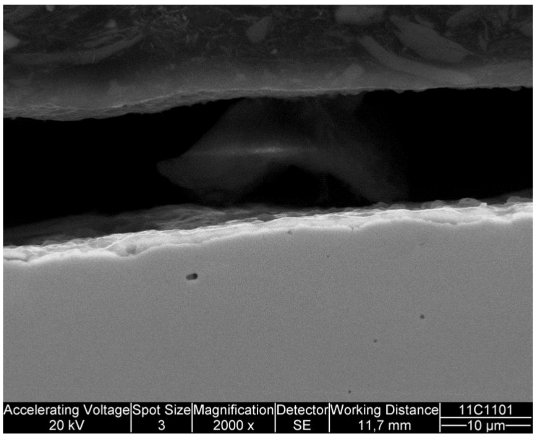
- **White outer layer – Low Fe, Ni**

---

# Results/observations from Probe No. 4 - 3R12 (304L)



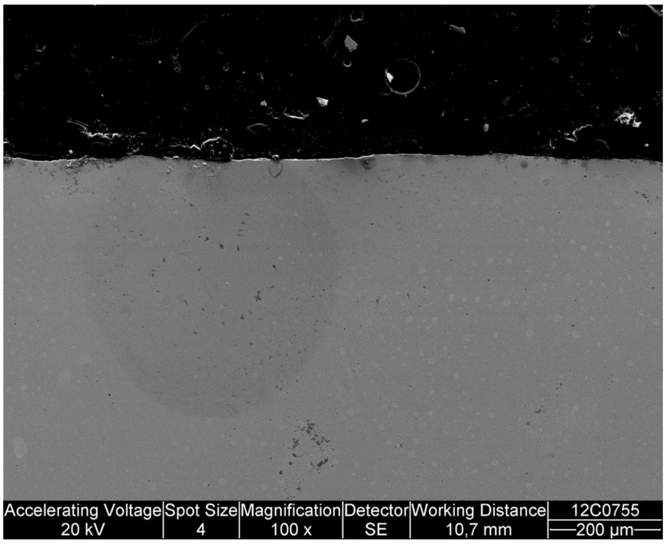
*Unexposed reference*

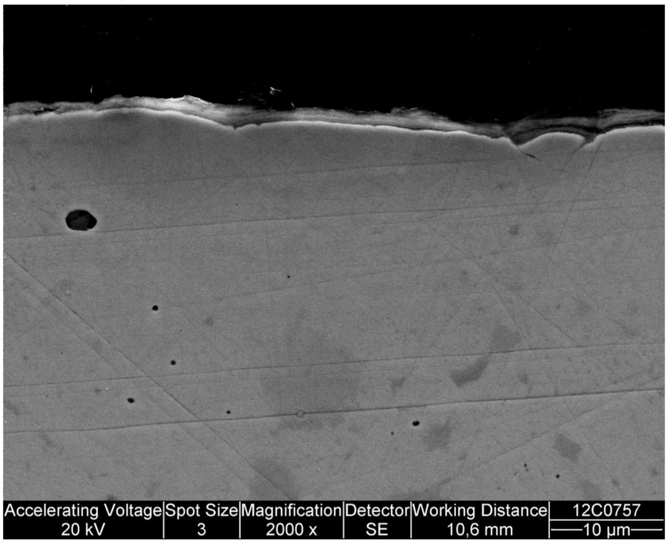


*After exposure – effective test duration 2154 h & temperature 440°C*

| **3R12 (304L) - P4** | **Composition wt.-%** | | | | | |
|---|---|---|---|---|---|---|
| | **Cr** | **Ni** | **Mo** | **Fe** | **S** | **O** |
| **Base material** | **18,8** | **9,6** | **0,4** | **69,3** | | |
| **Thin outer layer** | **25,0** | **3,6** | | **32,8** | **10,1** | **24,4** |

# 3R12 - Probe No. 5





# Conclusions

- Carbon steel corrodes at extremely high rate (4 mm/a) at the temperature of 440 °C.
- The 3R12 (AISI 304L) composite tube material corrodes in such high rate (average ca. 0.5-0.6 mm/a and maximum ca. 0.8 mm/a) that it can’t be safely used in the lower furnace
- Sanicro 38 (mod. UNS N08825) and HR11N are ca. 3-4 times better than the 3R12 (AISI 304L). *HR11N long term sample needs to be re-analysed (Probe No. 5)*
- Sanicro 28? - L*ong term sample needs to be re-analysed (Probe No. 5)*

# VTT creates business from technology

# APPENDIX 9
# SUMMARY
# Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment
final report 28.2.2012

# AKTIIVIHIILI, UV-KÄSITTELY JA KÄÄNTEISOSMOOSI SOODAKATTILALAITOKSEN LISÄVEDEN ORGAANISEN AINEEN VÄHENTÄMISESSÄ

## - TUTKIMUSRAPORTTI

JP|analysis

# Sisällysluettelo

# 1. Johdanto

Tämä tutkimus on jatkoa keväällä 2010 valmistuneelle pro gradu -työlle ”Soodakattilalaitoksen lisäveden orgaanisen aineen vähentäminen”.[1] Tutkimus on osa Suomen Soodakattilayhdistys ry:n SKYREC-projektia ja siihen kuuluvaa Kattilaveden ja höyryn laadun varmistaminen -osaprojektia. Tutkimuksen syynä on lisäveden orgaanisten yhdisteiden hajoamistuotteiden (hiilidioksidi ja pienen molekyylikoon orgaaniset hapot) aiheuttama korroosioriski tiettyihin soodakattilalaitoksen vesi-höyrykierron osiin.

Tutkimuksen tarkoituksena oli vertailla aktiivihiilisuodatusta, UV-säteilyn käyttöä ja käänteisosmoosia soodakattilalaitoksen lisäveden orgaanisten yhdisteiden poistossa. Kokeet toteutettiin kesän 2010 – syksy 2011 välillä. Vuoden 2010 osalta kokeet olivat pääasiassa esikokeita ja varsinainen aktiivihiilisuodattimen pitkän aikavälin seuranta toteutettiin vuoden 2011 aikana.

Aktiivihiilisuodatuksen osalta tutkimuksen tavoite oli selvittää mahdollisuutta integroida aktiivihiilisuodatin osaksi suolanpoistolaitosta. Tutkimuksessa verrattiin kolmea eri happopestyä aktiivihiililaatua jatkuvatoimisten suodatuskokeiden avulla. Pitkän aikavälin testiin valittiin kolmesta hiilestä parhaaksi osoittautunut, tosin erot olivat hyvin pienet. Lisäksi selvitettiin muun muassa aktiivihiilisuodattimen biologisen aktiivisuuden merkitystä puhdistustulokseen, johtokyvyn ja silikaattipitoisuuden muutosta aktiivihiilipatjassa ja orgaanisen aineksen kokojakauman ja koostumuksen vaihteluja aktiivihiilisuodattimessa ja aiemmin vedenpuhdistusprosessissa.

UV-säteilyn käyttö orgaanisten yhdisteiden hajotukseen ilman hapetinkemikaaleja on suhteellisen tuntematon tekniikka suuren mittakaavan sovelluksissa. Tutkimuksessa selvitettiin suolanpoistolaitoksen sivuvirtaukseen kytketyn UV-laitteen vaikutusta veden TOC-pitoisuuteen, johtokykyyn ja orgaanisten yhdisteiden koko- ja rakennejakaumaan. Lisäksi tutkittiin kontaktiajan, titaanidioksidikatalyytin ja vetyperoksidin vaikutusta UV-käsittelyn tehoon.

Käänteisosmoosin osalta tutkimuksessa selvitettiin laitteistojen hankinta- ja käyttökulut pyytämällä laitetoimittajilta tarjoukset soveltuvista laitteistoista.

Tutkimusta rahoittivat Suomen Soodakattilayhdistys ry, CEWIC-projekti (*Center of expertise in the water industry cluster),* Stora Enso Oyj ja Aquator Oy. Tutkimuksen toteutti JP-analysis ja yhteistyötahoina mukana olivat Oulun yliopiston kemian laitos, Hanovia, IP-Produkter Oy, Chemviron Carbon Ltd. ja Haarla Oy.

Tutkimuksen tuloksia on esitelty Soodakattilapäivillä Tampereella 27.10.2010 ja SKYREC-seminaarissa Helsingissä 20.10.2011. Lisäksi projektin aktiivihiilikokeiden tuloksista on laadittu tieteellinen julkaisu.

# 6. Johtopäätökset

## 6.1. Aktiivihiilikokeet

Aktiivihiilikokeissa tärkein mittausparametri oli orgaanisen hiilen kokonaispitoisuus (TOC). TOC:ta mitattiin offline- ja online-tyyppisesti sekä Saksassa tehtyjen LC-OCD-analyysien yhteydessä. Vaikuttaa siltä, että Oulun yliopiston laitteella saatavat absoluuttiset TOC-lukemat pienille pitoisuuksille sisältävät virhettä noin 50 – 150 ppb. TOC-reduktiot kuitenkin vaikuttavat luotettavilta (virhe supistuu suhteita laskettaessa pois).

### 6.1.1. Aktiivihiililaatujen vertailu TOC-poistossa

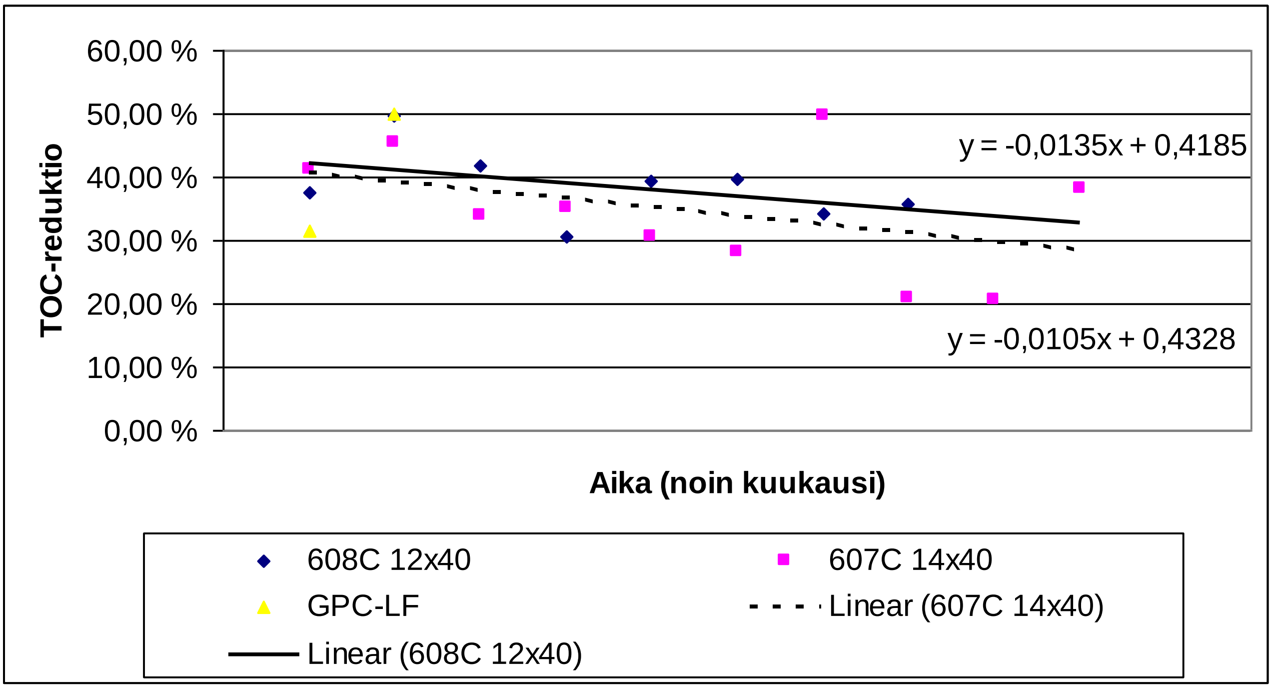
Aktiivihiililaatuja vertailtiin jatkuvatoimisilla suodatuskokeilla. Tavoitteena oli selvittää mikä kolmesta aktiivihiililaadusta poistaa orgaanisia yhdisteitä tehokkaimmin. Aktiivihiiliä testattiin erilaisilla suodattimilla (kuvat 2 ja 3), mikä vaikeuttaa suoraa tulosten vertailua. Kokeet tehtiin myös eri aikoina, joten tulevan veden orgaanisen aineksen koostumus on ollut erilainen. Vertailua on tässä yhteydessä tehty keskimääräisen TOC-reduktion perusteella (taulukko 13) ja noin kuukauden mittaisen koejakson tulosten perusteella (kuva 34). Kaikilla testatuilla aktiivihiilillä päästiin suodatusjakson alussa noin samoihin TOC-pitoisuuksiin.

CPG-LF 12X40 -aktiivihiili vaikuttaa taulukon 10 vertailun perusteella parhaalta, mutta sen suodatusjakso oli vasta alussa ja näytteitä ehdittiin analysoida vain kaksi. Kahdella AQUACARB -aktiivihiilellä ei ole merkittävää eroa keskimääräisen TOC-reduktion perusteella. Kuvan 34 perusteella AQUACARB 608C 12X40 vaikuttaa parhaiten toimivalta (GPC-LF -hiiltä ei voi kahden pisteen perusteella kuvasta 33 arvioida), mutta erot eivät ole suuria.

Aktiivihiilten vertailukokeiden perusteella parhaiten soveltuva aktiivihiili on joko AQUACARB 608C 12X40 tai GPC-LF 12X40. Ratkaiseva tekijä lienee hiililaadun hinta ja saatavuus.

Taulukko 13. Aktiivihiilillä saavutetut keskimääräiset TOC-reduktiot.

| **Aktiivihiili** | **Keskimääräinen TOC-reduktio** |
|---|---|
| AQUACARB 607C 14X40 | 37 % |
| AQUACARB 608C 12X40 | 39 % |
| GPC-LF 12X40 | 41 % |



Kuva 34. Aktiivihiililaatujen vertailu noin kuukauden kestäneellä aikajaksolla.

### 6.1.2. Johtokykymittaukset

Johtokykyä tarkkailtiin TSP-vedestä, aktiivihiilisuodatetusta vedestä ja koesekavaihtimen jälkeisestä vedestä.

Veden johtokyky kasvaa merkittävästi aktiivihiilisuodattimessa kaikilla aktiivihiililaaduilla. Tehdyissä alkuaineanalyyseissä ei kuitenkaan havaittu, että aktiivihiilestä irtoaisi epäpuhtauksia. Myöskään merkittävää orgaanisen aineen hajoamista ioniseksi orgaaniseksi aineeksi ei havaittu. Johtokyvyn nousun voisi selittää orgaanisen hiilen muuttuminen epäorgaaniseksi (karbonaatti, vetykarbonaatti), mikä viittaisi suodattimen mikrobiologiseen toimintaan. Kuitenkaan pesäkelukumittaukset eivät tue tätä tulkintaan. TOC-mittauksissa havaittiin aktiivihiilisuodatetussa vedessä kohonnut epäorgaanisen hiilen pitoisuus. Aktiivihiilisuodatetun veden johtokyvyn kasvun syy ja taustalla vaikuttava mekanismi jäi tutkimuksessa kuitenkin osittain tuntemattomaksi.

Tutkimuksessa havaittiin heikohkoa korrelaatiota ($R^2$-korrelaatiokerroin lineaariselle riippuvuudelle noin 0,5) aktiivihiilisuodattimen TOC-reduktion ja aktiivihiilisuodatetun veden johtokyvyn välillä (kuva 11). Johtokykymittausten data hyödyntäminen edellyttää johtokyvyn nousun syyn parempaa ymmärtämistä.

Havaittiin, että aktiivihiilisuodattimen jälkeinen johtokyky seuraa tietynlaista trendiä, jossa johtokyky nousee ensin tietylle tasolle ja alkaa sieltä hitaasti laskea (kuvat 19 ja 22).

Aktiivihiilisuodattimen jälkeisen sekavaihtimen tehtävä on alentaa aktiivihiilisuodattimessa noussut johtokyky takaisin hyväksyttävälle tasolle. Sekavaihdin poisti orgaanista hiiltä noin 10 - 20 % kun sekavaihtimeen pääsi epähuomiossa pieni määrä aktiivihiiltä ja aktiivihiilen likaista huuhteluvettä. Tällöin sekavaihtimen toimintamekanismi ei todennäköisesti ollut ioninvaihto. Vaihdettaessa sekavaihtimeen uusi ioninvaihtomassa, efekti poistui. Sekavaihdin ei tulosten perusteella tavallisesti alentanut TOC:ta merkittävästi.

### 6.1.3. Suodattimen biologisen aktiivisuuden herätys ja merkityksen arviointi

Aktiivihiilisuodattimen biologista aktiivisuutta tutkittiin pesäkelukumittauksilla, herätyskokeella ja kuumien lauhteiden suodatuskokeella.

Pesäkelukunäytteitä kerättiin TSP-vedestä, aktiivihiilisuodatetusta vedestä ja koesekavaihtimen jälkeisestä vedestä. Pesäkeluku kasvaa aktiivihiilisuodattimessa, mutta luvut ovat hyvin pieniä. Pesäkelukumittausten tulosten perusteella aktiivihiilisuodattimen biologinen aktiivisuus on vähäistä.

Herätyskokeessa (Oulun Veden Hintan vedenpuhdistuslaitokselta otetun käytetyn aktiivihiilen sekoittaminen uuden hiilen joukkoon) havaittiin hetkellinen kasvu TOC-reduktiossa, joka mahdollisesti liittyy käytetyn aktiivihiilen mukanaan tuomaan mikrobikantaan. Vaikutus poistui noin kahden viikon aikana. TSP-veden ravinne- ja orgaanisen hiilen pitoisuudet ovat niin pienet, että biologisen toiminnan muodostuminen ja ylläpito vaikuttavat epätodennäköisiltä.

Kuumien lauhteiden suodatuskokeessa kuuman lauhteen ajaminen suodattimen läpi alensi TOC-reduktiota noin 50 %. Kuuman lauhteen (lähes 100 ºC) oletettiin poistavan biologinen aktiivisuus suodattimesta. Pesäkelukumittaukset eivät kuitenkaan tue tulkintaa, jonka mukaan suodattimen toiminta olisi jopa 50 % biologinen.

Yhteenvetona voidaan todeta, että aktiivihiilisuodattimen toimintamekanismi vaikuttaa olevan käytännössä täysin adsorptioon perustuva. Biologisen aktiivisuuden herättäminen näyttäisi olevan mahdollista, mutta vaikutus on suhteellisen lyhytkestoinen.

### 6.1.4. Ominaispinta-alamääritykset

Ominaispinta-ala määritettiin käyttämättömästä, noin 4 kk ja noin 1 kk käytössä olleista AQUACARB 607C 14X40 -aktiivihiilinäytteistä. Käyttämättömän aktiivihiilen ominaispinta-ala vastasi valmistajan ilmoitusta. Käytettyjen aktiivihiilten pinta-alassa ei havaittu merkittäviä muutoksia (ks taulukko 6). Johtopäätöksenä voidaan sanoa, ettei aktiivihiilen ominaispinta-ala alentunut, mikä kertoisi huokosten tukkeutumisesta ja alentuneesta adsorptiokapasiteetista.

### 6.1.5. Kokojakaumamääritykset

Kokojakaumamääritysten perusteella Oulujoen vedessä on selvää vaihtelua orgaanisen aineen koostumuksessa. Tuloksissa näkyy koagulaatio-flokkaus-flotaatiovaiheiden orgaanista ainesta pilkkova vaikutus (kuva 23), joka ei todennäköisesti ole ko. vaiheiden toiminnan kannalta optimaalista. Mielenkiintoista on, että kokojakaumamääritysten perusteella AQUACARB 608C 12X40 -aktiivihiili toimisi merkittävästi tehokkaammin kuin GPC-LF 12X40 -aktiivihiili orgaanisten yhdisteiden poistossa (kuvat 28 ja 29). Eroa ei ole havaittavissa TOC-mittausten perusteella. Koesekavaihdin vaikuttaisi hieman vapauttavan orgaanista ainesta, mikä voi olla mahdollisesti näytteenotosta aiheutunut virhe (kuva 30).

### 6.1.6. LC-OCD-määritykset

LC-OCD-määritysten perusteella aktiivihiilisuodattimien poistamia orgaanisia yhdisteitä pystyttiin karakterisoimaan. Aktiivihiilisuodatin vaikutti poistavan muita orgaanisten yhdisteiden fraktioita paitsi biopolymeerejä melko tehokkaasti. Biopolymeerien huonompi poistoteho voi johtua niiden koosta: toisenlaista huokoskokoa oleva aktiivihiili mahdollisesti voisi poistaa niitä tehokkaammin.

### 6.1.7. Pitkän aikavälin seurantakoe (aktiivihiilen käyttöjakson pituus)

Aktiivihiilen TOC-poistoteho pysyi lähes vakiona koko 11 kuukauden koejakson ajan. Tämä näkyi sekä TOC-mittauksissa, että LC-OCD-määrityksessä, joka tehtiin noin 10 kuukautta pitkän aikavälin kokeen alettua. Aktiivihiilen käyttöjakson pituudesta voi tämän tutkimuksen perusteella todeta, että se on ainakin 11 kuukautta.

### 6.1.8. Tehdasmittakaavan aktiivihiilikoe

Tehdasmittakaavan koe kesti noin kolme kuukautta. Sinä aikana TOC-poistoteho oli noin 40 – 65 %, mikä vastasi pilot-kokeiden poistotehoa. Johtokyky nousi aktiivihiilisuodattimessa myös samoin kuin pilot-kokeissa. Tehdasmittakaavan kokeessa mitattiin aktiivihiilisuodatetun veden silikaattipitoisuutta, joka nousi huomattavasti: noin tasolle 200 mg/l aluksi. Kahden viikon aikana silikaattitaso aktiivihiilisuodatetussa vedessä laski tasolle noin 20 mg/l. Aktiivihiilisuodatinta seurannut sekavaihdin poistaa vapautuneen silikaatin ja sen rooli onkin tästä syystä erityisen tärkeä.

### *6.2. Oulun soodakattilan ja leijupetikattila K3:n vesi-höyrykierron TOC-, asetaatti- ja formiaattipitoisuudet*

Mitatut TOC-pitoisuudet olivat liian suuria suosituksiin ja kattiloissa käytettäviin paineisiin nähden. Kahden mittaussarjan (taulukot 11, 12 ja kuva 32) välillä oli aika suurta vaihtelua. Huomattavan suuri on taulukossa 11 esitetty lisäveden TOC-pitoisuus. Todennäköisesti tuloksessa on virheellisyyttä.

Asetaatti- ja formiaattipitoisuuksien mittaus ionikromatografilla kertoi orgaanisen aineksen hajoamisasteesta. Ensimmäisen näytesarjan mitatut pitoisuudet (taulukko 11) olivat yllättävän pieniä ja toisessa mittaussarjassa (taulukko 12) ei asetaattia ja formiaattia havaittu kuin ainoastaan kattilavedestä.

## 6.3. UV-kokeet

UV-valon käyttöä TOC:n hajotuksessa kokeiltiin yhteistyössä Hanovian (UV-lamppuvalmistaja) kanssa. Suurin kokeissa saavutettu TOC-reduktio oli noin 30 % (käytössä yksi UV-kammio ja keskipainelamppu). Kokeissa selvitettiin myös seuraavien tekijöiden vaikutusta TOC-poistotehoon:

- Viipymäaika UV-reaktorissa eli UV-säteilyannos.
- Lampun tyyppi (matalapaine- ja keskipainelamput).
- $TiO_2$-katalyytti.
- Vetyperoksidin käyttö hapettimena.

Tutkituista tekijöistä mikään ei oleellisesti parantanut TOC-poistotulosta. Vetyperoksidikokeen toteutus tosin epäonnistui, sillä käytetty putkimateriaali vapautti veteen muovinlisäaineita, mikä näkyi kohonneena TOC-pitoisuutena.

Tehtyjen kokeiden perusteella UV-käsittely TOC:n poistomenetelmänä soodakattilan lisävedestä ei ole kilpailukykyinen suuren energiankulutuksen ja alkuinvestoinnin vuoksi.

# 7. Jatkotutkimuskohteet

Tutkimuksessa avoimiksi tai osittain epäselviksi jääneitä kysymyksiä olivat:

- Aktiivihiilen käyttöjakson pituus: 11 kuukauden mittaisen koejakson aikana ei vielä ehtinyt tapahtua selkeää muutosta TOC-poistotehossa.
- Aktiivihiilen toimintamekanismi (oletus: adsorptio) ionivaihdetuissa vesissä ja johtokyvyn nousun täsmällinen syy.

# APPENDIX 10
# SUMMARY
# Cewic, Reduction of TOC in recovery boiler makeup water article Powerplant Chemistry 2/2012

# Reduction of Organic Carbon in Demineralized Make-up Water with Activated Carbon Filtration

*Tero Luukkonen, Reijo Hukkanen, Jaakko Pellinen, Jaakko Rämö, and Ulla Lassi*

## ABSTRACT

Organic compounds in the water-steam cycle are an emerging issue at recovery boiler plants. Decomposition products of organic compounds, mainly organic acids with low molecular weight and carbon dioxide, are often related to corrosion. Removal of organics from recovery boiler make-up water with activated carbon (AC) was investigated both in pilot and full scale 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. Total organic carbon (TOC), conductivity, silica concentration and composition of organic compounds were monitored during the experiments. Results show that AC filtration is a suitable technology for TOC removal from demineralized water. A TOC reduction of 38–70 % was achieved. Mixed-bed ion exchange after the AC filters proved to be necessary to remove conductivity, which was increased in the AC bed.

## INTRODUCTION

Recovery boilers are an essential part of pulp mills using sulphate process. They have two separate functions: recovery of pulping chemicals and steam production by combustion of waste materials (black liquor) [1]. 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. Make-up water requirements can be up to 50–70 $\mathrm{kg \cdot s^{-1}}$ 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. Mathews [2] lists organic compounds in the cycle as one of the most important challenges in water-steam cycle chemistry.

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.) [3–5]. Organic compounds decompose at high temperatures and pressures of the water-steam cycle. End products are low molecular weight organic acids (mainly formic and acetic acid), ammonia and carbon dioxide [4]. Organic acids and carbon dioxide are related to corrosion in a water-steam cycle although there is some controversy on their relevance [6,7]. One of the reasons for the aggressive corrosive nature of the decomposition products is the absence of a balancing counter cation for formed anions (e.g. formiate and acetate). Anionic decomposition products also mask cation conductivity measurements, preventing the detection of the potentially more corrosive chloride and sulphate [3,4]. Organic compounds can also contain harmful contaminants such as chloride and release them in decomposition processes [8].

The recommended limit for total organic carbon (TOC) in the make-up water is usually 100–200 $\mathrm{\mu g \cdot L^{-1}}$, depending on the operating temperature and pressure of the boiler [9,10]. There is a need to operate recovery boilers as well as other steam electric power plants at higher temperatures and pressures in order to produce electricity that is more energy efficient. 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.

Over 90 % of organic compounds are typically removed with the combination of conventional chemical water treatment and demineralization processes. There are however electrically neutral fractions (e.g. polysaccharides, proteins and low molecular weight compounds) present in surface waters that remain in the produced make-up water [8]. As a result, conventional demineralization performed by ion exchange cannot remove these fractions effectively [8]. Currently, there are a number of processes that can produce very low TOC level water: reverse osmosis (RO), electrodeionization (EDI) and short wavelength

UV radiation [11–13]. However, the production of high volumes of demineralized water can be expensive with these techniques.

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 [8,14]. 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.

In this study demineralized water was treated further with an AC filter followed by a mixed-bed ion exchanger (MB). There was also a subsequent AC filter after the MB unit. TOC reductions were monitored for 11 months and 3 months in pilot scale filters (Figure 1) and full scale AC filters (Figure 2), respectively. Our goal was to evaluate whether 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. We also hypothesized that the operation time of an AC filter could be very long due to low levels of TOC in the influent water.

## EXPERIMENTAL

### Experimental Setup

The first part of the 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). Process schemes of the studied processes are shown in Figures 3–5.

Two pilot scale AC filters and a mixed-bed ion exchange (MB) unit were installed inside a stream at plant A as shown in Figure 1. The volumes of the filters were 34 L (AC2), 18 L (MB) and 18 L (AC1). The ACs used in the experiments were acid washed low ash content CPG-LF 12X40 (AC1 filter) and AQUACARB 608C 12X40 (AC2 filter). The AC beds were wetted for about 24 h and then rinsed continuously until online conductivity measurements settled at a constant value. The MB resin used in the experiment was Purolite MB 400, and the flow at each filter was maintained constant at 1.5 L · min$^{-1}$ with rotameters. Samples for TOC analysis and side stream for online conductivity measurements were taken after each unit. The AC filters were monitored over the period 18.12.2010 – 12.10.2011.

A full scale AC filter (old anion exchanger tank, volume 3.86 m$^3$) was also studied at plant A, whose testing scheme is shown in Figure 2. The AC used in the full scale experiment was AQUACARB 608C 12X40. Once again the AC bed (volume 2.2 m$^3$) was wetted and rinsed in the same way as the pilot scale AC filters. Flow to the AC filter was approximately 8 L · sec$^{-1}$. Conductivity and silica were monitored online and TOC samples were taken before and after the AC filter and MB unit. The full scale AC filter was monitored over the period 23.3.2011 – 6.7.2011.

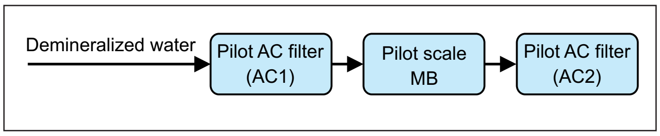


Figure 1:
Testing scheme of pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB). Demineralized water was taken from phase 6 in Figure 3.

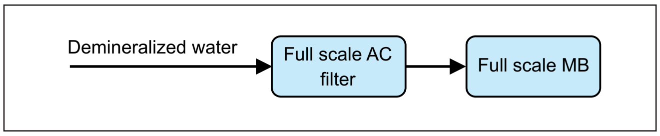


Figure 2:
Testing scheme of full scale activated carbon filter (AC) and mixed-bed ion exchanger (MB). Demineralized water was taken from phase 6 in Figure 3.

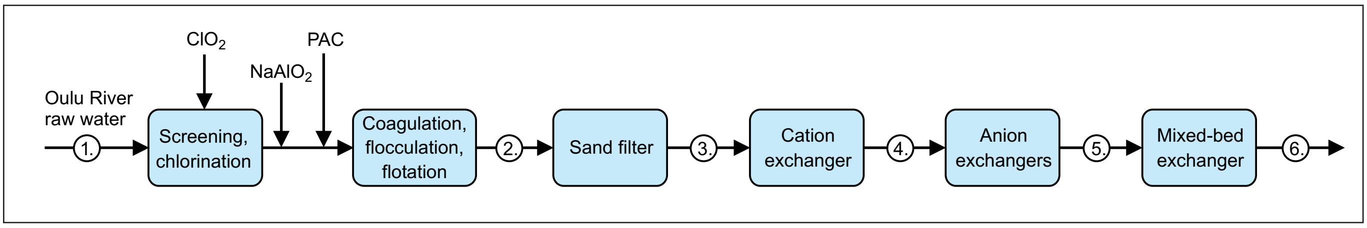


Figure 3:
Plant A water treatment process.
PAC polyaluminium chloride

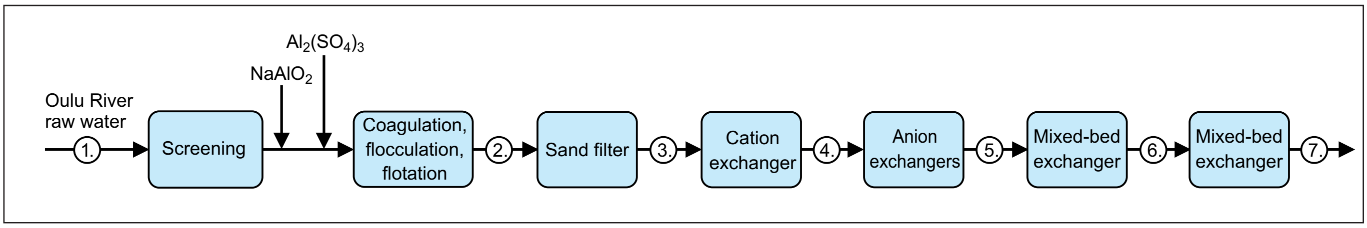


Figure 4:
Plant B water treatment process.

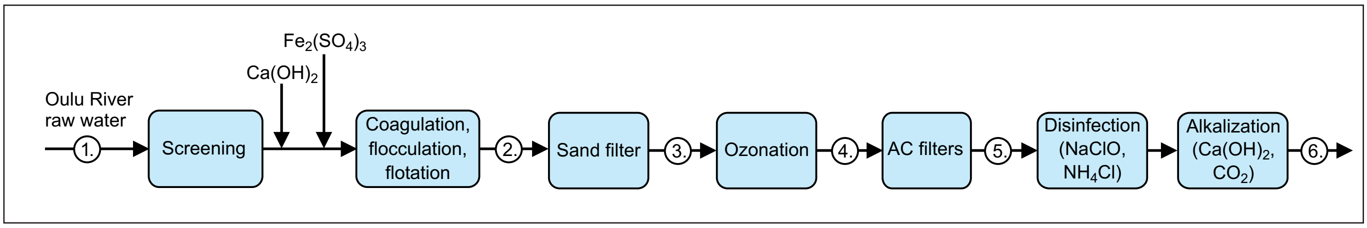


Figure 5:
Plant C water treatment process.

### Chemical Analysis

The total organic carbon (TOC, $mg \cdot L^{-1}$) of the water samples was measured with a Sievers 900 Portable TOC analyser according to the manufacturer specifications. TOC samples were collected in acid washed (1 h soaking in 10 % $HNO_3$ and rinsed with ultrapure water) vials and preserved at 4 °C before being measured. Control solutions with known TOC concentrations were prepared from glucose and measured occasionally to control the proper operation of the analyser. The analyser was also flushed carefully with ultrapure water before measurements to avoid contamination from the instrument itself.

The conductivity of the influent and AC filtered water was monitored online (Kemetron online conductivity probe) and the values were logged directly to a computer. Conductivity data was then manually edited to remove peaks which were the result of regeneration of ion exchange units or stopping of the water flow. Silica concentrations were also monitored online (Bran & Lübbe 6-channel analyser) during full scale AC tests.

The compositions of selected water samples were determined with the liquid chromatography – organic carbon detection (LC-OCD) method, which possesses a detection limit of 1 $\mu g \cdot L^{-1}$ as TOC. Details of the LC-OCD method are explained in [15]. Samples were again collected in acid washed bottles and preserved at 4 °C before being analysed.

## RESULTS AND DISCUSSION

### Comparison of Water Treatment Processes Using the Same Raw Water Source

Plant C (Figure 5) supplies potable water while plants A and B (Figure 3 and 4) 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 6. The comparison is based on three series of samples collected over the period 24.09.2009 – 20.10.2009.

As expected, raw water at all three plants had practically the same TOC level (11.7–11.9 $mg \cdot L^{-1}$) during the sampling period. There is a remarkable seasonal TOC variation in the Oulu River as shown in Figure 7. 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 remove NOM better than aluminium-based chemicals [16–18]. 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.

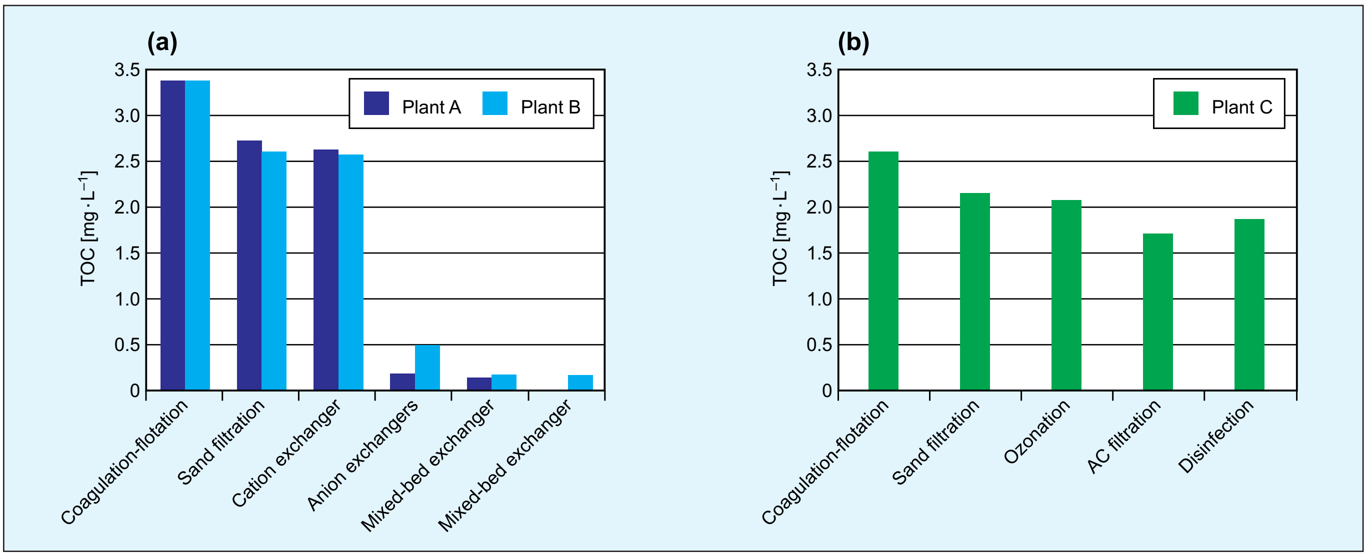


Figure 6:

Comparison of TOC levels after each process stage for all three water treatment plants using the Oulu River as a raw water source. Samples were collected between 24.9.2009 – 20.10.2009.

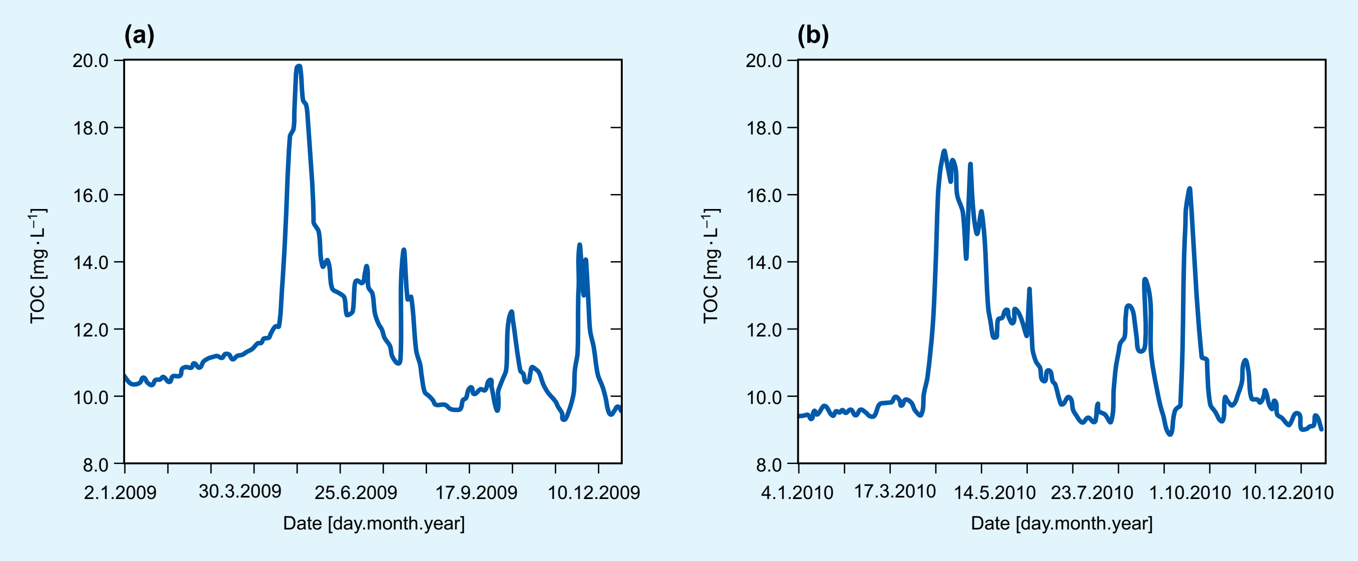


Figure 7:

Oulu River TOC levels in 2009 (a) and 2010 (b).

Data was provided by Oulu Waterworks.

## Activated Carbon Filtration

The results of TOC measurements during the pilot scale AC filter tests are presented in Figure 8a. 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 8a). 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 1). The role of the MB unit is important since conductivity increases extensively in an AC filter (Figure 9a). The MB unit removes ionized inorganic material which is released from the AC bed. However, the identity of this ionized material remains unclear.

TOC reductions measured in the full scale AC filter are shown in Figure 8b. The TOC reductions were between 40–65 % and were slightly higher than those measured with the pilot scale filters. The conductivity of filtered water (Figure 9b) increased similarly as with the pilot scale

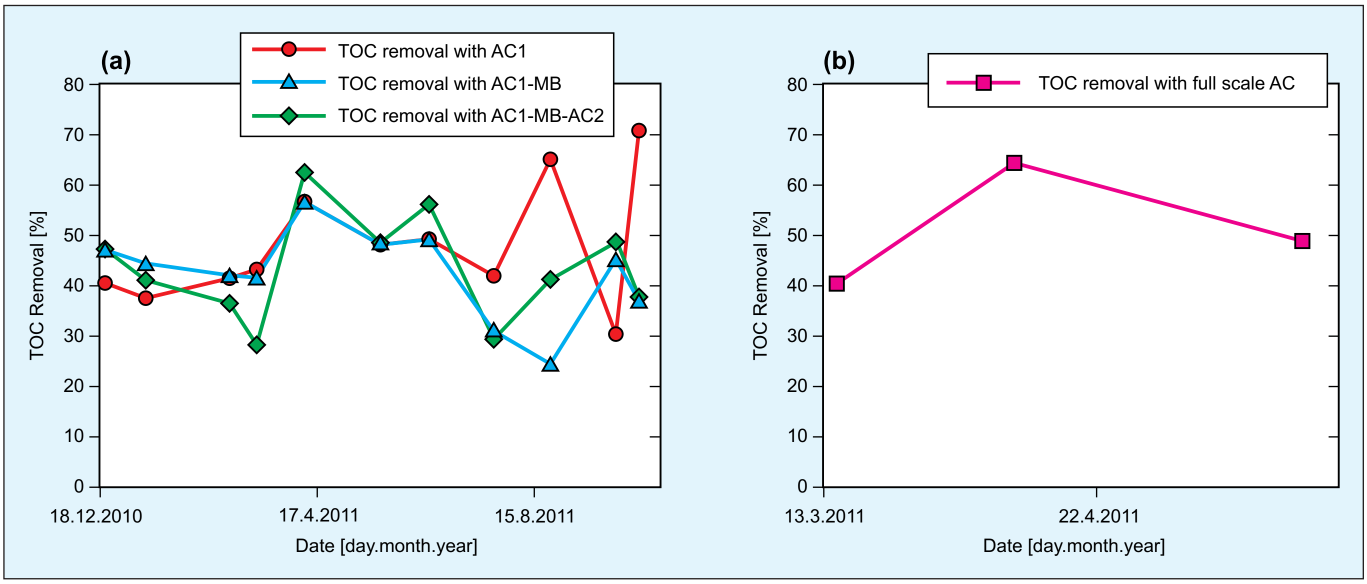


Figure 8:
TOC measurement results of pilot (a) and full scale AC filter tests (b).

| | 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 |

Table 1:
Composition of organic compounds in different parts of the plant A water treatment process. Samples were collected on 22.9.2011. All concentrations are stated in $\mu g \cdot L^{-1}$.
n.d. = not detectable (< $1\ \mu g \cdot L^{-1}$); LMW = low molecular weight

filters and so a subsequent MB unit was needed to reduce conductivity. The conductivity sensors used were not as accurate as the ones used with the pilot scale experiments so the actual conductivity values (Figure 9b) are not comparable with the readings in Figure 9a. The silica level of filtered water (Figure 10) was initially 212 $mg \cdot L^{-1}$ with a new AC bed, however it took about 14 days for the silica levels to settle to a constant value of 20 $mg \cdot L^{-1}$. By positioning the MB unit after the AC filter, the remaining silica was reduced to a concentration of 0.002–0.005 $mg \cdot L^{-1}$.

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. The CFU increase in the AC filter was

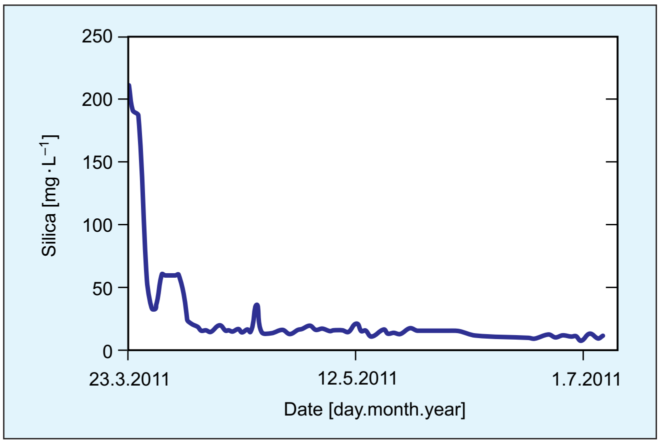


Figure 10:
Online silica measurement results of water after full scale activated carbon filter.

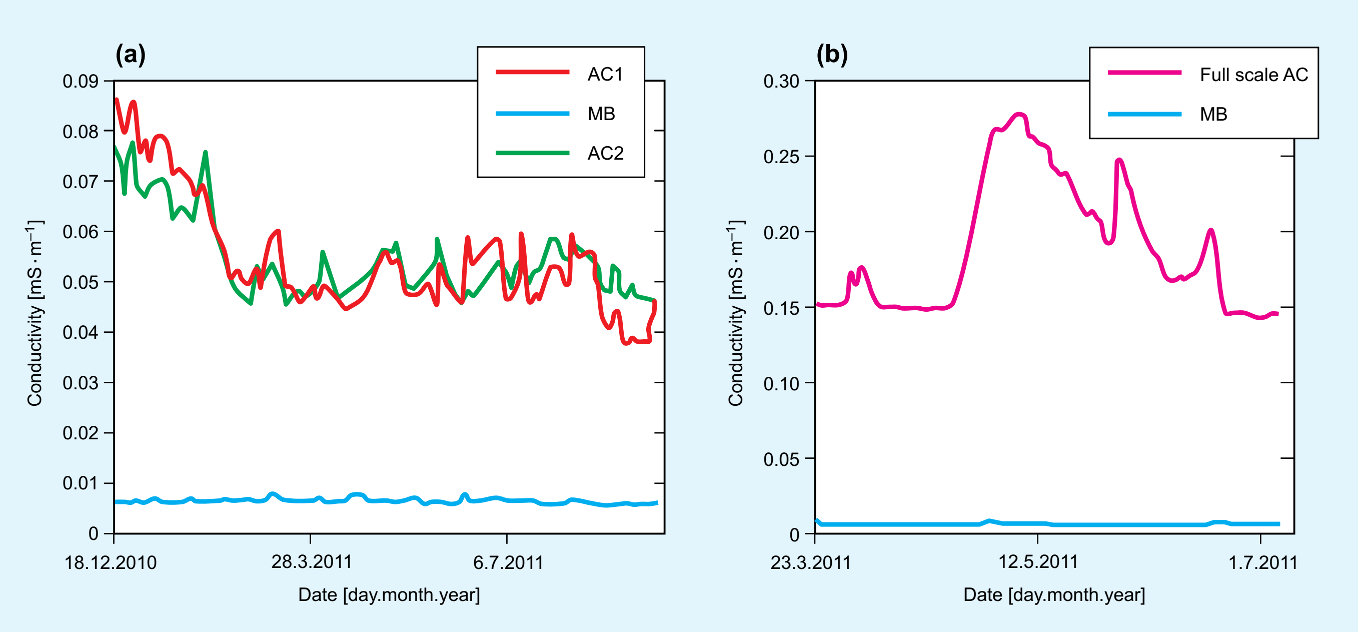


Figure 9:

Conductivity of water:
a) after pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB), and
b) after full scale activated carbon filter (AC) and mixed-bed ion exchanger (MB).

| | DOC | Hydrophobic | Hydrophilic | | | | |
|---|---|---|---|---|---|---|---|
| | | | Biopolymers | Humic substances | Building blocks | LMW neutrals | LMW acids |
| Raw water | 8 410 | n.d. | 169 | 5 833 | 1 259 | 1 140 | 9 |
| Chemically treated water | 2 646 | 100 | 74 | 835 | 1 009 | 619 | 8 |
| Demineralized water | 145 | n.d. | 21 | n.d. | 20 | 102 | 2 |
| AC1 filtered water | 109 | n.d. | 23 | n.d. | 15 | 70 | n.d. |
| After pilot MB | 86 | n.d. | 22 | n.d. | 12 | 51 | 1 |

Table 2:

Composition of organic compounds in different parts of the plant A water treatment process. Samples were collected on 9.12.2010. All concentrations are stated in $\mu g \cdot L^{-1}$.

n.d. = not detectable ($< 1\ \mu g \cdot L^{-1}$); LMW = low molecular weight

only 25 CFU per ml maximum. 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.

## Composition of Organic Compounds

The compositions of organic compounds at different stages of the plant A water treatment process are shown in Tables 1 and 2. Organic compounds are divided into hydrophobic and hydrophilic fractions, in which the latter is divided into biopolymers ($>> 20\,000\ g \cdot mol^{-1}$), humic substances ($1\,000\ g \cdot mol^{-1}$), building blocks, e.g. decomposition products of humic substances, ($300–500\ g \cdot mol^{-1}$), low molecular weight (LMW) neutrals ($< 350\ g \cdot mol^{-1}$) and LMW acids ($< 350\ g \cdot mol^{-1}$).

Raw water has high levels of humic substances as do most Finnish surface waters. The problematic fractions are biopolymers, building blocks and LMW neutrals, which comprise 1/6 of the DOC. These fractions are characterized by an electrically neutral structure, which is the reason why ion exchange cannot remove them effectively. The AC and MB units remove these fractions in part, resulting in a DOC level of 86 $\mu g \cdot L^{-1}$ (Table 2) in the produced water. After about 10 months of continuous use other sets of samples were analysed and it was discovered that the AC1 filter performance had actually improved. However, the pilot MB unit has started to release organic material, probably because it has reached its ion exchange capacity. Interestingly though, AC2 removes a substantial part of the residual DOC, which can't be seen with the TOC measurements (Figure 8a). The final DOC concentration with an AC-MB-AC set-up is comparable to the DOC achieved with reverse osmosis.

## CONCLUSIONS

Based on the results of pilot and full scale AC filtration experiments, the following conclusions can be made:

- 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.
- TOC removal of 38–57 % was achieved in activated carbon filter produced water; the TOC level ranged between 150–200 $\mu g \cdot L^{-1}$. DOC determined with the LC-OCD method was between 62–109 $\mu g \cdot L^{-1}$.
- With the AC-MB-AC set-up, as low as 37 $\mu g \cdot L^{-1}$ of DOC was achieved after 10 months of continuous operation.
- Organic fractions removed with AC were mainly decomposition products of humic substances (so-called building blocks) and low molecular weight neutral organic compounds.
- The AC bed releases silica and substantially increases the conductivity of the water.
- The AC filter needs a subsequent mixed-bed ion exchanger, which acts as a polishing filter. The role of the mixed-bed unit is to reduce conductivity and remove silica.
- There was no sign of reduction in the TOC removal efficiency in the pilot scale AC filters during the test period of 11 months.

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