SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

**Finnish Recovery Boiler Committee**

# SKYREC – Increasing recovery boiler electricity generation to a new level

**1.1.2008 – 31.12.2012**
**Summary Report**

**3/2013**
**(16A0913-E0142)**

# SKYREC Summary Report 1.1.2008-31.12.2012

# FOREWORD

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

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

In addition the directing committee was assisted by **Olli Talaslahti** and **Toni Orava** (chairmen of the liquor subcommittee), **Reijo Hukkanen** Stora Enso Oyj, Oulu (chairman of the durability sub-committee), project coordinator **Esa Vakkilainen** LappeenrantaUniversity of Technology and as secretary **Markus Nieminen** Pöyry Finland Oy, Vantaa.

Finnish Recovery Boiler Committee

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# 1 GENERAL

SKYREC-project was preceded by SoTuII- research program ” Recovery boiler of the future II – possibilities to increase power production 1.4.2003 – 30.10.2006” which results are utilized in this project. SKYREC project also concentrated issues that have not studied before.

The rise of oil world market price and EU $CO_2$ emission trade scheme has paid attention to $CO_2$ free bioenergy. The increase in the average cost of electricity has also paid attention to recovery boiler electricity production. For pulp mills the significance of electricity generation from recovery boiler has been secondary. The most important factor in recovery boiler process and steam cycle has been high availability. Increasing electricity production means changes in recovery boiler parameters, typically main steam pressure and temperature or black liquor (BL) dry solids. A higher dry solids content of BL increases boiler efficiency, since the flue gas loss decreases and the heat needed to evaporate moisture from BL is lower. The higher recovery boiler main steam temperature affects the corrosion of superheaters. Higher recovery boiler main steam pressure increases the design pressure for in all boiler parts. The recovery boiler lower furnace heat flux increase with higher BL dry solids and operating pressure. Increasing pressures and temperatures require new materials and attention to feedwater quality.

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

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

# 2 SUMMARY OF THE PROJECT

SKYREC- research program ”Possibilities to increase recovery boiler power production into a new level 1.1.2008 – 31.12.2012” was divided into several sub-programs. The program was part of TEKES (Finnish Funding Agency for Technology and Innovation) funded activities. It received 50 % public support. Without this funding the project could have not been started.

## 2.1 Project schedule and budget

Project time frame was 2.5 years (1.1.2008 – 30.6.2010). The project had to apply for 12 months extension. The reason was the economic turndown in 2009 which caused temporary shutdowns to pulp mills and measurement projects in operating recovery boilers could not be completed as planned. The length was rather long, but as the project had lots of measurement activities at operating recovery boilers, all time was needed.

The original budget for the project was 700 000 € (of which TEKES 350 000 €). When Sumitomo joined the project autumn 2008, budget increased to 805 000 €. With extra funding additional projects could be performed and schedule was extended to the end of 2012. The project was coordinated and the funding administrated by the Finnish Recovery Boiler Committee (FRBC). Almost all of the funding was spent by various universities and research organizations.

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

## 2.2 Background

### 2.2.1 Basis for project

The rise of oil world market price and EU $CO_2$ emission trade scheme has paid attention to $CO_2$ free bioenergy. The increase in the average cost of electricity has also paid attention to recovery boiler electricity production. For pulp mills the significance of electricity generation from recovery boiler has been secondary. The most important factor in recovery boiler process and steam cycle has been high availability. Traditionally, recovery boilers have operated at moderate steam pressures (≤80 bar) and temperatures (≤480 °C) due to concerns over superheater corrosion and high costs of materials for construction. The amount of power a recovery boiler can generate from BL combustion depends on the pressure and temperature of the steam that the boiler produces. However, the main barriers to increased steam parameters in recovery boilers are the materials of heating surfaces. Sulfide corrosion of the furnace walls and molten-phase corrosion in the superheater area are the biggest concerns related to steam parameters. The maximum steam temperature can be limited by the ash properties. So either new materials are needed or the ash chemistry needs to be redesigned with high temperatures in mind. Increased steam pressure and temperature raises the feedwater and steam purity standards. High pressure boilers require high purity demineralized water as even very low levels of contaminants can cause deposits and corrosion inside the boiler and condensate systems.

### 2.2.2 What we knew

Before the project started we knew reliable and proven methods to increase electricity production which are  increase of (1) BL dry solids over 80%, (2) air preheating to 190 °C, (3) feedwater preheating to 160 °C and (4) main steam parameters to 490 °C and 90 bar. Sootblowing steam taken from turbine outlet instead of superheater/boiler also increases electricity generation.

The four principal corrosion mechanisms can be identified as (1) high-temperature oxidation, (2) sulfidation, (3) active oxidation, and (4) hot corrosion. These can be present individually or as a mixture of two or more different mechanisms. High-temperature oxidation and active oxidation are typically present in oxidizing conditions, whereas sulfidation requires reducing conditions. Hot corrosion may occur both in reducing and oxidizing conditions. Earlier project (SOTU II) studied resistance/behavior of the chosen boiler steam/superheater tube materials under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in an oxidizing atmosphere, but resistance/behavior of tube materials in reducing conditions was needed. In recovery boilers, sulfur-rich reducing atmospheres in the superheater area are mainly due to high gaseous $H_2S$ concentrations or high amounts of unburnt carryover particles depositing on the tube surface.

High-temperature oxidation is normally not considered as a problem in modern recovery boilers due to moderate steam parameters applied. However, when increasing the steam temperature and pressure oxidation of tubes may become an issue. Sulfidation typically occurs when the metals are exposed to temperatures above

200 °C in gases that contain more than 1 ppm $H_2S$. Sulfidation can be effectively avoided by proper combustion control and by limiting the amount of carryover. Hot corrosion, however, is not that easy to avoid by these methods. Hot corrosion is related to deposit properties, which are a consequence of the BL composition (especially the amount of potassium and chloride). Corrosion rate increases when the first melting temperature ($T_0$ or FMT) in the deposits is exceeded. The only way to limit material loss via hot corrosion is to keep the material temperatures below the FMT of the deposits.

Material composition affects the corrosion rate. Chromium is stable in sulfidizing atmospheres, and therefore high Cr alloys should be used to avoid extensive sulfide-induced corrosion. Similarly nickel increases the resistance to chloride corrosion but is very susceptible to sulfidation and alloys composed of high Ni contents can sulfidize very rapidly at temperatures higher than 630 °C.

It was known from previous studies that the conventional 3R12 (AISI 304L) composite tube material can't be safely used in the future high pressure recovery boiler. Other currently used compound materials, such as Sanicro38 and HR11N, have shown good corrosion resistance in existing recovery boilers, but their corrosion resistance at high temperatures has not been thoroughly studied and operational experiences are still limited. Also other highly alloyed materials are available, but data on their corrosion resistance is lacking. We knew from refractory materials that resistance of silicon based ceramics in oxidizing-reducing at lower furnace atmosphere is unsatisfactory, aluminum based ceramics react with sodium and magnesium based ones don't endure the effect of water vapour.

Extensive waterside corrosion has been discovered in two recovery boilers in Finland during the 21st century. Cost of several weeks unplanned shutdown was tens of millions of euros.

### 2.2.3 Things we wanted to know

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

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

Organic burden of recovery boiler waterside can be mitigated by improving the effectiveness of make-up water treatment process to filter organic substances. One objective was to test different filter methods and their applicability in recovery boiler make-up water treatment.

Recovery boiler operators need to monitor and control steam/water cycle chemistry to protect recovery boilers and turbines. There was a need for updating and standardizing the recovery boiler water treatment and water chemistry guidelines, since the boiler pressure has increased in new and future boilers, the capacities of the old plants have been increased, the usage of the new chemicals has increased, and the monitoring of the water chemistry is largely done by on-line measurements.

### 2.2.4 Aims

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

- Study the future recovery boiler concepts, especially once-through recovery boiler
- Increase electricity production from recovery boiler
- Performance of tube materials for recovery boilers at high material temperatures
- Test different TOC removal methods and their applicability in recovery boiler make-up water treatment.
- Update the water treatment and water chemistry guidelines for future recovery boilers

### 2.2.5 Work Packages

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

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

Each work package consisted several subprojects which were done by various universities and research organizations. Work packages consisted of the following subprojects (Author appears in brackets):

WP1: NEW RECOVERY BOILER CONCEPTS
- Once-through and reheater recovery boiler – concept studies (LUT)
- Co-firing black liquor and biomass (ÅA)
- Utilization of pyrolysis gases from the recovery boiler - Preliminary studies (ÅA)
- Pulp mill optimal steam pressure levels (LUT)
- Dew point measurements in Rauma and Heinola mill (ÅA)
- Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler (ÅA)

WP2: INCREASING SUPERHEATED STEAM TEMPERATURE
- Corrosion tests of superheater materials in reducing conditions (ÅA)
- Full scale material exposure in Joutseno (VTT)

WP3: INCREASING RECOVERY BOILER PRESSURE
- Phenomena of transformation in recovery boiler char bed (LUT)
- Refractory material/ceramics in recovery boiler furnace (UO)
- Field tests of furnace materials / Characterization of probe test samples (Boildec/VTT)

WP4: ENSURING BOILER AND FEEDWATER QUALITY
- Organic amines and natural organic matter in steam water cycle (VTT)
- Effect of organic amines to magnetite layer formation (VTT)
- TOC balance of Stora Enso Laminating Paper mill (Teollisuuden Vesi)
- TOC removal methods and their applicability in make-up water treatment (Teollisuuden Vesi)
- Water quality and water treatment guidelines (Teollisuuden Vesi)
- Reduction of TOC from recovery boiler make-up water (UO)
- Activated carbon and UV-treatment - field tests (Cewic/UO/JP-analysis)
- Comparison study of active carbon grades (Cewic/UO/JP-analysis)

LUT = Lappeenranta University of Technology
ÅA = Åbo Akademi
VTT = Technical Research Centre of Finland
UO = University of Oulu
Cewic = Centre of Expertise in the Water Industry Cluster
Boildec = Boildec Oy
Teollisuuden Vesi = Teollisuuden Vesi Oy / Industrial Water Ltd.

### 2.2.6 Experiences from SKYREC

SKYREC-project was a large endeavor to the whole FRBC. Both the done quantity of research and needed financing have been large compared to the normal routine work for the committee. Project budget for SKYREC was several times the normal yearly budget.

Coordinating the project could be done within the organization of FRBC. Hence, the capability of doing ”large” projects exists. Division of responsibilities and daily routines between the working groups and the steering committee needs sharpening especially coordination and information sharing.

### 2.2.7 What was accomplished?

Project produces vast amounts of solid research. Several new hypotheses were confirmed. Study made in Lappeenranta University of Technology compared several future recovery boiler concepts and confirmed the rationality of design choices that have led to the present recovery boiler. One of the most successful ways to increase electricity generation from recovery boilers has been the implementation of different preheating schemes. Reheating and once-through concepts appear only marginally better when considering the recovery boiler electricity generation. From cost of additional power point of view assisted circulation concept in 540 °C steam temperature seems desirable.

One way to improve electricity production in mills is to lower steam pressures in pulping processes. In that case steam can be expanded to lower pressure in turbine. However, lowering the steam pressures increases also investment costs of mill because of bigger pipe sizes and heat transfer areas. On the bases of the study it is economically profitable to choose the lowest possible steam pressure levels defined by pulping processes and equipment’s.

Åbo Akademi studied co-firing BL and biomass in a recovery boiler that has excess capacity to increase the amount of bio-electricity. The results of the study indicate that from a combustion chemistry standpoint, there is potential to add biofuels to BL. The mixtures containing bark, wood, or biosludge appear to burn much like the original BL based on single particle combustion tests. Additional work should be carried out to determine the impact of this moisture on the burning characteristics. Additionally, for the mixtures considered here the BL appears to coat the solid material rather than form a solution with suspended solids. At firing temperatures the mixtures could look different, but spraying studies are certainly required to determine how to feed such mixtures in the best way. Åbo Akademi also studied possibilities for extracting gases from the lower part of a recovery boiler to be used in the lime kiln instead of fossil fuels. Preliminary studies showed that extraction of gas with a heating value of 3 MJ/kg could be feasible with normal recovery boiler operation. Additional work should be done to remove sodium and dust from pyrolysis gas.

Other sub-project concentrated to get reliable information of the dew point and low temperature corrosion conditions in recovery boiler flue gas ducts and flue gases coolers. The study would indicate that there was no acid dew point corrosion due to $H_2SO_4$ formation and mills can take more energy out of the flue gas without dew point corrosion under normal operational conditions.

Superheater tube material projects were carried out by Åbo Akademi and VTT. VTT tested the corrosion performance of various superheater tube materials in recovery boilers at high material temperatures. Performance of the six materials tested was considered as unsatisfactory, Super 625 and possibly SAN 69 excluded, in the actual test conditions; i.e., at such conditions where the probes were exposed to steam blowing from a close vertical distance and at average tube material temperatures of about 570 °C and 540 °C, peaking for a short time up to 590 °C. Åbo Akademi studied the resistance/behaviour of the superheater tube materials under reducing conditions and compared those results to previous material studies in oxidizing conditions. 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 results were obtained at a lower temperature. The results for HR11N with under reducing conditions at 565°C were comparable to the results obtained from tests under oxidizing conditions at 600°C while Sanicro 28 performed better in a reducing environment.

Several furnace material tests were performed by in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The test materials were carbon steel (CS); austenitic stainless steels 3R12 (304L), 3RE28 (310S) and 3XRE28 (310S); high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67.The corrosion rate, ca. 4 mm/a, was measured for CS. The rate was as high as expected. The traditional composite tube material 304L had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C. No marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were about four times lower than that of 304L in the long term (>2000 h) test. In short term (<1000 h) tests the corrosion resistance of 310S and Sanicro 28 were as good as or even slightly better than that of Sanicro 38 or HR11N. Because 310S were not included in the long term tests and no results were obtained for the Sanicro 28, it is recommended to verify their promising performance with long term tests in the future. The results for Super 625 were inconsistent. In short term it's corrosion resistance was only slightly better than that of 304L, but in the long term its resistance was even better that of Sanicro 38 and HR11N. Similar kind of behaviour was observed in Sanicro 67. In short term its corrosion resistance was only slightly better than that of Sanicro 38 and HR11N, but in the long term its corrosion rate was only 1/10 of that of Sanicro 38 and HR11N and 1/5 of Super 625.

New and currently used refractory materials were tested in actual recovery boiler lower furnace condition. Field test data also indicated that mechanically weak materials won’t last. Although they are chemically stable against BL char. These dense materials wear off by thermal shock and cracks easily. Findings of the study were that best material is Hassle D39A castable which is already in use. $ZrO_2$, full spinel and nanospinel castables could have the potential but lacking of manufacturers. More tests need to be made before final conclusion can be made for MgO*Cr2O3 spinel castable potential against Hassle D39A castable.

VTT studied the effect of alkaline chemicals to the protective oxide layer (magnetite) on the inner surface of the recovery boiler tubes in 340 °C. The rate of thermal degradation and concentration of decomposition products alkaline were also studied. Alkaline amines had effect on magnetite layer properties of polished and pre-oxidized samples. Ammonia and morpholine had more large oxide particles on the sample surface. According to mass transfer resistance there was no significant difference in corrosion rate between the tested amines. According to newest findings organic acids, mainly acetic and formic acid, are more intense to cause corrosion in water-steam cycle of recovery boiler. Organic acids concentrate in the condensate droplets that are formed when steam starts to condensate and cause pH to drop drastically. pH drop accelerates dissolution of the protecting magnetite layer on metal surfaces. It also makes the forming of a new layer more difficult.

Conventional chemical water treatment and demineralization processes cannot remove electrically neutral fractions. Organic burden can be mitigated by improving the effectiveness of make-up water treatment process to filter organic substances with different methods. UV treatment should have about 30 % TOC reduction rate but the efficiency depends on the inlet of TOC and actual organic components present in the water. Reverse osmosis removes over 95% of TOC and it is the best available technology to remove biopolymers and organic molecules. Nanofiltration has 80-90% TOC reduction rate with simultaneous salt removal (60-80%). Activated carbon removes 20 to 80 % of TOC but the removal efficiency retains over time.

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

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

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

# 3 REPORTS

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

## 3.1 Sub-project reports

Sub-projects reports listed by author:

**VTT (Technical Research Centre of Finland) reports:**

- Organic amines and natural organic matter in steam water cycle
  Jouko Hildén, Pekka Pohjanne. Report 27.4.2009.

- Effect of organic amines to magnetite layer formation
  Mikko Vepsäläinen, Petri Kinnunen, Timo Saario, Pekka Pohjanne, Stella Rovio. Report 29.6.2010.

- Full scale material exposure in Joutseno
  Martti Mäkipää, Janne Kärki, Markku Orjala. Report 21.4.2011

- Characterisation of probe test samples exposed to BLRB lower furnace environments
  Pekka Pohjanne. Report 4.4.2013

**Industrial Water Ltd. / Teollisuuden Vesi Oy reports:**

- TOC balance of Stora Enso Laminating Papers mill
  Jani Vuorinen. Report 26.5.2009

- TOC removal methods and their applicability in make-up water treatment
  Jani Vuorinen, Maija Vidqvist. Report 20.1.2010

- Water quality and water treatment guidelines
  Maija Vidqvist, Jani Vuorinen Report 2011

**Boildec Oy reports:**

- Field tests of furnace materials - test No 1
  Timo Karjunen. Report 27.4.2010.

- Field tests of furnace materials - test No 2
  Timo Karjunen. Report 6.7.2010.

- Field tests of furnace materials - test No 3
  Timo Karjunen. Report 17.9.2010.

- Field tests of furnace materials - test No 4
  Jussi Vänskä. Report 7.6.2011

- Field tests of furnace materials - test No 5
  Jussi Vänskä. Report 22.12.2011

**Åbo Akademi (ÅA) reports:**

- Co-firing black liquor and biomass
  Nikolai DeMartini, Esperanza Monedero, Patrik Yrjas, Mikko Hupa. Report 24.8.2009

- Corrosion tests of superheater materials in reducing conditions – Part 1
  Patrik Yrjas, Dorota Bankiewicz. Report June 2010

- Utilization of Pyrolysis Gases from the Recovery Boiler - Preliminary studies
  Mikko Hupa, Nikolai DeMartini, Anders Brink, and Markus Engblom. Report 15.12.2010

- Co-firing black liquor and biomass, Phase 2 - report
  Nikolai DeMartini, Niklas Vähä-Savo, Mikko Hupa, Report 19.4.2011.

- Corrosion tests of superheater materials in reducing conditions – Part 2
  Patrik Yrjas, Dorota Bankiewicz. Report February 2012.

- Dew Point Measurements in Rauma and Heinola mill
  Nikolai DeMartini, Emil Vainio, Tor Lauren, Mikko Hupa. Report December 2011.

- Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler
  Tor Lauren, Emil Vainio, Nikolai DeMartini, Mikko Hupa. Report December 2012.

**Lappeenranta University of Technology (LUT) reports:**

- Phenomena of transformation in recovery boiler char bed
  Tanja Pentinsaari. Report 5.11.2009.

- Once-through and reheater recovery boiler – concept studies
  Vakkilainen Esa, Kaikko Juha, Hamaguchi Marcelo. Report 15.2.2010.

- Pulp mill optimal steam pressure levels
  Aapo Hiltunen, Esa Vakkilainen, Report 26.7.2011.

**University of Oulu (UO) / CEWIC reports:**

- Reduction of TOC from recovery boiler make-up water
  Tero Luukkonen. Report 18.4.2010.

- Recractory materials/ceramics in recovery boiler furnace
  Riku Mattila. Report 2.5.2011.

- Activated carbon and UV-treatment in TOC removal- field tests
  Tero Luukkonen, (JP-Analysis) Jaakko Pellinen (JP-analysis), Jaakko Rämö (UO), Ulla Lassi (UO). Report February 2011

- Comparison study of active carbon grades
  Emma Tolonen (UO), Jaakko Pellinen (JP-analysis), Tero Luukkonen (Pacs), Hanna Runtti (UO), Ulla Lassi (UO), Jaakko Rämö (UO).
  Report June 2012

## 3.2 SKYREC seminar

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

- Project summary
  Esa Vakkilainen, Lappeenranta University of Technology

- Co-firing black liquor and biomass - laboratory tests
  Nikolai DeMartini, Åbo Akademi

- Dew point measurements in Rauma and Heinola
  Nikolai DeMartini, Åbo Akademi

- Improving heat recovery in biomass-fired boilers - project presentation
  Doug Singbeil, FPInnovations

- Full scale material exposures in Joutseno recovery boiler
  Martti Mäkipää/Markku Orjala, VTT

- Corrosion tests of superheater materials in reducing conditions
  Dorota Bankiewicz, Åbo Akademi

- Field tests of furnace materials
  Timo Karjunen, Boildec Oy / Pekka Pohjanne, VTT

- Refractory materials/ceramics in recovery boiler furnace
  Riku Mattila, University of Oulu

- TOC removal methods and water quality guidelines
  Maija Vidqvist, Teollisuuden Vesi Oy

- Activated carbon and UV-treatment in TOC removal- field tests
  Tero Luukkonen, JP-Analysis / University of Oulu

## 3.3 International co-operation

SKYREC project was presented the following papers/seminars.

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

# 4 PROJECT BACKGROUND

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

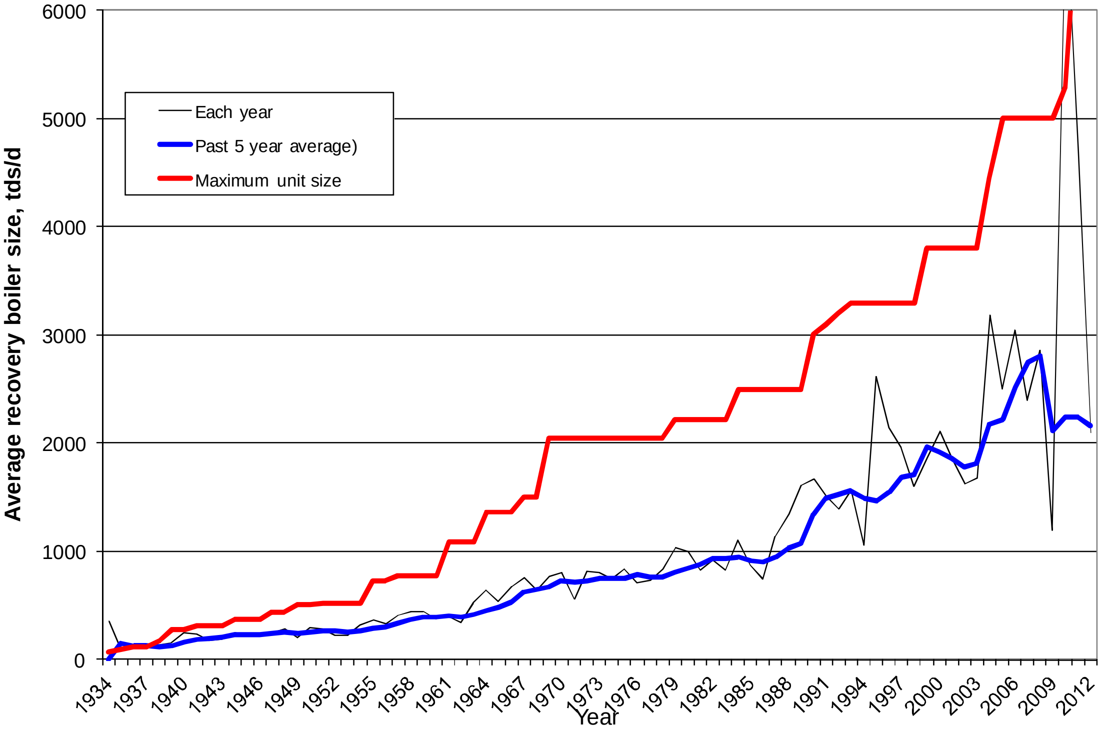


**FIGURE 4-1. Size of the recovery boiler as a function of purchase year.**

Black liquor dry solids has always been limited by the ability of available evaporation technology to handle highly viscous liquor. As technology has evolved so has the final BL dry solids. The higher the dry solids, the less water the BL contains and the hotter the adiabatic combustion temperature. Higher BL dryness significantly increases steam generation and improves combustion stability, resulting in lower TRS and $SO_2$ emissions, and less boiler fouling and plugging. It also provides for more capacity in existing units.

On average the virgin BL dry solids content has increased. This is especially true for latest very large recovery boilers. Design dry solids for the new green field mills and new recovery islands have been either 80 or 85 % dry solids. In Asia and South America 80 % (earlier 75 %) dry solids is in use. In Europe 85 % (earlier 80 %) dry solids is in use. Dry solids content of virgin BL (without ash recycle) is shown in FIGURE 4-2 as a function of purchase year of that boiler.

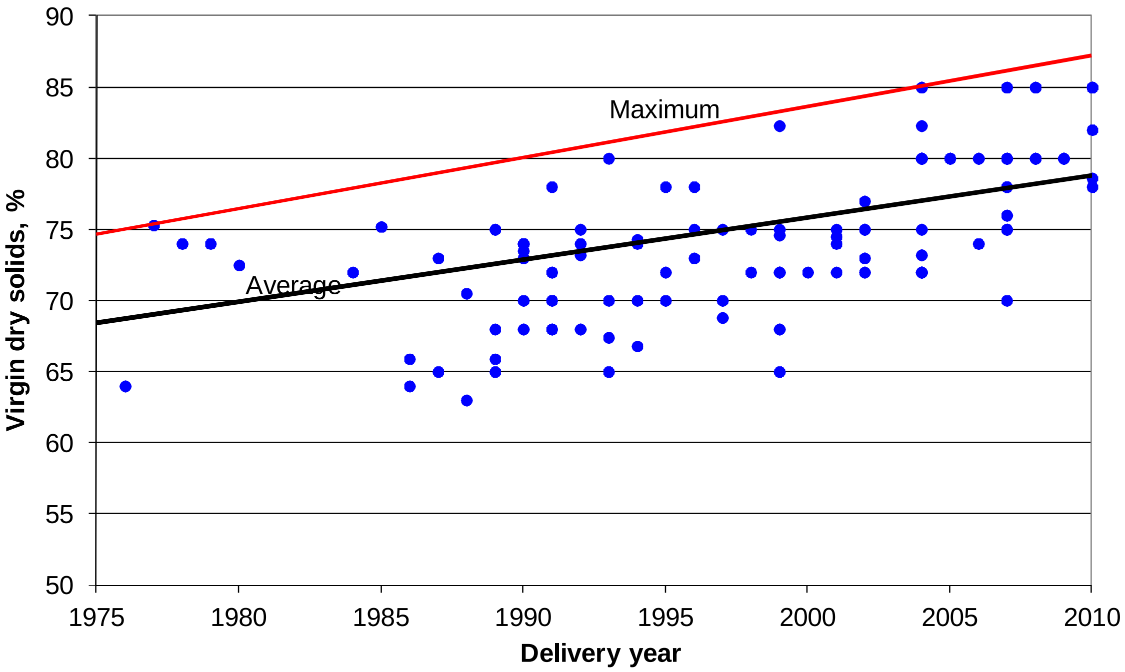


**FIGURE 4-2. Virgin black liquor dry solids as a function of purchase year of the recovery boiler.**

The main steam temperature of recent recovery boilers is shown in FIGURE 4-3 as a function of MCR capacity of that boiler. The average steam temperature increases with size. Small boilers tend to have lower pressures to reduce specific cost. An increase in main steam temperature is usually accompanied by an increase in main steam pressure. An increase either in steam pressure or temperature has only a small effect on back-pressure electricity generation. There are many boilers with main steam parameters higher than 500 °C.

This project has had important role in the recovery island research in Finland. Project has given valuable information to the recovery boilers users and manufacturers. Project aim wasn’t to resolve single company research and development issues, but to gain general knowledge for number of companies to utilize. Recovery boiler market share development is shown in FIGURE 4-4.

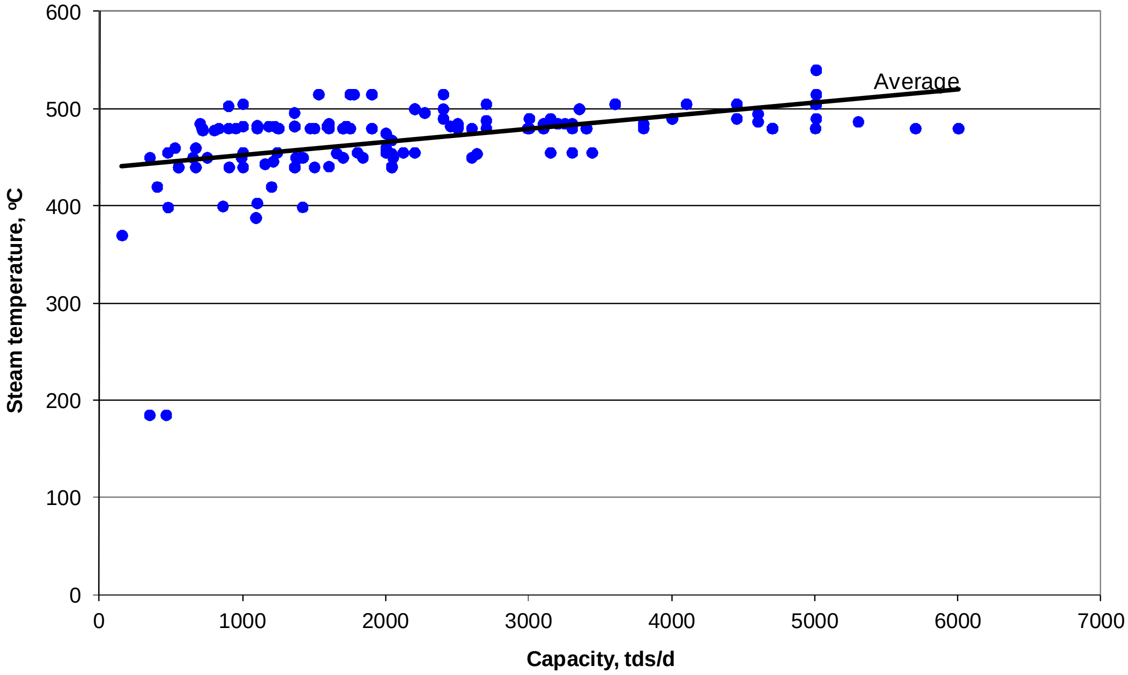


FIGURE 4-3. Main steam temperature as a function of recovery boiler capacity.

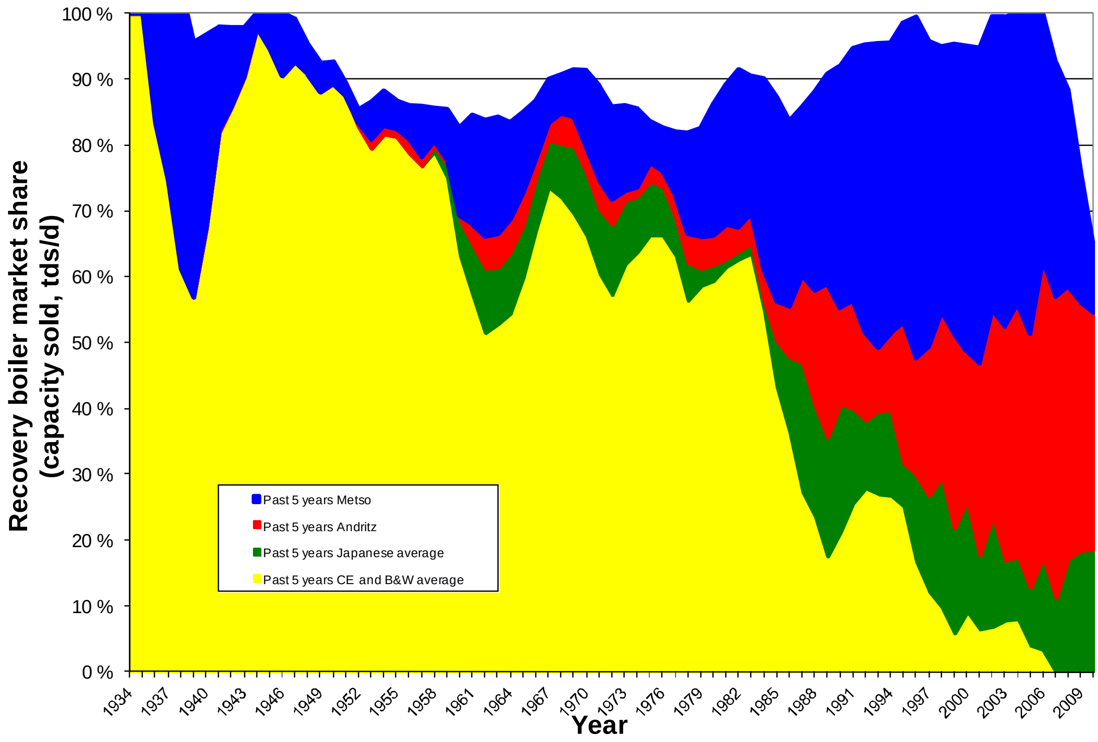


FIGURE 4-4. Recovery boiler market share

## 4.1 Objectives

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

Emphasis was on the in situ tests which would provide practical information to increase the recovery boiler power-to-heat ratio and maximize electricity production. This meant several tests of different furnace and superheater materials in actual recovery boiler conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery. Project wanted to think “outside the box” and study the new recovery boiler concepts, especially once-through recovery boiler. Recovery boilers usually have high demand for make-up water compared to utility boilers. This calls for care in eliminating organic matter in water treatment when increasing main steam pressure and temperature. Objective was to improve the effectiveness of make-up water treatment process to filter organic substances and study effect and behavior of water chemicals in elevated temperature and pressure. There is a need for updating and standardizing the recovery boiler water treatment and water chemistry guidelines since the boiler pressure has increased in new and future boilers, the capacities of the old plants, have been increased, the usage of the new chemicals has increased, and the monitoring of the water chemistry is largely done by on-line measurements.

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

## 4.2 Ways

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

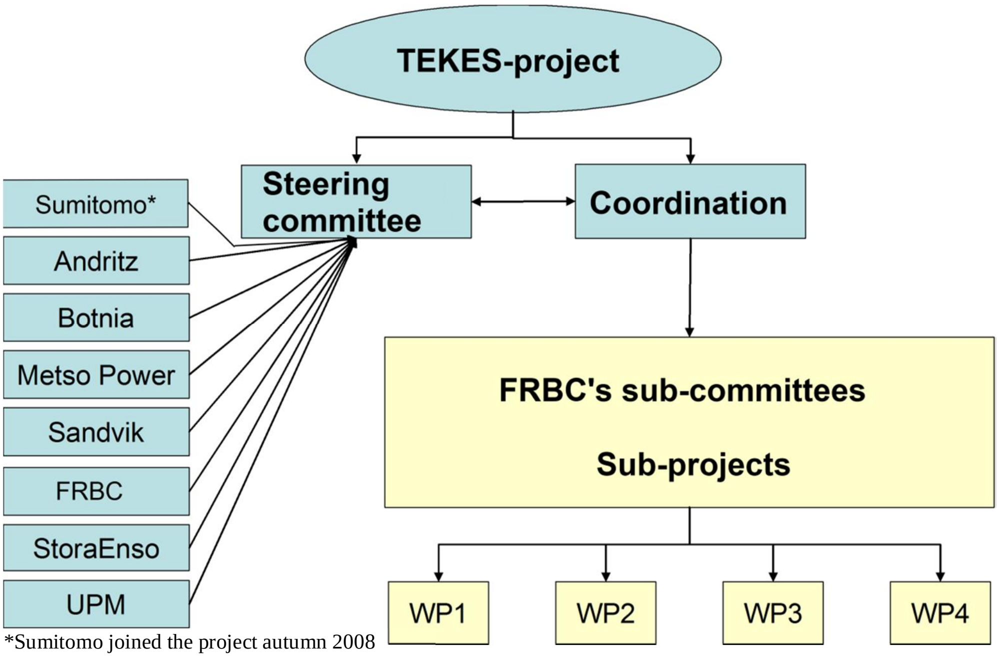
- Literary research
- Laboratory tests
- In situ tests
- Writing guidelines and distributing information

## 4.3 Organisation

Steering committee was established to manage the project economics and scientific orientation. Every cost sharing partner had member in the steering committee. FRBC's sub-committees, mostly durability sub-committee and black liquor sub-committee participated by directing the sub-projects. Steering committee members are presented in TABLE 4-1 and project organization in FIGURE 4-5.

**TABLE 4-1. Members of steering committee**

| Voting members: | |
|---|---|
| Matti Tikka | UPM-Kymmene Oyj, Kymi, chairman |
| Martti Korkiakoski | TEKES |
| Lasse Koivisto | Andritz Oy, Varkaus |
| Timo Peltola | Sandvik Materials Technology, Helsinki |
| Mika Paju | Metsä Fibre Oy, Joutseno |
| Kalle Salmi | Metso Power Oy, Tampere |
| Keijo Salmenoja | Andritz Oy, Helsinki |
| Kaj Nordbäck | UPM-Kymmene Oyj, Pietarsaari (Chairman of FRBC) |
| Timo Pekka Veijonen | Stora Enso Oyj, Pulp Competence Center, Imatra |
| Hidenori Ogawa | Sumitomo Metal Industries Ltd |
| | |
| **Non-voting members:** | |
| Reijo Hukkanen | Stora Enso Oyj, Oulu (Chairman of durability committee) |
| Olli Talaslahti / Toni Orava | (Chairman of black liquor committee) |
| Esa Vakkilainen | Lappeenranta university of technology (coordinator) |
| Markus Nieminen | Secretary of FRBC |



*Sumitomo joined the project autumn 2008

FIGURE 4-5. Project organisation and coordination.

## 4.4 Budget

The original project budget was 700 000 € (of which TEKES 350 000 €). When Sumitomo joined the project autumn 2008, budget increased to 805 000 €. Project funding is presented in TABLE 4-2.

**TABLE 4-2. SKYREC funding**

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

FRBC coordinated and administrated funding and budget. Committee was also one of the project cost share partners that formed a directing committee. Most of the funding was spent by various universities and research organizations. Allocation of funding between small and medium sized enterprises (SME) and universities and research organizations is presented in TABLE 4-3. SKYREC budget is shown in TABLE 4-4.

**TABLE 4-3. SKYREC funding allocation**

| | 2 008 | 2 009 | 2 010 | 2 011 | 2 012 | Total | Share |
|---|---|---|---|---|---|---|---|
| **Small and medium-sized enterprise** | 19 600 € | 44 900 € | 95 300 € | 80 600 € | 31 500 € | 271 800 € | 34 % |
| **Universities and research institutes** | 5 300 € | 134 800 € | 167 800 € | 158 000 € | 30 300 € | 496 100 € | 62 % |
| **Other companies** | 0 € | 12 300 € | 14 700 € | 7 600 € | 2 500 € | 37 200 € | 5 % |
| **Total** | **24 900 €** | **192 000 €** | **277 800 €** | **246 200 €** | **64 200 €** | **805 100 €** | **100,0 %** |

**TABLE 4-4.SKYREC budget**

| Project | Cost |
|---|---|
| **WP1: New recovery boiler concepts** | |
| Once-through and reheater recovery boiler – concept studies (LUT) | 33 800 € |
| Co-firing of black liquor and biomass, part 1 and 2 (ÅA) | 31 100 € |
| Utilization of Pyrolysis Gases from the Recovery Boiler (ÅA) | 8 500 € |
| Pulp mill optimal steam pressure levels (LUT) | 16 000 € |
| Dew point measurements in Rauma and Heinola mill (ÅA) | 30 000 € |
| Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler (ÅA) | 14 900 € |
| | **134 300 €** |
| **WP2 Increasing superheated steam temperature** | |
| Corrosion tests of superheater materials in reducing conditions, part 1 (ÅA) | 37 000 € |
| Corrosion tests of superheater materials in reducing conditions, part 2 (ÅA) | 30 700 € |
| Full scale material exposure in Joutseno (VTT) | 104 000 € |
| | **171 700 €** |
| **WP3: Increasing recovery boiler pressure** | |
| Phenomena of transformation in recovery boiler char bed (LUT) | 14 800 € |
| Refractory material/ceramics in recovery boiler furnace (UO) | 15 000 € |
| Field tests of furnace materials / Characterisation of probe test samples (Boildec/VTT) | 175 600 € |
| | **205 400 €** |
| **WP4: Ensuring boiler and feedwater quality** | |
| Organic amines and natural organic matter in steam water cycle (VTT) | 17 700 € |
| Effect of organic amines to magnetite layer formation (VTT) | 65 000 € |
| TOC balance of Stora Enso Laminating Paper mill (Teollisuuden Vesi) | 24 600 € |
| TOC removal methods and their applicability in make-up water treatment (Teollisuuden Vesi) | 45 000 € |
| Water quality and water treatment guidelines (Teollisuuden Vesi) | 31 500 € |
| Reduction of TOC from recovery boiler make-up water (UO) | 10 000 € |
| Activated carbon and UV-treatment - field tests (Cewic/UO/JP-analysis) | 34 500 € |
| Comparison study of active carbon grades (Cewic/UO/JP-analysis) | 23 400 € |
| | **251 700 €** |
| **Coordination, meetings, translations etc.** | **42 000 €** |
| **Project total** | **805 100 €** |

## 4.5 Schedule

The project time frame was 2.5 years (1.1.2008 – 30.6.2010). The project had to apply for 12 months extension. The reason was the economic turndown in 2009 which caused temporary shutdowns to pulp mills and measurement projects in operating recovery boilers could not be completed as planned. With extra funding from Sumitomo additional projects could be performed and schedule was extended to the end of 2012. So, total schedule was 5 years (1.1.2008 – 31.12.2012). The length was rather long, but as the project had lots of measurement activities at operating recovery boilers, all time was needed.

# 5 SUMMARY OF THE SUB-PROJECTS

The SKYREC-project was divided into four work packages:

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

## 5.1 NEW RECOVERY BOILER CONCEPTS (WP1)

The work package 1 (WP1) studied the new recovery boiler concepts to increase the electricity generating potential and energy efficiency of recovery boilers. Most of the concepts weren’t studied previously. One way to improve electricity production in mills is to lower steam pressures in pulping processes. In that case steam can be expanded to lower pressure in turbine.

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

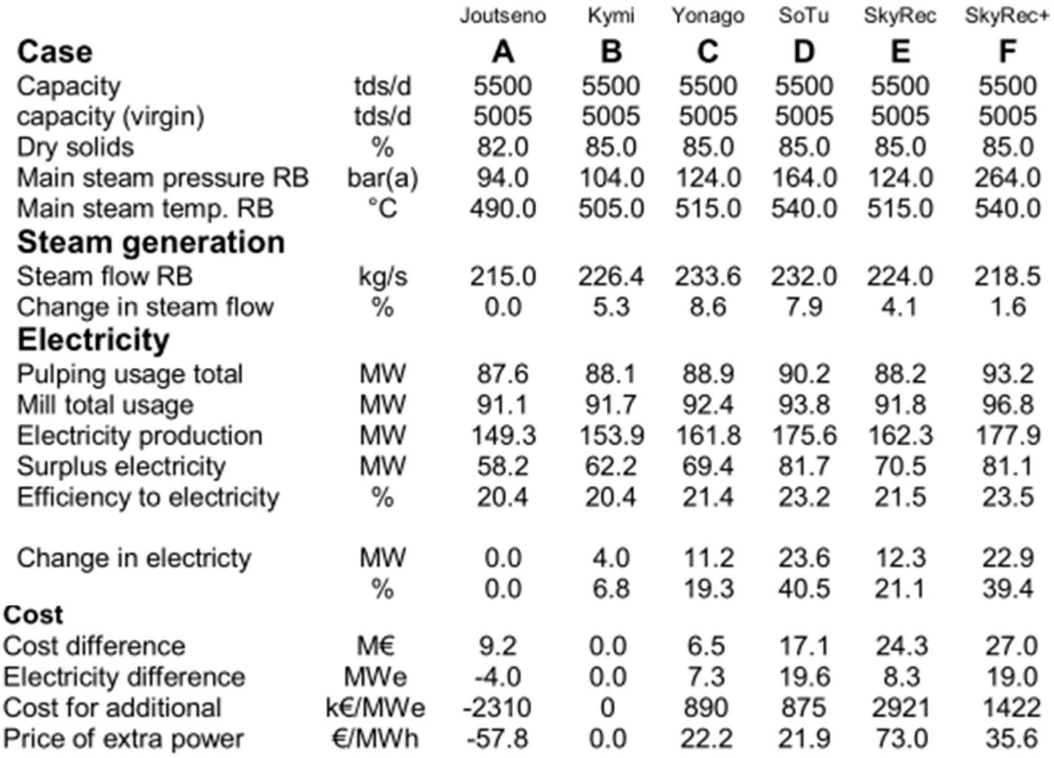
### 5.1.1 Once-through and reheater recovery boiler – concept studies

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

The studied concepts were:

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

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



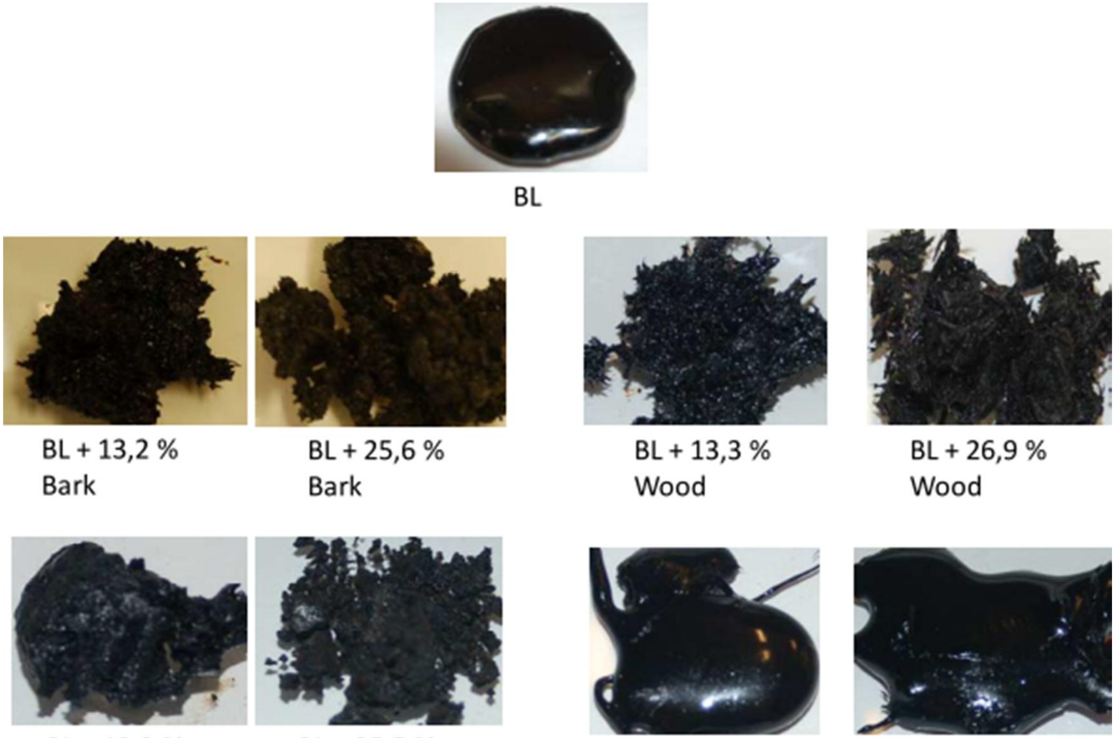
| | | Joutseno | Kymi | Yonago | SoTu | SkyRec | SkyRec+ |
|---|---|---|---|---|---|---|---|
| **Case** | | **A** | **B** | **C** | **D** | **E** | **F** |
| Capacity | tds/d | 5500 | 5500 | 5500 | 5500 | 5500 | 5500 |
| capacity (virgin) | tds/d | 5005 | 5005 | 5005 | 5005 | 5005 | 5005 |
| Dry solids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

Conclusions:

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

### 5.1.2 Co-firing black liquor and biomass

If mills have excess capacity in recovery boilers, they can potentially mix other biofuels into the BL to produce more bio-energy. The objective of this work was to determine if mixing other biofuels within BL would alter the combustion characteristics of the BL. Two different concentrations of bark, wood, peat and biosludge were added and mixed into BL of 80.4% d.s. All fuel mixtures except the biosludge mixtures looked more like wet solid fuels than liquid fuels, FIGURE 5-1. Droplets of the mixed fuels were burned at 1100 °C and 3% $O_2$ in a droplet furnace. Video and on-line gas analyzers for CO, $CO_2$ and NO were used to measure swelling, combustion times, carbon evolution ($CO_2$ + CO), and NO formation tendency. We found changes in swelling, char burning and NO formation.


BL

BL + 13,2 %
Bark

BL + 25,6 %
Bark

BL + 13,3 %
Wood

BL + 26,9 %
Wood

BL + 13,3 %
Peat

BL + 25,5 %
Peat

BL + 0,82 %
Bio-sludge

BL + 1,84 %
Bio-sludge

**FIGURE 5-1. Fuel mixtures of black liquor with bark, wood, peat or bio-sludge.**

The mixtures containing bark, wood or biosludge appear to burn much like the original BL based on single particle combustion tests. The largest changes in swelling were seen for peat and bio-sludge addition. The cause of these changes is not clear as 13,2 % and 25,5 wt% peat addition resulted in higher and lower swelling respectively when compared to the BL. Similarly, the 0,8 % biosludge mixture resulted in more swelling, while the swelling of the 1,8 % biosludge mixture had swelling similar to the BL.

The char burning stage is on average increased only slightly by the addition of bark, wood chips and biosludge, but more significantly by peat, especially the 25,5 wt% peat mixture FIGURE 5-2. This was caused in part by the significantly lower swelling of this mixture. All mixtures result in a higher NO formation with peat resulting in a significantly higher NO formation. Changes in air distribution should minimize any increase in NO. Cyanate also increased with all the fuel mixtures with peat resulting in the largest increase. Results are consistent with the nitrogen content of the mixtures, with the peat-BL mixture having the highest nitrogen content.

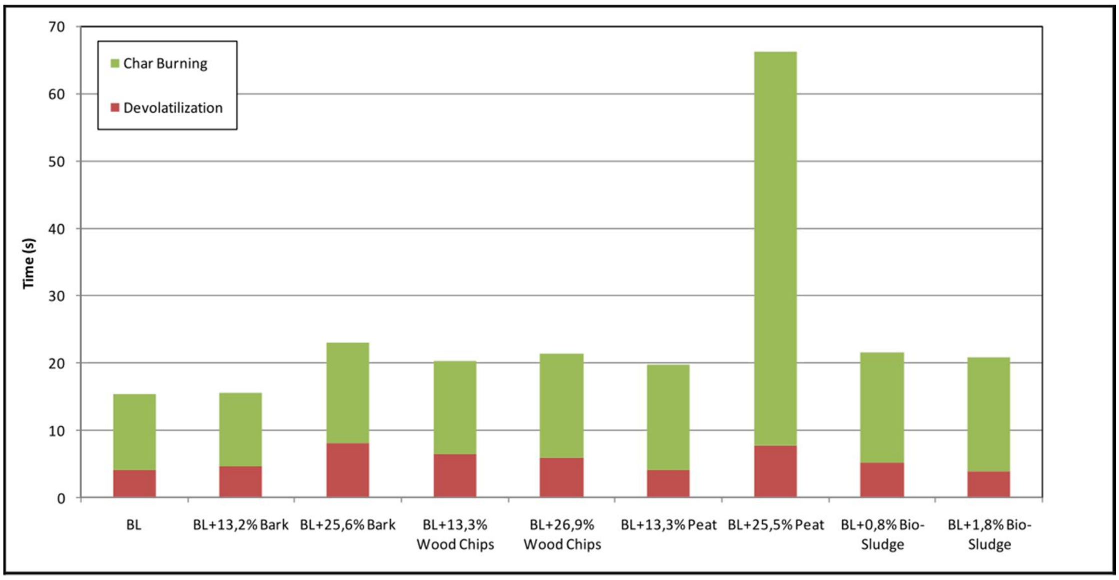


**FIGURE 5-2. Times of the combustion stages (drying, devolatilization, and char burning) for the fuel mixtures**

Increasing wood generally resulted in longer char burning and total combustion times while devolatilization times were about the same for all wood addition levels, FIGURE 5-3. There was no sharp transition as there had been with 26% peat, though the 50 wt% d.s. wood appeared to result in a significant increase in combustion time and therefore 35 wt% wood was also studied. Combustion times for the 26% and 35% wood mixtures were similar and longer than for 13%, but shorter than for 50%.

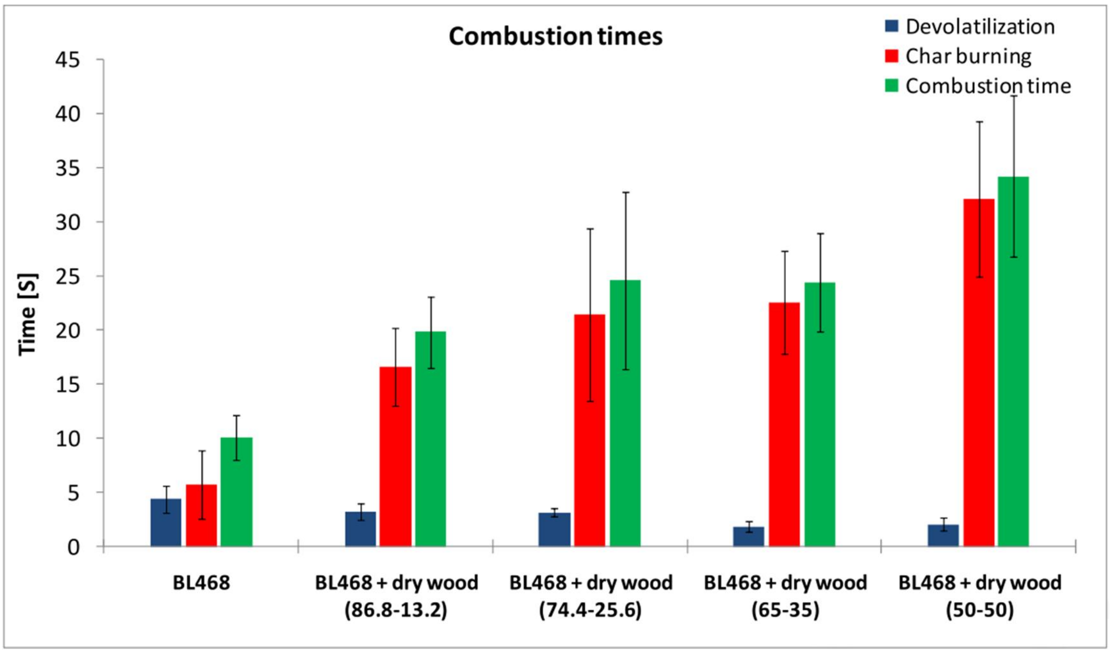


**FIGURE 5-3. Devolatilization, char burning and total combustion times for 4 different addition levels of dry wood with black liquor.**

The results of this preliminary study indicate that from a combustion chemistry standpoint, there is potential to add biofuels to BL for firing of the mixtures in a recovery boiler that has excess capacity to increase the amount of bio-electricity. The addition of elements to the recovery cycle can be accurately estimated and accounted for though the release of potassium from mixtures for example should be studied further. The fuels added here were air dried in the laboratory and therefore quite dry relative to the fuels as mills would receive them. Additional work should be carried out to determine the impact of this moisture on the burning characteristics. Additionally, for the mixtures considered here the BL appears to coat the solid material rather than form a solution with suspended solids. At firing temperatures the mixtures could look different, but spraying studies are certainly required to determine how to best feed such mixtures.

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

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

FIGURE 5-4 presents the heating value of the gas as air factor corresponding to the composition (chemical equilibrium at 900°C). The amount of gas to be extracted to cover 30 MW is indicated for two cases. The sensible enthalpy is excluded in calculation of the amount of gas needed. In addition to the heating value, the gas would contain some energy because of its temperature. Taking zero degrees Celsius as the reference temperature, in the case of 10kg/s extracted, the gas would contain 30 MW as heating value and about 9 MW as sensible enthalpy; the sensible enthalpy being 30% compared to the heating value of the gas. In the case of 3 kg/s extracted, there would be about 3 MW sensible enthalpy, which is 10% compared to the heating value. Results from existing CFD simulations of two recovery furnaces were analyzed for the local gas composition in the lower furnace.

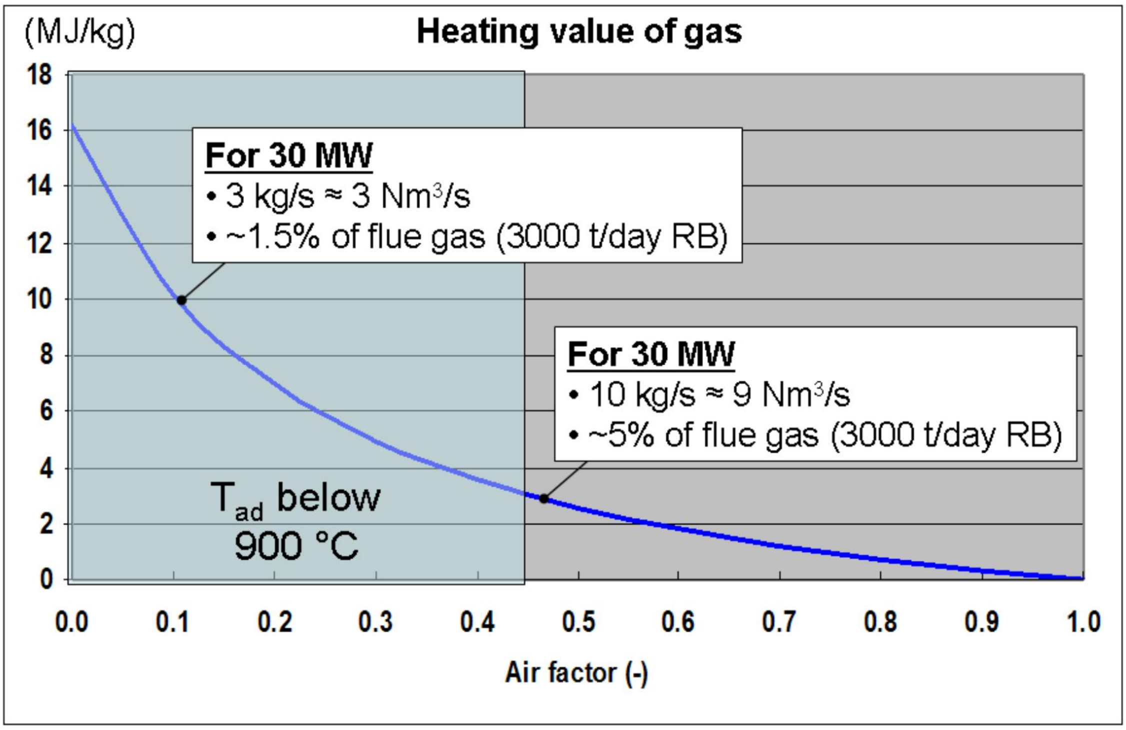


**FIGURE 5-4. Gas heating value as function of air factor, from equilibrium calculations at 900°C. Region of air factors which would result in adiabatic temperatures below 900°C also indicated**

The following conclusions are made:

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

### 5.1.4 Pulp mill optimal steam pressure levels

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

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

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

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

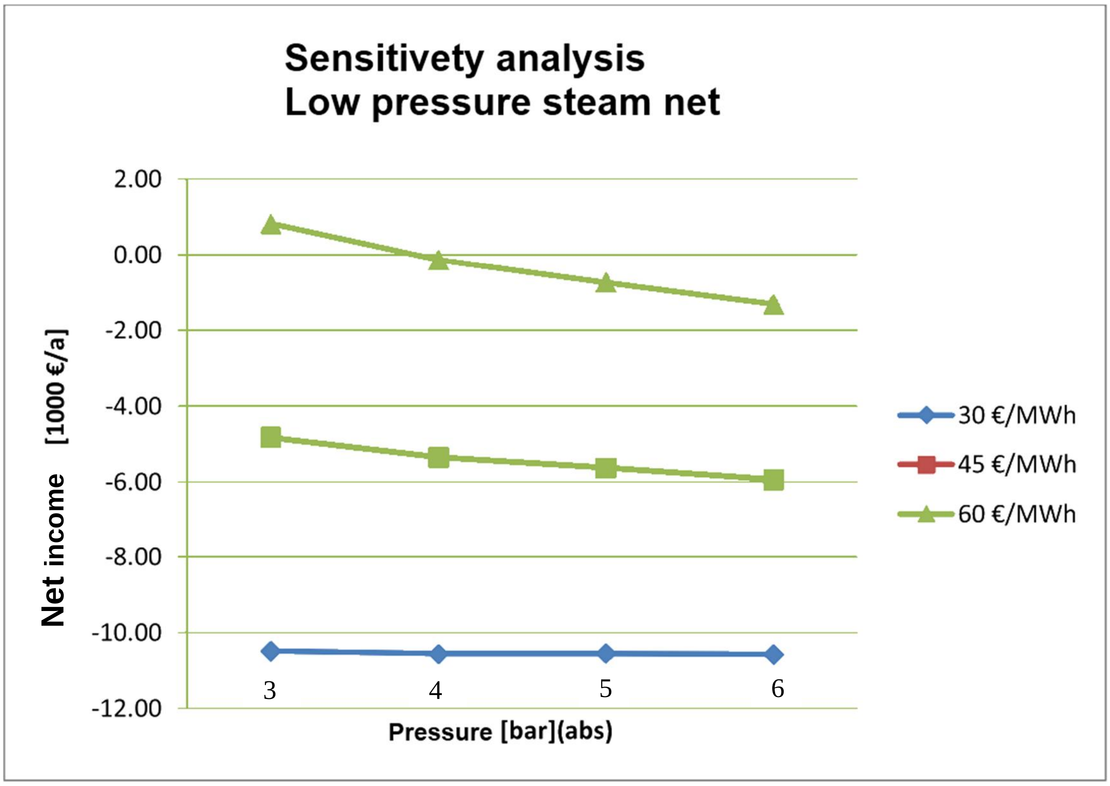


**FIGURE 5-5. Electricity price and steam pressure level effect to sale income in traditional pulp mill**

### 5.1.5 Dew Point Measurements in Rauma and Heinola mills

In modern recovery boilers an extra heating surface can be located after the electrostatic precipitator (ESP). Recovered heat replaces a certain amount of back-pressure steam and thus releases steam to be used for power generation with the condensing turbine. It is possible to reduce the temperature of flue gas safely down to 145°C. There is an increased interest in efficient use of the flue gas energy even down to temperatures lower than today and clearly below the normal acid due point temperatures (< 120°C).

Severe low-temperature corrosion may occur on cold surfaces, e.g., the air-preheaters or flue gas duct if their material temperature is below the acid dew point. This kind of corrosion can be avoided by keeping all cold end surfaces above the acid dew point. However, very little information is available for the corrosion tendency in recovery boiler flue gases at these lower temperatures. The objective of this study was to get reliable information of the dew point in recovery boiler flue gas ducts and of corrosion tendencies of surfaces having these low temperatures 70-110°C.

Dew point measurements were made with a commercial instrument (“Land”). $H_2SO_4$-concentration was measured with salt method were $H_2SO_4$ is absorbed into a salt, e.g. potassium chloride, then dissolved in water and analyzed for sulfate ions by ion chromatography. At the same time corrosion measurements were made with air-cooled probes. Metal samples on probes were analyzed after test time with SEM-EDS.

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

$SO_3$ (g) + $H_2O$(g) -> $H_2SO_4$ (g)

The gaseous sulfuric acid starts to form an acid mist below the acid dew point or condensate on cold surfaces. The sulfuric acid dew point temperature at different $H_2SO_4$ (g) concentrations is shown in FIGURE 5-6. Below 100°C practically no gaseous $H_2SO_4$ is found in the flue gas.

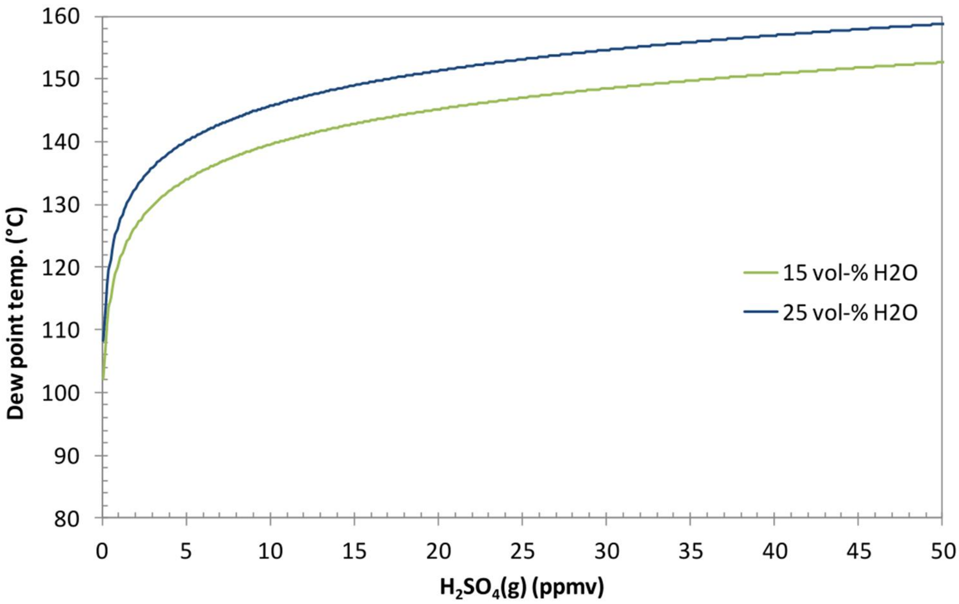


**FIGURE 5-6. Sulfuric acid dew point temperature in a flue gas with 15 and 25 vol-% $H_2O$**

At the Rauma Kraft mill the dew point measured was equal to the water dew point, 62-64°C, FIGURE 5-7. 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.

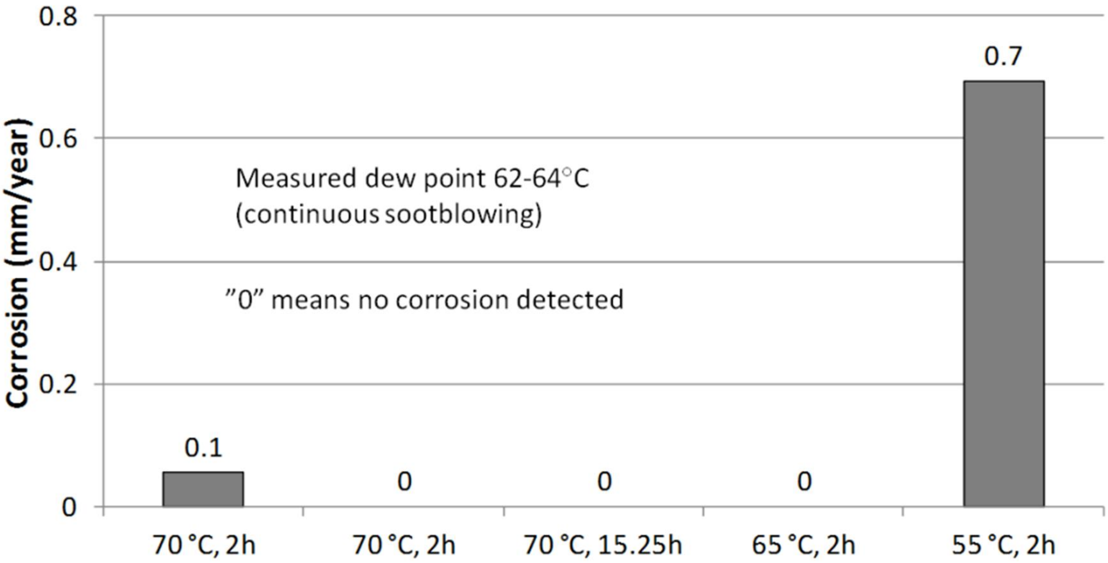


**FIGURE 5-7. Corrosion test results (Rauma mill)**

At the Heinola sulfite mill a somewhat elevated dew point of water was found. This can be the high amount of and the hydroscopic nature of $Na_2SO_4$. The concentration of $SO_2$ was between 1200-1600 ppmv, in dry gas, before the scrubber. The measured $H_2SO_4$ was below 1 ppmv measured with the salt method and 1-4 ppmv measured with controlled condensation method. This implies that there is a reaction between $H_2SO_4$ with $Na_2SO_4$ to form acidic $NaHSO_4$. At 80°C significant corrosion was observed.

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

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

The objective of this work was to better understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler. In particular this work was to clarify the conclusion of the dew point measurements at Rauma and Heinola in the previous study which indicated that there is no $H_2SO_4$ acid dew point. The question then came up, why some mills see corrosion in the economizers. One subsequent hypothesis was that corrosion was promoted during the water wash. This long term probe test was designed to help clarify these earlier findings and questions.

Two probes were inserted into the economizer section at Rauma at the same time. Both probes were kept at 90 °C by air cooling. One was pulled just prior to the planned recovery boiler shutdown and the second was pulled after the water wash. A temperature of 90°C was chosen because it is well above the water dewpoint, even in the presence of HCl and salt, but below a $H_2SO_4$ dewpoint, FIGURE 5-8.

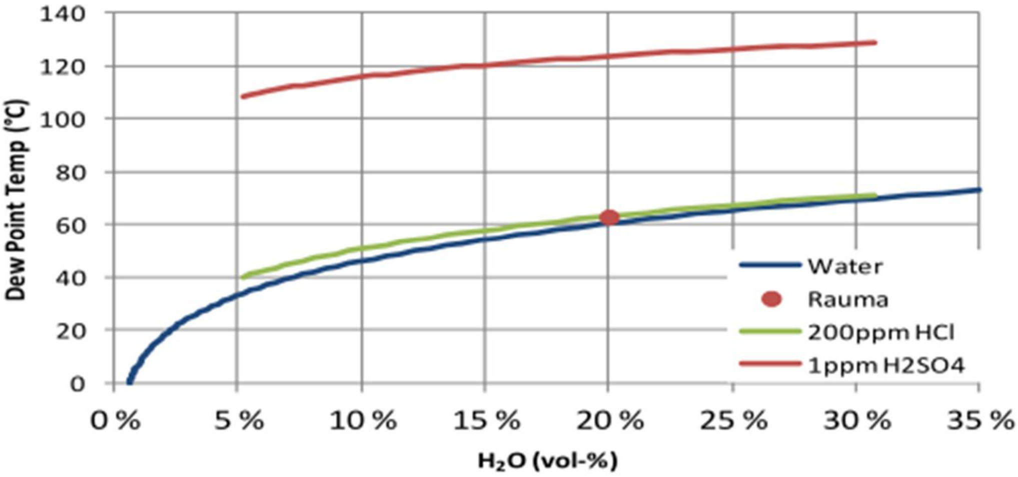


**FIGURE 5-8. Water dew point and acid dew points based on 200 ppm HCl or 1 ppm $H_2SO_4$ as well as the measured dew point at Rauma.**

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

The first probe was pulled out after 811h of normal operation and the probe was covered in ash. There was virtually no corrosion on the probe, FIGURE 5-9. Only a little corrosion was found on the top of the probe, but not on the bottommost edge of the probe. The probe was placed in one of the lower turns in the economizers and it is not clear which were the windward and leeward sides of the probe.

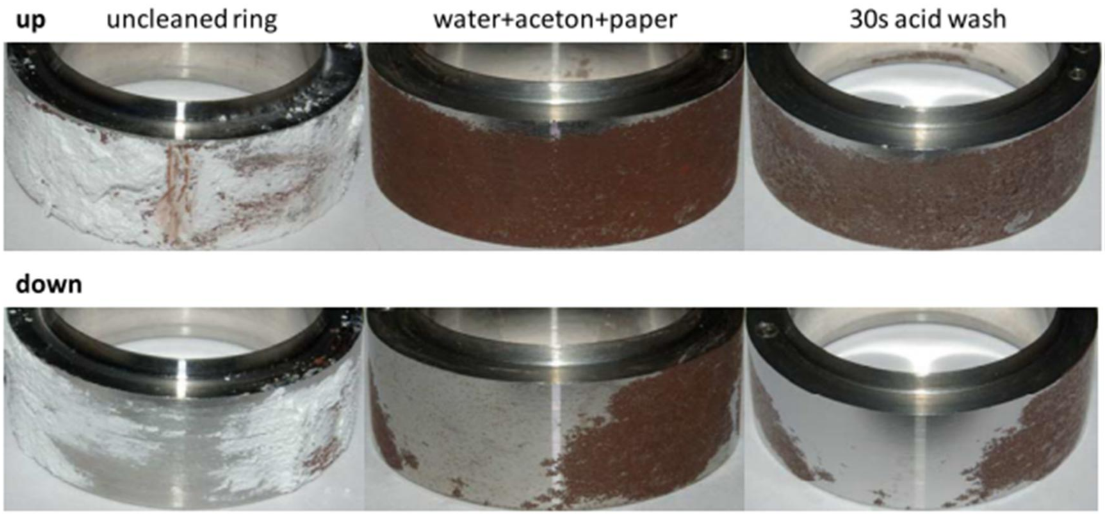


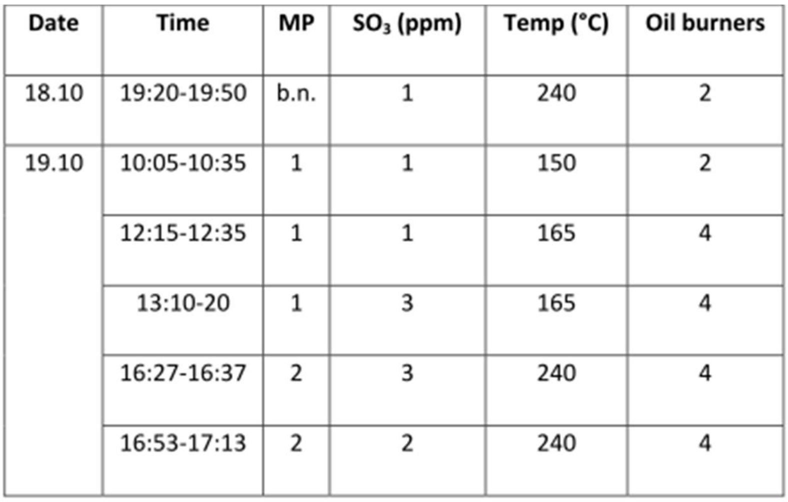
**FIGURE 5-9 Ring after 811h normal operation. No iron oxide was found on the bottom edge of the probe.**

The corrosion layer was pitting up to approximately 10 µm. In some spots of the corrosion layer, the chloride was not balanced by alkali indicating iron chloride and chloride induced corrosion. One explanation for the combined observations of corrosion being present on the top but not bottom and the presence of chloride in the corrosion layer is that a small amount of water is dropping on the probe from the sootblowers. This would dissolve NaCl in the salt resulting in a chloride containing solution until the water evaporates. The negligible amount of corrosion seen along with the lack of sulfur in the corrosion layer indicated clearly that there is no acid dew point corrosion.

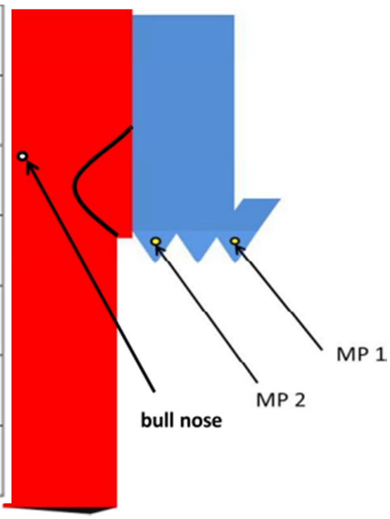
The second probe that was pulled out after the water wash and annual shutdown had more corrosion than the probe pulled out before the water wash, but there was still virtually no corrosion. Again, the bottommost edge was not corroded. The average corrosion for the two probes estimated on an annual basis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

After the water wash and after acid washing the tubes inside, oil was burned in the boiler. The air ratio used was extremely high, resulting in a flue gas with a high oxygen content and low $H_2O$ and $SO_2$ content due to the high level of dilution. Dew point and $SO_3$ were measured during oil burning at three different points, the bull nose and two different points in the economizer. No acid dew point was measured. The highest $SO_3$ level measured was about 3 ppm when four burners were firing oil, TABLE 5-2.

**TABLE 5-2. Sampling positions and $SO_3$ results. b.n.:bull nose.**



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



**Conclusions:**

No significant corrosion seen under normal operation or after the water wash for the probes held at 90°C. It was clear that there was no acid dew point corrosion due to $H_2SO_4$ formation during normal operation and mills can take more energy out of the flue gas without dew point corrosion under normal operational conditions. There was also no dew point corrosion seen during the oil firing. This may be due to the high air ratios used in this instance, but the results clearly show no acid dew point corrosion during normal operation of a modern Kraft recovery boiler.

## 5.2 INCREASING SUPERHEATED STEAM TEMPERATURE (WP2)

Fireside corrosion of recovery boiler superheaters has become increasingly common due to increasing closure of the chemical cycles and increasing steam parameters. Therefore, present and forthcoming conditions may accelerate metal loss by corrosion, unless proper preventive measures are applied. There are several different methods to limit the corrosion rate of superheaters in recovery boilers. The physical arrangement of recovery boiler superheaters plays an important role in preventing fireside corrosion. Several factors are critical in superheater design, including the location, tube geometry, arrangement, materials, and the direction of the steam flow. If neither the design nor the tube arrangement is enough to avoid high material temperatures and excessive tube wastage, improvements can be achieved by selecting better materials. Objective of the work package was to study the corrosion performance of various superheater tube materials in recovery boilers at high material temperatures.

In recovery boilers, sulfur-rich reducing atmospheres in the superheater area are mainly due to high gaseous $H_2S$ concentrations or high amounts of unburnt carryover particles depositing on the tube surface. Carryover particles may contain high amounts of sodium sulfide ($Na_2S$) and unburnt carbon. Unburnt carbon in the deposit is able to keep the local atmosphere reducing and thus initiate sulfide-induced corrosion. One goal of the project was to estimate the resistance/behaviour of the superheater tubes in a reducing atmosphere.

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

**Part 1**

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

The material samples were exposed to high temperature in a horizontal tube furnace for 168 h (7 days), at 450°C - 600°C. The furnace was equipped with a tightly closed glass reactor. The composition of the gas flowing through the reactor during the tests was 5% CO, 95% $N_2$ with a flow of 2.0 l/min. After the corrosion test, the specimens were allowed to cool down to room temperature inside furnace with a continuous flow of the gas mixture through the reactor. The samples were then ready to be analyzed with SEM/EDX in order to identify various chemical elements. The corrosion products were identified using x-ray images. The corrosion layer thickness was determined using scanning electron microscope back-scatter images.

The materials can be classified as two low alloy steels: ferritic (10CrMo9-10) and martensitic (T91), high nickel austenitic stainless steel (S28) and nickel based austenitic stainless steel (HR11N). Synthetic ashes salt 5, salt 8, salt 9 and salt 10 are introduced with respect to previous project dealing with the same salts and are used for comparison and recognition purposes. The chemical compositions of the synthetic ashes used in the experiments are shown in FIGURE 5-10.

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

- Salt 5 – reference salt – only sodium sulfate containing BL does not exist
- Salts 8 and 10 – “represent” BL with low and low/medium Cl content
- Salt 9 – no potassium – unlikely for the BL. Check what is the role of K.

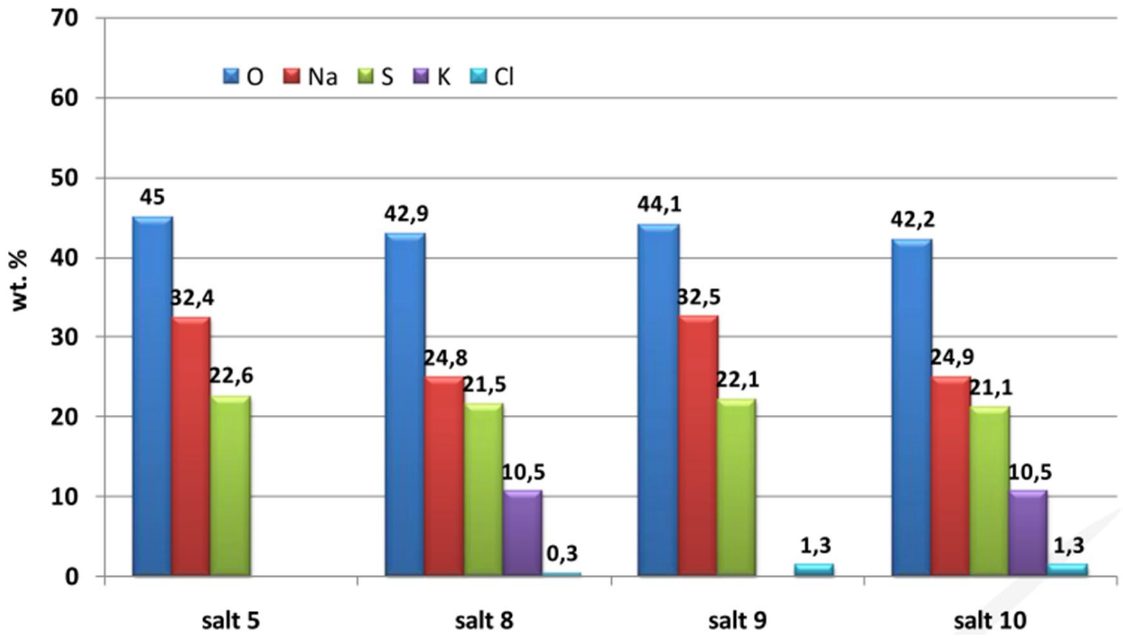


**FIGURE 5-10. The chemical compositions of the synthetic ashes used in the corrosion tests (wt%) (Part 1)**

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

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

- at reducing conditions for all steels ≥ 550ºC
- at ambient conditions for low grade steels especially ≥ 500ºC, for all steels ≥ 550ºC ($T_0$ of the K containing salts slightly above 500ºC)

In reducing conditions and high temperature (600ºC):

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

Sulfur was often found on the corrosion front beneath the depleted surface of the bulk material suggesting formation of metal sulfides. This was typically but not exclusively observed in the cases of high alloy steels, S28 and HR11N. In a previous project (SOTU2) the same salts have been used for corrosion tests in ambient atmosphere. A comparison of these results for Salts 5, 8, 9, and 10 in ambient and reducing atmosphere is presented below on separate graphs (FIGURE 5-11).

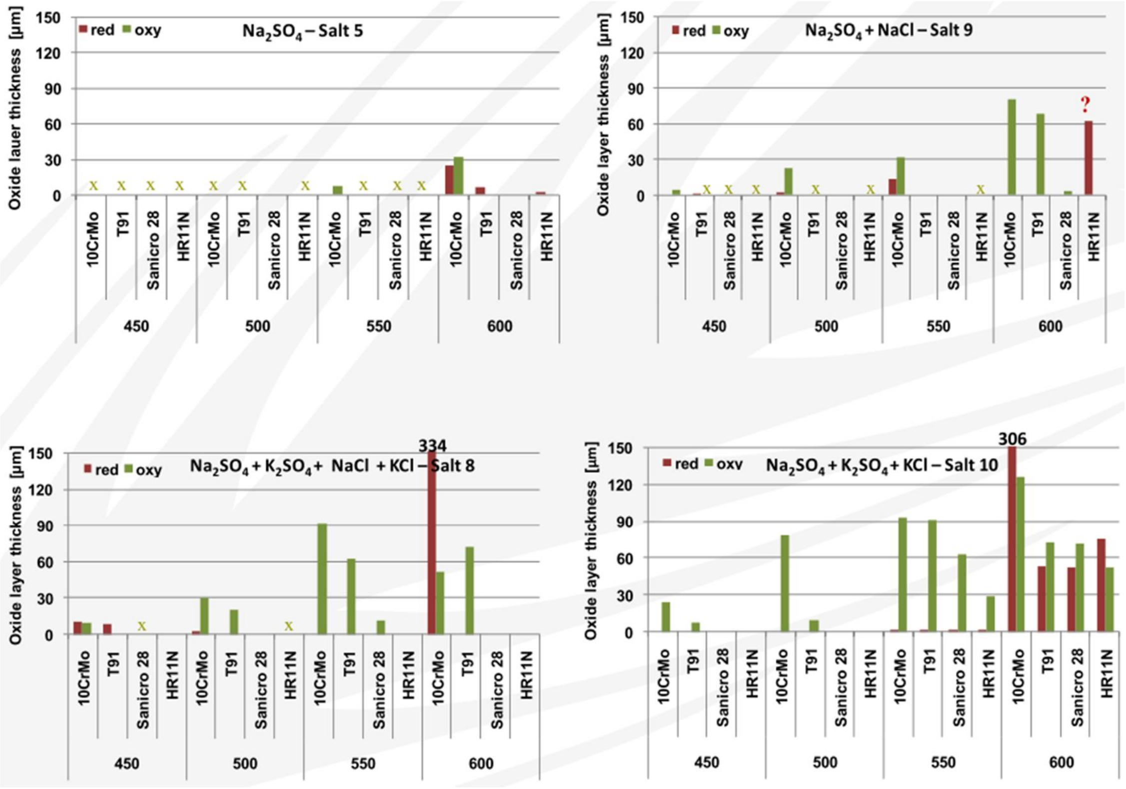


FIGURE 5-11. The mean oxide layer/corrosion product thickness of the tested materials in ambient (green bars - oxy) and reducing atmosphere (red bars- red). The corrosion tests duration 168h.

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

## Part 2

In the part 1 of the project it was concluded that only a low reduction level of sulfate to sulfide was achieved with the test setup used. Thus, in Part 2 (BL) char and $Na_2S$ (simulating reduced $Na_2SO_4$) were added to the previously tested salts (5 and 10). Same four materials (10CrMo9-10, T91, Sanicro 28 and HR11N) were tested in reducing atmosphere ($95N_2$ -5CO vol%) at 525°C and 565°C.

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

**TABLE 5-3. The detailed compositions of the salts and their first calculated melting points, $T_0$.(Part 2)**

| Salt | $Na_2SO_4$ | $Na_2S$ | $K_2SO_4$ | KCl | BL char | T0, °C |
|---|---|---|---|---|---|---|
| | mol% | | | | wt% | |
| **5** | 100 | | | | | 886 |
| **5r10** | 90 | 10 | 0 | 0 | 5 | 585* |
| **5r50** | 50 | 50 | 0 | 0 | 5 | 583* |
| **5r80** | 20 | 80 | 0 | 0 | 5 | 571* |
| **10** | 78 | | 17 | 5 | | |
| **10r10** | 70 | 8 | 17 | 5 | 5 | 494 |
| **10r50** | 39 | 39 | 17 | 5 | 5 | 498 |
| **10r80** | 15 | 62 | 17 | 5 | 5 | 513 |

The exposures to Salt 5r10, Salt 5r50 and Salt 5r80 resulted in high corrosion of the low alloy materials, 10CrMo9-10 and T91, FIGURE 5-12. 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.

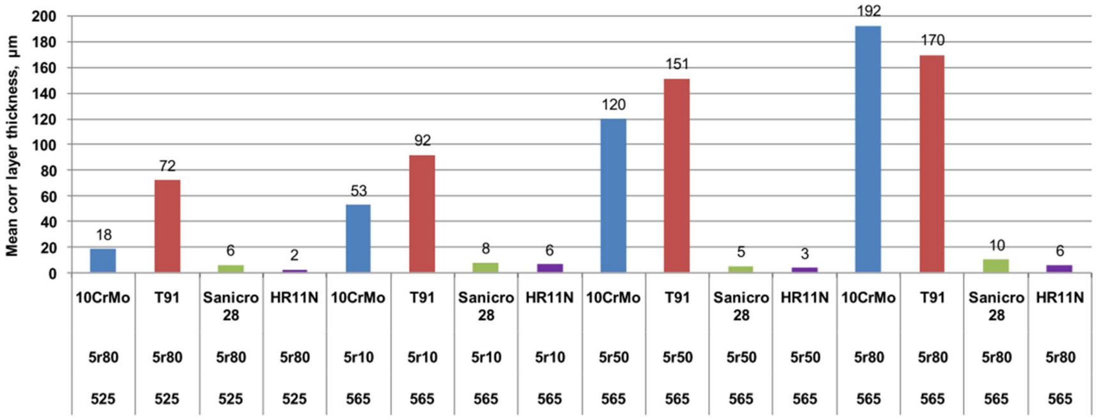


**FIGURE 5-12. The mean corrosion layer thickness of the tested materials with Salts 5r10, 5r50 and 5r80 in reducing atmosphere at 525°C and 565°C. Test duration 168 h.**

The exposures to Salt 10r10, Salt 10r50 and Salt 10r80 resulted in an extreme corrosion of low alloy materials, 10CrMo9-10 and T91, FIGURE 5-13. 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.

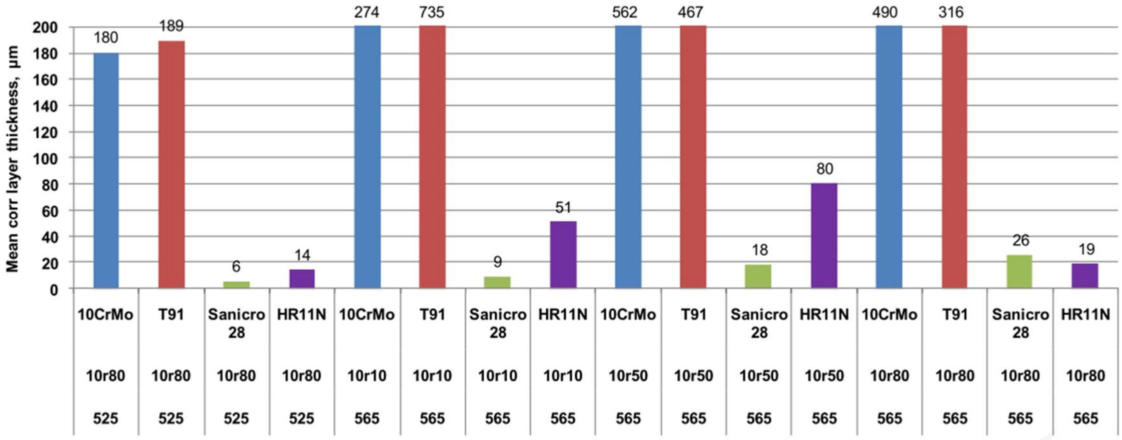


**FIGURE 5-13. The mean corrosion layer thickness of the tested materials with Salts 10r10, 10r50 and 10r80 in reducing atmosphere at 525°C and 565°C. Test duration 168 h**

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

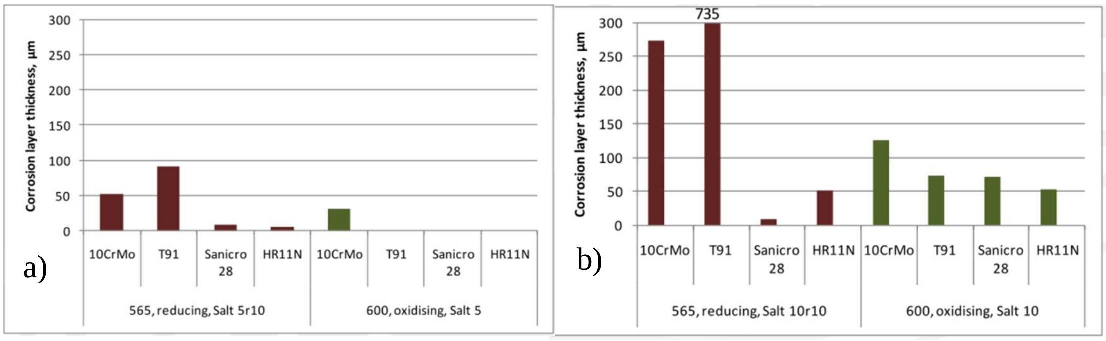


**FIGURE 5-14. The mean corrosion layer thickness with Salt 5r10 at 565°C in reducing atmosphere and Salt 5 at 600°C in oxidising atmosphere (a) and with Salt 10r10 at 565°C in reducing atmosphere, Salt 10 at 600°C in oxidising atmosphere (b)**

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 oxidizing conditions with Salt 5 no corrosion was detected. The results for HR11N with Salt 10r10 under reducing conditions at 565°C were comparable to the results obtained from tests under oxidizing conditions with Salt 10 at 600°C while Sanicro 28 performed better in a reducing environment with Salt 10rX (10r10, 10r50 and 10r80).

### 5.2.2 Full scale material exposure in Joutseno

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

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

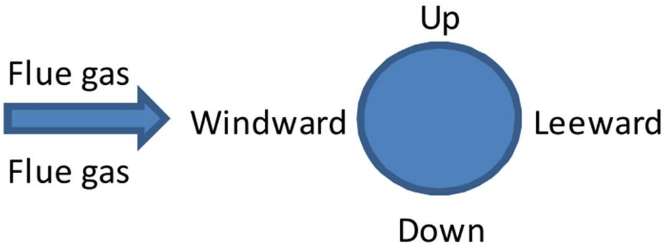


**FIGURE 5-15.The terminology of different measuring directions on the probe referring the flue gas flow is presented above.**

**FIGURE 5-16. Probe ready for insertion through an inlet located about one meter below the sootblower at level 10½, between 2nd and 3rd superheater.**

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

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

Performance of the six materials tested is considered as unsatisfactory, Super 625 and possibly SAN 69 excluded, in the actual test conditions; i.e., at such conditions where the probes were exposed to steam blowing from a close vertical distance and at average tube material temperatures of about 570 and 540 °C, peaking for short time up to 590°C. There exist, however, no major quantitative or qualitative differences between the results of the present study and recent full scale recovery boiler and laboratory test data available in the literature taking in regard the temperature sensitivity of the corrosion phenomena in question and the statistical nature of the extent of localized corrosion in place and time, FIGURE 5-17.

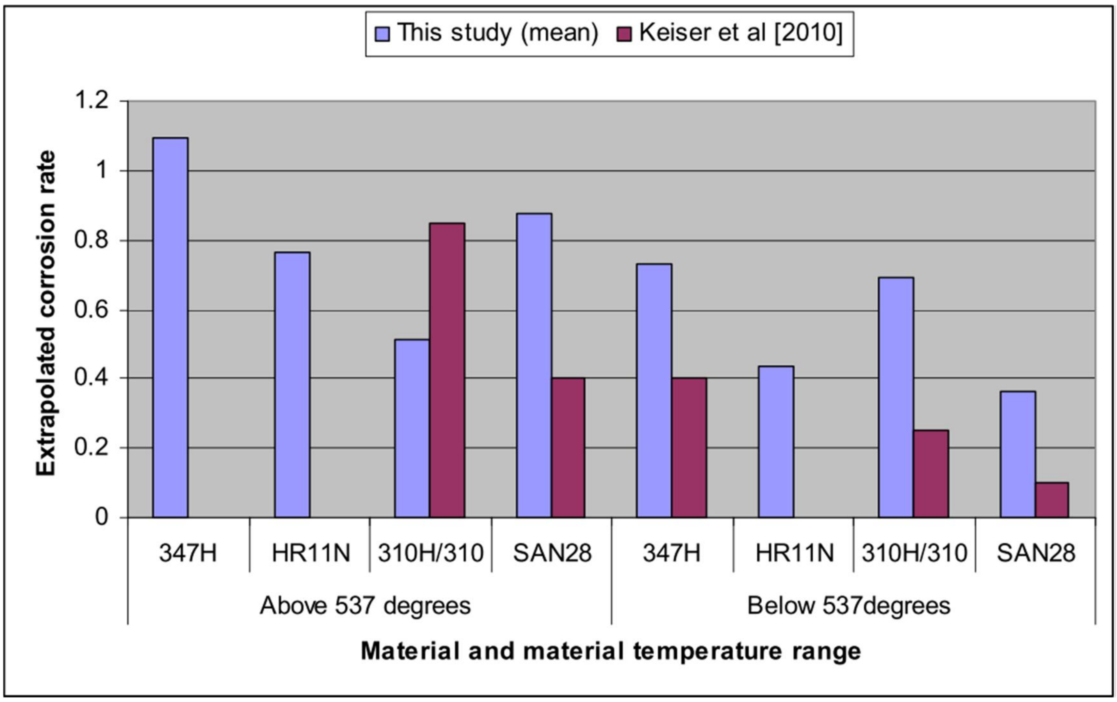


**FIGURE 5-17. Schematic presentation of extrapolated corrosion data applied from two different sources. Experimental exposure time in RB superheater area in each case is as follows. This study: 600 h; Keiser et al [2010]: 1000 h.**

## 5.3 INCREASING RECOVERY BOILER PRESSURE (WP3)

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

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

### 5.3.1 Phenomena of transformation in recovery boiler char bed

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

The overall shape and composition of char bed is well defined. Recovery boiler char bed consists mostly of combustion residue. It contains unreacted carbon, sodium carbonate ($Na_2CO_3$), sodium sulfate ($Na_2SO_4$), sodium sulfide ($Na_2S$) and sodium chloride (NaCl) with smaller amounts of similar potassium compounds. The structure is partly porous, but contains rocklike sintered sections. Both passive and active parts of the char bed are relatively porous and light. The heat capacity per volume is much less than e.g. rocks. Thermal conductivity of char bed is close to insulating materials. The heat stored in the char bed is about 4200MJ/m 2 and the heat stored in smelt is 340MJ/m$^2$. At full capacity new heat is brought at about 3MJ/s. The char bed contains considerable amount of heat.

Cooling of the char bed has been problematic especially when the boiler has been stopped though emergency shutdown. Then it can happen that the char bed is large and contain molten smelt. One must prevent smelt water contact. This can best be done so that the char bed is disturbed as little as possible. The char bed is let to cool and all smelt is let to solidify before the water wash is started to minimize the possibility of explosion. During emergency stoppage the fuel flow is closed and most of the water in the boiler is drained. The char bed top surface cools by convection and the bottom tubes are operated at temperature corresponding to the boiler pressure. These outside changes are fast compared to char bed cooling time. The bed has been cooled with sodium bicarbonate ($NaHCO_3$), which is a solid powder like chemical. Another tried cooling chemical has been liquid carbondioxide ($CO_2$), which in storage pressure to atmospheric pressure causing cooling. The cooling increase from additional cooling remains unproven.

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

| Bed height [m] | Cooling time [h] |
|---:|---:|
| 0.1 | 2.5 |
| 0.2 | 6.5 |
| 0.4 | 19 |
| 0.6 | 39 |
| 0.8 | 69 |
| 1 | 108 |
| 1.2 | 154 |
| 1.4 | 202 |
| 1.6 | 255 |
| 1.8 | 313 |
| 2 | 382 |

**FIGURE 5-18. Total required time to cool charbed to less than 500ºC.**

### 5.3.2 Refractory materials/ceramics in recovery boiler furnace

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

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

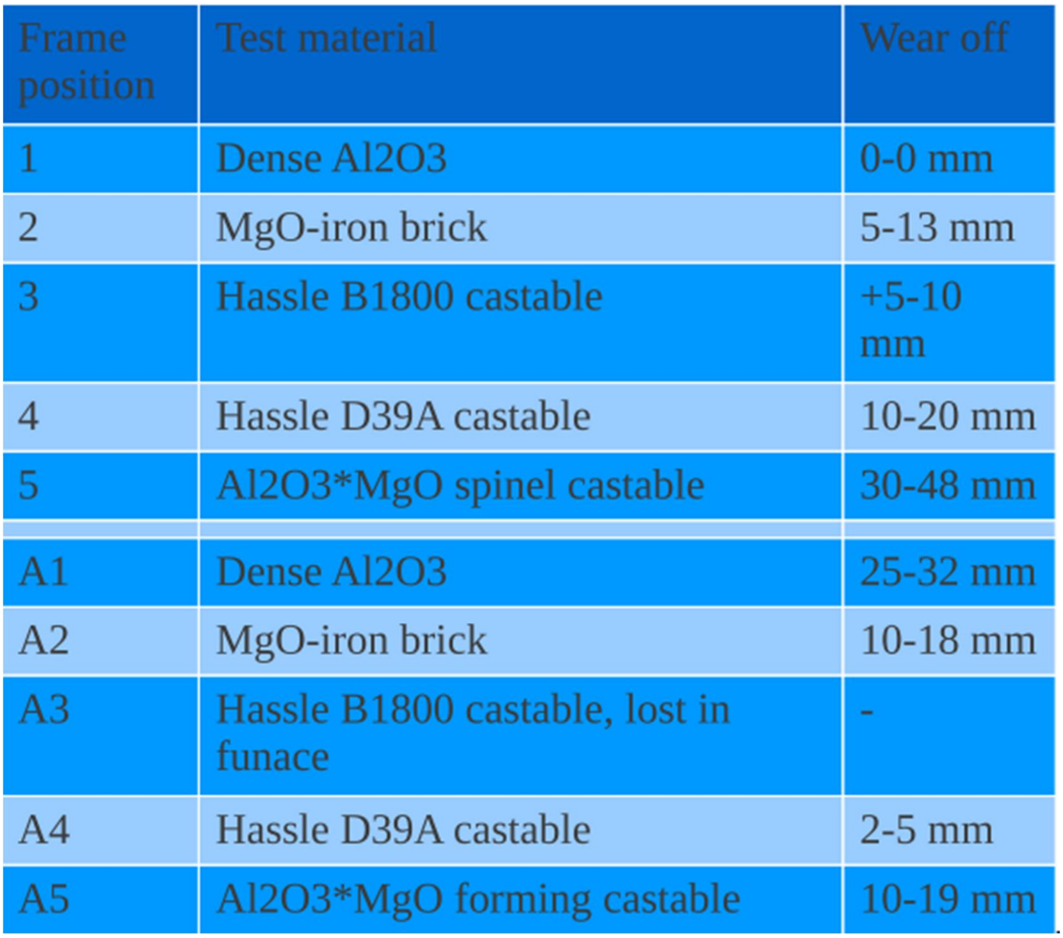
**FIGURE 5-19. Refractory materials after test**

Because of this performance, the decision was to find harder $ZrO_2$ castable and improve spinel and other castables bonding to be more chemically resistant by nanospinel. Result was that there is no harder $ZrO_2$ castable in the market and nanospinel manufacturing failed due to laboratory accident. For the 2nd test it was decided to use best from 1st test and Hassle B1800 castable.

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

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

**TABLE 5-4. Second test wear-off results**



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

### 5.3.3 Field tests of furnace materials / Characterisation of probe test samples

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

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

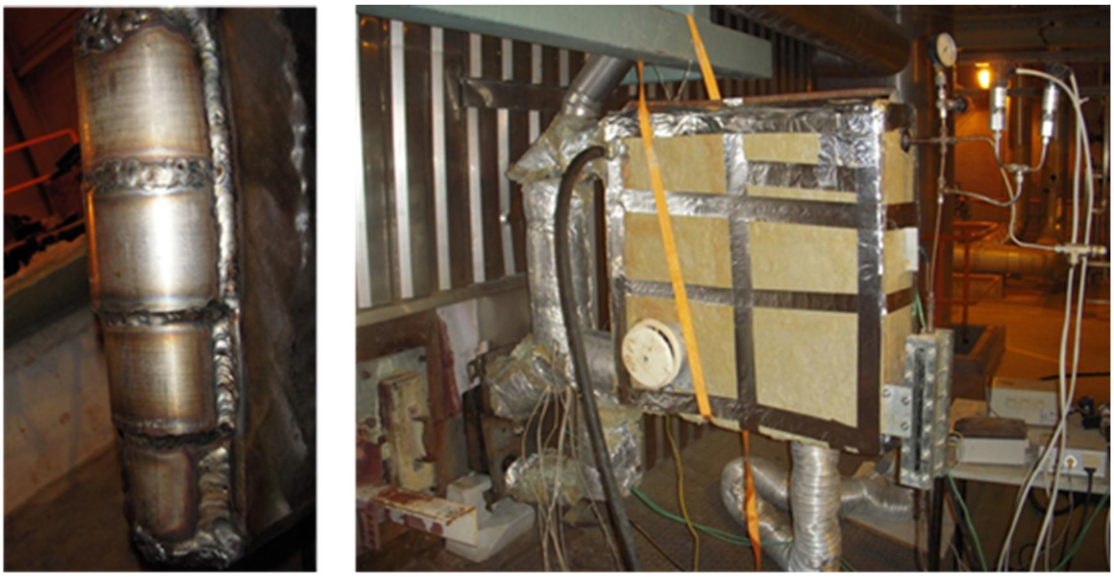


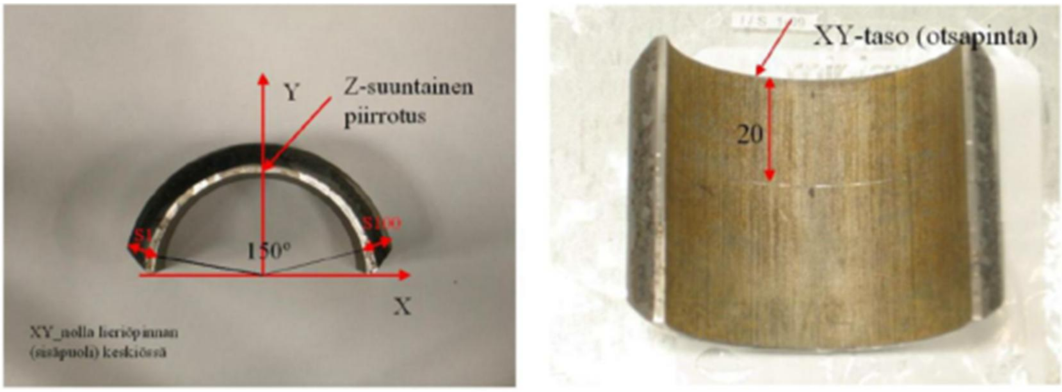
**FIGURE 5-20. Steam generator front wall with tested materials and experimental setup before installation into liquor gun**

The test materials were carbon steel; austenitic stainless steels 3R12 (304L), 3RE28 (310S) and 3XRE28 (310S); high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test matrix is shown in TABLE 5-5.

**TABLE 5-5. Test schedule and chosen 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 |

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



a)

b)

**FIGURE 5-21. The wall thickness profiles were measured before and after testing with coordinate measurement machine a) as a function of circumference b) from three axial locations (Z = 15, 25 and 32 mm).**

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

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

**Results**

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

In current tests highest corrosion rate, ca. 4 mm/a, was measured for the carbon steel as expected. The traditional composite tube material 3R12 (304L) had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C. Based on the results of 3R12 (304L) the reproducibility of the probe tests was so good that different probe tests can be used to compare different materials to each other. No marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were in the order of 0.15...0.2 mm/a in the long term (>2000 h) test, i.e. about four times lower than that of the 3R12 (FIGURE 5-22).

The results for the Super 625 were inconsistent. In short term 750 h test at 430 °C it's corrosion resistance was only slightly better than that of the 3R12 (304L), but in the long term 2154 h test at 440 °C it's resistance was even better that of the Sanicro 38 and HR11N (FIGURE 5-22). Similar kind of behaviour was observed in Sanicro 67. In short term 744 h test at 440 °C its corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C its corrosion rate was only 1/10 of that of the Sanicro 38 and HR11N and 1/5 of the Super 625.

In short term (<1000 h) tests the corrosion resistance of the 3RE28, 3XRE28 and Sanicro 28 were as good as or even slightly better than that of the Sanicro 38 or HR11N (FIGURE 5-23). Because the 3RE28 (310S) and 3XRE28 (310S) were not included in the long term tests and no results were obtained for the Sanicro 28 from the long term test No. 5, due to the misplaced thermocouple, it is recommended to verify their promising performance with long term tests in the future.

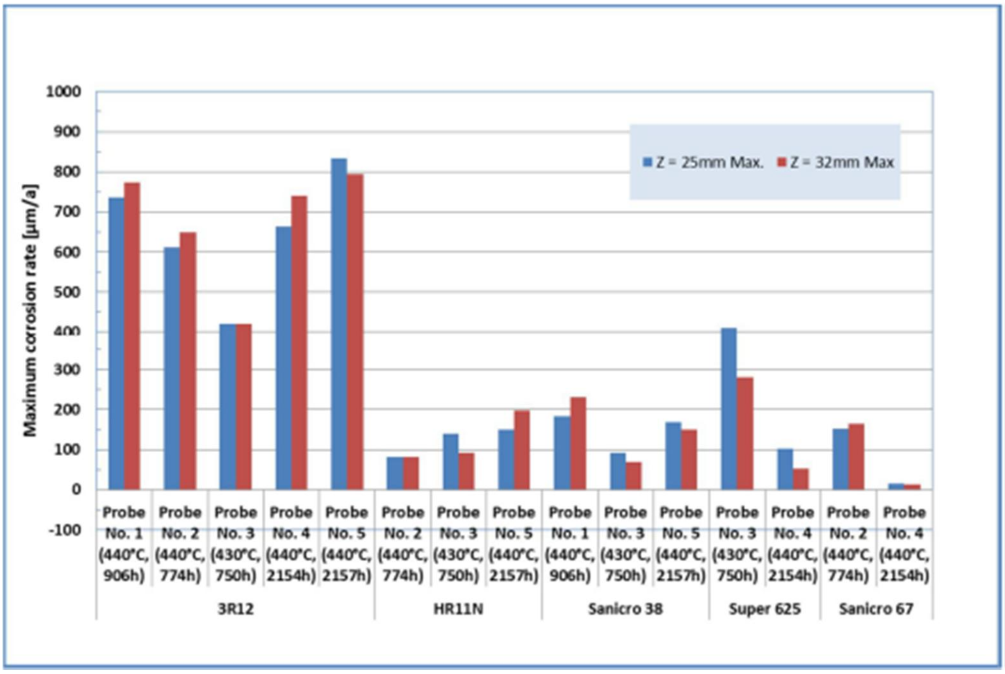


**FIGURE 5-22. Calculated maximum corrosion rates for the 3R12, HR11N, Sanicro 38, Super 625 and Sanicro 67 materials from the probe test No. 1 - 5.**

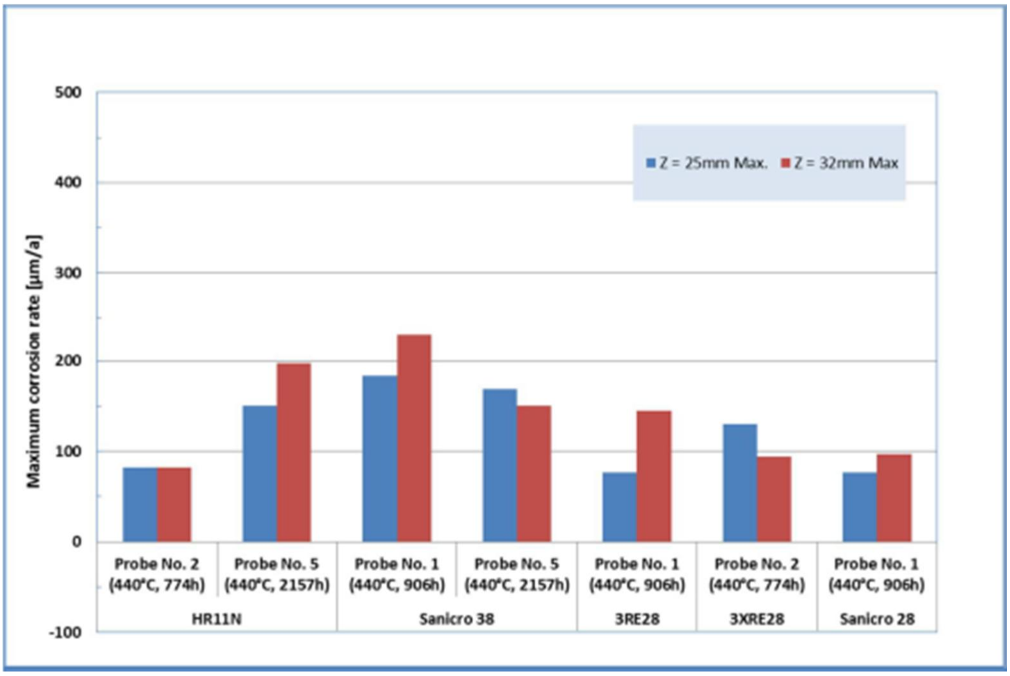


**FIGURE 5-23. Calculated maximum corrosion rates for the 3RE28, 3XRE28, HR11N and Sanicro 38 from the probe test No. 1-3 and 5.**

## 5.4 ENSURING BOILER AND FEEDWATER QUALITY (WP4)

Water treatment and water chemistry are essential to the safe operation of black liquor recovery boilers. Boiler feedwater requires treatment, the level of treatment depending on the operating pressure of the boiler and the specific raw water used. High pressure boilers require high purity demineralized water as even very low levels of contaminants can cause deposits and corrosion inside the boiler and condensate systems.

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

There are two primary sources of carbon-based molecules in a recovery boiler or in the steam it produces: compounds that enter with makeup water and organic treatment chemicals. Organic compounds in the make-up water originate from raw water (mainly natural organic matter, NOM), organic internal water treatment chemicals and impurities (lubricants, oils, degraded ion exchange resins etc.). Amount of organic matter can be measured by TOC (total organic carbon) analyzers (down to ppb-level). Conventional chemical water treatment and demineralization processes cannot remove electrically neutral fractions. Organic burden can be mitigated by improving the effectiveness of make-up water treatment process to filter organic substances with different methods.

Organic compounds decompose at high temperatures and pressures of the water-steam cycle. The higher the temperature and pressure, the greater the decomposition of organic compounds occurs. Therefore organic content in boiler water-steam cycle has a link to energy efficiency. End products are low molecular weight organic acids (mainly formic and acetic acid), ammonia and carbon dioxide. Organic acids and carbon dioxide are related to corrosion in a water-steam cycle although there is some controversy on their relevance.

Work package 4 (WP4) objectives was to study the characteristic of carbon-based molecules and their effect on water-steam cycle corrosion. The effect and behavior of water chemicals degradation products in elevated temperature and pressure was also studied. Several sub-projects studied different removal methods and their applicability in recovery boiler make-up water treatment. There was a need for updating and standardizing the recovery boiler water treatment and water chemistry guidelines since the boiler pressure has increased in new and future boilers, the capacities of the old plants, have been increased, the usage of the new chemicals has increased, and the monitoring of the water chemistry is largely done by on-line measurements. The guidelines presently used in the plants are based on old norms, on the values given by boiler or by chemical suppliers, and on best practices based on plants' own experiences.

### 5.4.1 Organic amines and natural organic matter in steam water cycle

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

Organic matter may be present as unwanted impurities (natural organic matter by make-up water or cooling water leak, residual from plant erection or by maintenance procedures) or functional additives (alkalizing amines, organic oxygen scavengers, dispersant and chelants, polyamines). Alkalizing amines are used as functional additives because of reduction of corrosion generation and corrosion product transport into the boiler and improvement in the feedwater purity, which results in decreased blowdown losses. Alkalizing amines provide also faster startup which lowers corrosion product transport during start up. These advantages are expected to be achieved by increased pH in the condensing steam which is due the more favorable distribution behavior of amines in comparison to ammonia. Alkalizing amines and their trade names used in Finland are listed in TABLE 5-6.

**TABLE 5-6. Alkalizing amines in Finland.**

| Alkalizing amine | Trade name |
|---|---|
| Cyclohexylamine (CHA) | Boilex 510A ja Amercor 853s |
| Aminoethylpropanol (AMP) | Boilex 510A ja Amercor 853s |
| Morpholine (Morph) | KK-Amina 8026 ja Eliminox-Mor |
| Diethylaminoethanol (DEAE) | KK-Amina 8026 |
| Ethanolamine (ETA) | KK-Amina 8026 |

When introduced in the steam water cycle all organics also alkalizing amines are subject to hydrolysis and thermal degradation (decomposition and oxidation). An external supply of oxygen will accelerate oxidation process. As a general rule volatile acidic degradation products are produced, such as acetic acid and carbon dioxide, but also other organic acids are found. The decomposition products result in lowering of pH. Organic amines on the other hand produce, beside volatile acids, also ammonia. Both the remaining amine and ammonia dissociate into cations that will act to increase the pH.

Recovery boilers which supply steam to many separate processes, resulting in incomplete recovery and losses of condensate, are often integrated as part of a large factory complex. Therefore large quantities of make-up water are needed and even relatively very small amounts of impurities (natural organic matter, NOM) present in the make-up water can have dramatic negative effects on the operation of a water-steam cycle. Amount of organic matter can be measured by TOC (total organic carbon) analyzers (down to ppb-level). TOC has (especially NOM) many forms and often associated with inorganic ions (chloride, sulfate etc.). Individual substances of NOM not feasible fractionated and identified. Liquid Chromatography – Organic Carbon Detection (LC-OCD) method separates organic matter to seven different groups according to size. Example of LC-OCD method is presented in FIGURE 5-24.

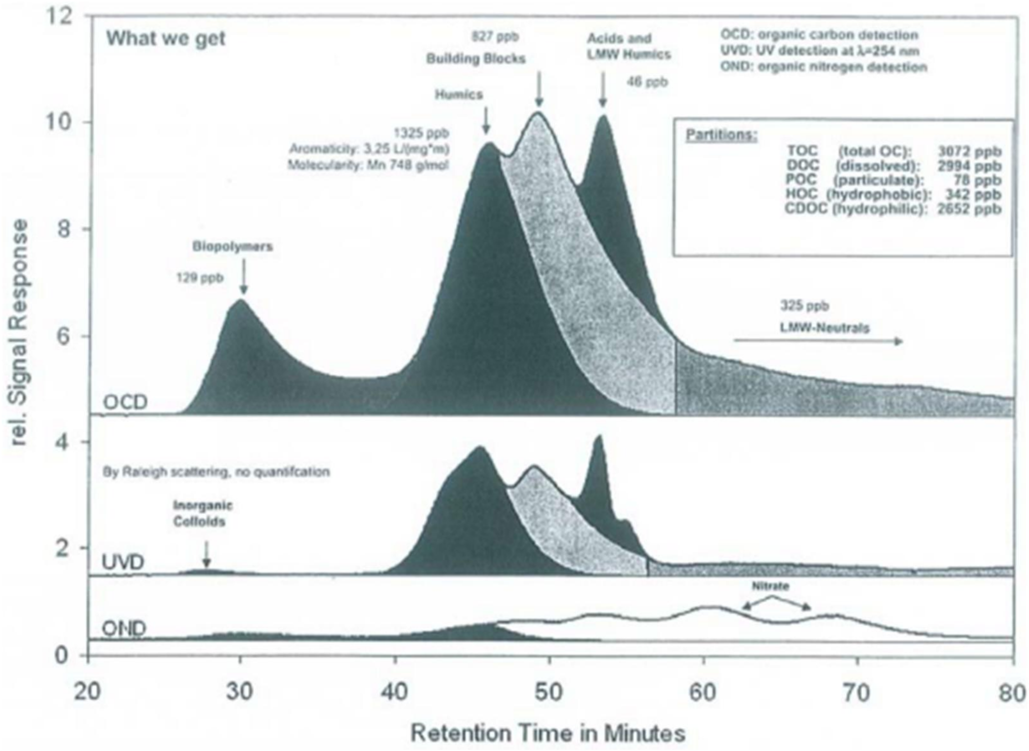


**FIGURE 5-24. Example composition of organic compounds in surface water with LC-OCD method.**

Organic matter in the form of NOM or alkalizing amines, polyamines or organic oxygen scavengers is not harmful for materials of construction. Greatest effect of organic matter is caused by its break-down products – low molecular mass organic acids (LMMOA), carbon dioxide and inorganic acids (formed as a result of inorganic ions bound to organic structure) Above mentioned cause changes in pH, especially condensate pH on varying steam quality. Most pronounced corrosion mechanism enhanced by organic matter, by affecting pH is concluded to be Flow Accelerated Corrosion (FAC).

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

Limit values for organics difficult to set:

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

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

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

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

Prevention of FAC:

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

### 5.4.2 Effect of organic amines to magnetite layer formation

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

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

During the tests degradation of chemicals where monitored with on-line pH-measurement and concentration of amines with capillary electrophoresis (ppb level). Magnetite layer formation to polished and pre-oxidized samples was monitored by EIS (Electrochemical Impedance Spectroscopy). Test arrangement is shown in FIGURE 5-25.

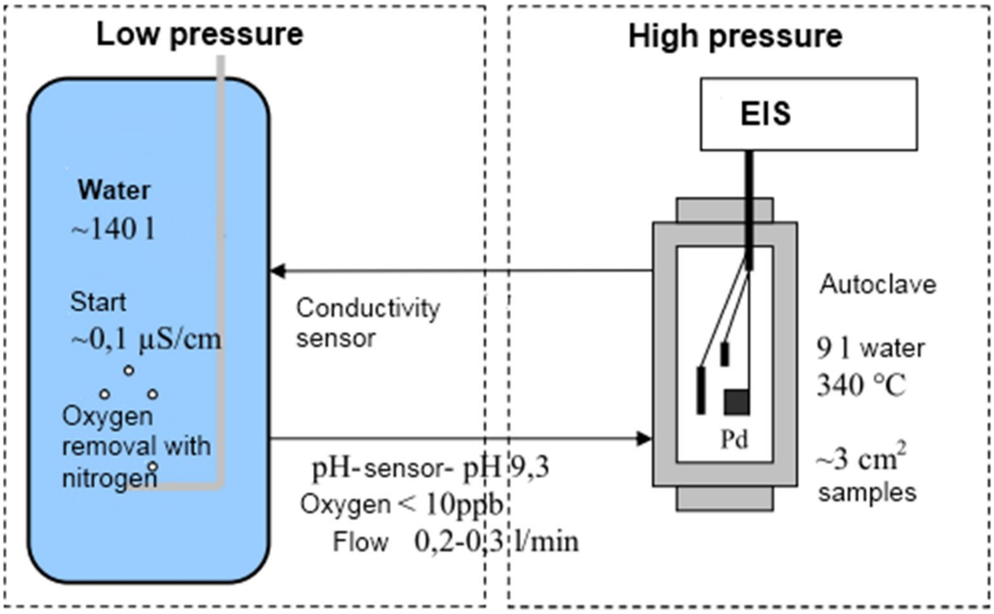


**FIGURE 5-25. Test arrangement**

From studied amines morpholine had the best thermal resistance (340 °C) and 2-amino-2-methyl-1-propanol the weakest, FIGURE 5-26. Concentration of decomposition products was minimal, in low-oxygen water degradation products are mainly low molecular weight amines and alcohols, not organic acids. Accurate analysis of low concentration degradation products needs qualitative methods.

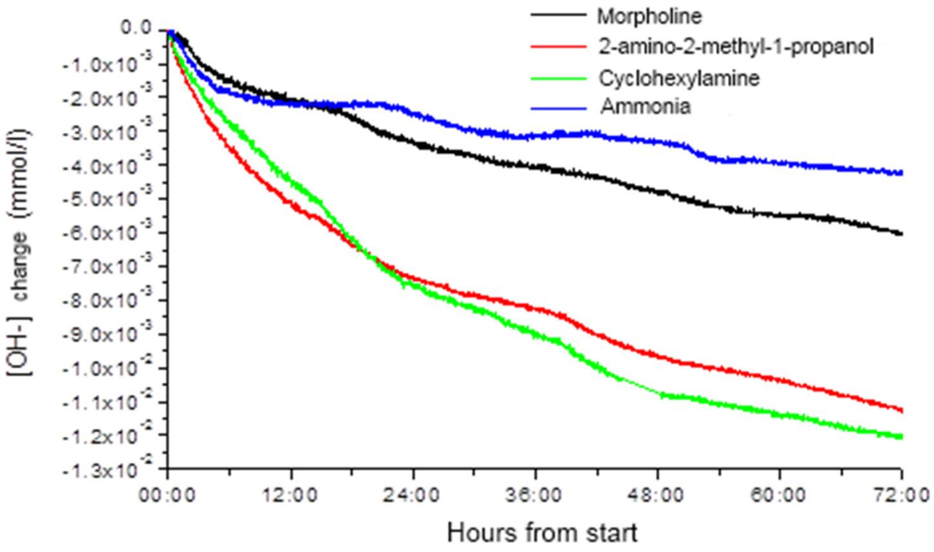


**FIGURE 5-26. Change in hydroxyl ion concentration during test (≈ 340 °C)**

After 12 hours the magnetite layer had been developed on the surface of polished samples, FIGURE 5-27. Potential was on the thermodynamic stability zone of magnetite. Alkaline amines had effect on magnetite layer properties of polished and pre-oxidized samples. Ammonia and morpholine had more large oxide particles on the sample surface. According to mass transfer resistance there was no significant difference in corrosion rate between the tested amines.

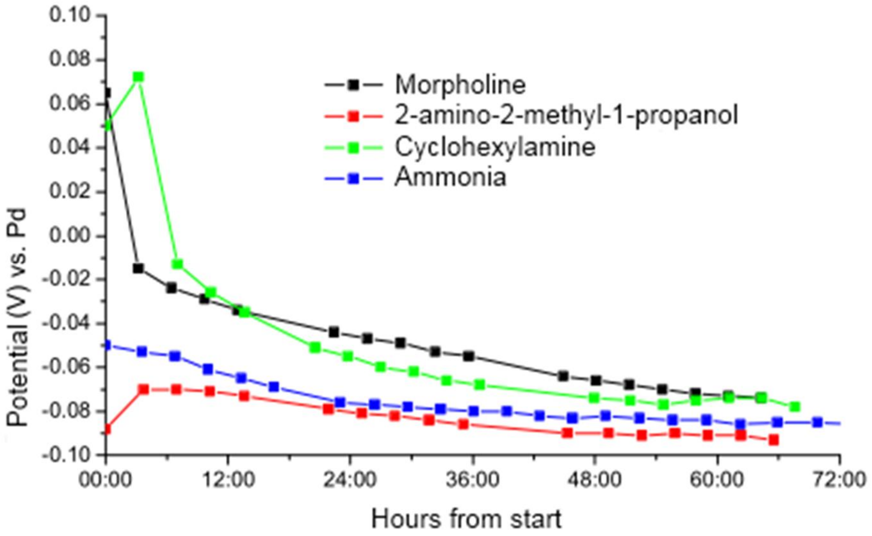


**FIGURE 5-27. Change in potential (funktion on time) of polished carbon steel sample (≈ 340 °C)**

### 5.4.3 TOC balance of Stora Enso Laminating Papers mill

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

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

Normal water chemistry balance, FIGURE 5-28:

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

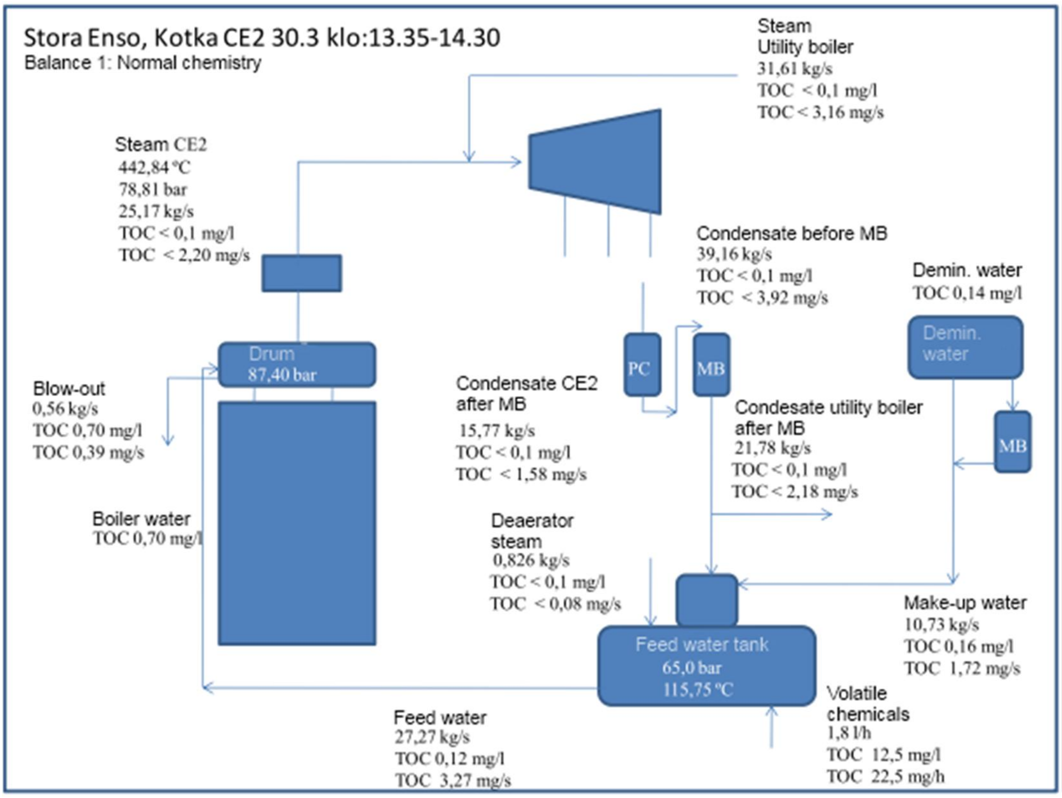


FIGURE 5-28. TOC-balance, normal water chemistry

TOC-balance without volatile organic water treatment chemicals was also measured, FIGURE 5-29. Balance was made after chemical dosing pumps were stopped and when condensate direct conductivity and cation conductivity before mixed bed exchanger was almost same. The process was without volatile chemicals over 10 hours.

Balance without volatile chemicals

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

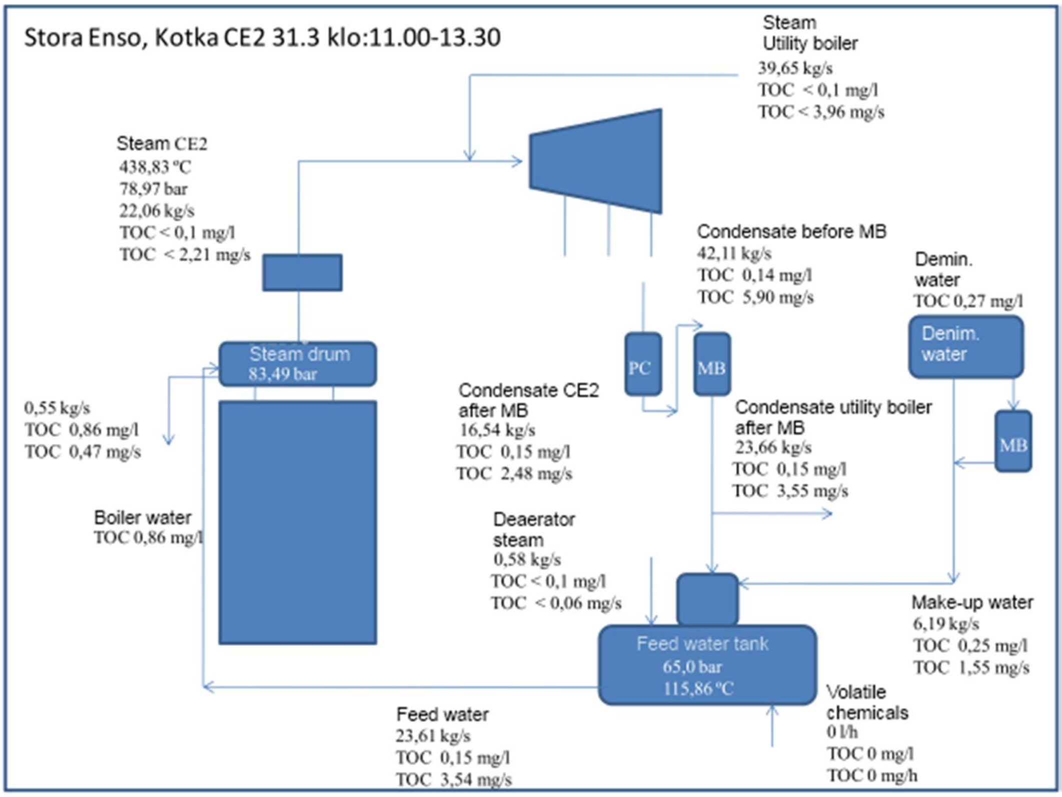


**FIGURE 5-29. TOC-balance without volatile organic water treatment chemicals**

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

The aim of this this literature study was to clarify different water treatment methods and their TOC removal efficiency. As conclusion, the conventional way (chemical precipitation + ion exchange) has long been recognized as a technology capable to remove many dissolved compounds from water that cause water quality problems, but in the future there will be other methods as well. Summary of different water treatment methods is presented in TABLE 5-7.

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

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

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

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

Reverse Osmosis is one of the best technologies removing TOC from waters. RO is a membrane treatment technology and can achieve up to 90% removal of low-molecular-weight organic compounds and organic acids. Nanofiltration (NF) efficiency to remove these low-molecular-weight organic compounds is lower, but in some cases nanofiltration is feasible.

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

**TABLE 5-7. Summary of the different water treatment methods and TOC removal**

| Removal method | Principle | TOC-reduction rate | Comments and notes |
|---|---|---|---|
| **UV-AOP** | Destroys neutral organic molecules with the help of OH-radicals. Decomposition products are carbon dioxide and organic acids, which can be removed with ion exchange. | 30 %<br>> 30 % when combined with ion exchange | Efficiency depends on the inlet TOC and actual organic components present in the water. Could be installed also before ion exchange, but preferably after strong anion before mixed bed filter. Some units installed to achieve TOC guarantee level of 0,2 mg/l. |
| **UV- 185 nm** | Destroys smaller organic non-ionic components to $CO_2$. | 20…70 % | The system is used in ultrapure water units. Not competitive, if TOC concentration > 0,1 mg/l |
| **Reverse osmosis** | Removes efficiently TOC. Cut-off value for non-ionic compounds > 100 g/mol. | > 95 % | The best available technology to remove biopolymers and unharged organic molecules. |
| **Nanofiltration** | Removes efficiently both organics and ionic compounds. Cut-off value for non-ionic compunds is > 300…500 g/mol. | 80…90 % | Alternative treatment for chemical treatment with simultaneous salt removal (60…80 %). Colour removal units in operation e.g. in Norway for waters with high TOC values. |
| **Activated Carbon** | Based on adsorption. Capacity dependent on water quality and TOC components. Efficiency may be very high with the new filters. | 20..80%, 50% for biological filters with high retention times. | Is used within drinking water treatment units to remove taste and odour. After first operation period the efficiency in TOC removal retains. |

### 5.4.5 Water quality and water treatment guidelines

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

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

The report has been structured in a way it is both the guide book and the water chemistry work book. The guidelines have been shown in the separate tables and figures, for example operation area of phosphate chemistry, FIGURE 5-30 and condensate quality requirements, TABLE 5-8.

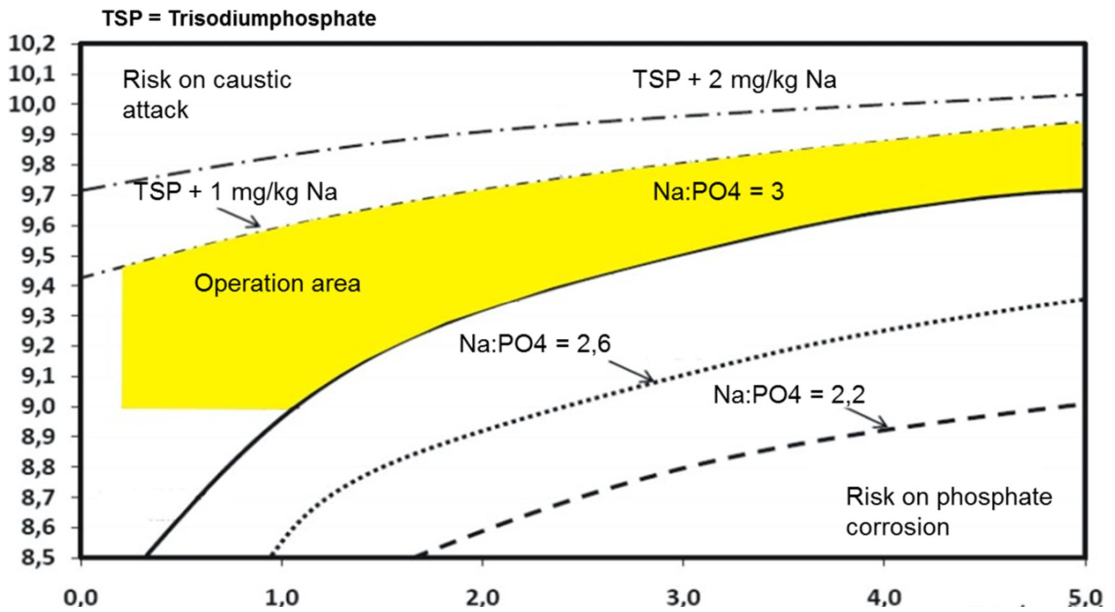


FIGURE 5-30. Phosphate Chemistry/Operation area

**TABLE 5-8. Condensate quality (minimum requirement)**

| **Condensate** | | | |
|---|---|---|---|
| | | Ammonia | Ammonia and organic amine |
| **pH** | | 8.5 - 10.0 | |
| **Cation conductivity** | mS/m | < 0.05 | <0.08 |
| **Direct conductivity** | mS/m | < 1.0 | |
| **$SiO_2$** | µg/kg | < 20 | |
| **Na** | µg/kg | < 20 | |
| **TOC** | µg/kg | <200 | <600 |
| **$O_2$** | µg/kg | ≤ 20 | |
| **Fe** | µg/kg | ≤ 10 | |
| **Cu** | µg/kg | ≤ 5 | |
| **Hardness** | dH | < 0.01 | |

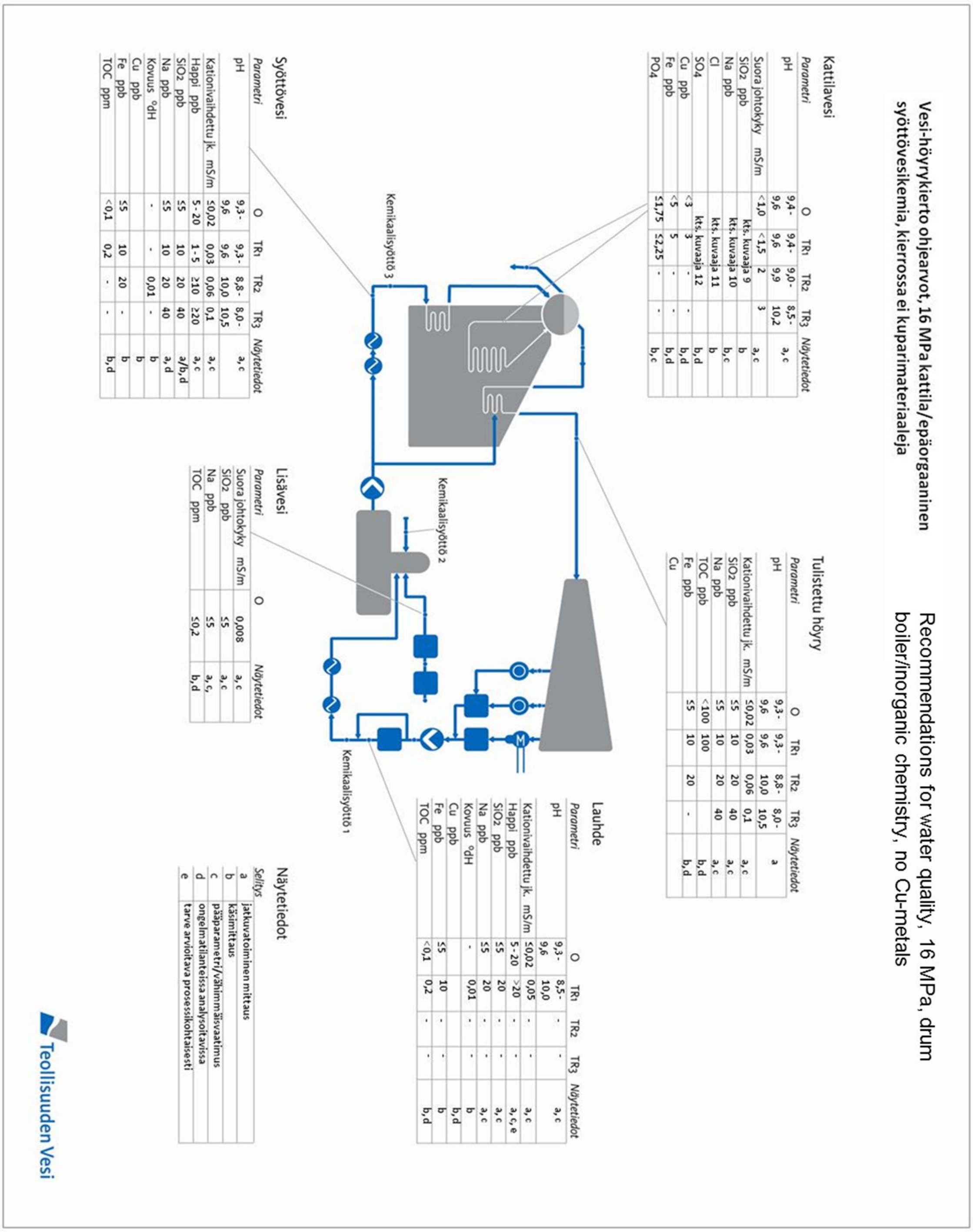
Compared to the heat and power boilers, recovery boilers have special features not found in the other power plants. They are the high heat flux in the boilers, the steam usage in the air pre-heaters, the probable contamination of the process condensates, the great portion of the make-up water in the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

One of the main objectives of this work is the increase of the control of the steam-water cycle in the situations, when there is a high concentration of the organic substances in the feed water, when there are possible leakages to the condensates and when the feed water consists 30…40 % of make-up water. Different action levels and responsible person are presented in TABLE 5-9.

TABLE 5-9. Action levels and responsible persons

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

The second important part of the guidelines is to give instructions how to control and follow water chemistry. It emphasizes the use of most comprehensive and reliable on line analyzers combined with the manual sampling and the laboratory analysis. The alternatives for the extensive and time consuming measuring routines have been found from the other standards, e.g. ASME and EPRI. The objective has been to find the required minimum number of the measurements by putting the emphasis on the quality of the measurements instead of quantity. Quality recommendation for 16 MPa drum boiler, inorganic chemistry with no Cu-metals is presented in FIGURE 5-31.



Vesi-höyrykierto ohjearvot, 16 MPa kattila/epäorgaaninen syöttövesikemia, kierrossa ei kuparimateriaaleja

Recommendations for water quality, 16 MPa, drum boiler/inorganic chemistry, no Cu-metals

Kattilavesi

| *Parametri* | O | $TR_1$ | $TR_2$ | $TR_3$ | *Näytetiedot* |
|---|---|---|---|---|---|
| pH | 9,4 - 9,6 | 9,4 - 9,6 | 9,0 - 9,9 | 8,5 - 10,2 | a, c |
| Suora johtokyky mS/m | <1,0 | <1,5 | 2 | 3 | a, c |
| $SiO_2$ ppb | kts. kuvaaja 9 | | | | b |
| Na ppb | kts. kuvaaja 10 | | | | b, c |
| Cl | kts. kuvaaja 11 | | | | b |
| $SO_4$ | kts. kuvaaja 12 | | | | b, d |
| Cu ppb | <3 | 3 | - | - | b, d |
| Fe ppb | <5 | 5 | - | - | b, d |
| $PO_4$ | ≤1,75 | ≤2,25 | - | - | b, c |

Tulistettu höyry

| *Parametri* | O | $TR_1$ | $TR_2$ | $TR_3$ | *Näytetiedot* |
|---|---|---|---|---|---|
| pH | 9,3 - 9,6 | 9,3 - 9,6 | 8,8 - 10,0 | 8,0 - 10,5 | a |
| Kationivaihdettu jk. mS/m | ≤0,02 | 0,03 | 0,06 | 0,1 | a, c |
| $SiO_2$ ppb | ≤5 | 10 | 20 | 40 | a, c |
| Na ppb | ≤5 | 10 | 20 | 40 | a, c |
| TOC ppb | <100 | 100 | | | b, d |
| Fe ppb | ≤5 | 10 | 20 | - | b, d |
| Cu | | | | | |

Lauhde

| *Parametri* | O | $TR_1$ | $TR_2$ | $TR_3$ | *Näytetiedot* |
|---|---|---|---|---|---|
| pH | 9,3 - 9,6 | 8,5 - 10,0 | - | - | a, c |
| Kationivaihdettu jk. mS/m | ≤0,02 | 0,05 | - | - | a, c |
| Happi ppb | 5 - 20 | >20 | - | - | a, c, e |
| $SiO_2$ ppb | ≤5 | 20 | - | - | a, c |
| Na ppb | ≤5 | 20 | - | - | a, c |
| Kovuus °dH | - | 0,01 | - | - | b |
| Cu ppb | | | | | b, d |
| Fe ppb | ≤5 | 10 | - | - | b |
| TOC ppm | <0,1 | 0,2 | - | - | b, d |

Syöttövesi

| *Parametri* | O | $TR_1$ | $TR_2$ | $TR_3$ | *Näytetiedot* |
|---|---|---|---|---|---|
| pH | 9,3 - 9,6 | 9,3 - 9,6 | 8,8 - 10,0 | 8,0 - 10,5 | a, c |
| Kationivaihdettu jk. mS/m | ≤0,02 | 0,03 | 0,06 | 0,1 | a, c |
| Happi ppb | 5 - 20 | 1 - 5 | ≥10 | ≥20 | a, c |
| $SiO_2$ ppb | ≤5 | 10 | 20 | 40 | a/b, d |
| Na ppb | ≤5 | 10 | 20 | 40 | a, d |
| Kovuus °dH | - | - | 0,01 | - | b |
| Cu ppb | | | | | b |
| Fe ppb | ≤5 | 10 | 20 | - | b |
| TOC ppm | <0,1 | 0,2 | - | - | b, d |

Lisävesi

| *Parametri* | O | *Näytetiedot* |
|---|---|---|
| Suora johtokyky mS/m | 0,008 | a, c |
| $SiO_2$ ppb | ≤5 | a, c |
| Na ppb | ≤5 | a, c, |
| TOC ppm | ≤0,2 | b, d |

Näytetiedot

| *Selitys* | |
|---|---|
| a | jatkuvatoiminen mittaus |
| b | käsimittaus |
| c | pääparametri/vähimmäisvaatimus |
| d | ongelmatilanteissa analysoitavissa |
| e | tarve arvioitava prosessikohtaisesti |

**FIGURE 5-31. Water quality recommendation for 16 MPa drum boiler, inorganic chemistry**

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

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

### 5.4.6 Reduction of TOC from recovery boiler make-up water

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

Plant C supplies potable water while plants A and B produce demineralized process water. The main differences in the processes are the coagulation-flocculation chemicals employed and the use of an ozone-AC combination at plant C. A comparison of the results of the three water treatment processes is shown in FIGURE 5-32. The comparison is based on three series of samples collected over the period 24.09.2009 – 20.10.2009.

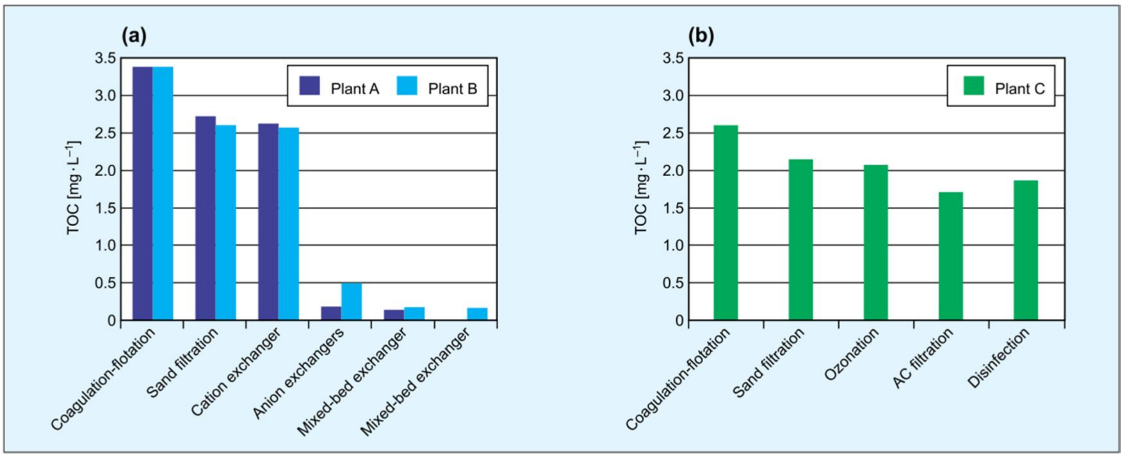


**FIGURE 5-32. Comparison of TOC levels after each process stage for all three water treatment plants using the Oulu River as a raw water source.**

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

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

Removal of organics from recovery boiler make-up water with (AC) was investigated in pilot scale experiment. One pilot scale AC filter unit was installed inside a stream at plant A and monitored over the period 19.12.2009– 27.2.2010. The ACs used in the experiment were acid washed low ash content AQUACARB 607C 14X40. The results of TOC measurements are presented in FIGURE 5-33.

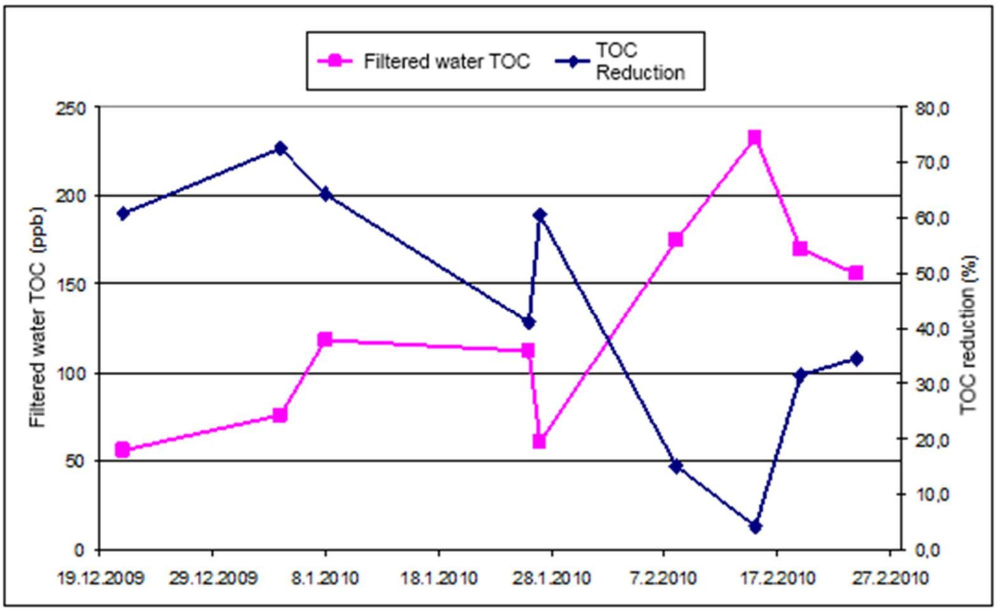


**FIGURE 5-33. TOC measurement results of pilot AC filter test**

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

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

### 5.4.7 Activated carbon and UV-treatment - field tests

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

AC was used in a novel way to remove organic compounds from demineralized water. AC is conventionally used before demineralization, but when implemented later in the process the lifetime of AC can be extended. Demineralized water was treated further with an AC filter followed by a mixed-bed ion exchanger (MB). In pilot scale tests there was also a subsequent AC filter after the MB unit, FIGURE 5-34. TOC reductions were monitored for 11 months and 3 months in pilot scale filters and full scale AC filters, respectively.

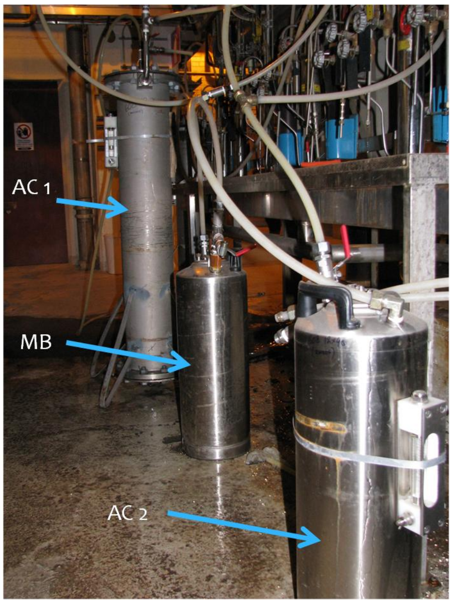


**FIGURE 5-34. Testing scheme of pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB).**

Other task of the project was to evaluate whether UV treatment can be used to treat demineralized water in order to reduce the residual TOC level. Also contact time and use of oxidizing chemicals effect on removal rate was studied. Experimental setup of pilot scale UV treatment is presented in FIGURE 5-35.

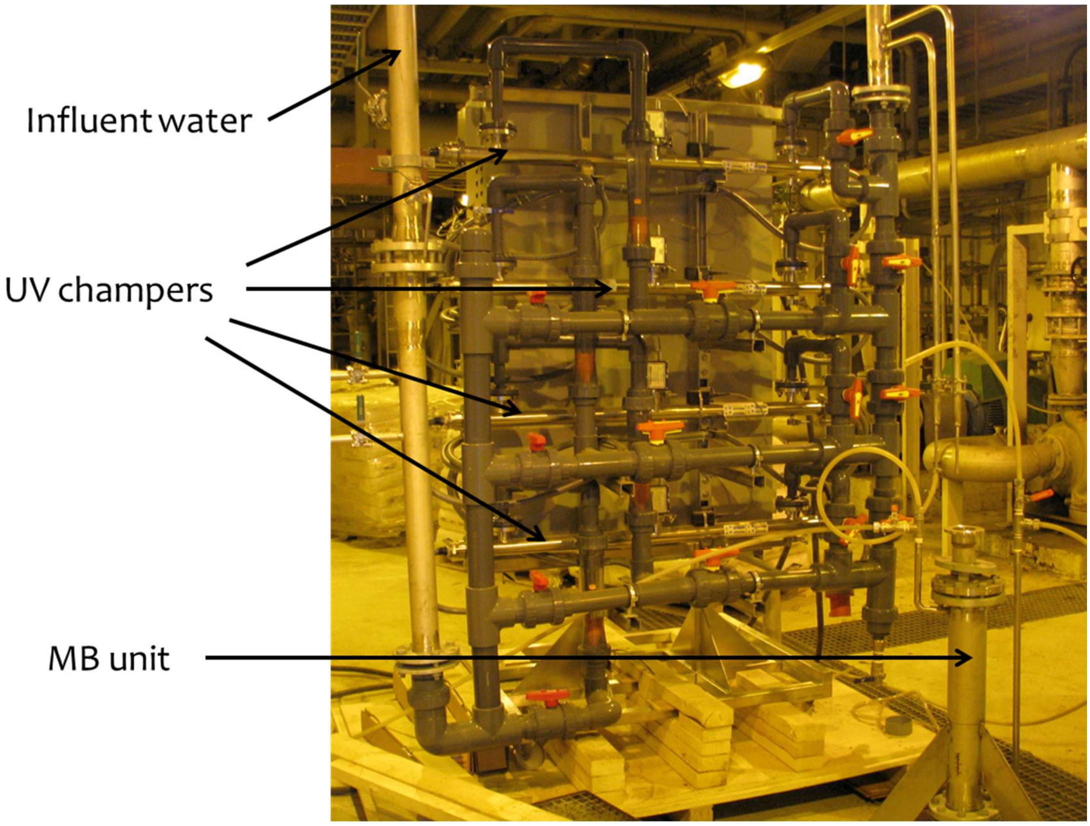


**FIGURE 5-35. Experimental setup of pilot scale UV treatment tests.**

As result UV treatment was able to remove up to 30 % of residual TOC but removal efficiency did not improve with increased number of UV chambers (contact time), wave length (more energy), $H_2O_2$ (oxidant) and $TiO_2$ (catalyst).

One possible reason for this result is that demineralized water TOC content is too high for UV treatment. Water should be pretreated with e.g. RO which is normal procedure in microelectronic or pharmaceutical industry water treatment. Reason for negligible effect of $TiO_2$ catalyst might be due to type of catalyst porous net. Experimental set-up with $H_2O_2$ oxidant failed because plastic piping released organic compounds. Medium pressure lamp (wavelength peaks at 254 nm and 185 nm) was much better (30 % TOC removal) than low pressures lamp (wavelength peak sharply at 185 nm) which effect was negligible.

The results of TOC measurements during the pilot scale AC filter tests are presented in FIGURE 5-36a. Overall, the first AC filter removed 38–70 % of TOC, the MB unit up to 12 % and the second AC filter up to 13 %. Furthermore, the MB unit and especially the second AC filter occasionally increased the TOC level.

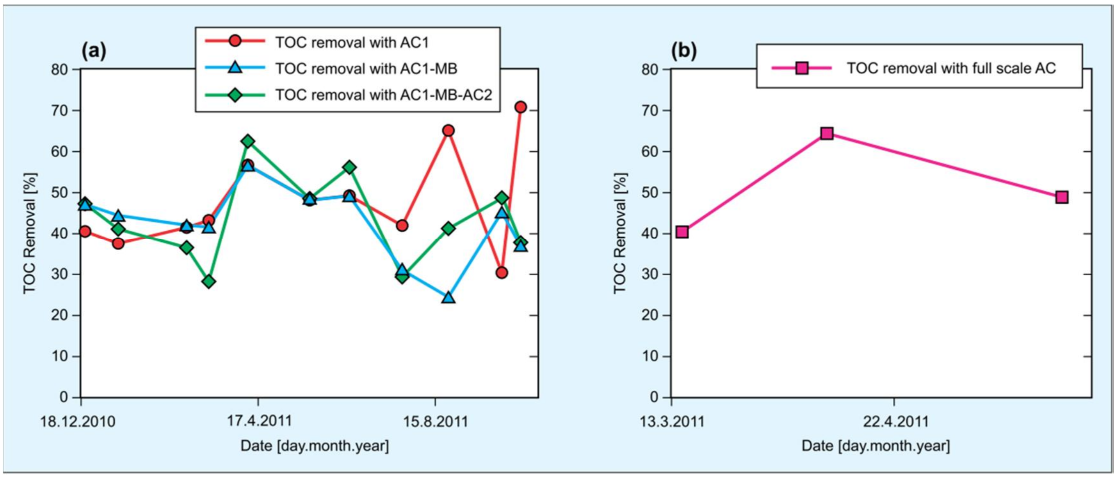


**FIGURE 5-36. TOC measurement results of pilot (a) and full scale AC filter tests (b)**

The role of the second AC filter after the MB unit seems to be insignificant in terms of TOC reduction, however dissolved organic carbon (DOC) levels measured with the LC-OCD method showed that the second AC filter removed a substantial part of residual DOC (TABLE 5-10). The role of the MB unit is important since conductivity increases extensively in an AC filter. The MB unit removes ionized inorganic material which is released from the AC bed. However, the identity of this ionized material remains unclear.

**TABLE 5-10. Composition of organic compounds in different parts of the water treatment process. Samples were collected on 22.9.2011. All concentrations are stated in µg L $^{-1}$**

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

TOC reductions measured in the full scale AC filter are shown in FIGURE 5-36b. The TOC reductions were between 40–65 % and were slightly higher than those measured with the pilot scale filters. The conductivity of filtered water increased similarly as with the pilot scale filters and so a subsequent MB unit was needed to reduce conductivity.

It was hypothesized that if an AC filter could operate biologically. However, colony forming unit (CFU) counts of the AC filtered water showed that there was no or insignificant biological activity. Furthermore the nutrient content of demineralized water is too low to allow microorganisms to accumulate. This is actually beneficial as microbial activity in the AC bed could possibly endanger the water quality.

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

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

### 5.4.8 Comparison study of active carbon grades

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

Comparison between AC grades was carried out in pilot scale; test arrangement is presented in FIGURE 5-37. Totally four grades were chosen, three acid washed ACs (AQUACARB 607C, CPG-LF, GAC 1240 PLUS) and one non-acid washed AC (GCN 1240). Technical data of AC grades are presented in TABLE 5-11.

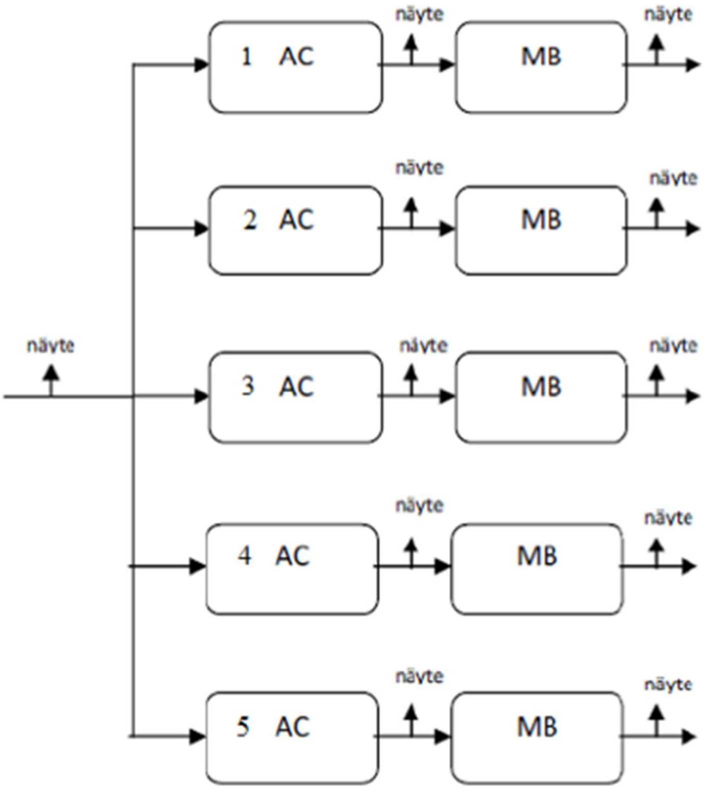


**FIGURE 5-37. Test arragement comparing different active carbon grades**

**TABLE 5-11. Technical data of tested active carbon grades**

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

Adsorption of organic molecules from demineralized water on AC material is depending on the characteristics of the organic molecules and the AC and the solution chemistry. The specific mechanisms by which the adsorption of many compounds, especially organic compounds, takes place on AC are still not clear.

There were no differences between AC grades regarding TOC removal efficiency. TOC removal efficiency was about ~40%. This is in line with previous AC studies. Non-acid washed was as effective as acid washed AC. Dissolved organic carbon (DOC) level and composition of organic compounds (ppb) measured with the LC-OCD method is presented in FIGURE 5-38. All AC grades removed the hydrophobic compounds, part of neutral organic compounds and decomposition products.

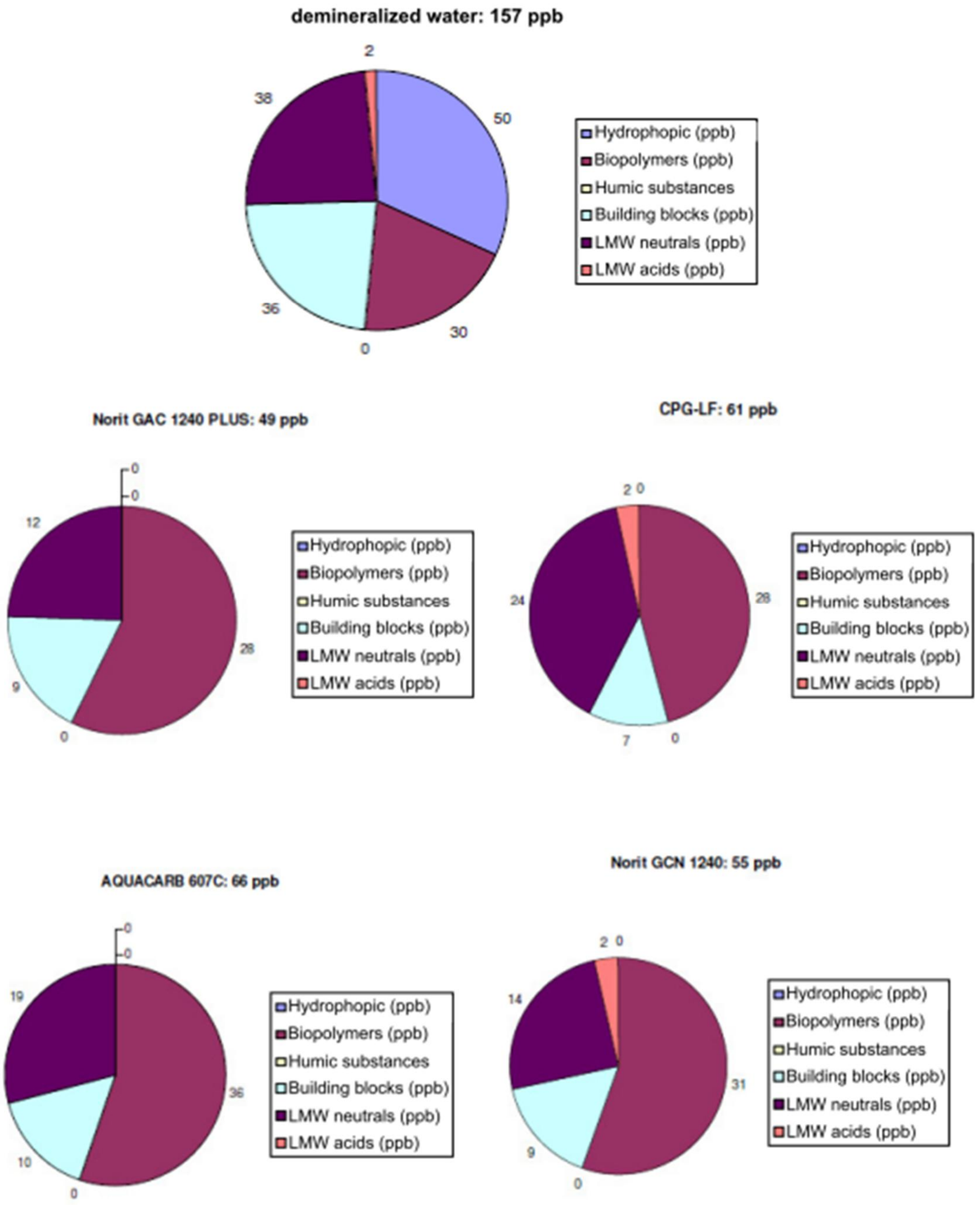


**FIGURE 5-38. Composition of organic compounds in deminaralized water and after AC filter (ppb).**

The term impregnation is defined as the fine distribution of chemicals and metal particles in the pores of AC. It is known that AC absorption capability or reactivity towards certain molecules can be enhanced by impregnation with metals such as silver, copper, nickel, aluminum and iron. In this study TOC removing efficiency of silver impregnated AC (silver content 0.1 m-%) , Fe(III) impregnated AC and Fe(IV) impregnated AC (iron content 1 m-%) from demineralized water was tested in pilot scale. Water flow was set to 4 l/s through AC filter (ab. 80 ml), experimental setup of pilot scale impregnated activated carbon tests is presented in FIGURE 5-39a. The measured TOC removal efficiency was about ~40% which is the same efficiency as AC without any impregnation.

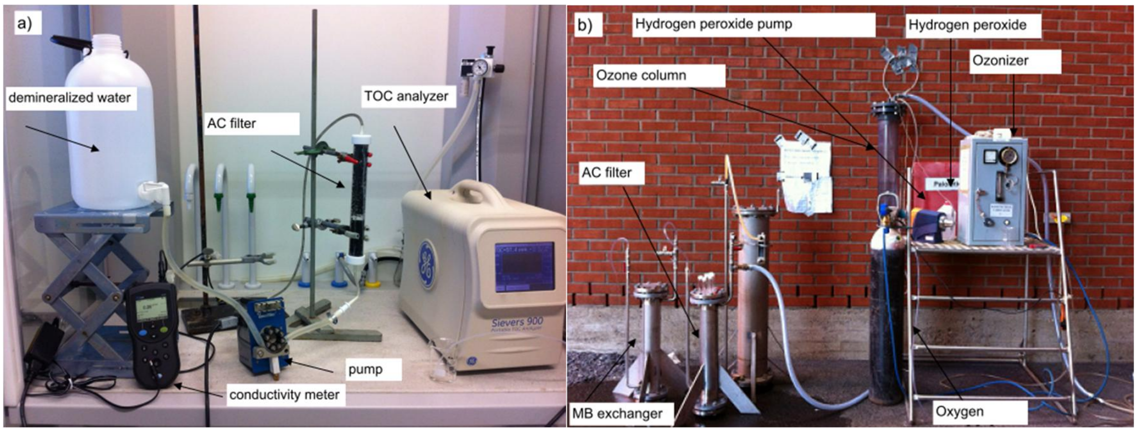


**FIGURE 5-39. Testing scheme of pilot scale impregnated activated carbon (a) and oxidation (b) tests**

Oxidation before AC filter can used to increase the removal of organic compounds. Ozone is a powerful oxidant which reacts with organic matter in water through two different ways, the so-called direct and indirect reactions. Ozone/AC system could eliminate organic micropollutants of low reactivity with ozone by enhancing ozone transformation process into OH radicals and/or adsorption on the surface of activated carbon. Ozone (54,73 mg $O_3$/min) and hydrogen peroxide (1 ppm) was applied in a vessel (45 l) filled with demineralized water with a residence time of 40 minutes. Oxidized demineralized water was passed through the AC filter (CPG-LF, capacity 5 l) and mixed-bed ion exchanger (Purolite MB400, capacity 5 l) with flow rate 0,8 l/min, test arrangement is presented in FIGURE 5-39b. Ozone and hydrogen peroxide was tested separately and together. Either ozone or hydrogen peroxide did not lower the TOC, so the role of the oxidation before the AC filter unit seems to be insignificant in terms of TOC reduction.

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