SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Suomen Soodakattilayhdistys ry

SKYREC-seminar 2011

Sokos Hotel Presidentti, Helsinki

20.10.2011

Raportti 8/2011

SKYREC SEMINAR 2011

Sokos Hotel Presidentti, Helsinki, 20.10.2011

PROGRAM

08.30 - 08.55	**Registration open**
08.55	**Welcoming words** ***Matti Tikka, UPM-Kymmene Oyj***
09.00 – 09.30	**Project summary** ***Esa Vakkilainen, Lappeenranta University of Technology***
09.30 - 10.00	**Co-combustion of mixed fuels** ***Niklas Vähä-Savo, Åbo Akademi***
10.00 - 10.15	**Coffee break**
10.15 – 10.45	**Dew point measurements** ***Emil Vainio, Åbo Akademi***
10.45 – 11.15	**Improving heat recovery in biomass-fired boilers - project presentation** ***Doug Singbeil, FPInnovations***
11.15 – 12.15	**Lunch**
12.15 – 12.45	**Field tests of superheater materials** ***Martti Mäkipää/Markku Orjala, VTT***
12.45 – 13.15	**Corrosion tests of superheater materials in reducing conditions** ***Dorota Bankiewicz, Åbo Akademi***
13.15 – 13.45	**Coffee break**
13.45 – 14.15	**Field tests of furnace materials** ***Timo Karjunen, Boildec Oy / Pekka Pohjanne, VTT***
14.15 – 14.45	**Ceramics in furnace** ***Riku Mattila, Oulu University***
14.45 – 15.00	**Coffee break**
15.00 – 15.30	**TOC removal methods and water quality recommendation** ***Maija Vidqvist, Teollisuuden Vesi Oy***
15.30 – 16.00	**Activated carbon and UV-treatment in TOC removal- field tests** ***Tero Luukkonen, JP-Analysis***
16.00	**Closing the seminar**

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PROJECT SUMMARY

Esa Vakkilainen
Lappeenranta University of Technology

SKYREC-Project

1.1.2008-30.6.2011

Esa Vakkilainen

SKYREC

Increasing recovery boiler electricity generation to a new level

Finnish Recovery Boiler Committee,
Andritz, Metso Power, Sandvik, Sumitomo,
Metsä-Botnia, Stora Enso, UPM-Kymmene,
Tekes

Work packages

- WP1 New concepts for increased electricity generation
- WP2 Increasing main steam temperature
- WP3 Increasing recovery boiler pressure
- WP4 Ensuring the steam and feedwater quality

- Total budget ~805 000 €
- Spent ~760 000 €

- TEKES project done, finishing the project ongoing

New concepts for increased electricity generation

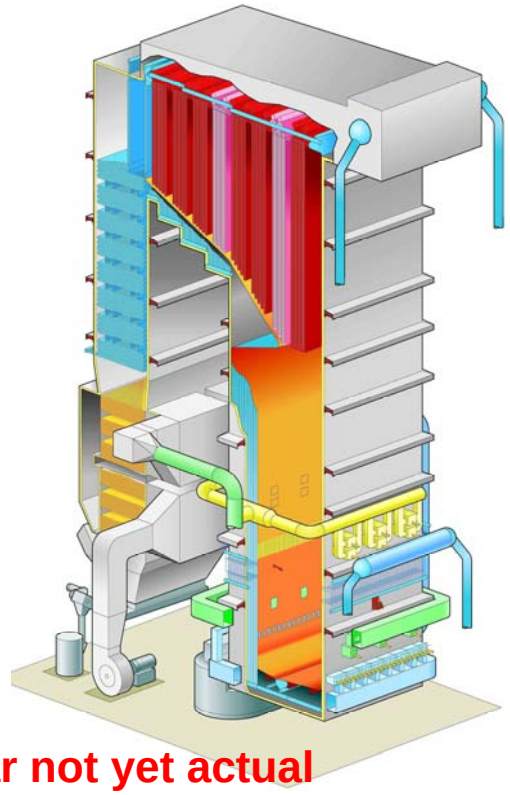
= More electricity **120 000 €**

- Once through boiler concept, LUT
- Wider quality of fuels to recovery boiler, ÅA
- Optimum steam pressure levels, LUT
- Use of recovery boiler furnace gases in lime kiln, ÅA
- Flue gas dew point measurements, ÅA (ongoing)

New generation recovery boilers

= change the heat transfer surfaces

- LUT has studied once through and reheater concepts
- The most important are pressure and preheating
- Once through if pressure high
- Reheating gives 4-5 % more electicity
- From Joutseno we have improved 20 %
- Investing in additional electricity is very profitable



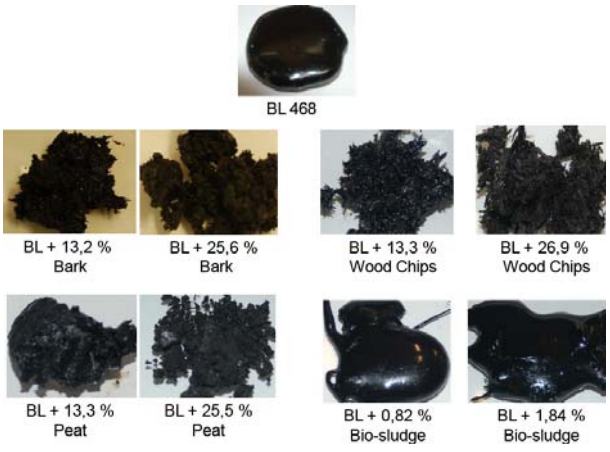
Increasing pressure to 200 bar not yet actual

Wider quality of fuels to recovery boiler

= burn wood based residuals if possible

- Åbo Akademi made combustion tests by mixing bark, peat, wood and biosludge to black liquor
- Mixture burns like BL
- Biosludge increases NO, lignin removal decreases NO, wood increases NO, typically longer combustion times, but changes not large

➡ **Need for industrial testing**

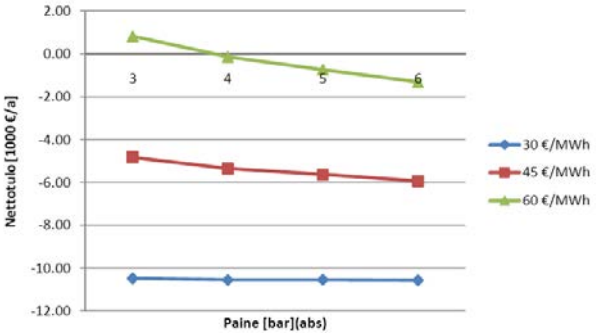


Biomass can be burned with black liquor

Optimal pressure levels in a pulp mill

= is it profitable to aim to lower LP and MP pressures

- Lappeenranta looked at steam pressure levels in pulp mills
- Economical optimum seems now to be at lowest technically possible
- If we can replace 50 kg/s of 5 bar steam with 3.5 bar steam we can get almost1 million € more profit per year

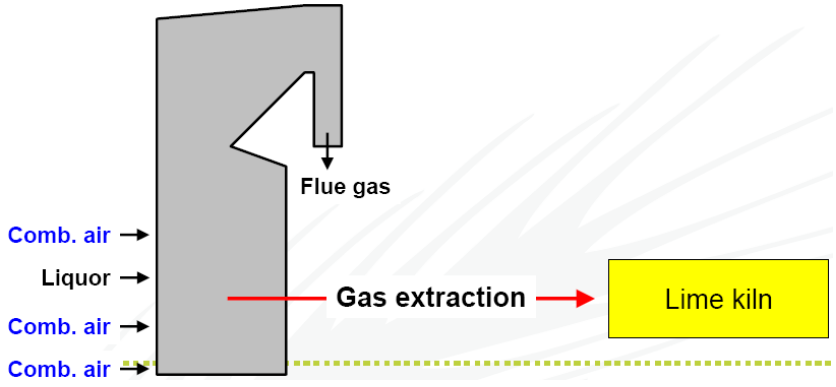


Decreasing pressure is profitable if investing in a turbine

Use of RB lower furnace gases at lime kiln

= direct biofuel from recovery boiler

- Åbo Akademi studied use of recovery boiler lower furnace gases to fire a lime kiln
- 5 % gases with HV = 3 MJ/kg would be enough
- Dust 30-80 g/Nm^3



Alkali in gases will cause problems

Dew point measurements

= as low as possible end temperature

- Not measured before at new recovery boilers
- How long SO_2/SO_3-emission periods are enough to cuse corrosion
- Åbo Akademi probe work (measuring of SO_2/SO_3 contents and dewpoints)
- May at Heinola
- Week 37 at Rauma

Increasing main steam temperature

= How to design the superheater to high temperatures

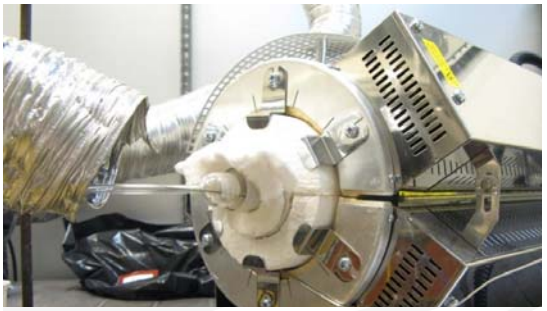
170 000 €

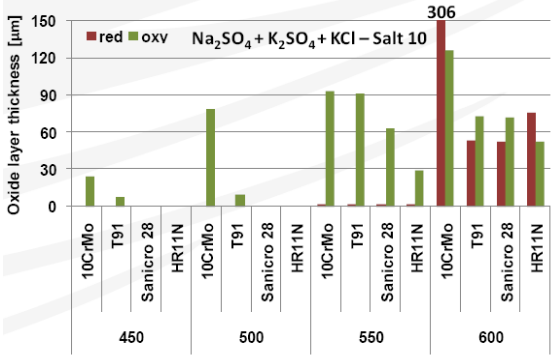
- Superheater corrosion tests at laboratory, ÅA (partly ongoing)
- Superheater corrosion tests at Joutseno, VTT

Steels in reducing conditions

= previously oxidizing now reducing

- Åbo Akademi tested 10CrMo9-10, T91, Sanicro 28 and HR11N in reducing conditions
- Pure Na_2SO_4 did not corrode
- Adding potassium to ~10 % not a problem
- Adding chloride ~ 1,3 % 10CrMo corroded
- If chlor and potassium then >550 °C means corrosion
- Ongoing tests where part of Na_2SO_4 is replaced with Na_2S





Mixed results between reducing and oxidizing

Superheater corrosion tests in a boiler

= real tests in real boiler

- VTT-Jyväskylä did corrosion testing with special probe
- fall 2010 – spring 2011
- Probe set to 530 °C & 570 °C
- SAN 28 < 347H < AISI 310 < HR11N < SAN 69 ~ Super 625
- Below 520 °C corrosion speed low
- Over 520 °C corrosion speed 0.5 – 1 mm/a

Problems in building a boiler to 540 °C

Increasing recovery boiler pressure

= Will the boiler furnace stay solid

- Charbed cooling, LUT;
- Ceramic materials in furnace, OY
- Corrosion testing in furnace Boildec; after several failures now successful tests, finally some results ongoing

Ceramic materials

= Something that lasts

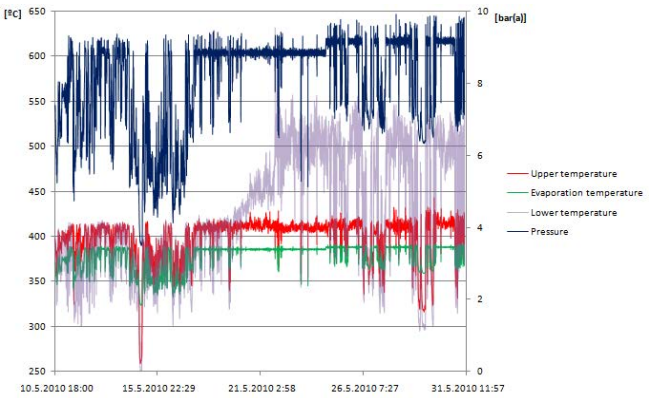
- Oulu university put material samples to furnace
- Tests will tell how new ceramics hold up

Still no sign of everlasting refractory

Boildec probe tests in a boiler

= Will the boiler furnace last with higher pressure

- Joutseno boiler probe tests with different materials
- Probe at liquor gun level
- VTT analyses the probes
- Corrosion low, except CS and 304L
- First (1006h) 15.4.2010.
- Second (1023h) 23.6.2010
- Third (1250h) 6.9.2010
- Fourth (2720h) 6.6.2011
- Test 5. ongoing



Test 4 results:
CS ~4 mm/a > 304L ~0.5 mm/a > Sanicro 67, Super 625

Ensuring the steam and feedwater quality

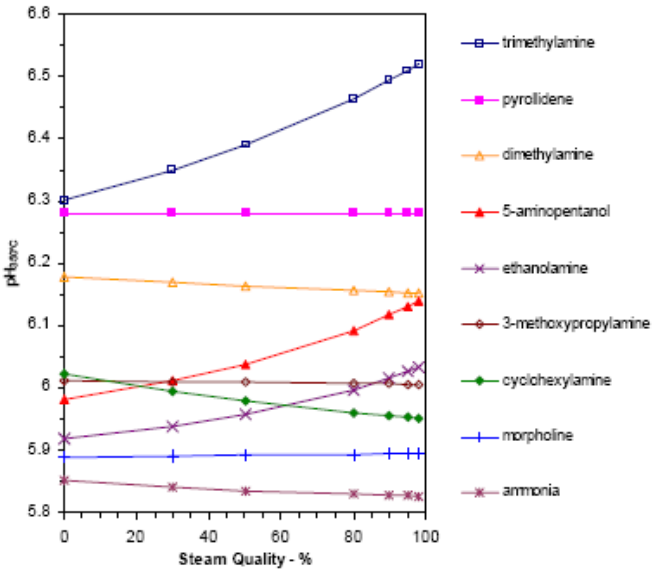
= Making sure we can run our boilers 230 000 €

- Effect of alkalizing amines to magnetite layer in carbon steels, VTT
- Methods for TOC-removal Teollisuuden Vesi; comparisions; measurements of TOC-contents
- Reducing the organics in recovery boiler feedwater, Oulun Yliopisto
- Use of activated carbon filtration and UV to treat water, Cewic/JP-analysis
- Water quality recommendation

VTT – water quality

= How does the magnetite layer form and hold

- Study on *Organic components in boiler water*
- Organics cause air preheater corrosion
- How does the water quality and the chemicals injected affect the magnetite layer of carbon steels
- Thermal decomposition of various amines

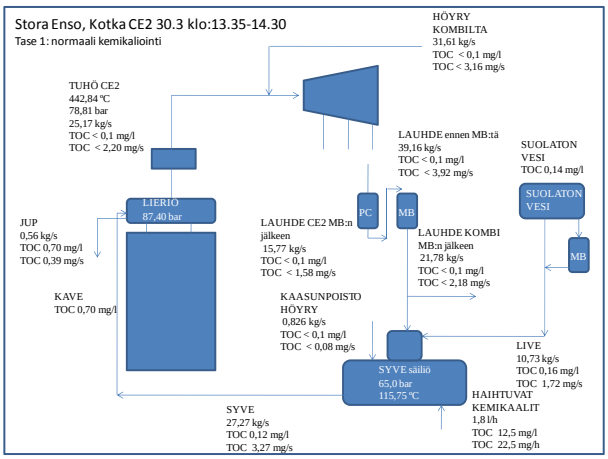


Morfoline thermally most stable

Teollisuuden Vesi – water quality work

= Role of TOC in water quality

- TOC-measurements Kotka
- Mixed bed does not remove organics
- TOC – in control at Kotka
- TOC removal methods
- Further studies of organics in water

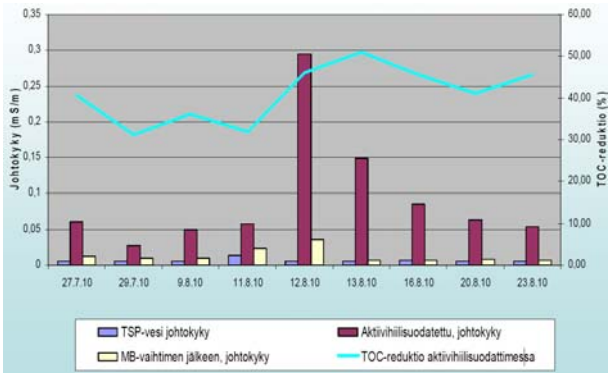


Needed information steadily accumulation

Cewic/JP-analyses – Activated carbon filtration (TOC-removal)

= How does UV and activated carbon remove TOC

- Tests in actual industrial conditions to find out the removal rate and carbon renewal rate
- Also trials for UV-light.
- Tests at Oulu



Industrial size active carbon filter works

Water quality recommendation

- Recommendation drafted by Teollisuuden Vesi Oy
- Recommendation commented during drafting
  - Andritz Marja Heinola
  - Botnia Toni Wahlman
  - Metso Anja Lehikoinen
  - UPM Toni Orava
  - Stora Enso Tero Arvilommi
- Recommendation is now circulating for comments

SKYREC continues to the end of 2011

Project reporting in committees

Reports available

http://www.soodakattilayhdistys.fi/secure/SKYREC.html

International co-operation

- “Improving Heat Recovery in Biomass-Fired Boilers” Jim Keiser, Oak Ridge National Laboratory
- Results published in 2010 International Chemical Recovery Conference
- Co-operation with Sodahuskommittee
- More reporting forthcoming during 2014 International Chemical Recovery Conference in Tampere

SKYREC – project

Steering committee

Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman
Martti Korkiakoski	Tekes
Lasse Koivisto	Andritz Oy, Varkaus
Timo Peltola	Sandvik Materials Technology, Helsinki
Mika Paju	Oy Metsä-Botnia Ab, Joutseno
Kalle Salmi	Metso Power Oy, Tampere
Keijo Salmenoja	Andritz, Helsinki
Kaj Nordbäck	UPM-Kymmene Oyj (Chairman 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, Fine Paper, Oulu (KTR)
Esa Vakkilainen	Lappeenranta university of technology (coordinator)
Markus Nieminen	Secretary FRBC

CO-COMBUSTION OF MIXED FUELS

Niklas Vähä-Savo
Åbo Akademi

Co-firing Black Liquor and Biomass - Laboratory Tests II

Nikolai DeMartini
Niklas Vähä-Savo

Conclusions of Phase I

- Results show promise for co-combustion
- For wood and bark addition, up to 25% appears reasonable from a combustion chemistry perspective
- An increase in NO was observed and found to correlate to an increase in fuel-N
- Presumably, this observed increase could at least partially be handled by air staging

Questions

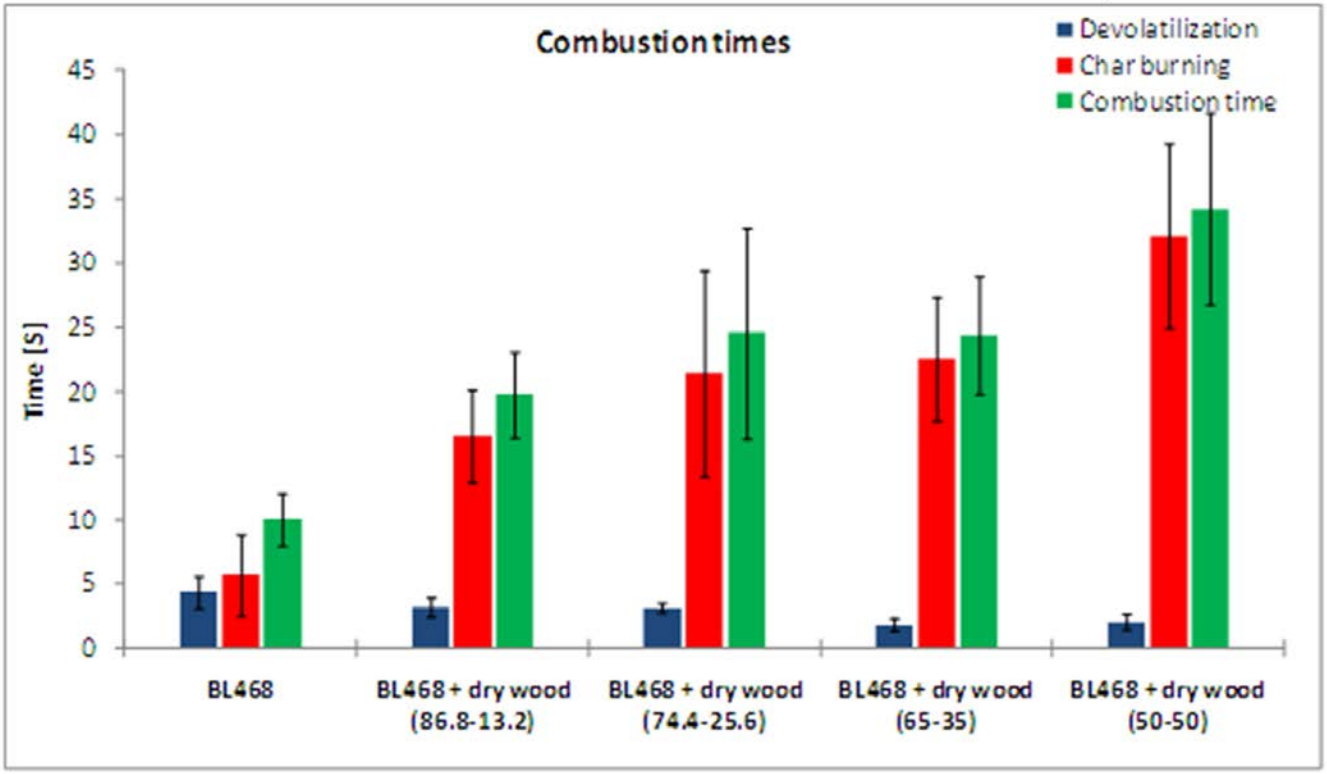
BL-Wood & Lignin Lean BL

1. At what addition level does the mixture burn more like wood than black liquor?
2. What is the fate of nitrogen in BL+wood mixture - does the char have more cyanate?
3. What are the burning characteristics of reduced lignin black liquor?
4. What is the fate of nitrogen in lignin lean black liquor?
5. What is the impact of wood on the combustion properties of lignin lean BL?

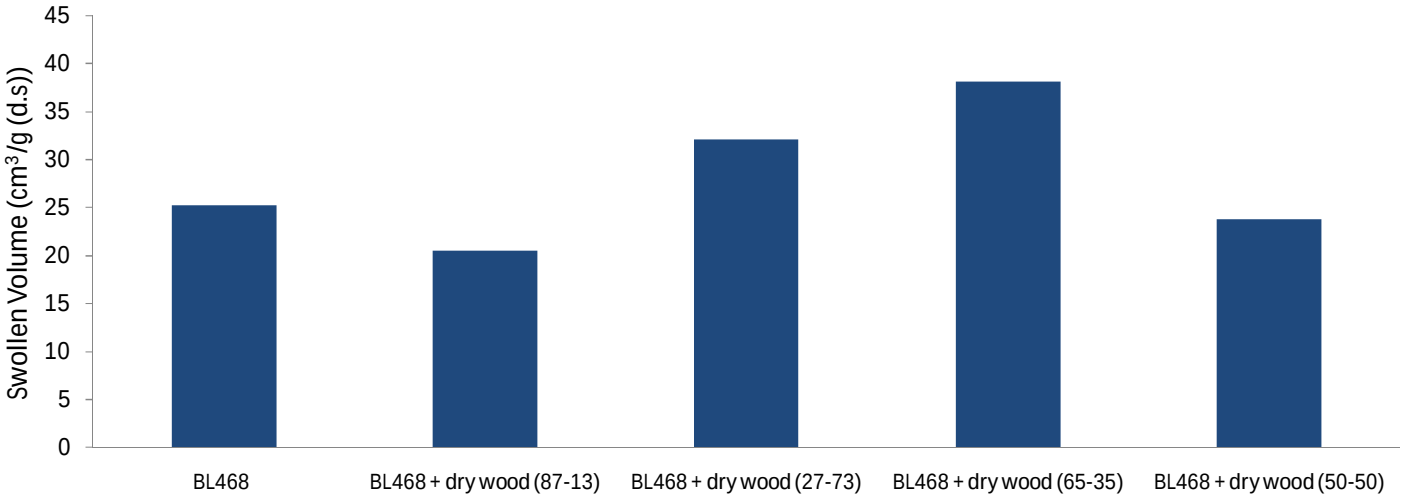
BL-Biosludge

1. How much of the nitrogen in biosludge nitrogen is lost from biosludge + black liquor mixtures after heat treatment?
2. How does a 5 wt% d.s. biosludge addition affect black liquor combustion?
3. Does biosludge addition change the cyanate concentration in smelt?

At what addition level does the mixture burn more like wood than black liquor?



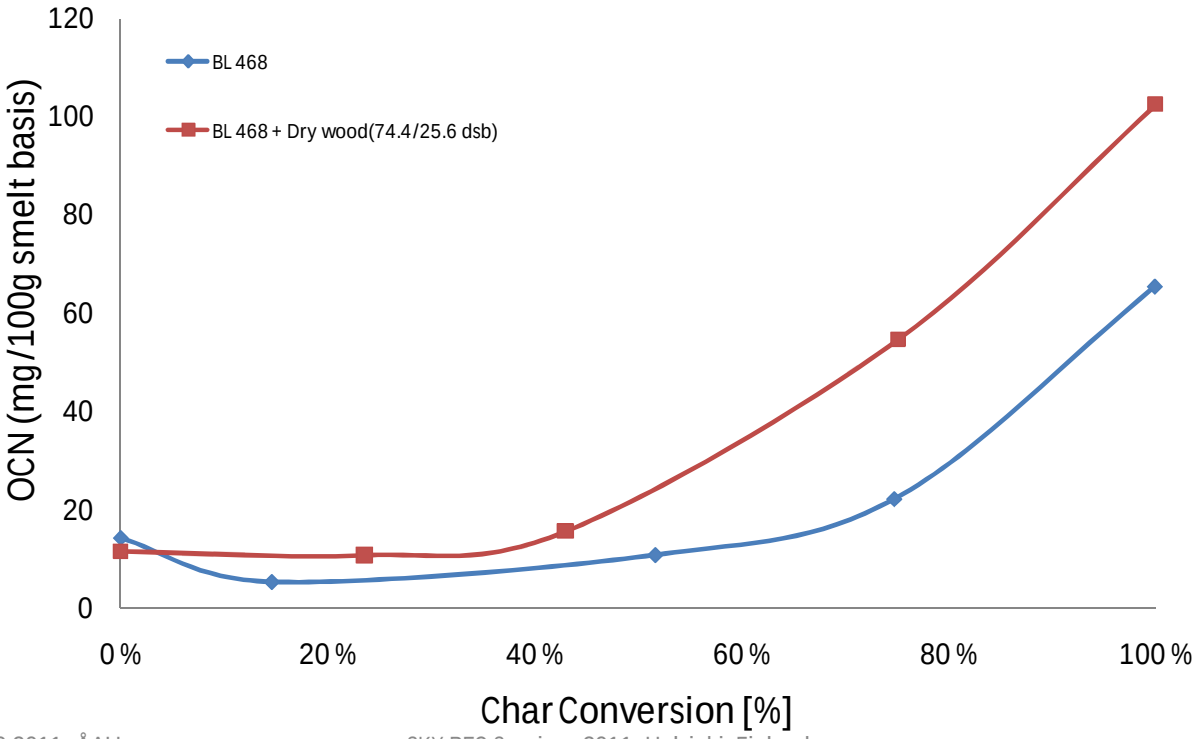
Swelling of BL-Wood Mixtures



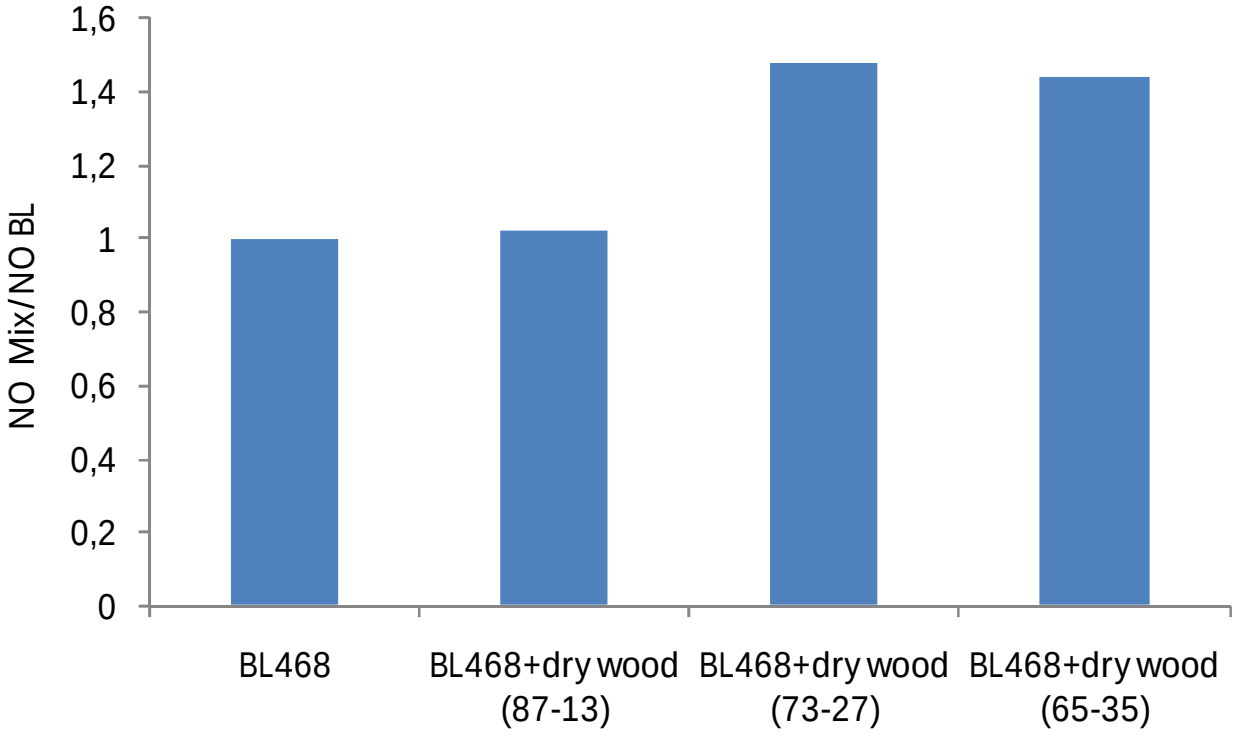
Videos-BL/Wood

- Sequence in Video:
  1. BL 468
  2. BL 468 + Wood (87-13% on d.s. Basis)
  3. BL 468 + Wood (73-27)
  4. BL 468 + Wood (65-35)
  5. BL 468 + Wood (50-50)

What is the fate of nitrogen in BL+wood mixture - does the char have more cyanate?



NO BL-Wood Mixtures



* Based on old NO analyzer

Videos Do Dry and Wet Wood Behave Similarly

- Sequence in Video:
  1. BL 468
  2. BL 468 + Dry Wood (73-27% on d.s. Basis)
  3. BL 468 + Wet Wood (73-27)

Lignin-Lean BL: Experimental

- To precipitate the lignin we bubbled CO_2 in the BL to reduce the pH
- Centrifuged to separate the lignin
- Washed with H_2O, then 0.05 M H_2SO_4, then H_2O (multiple stages of each)
- We added NaOH to the lignin lean BL to raise the pH back up, but not the wash solution

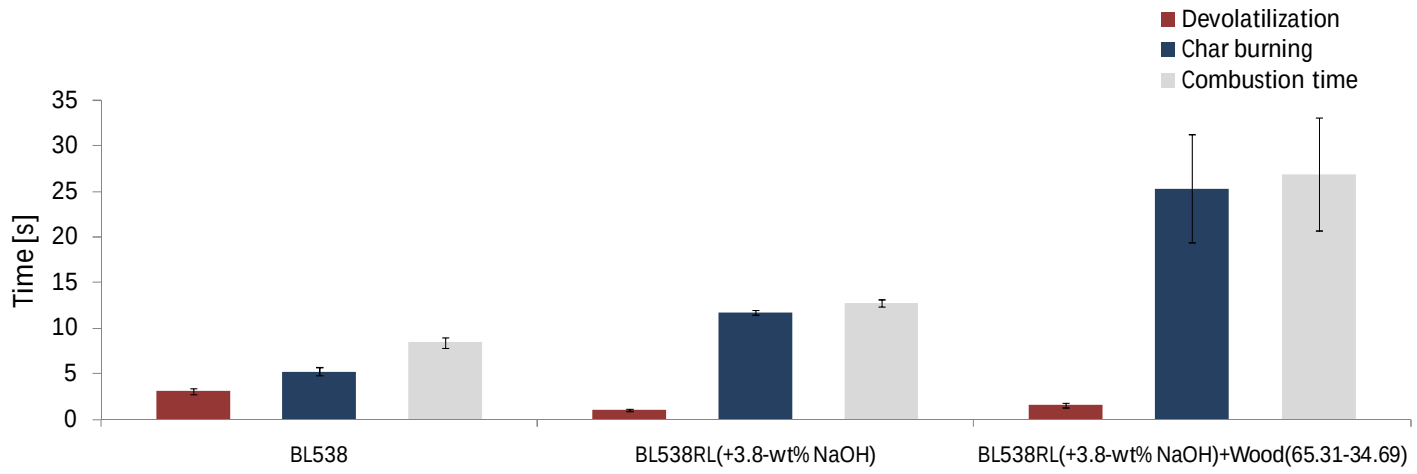
Lignin-Lean BL: Experimental

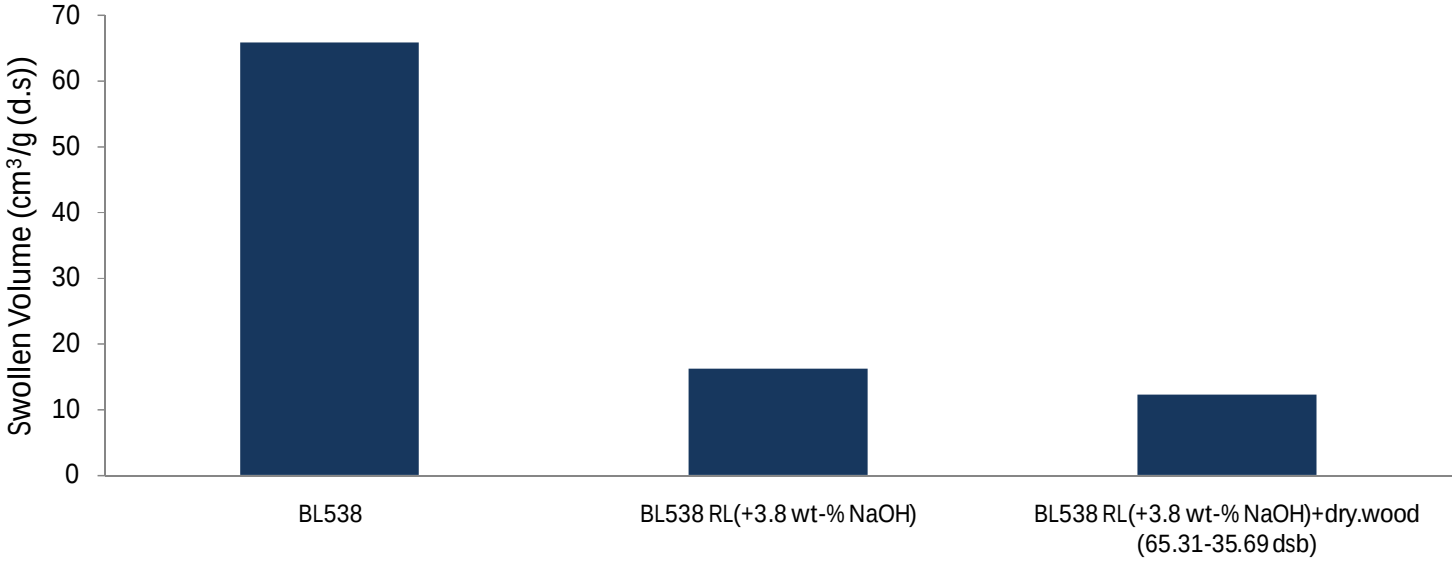
- The results are consistent with what might be expected for reduced lignin, but may not be representative of the LignoBoost process

1. What are the burning characteristics of reduced lignin black liquor?

2. What is the impact of wood on the combustion properties of lignin lean BL?

What are the burning characteristics of reduced lignin black liquor?

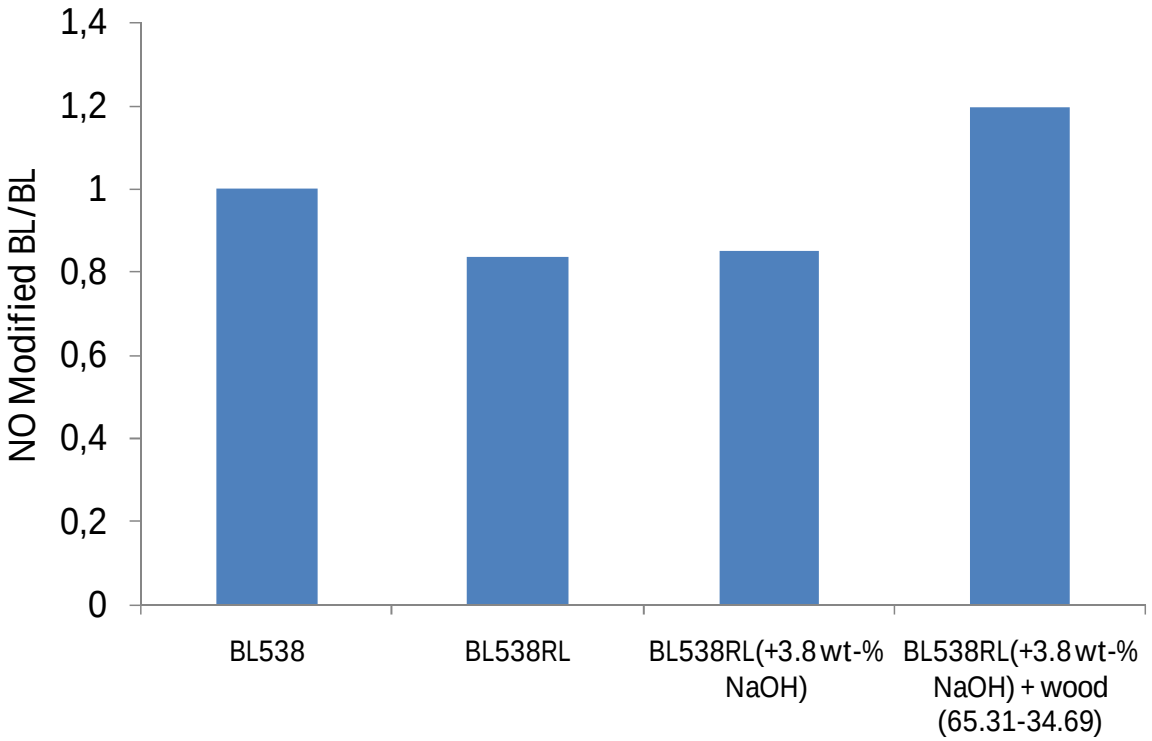




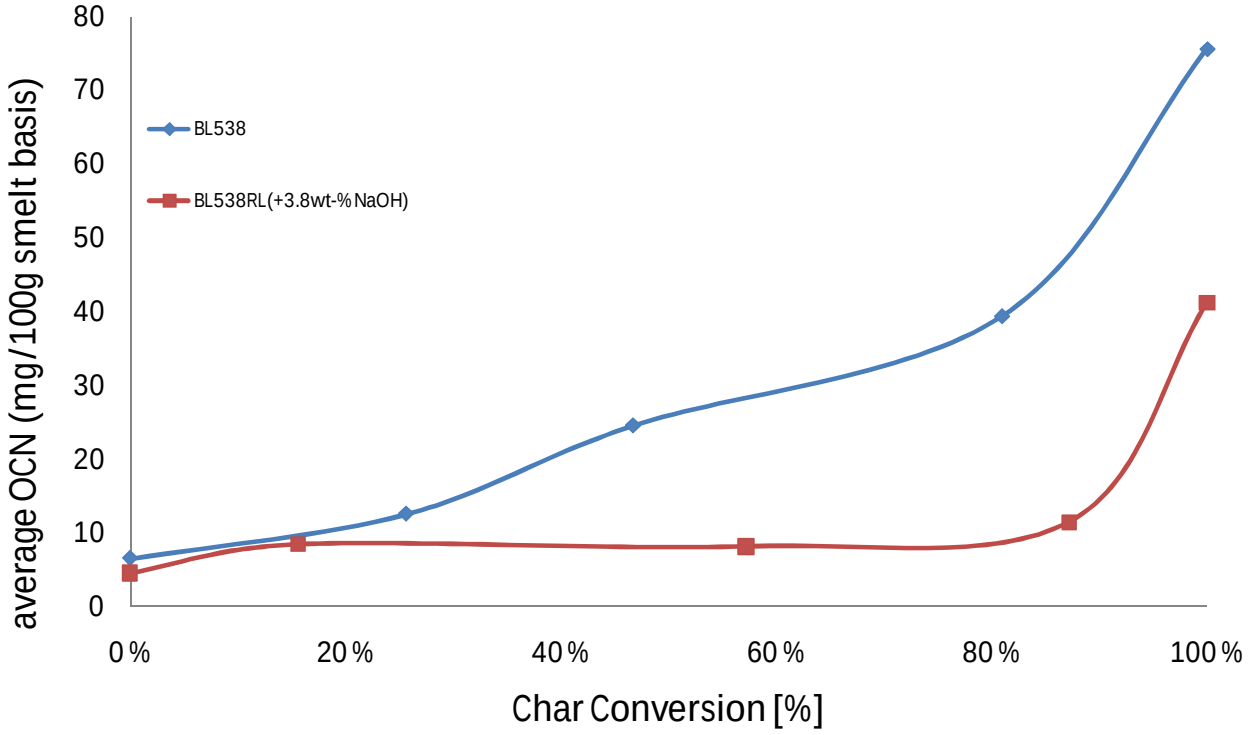
Videos Lignin Lean BL

- Sequence in Video:
  1. BL 538
  2. BL 538 RL (+3.8 wt % NaOH)
  3. BL 538 RL (+3.8 wt % NaOH) + Dry Wood (65-35)

What is the fate of nitrogen in lignin lean black liquor?



Cyanate Formation



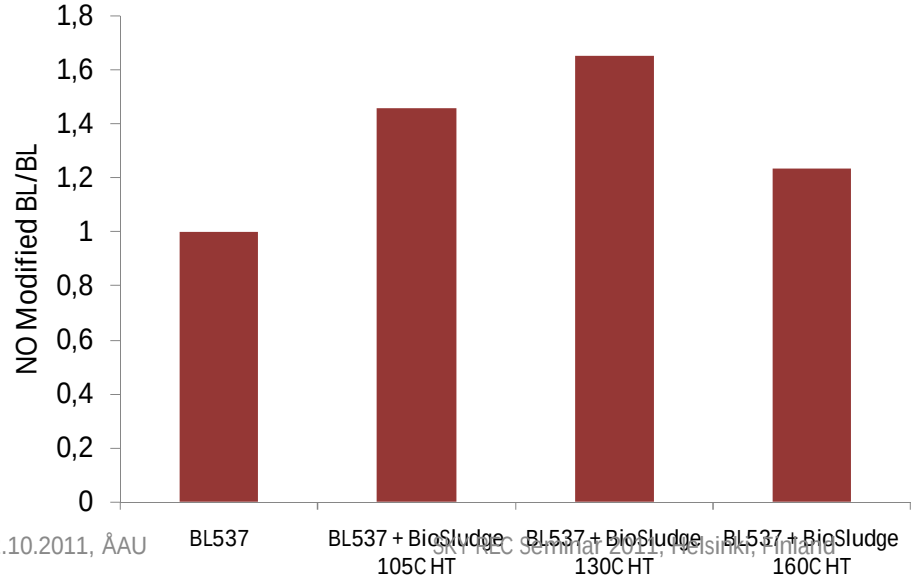
How much of the nitrogen in biosludge nitrogen is lost from biosludge + black liquor mixtures after heat treatment?

sample	Dry solids (wt % d.s)	Kjeldahl-N g/kg d.s.	NH3-N g/kg d.s.
BL537	81.93 %	0.9	-
Biosludge	2.10 %	47	3.8

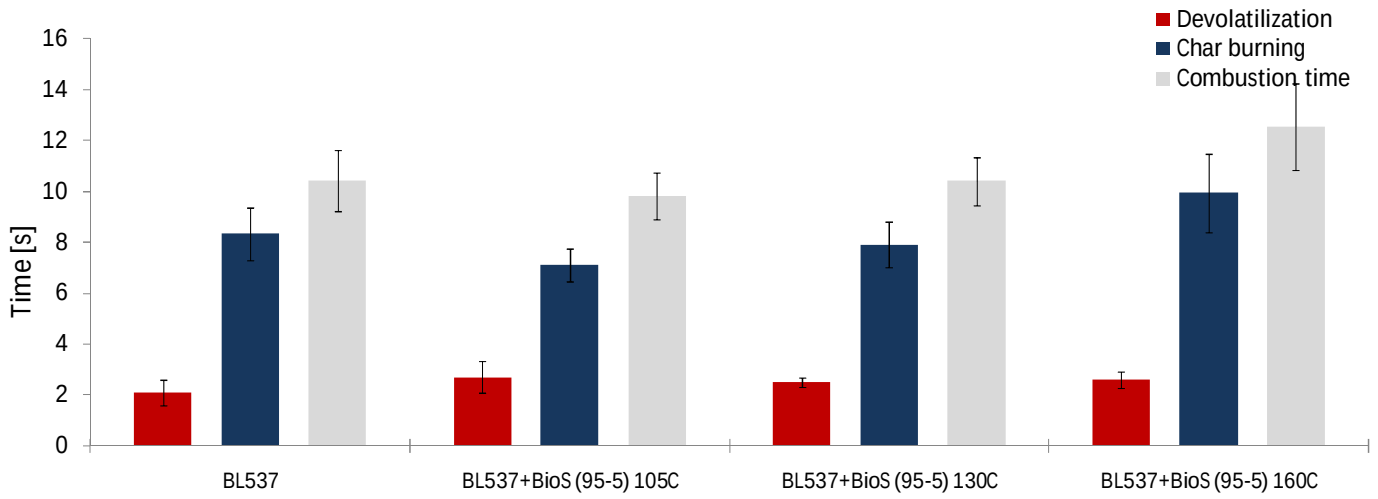
- Experimental
  - Mix BL + Biosludge (95-5 wt% on d.s. basis respectively)
  - Heat in a sealed vessel at 105, 130 or 160 °C for 60 minutes
  - Cool and vent vessel, blowing N_2 across the headspace and bubbling through 0.05M H_2SO_4 to capture NH_3
  - Question: Is NH_3 formed when mixed with BL and heated to evaporator temperatures.

sample	Kjeldahl-N in mixture g	NH_3 in initial mixture g	NH3 in vent gases g
105C 60min HT	0.068	0.0040	0.0013
130C 60min HT	0.066	0.0039	0.0010
160C 60min HT	0.070	0.0042	0.0010

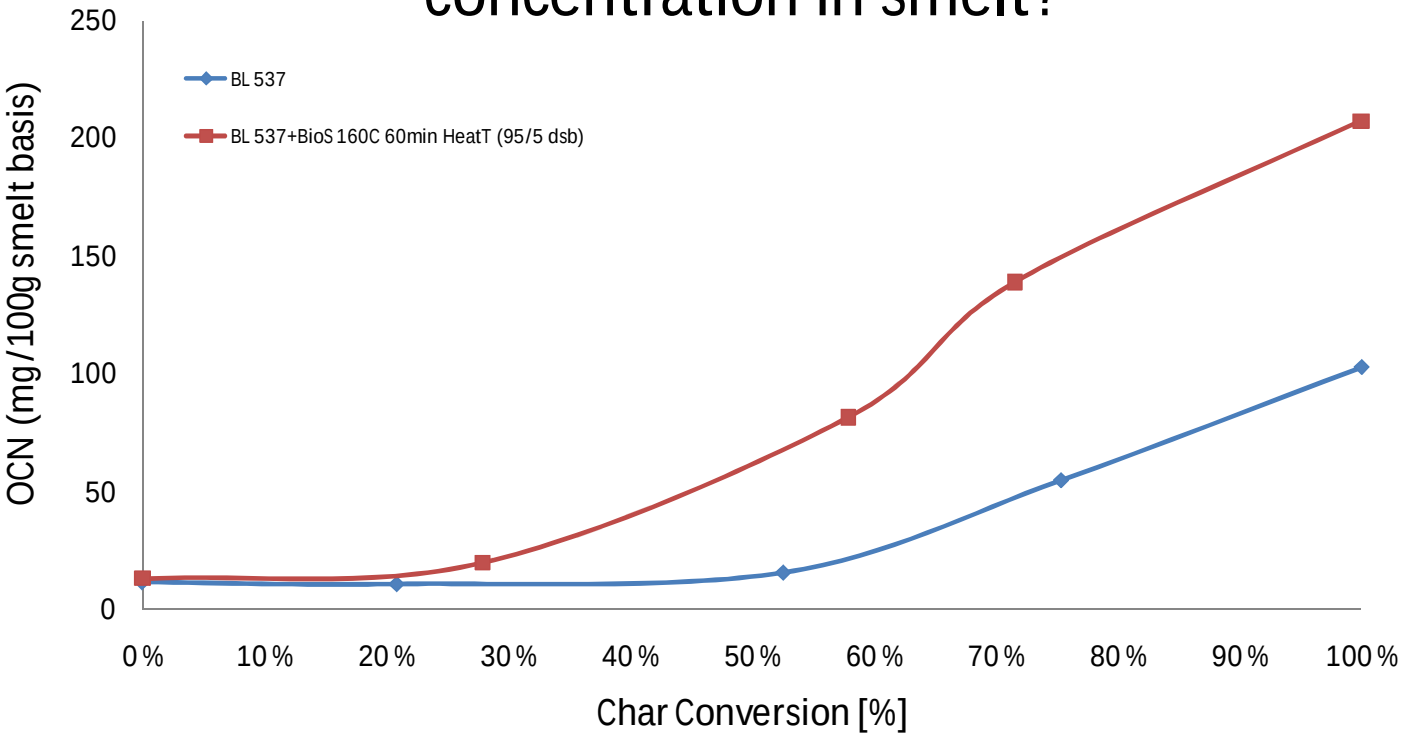
Conclusion is that no significant amount of NH_3 was formed



How does a 5 wt% d.s. biosludge addition affect black liquor combustion?



Does biosludge addition change the cyanate concentration in smelt?



Conclusions

- The transition between BL-wood mixtures burning like BL appears to be between 25 & 35 % wood on a dry basis
- BL-wet wood should be ok from a combustion standpoint
- More work needed with lignin-lean black liquor – preliminary results should not be considered representative of the LignoBoost process
- More work – mill & lab needed around bio-sludge

DEW POINT MEASUREMENTS

Emil Vainio
Åbo Akademi

Dew Point Measurements in Rauma and Heinola

Emil Vainio
Tor Lauren
Nikolai DeMartini
Mikko Hupa

Objective/Methodology

Purpose: to get reliable information of the low temperature corrosion in recovery boiler flue gases being cooled further.

1.Dew point measurements made with a commercial instrument (Land).

2.Corrosion measurements made with our air-cooled probes and samples analyzed with SEM-EDS.

3.H_2SO_4 analysis planned with Isopropanol. This was found to not be sensitive enough and an two alternative methods (salt and controlled condensation) were used at Heinola and the salt method was used at Rauma.

Mills

- Two mills chosen –Rauma (Kraft) and Heinola (sulfite)
- Rauma chosen as a representative Kraft pulp mill

  $O_{2,excess}$ = 2.3 % (mill measurement)

  H_2O flue gas = 20% (calculated based on excess O_2)
- Heinola chosen because of high SO_2

  SO_2 = 1200-1600 ppm (before scrubber, our measurements)

  $O_{2,excess}$ = 5.0 % (mill measurement)

  H_2O flue gas = 14% (calculated based on excess O_2)

Mill Measurements

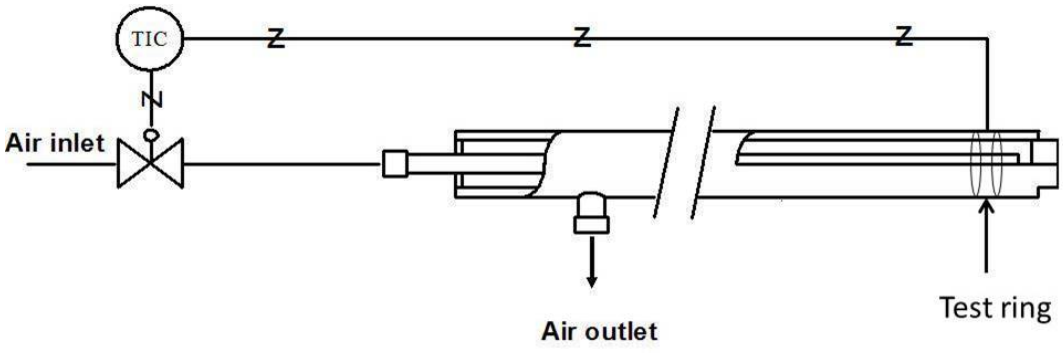
- Measurements
  - Dew point measured with a commercial dew point analyzer (Land)
  - Corrosion probe (temperature controlled to within +/- 5°C)
  - H_2SO_4 (salt method and controlled condensation)
  - SO_2
- The measurements were carried out between the ESP and scrubber
  - Rauma: average gas temperatures: 180/182/165 °C for days 1/2/3 respectively (low load + oil on day 3)
  - Heinola: average gas temperature 152 °C in two days of sampling

Dew Point Measurements

- Dew point probe made by Land
- Cooled probe has two electrodes at the end
- When an electrolyte (acid or water) condenses between electrodes, electricity is conducted resulting in a signal

Corrosion Experiments

- Conducted with air cooled probe
- 1 ring of carbon steel
- Thermocouple in the ring to measure/control the ring material temperature - PID controller used to adjust air flow

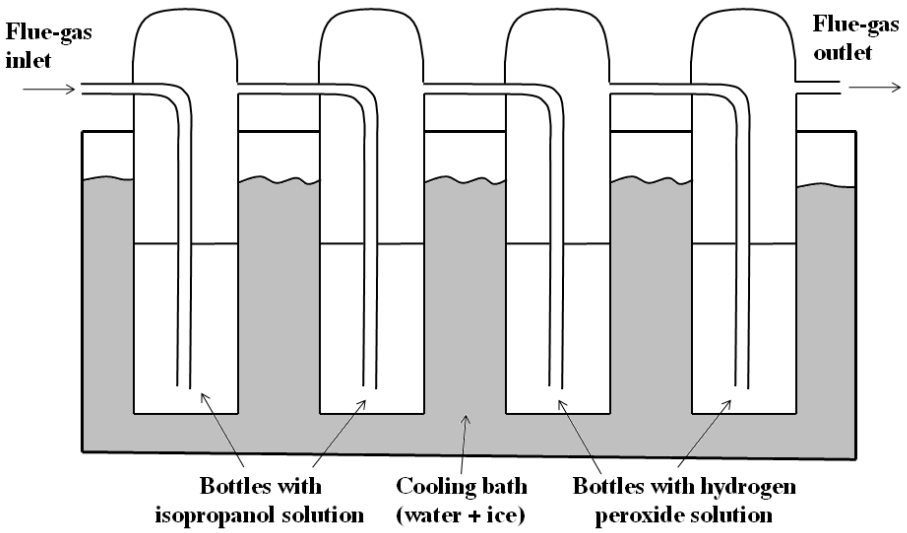


SO_2 & H_2SO_4 Measurements

- Plan was to use Isopropanol (IPA) to capture H_2SO_4 followed by hydrogen peroxide to capture SO_2
- SO_2 was successfully captured in hydrogen peroxide solution (4 vol-%) and subsequently analyzed by titration
- Isopropanol found to also absorb some SO_2 (some literature references found the same) – too much for observing small amounts of H_2SO_4
- Two new methods were tested
  - Salt method
  - Controlled condenstation

SO_2 & H_2SO_4 Analysis: IPA method (EPA method 8)

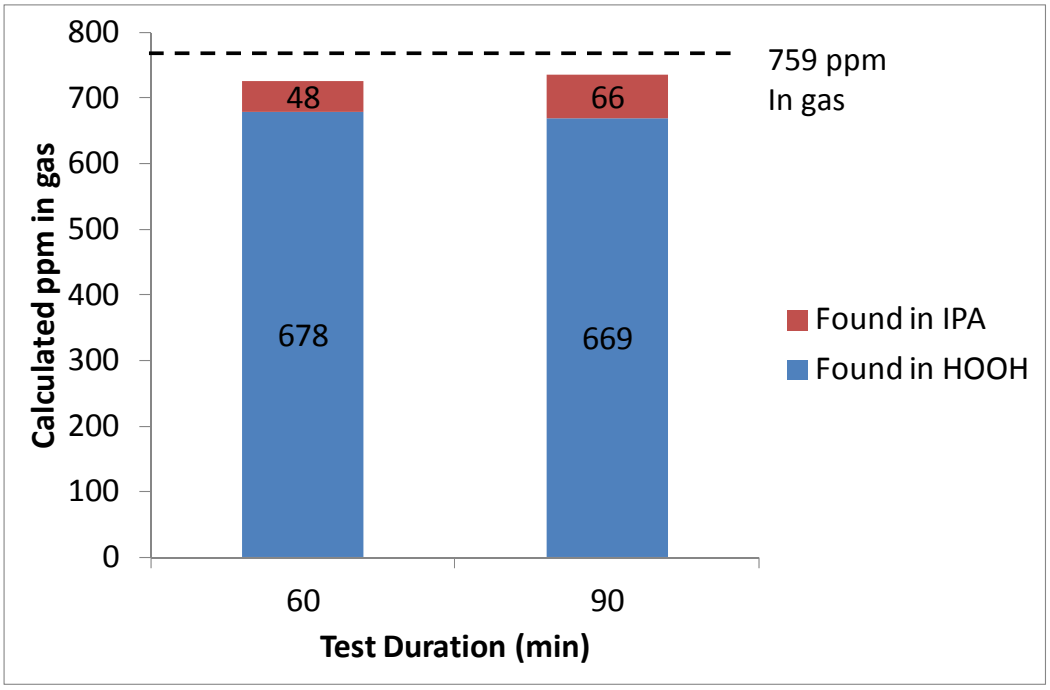
- Isopropanol solution to absorb H_2SO_4
- Hydrogen peroxide solution to aborb SO_2



SO_2 & H_2SO_4 Analysis: IPA method (EPA method 8)

- Prior to Heinola, we bubbled SO_2 calibration gas (759 ppm SO_2 in N_2) through the isopropanol and hydrogen peroxide solutions
- There is no H_2SO_4 in the calibration gas, so expectation of no H_2SO_4 in the isopropanol
- SO_2 absorbtion by hydrogen peroxide was complete (no SO_2 in gas after HOOH) and titration of the hydrogen peroxide gave accurate results

SO_2 & H_2SO_4 Analysis: IPA method (EPA method 8)



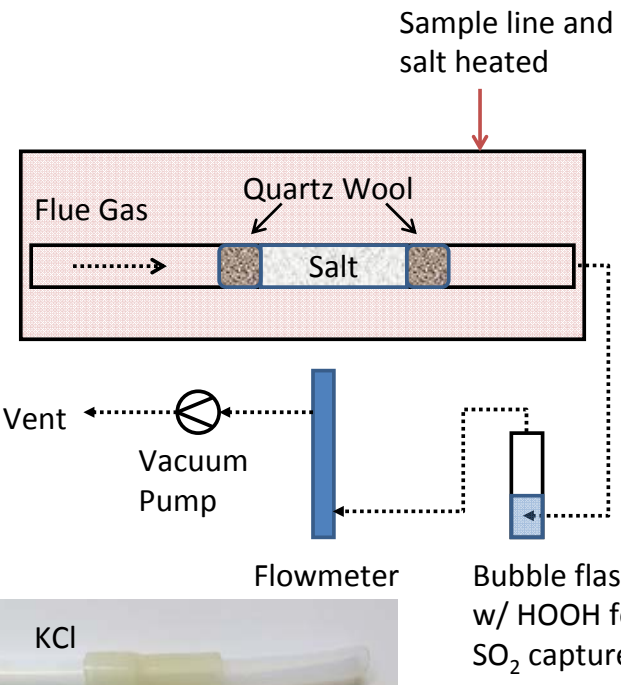
SO_2 & H_2SO_4 Analysis: Salt Method

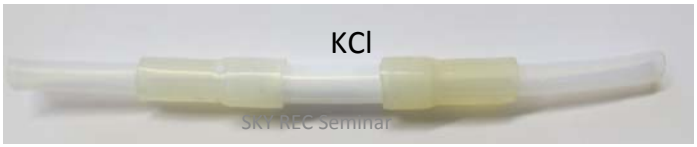
- Salt method
  - Gas is passed through a tube of KCl that will react with H_2SO_4 to form a sulfate salt

SO_3 (g) + H_2O(g) → H_2SO_4 (g)

2KCl (s) +H_2SO_4 (g)→K_2SO_4(s) + 2HCl(g)

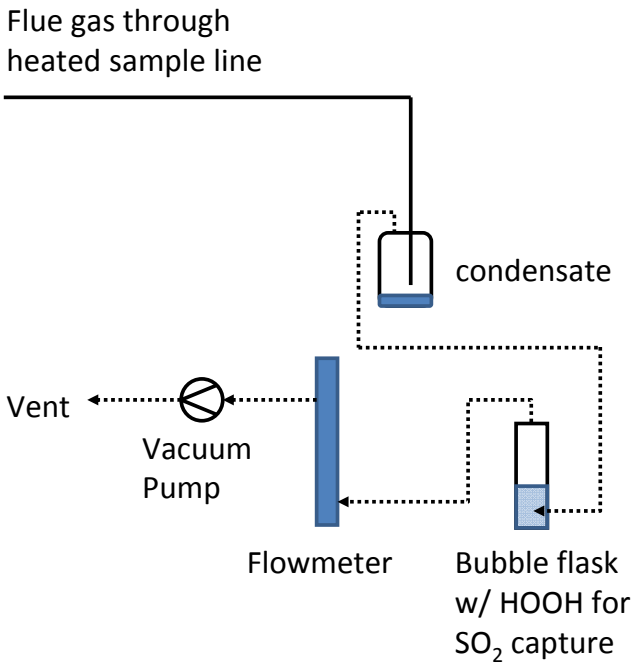
  - Salt then analyzed for sulfur. Advantage of of KCl is that K and Na can be analyzed, with Na associated with fume





SO_2 & H_2SO_4 Analysis: Controlled Condensation

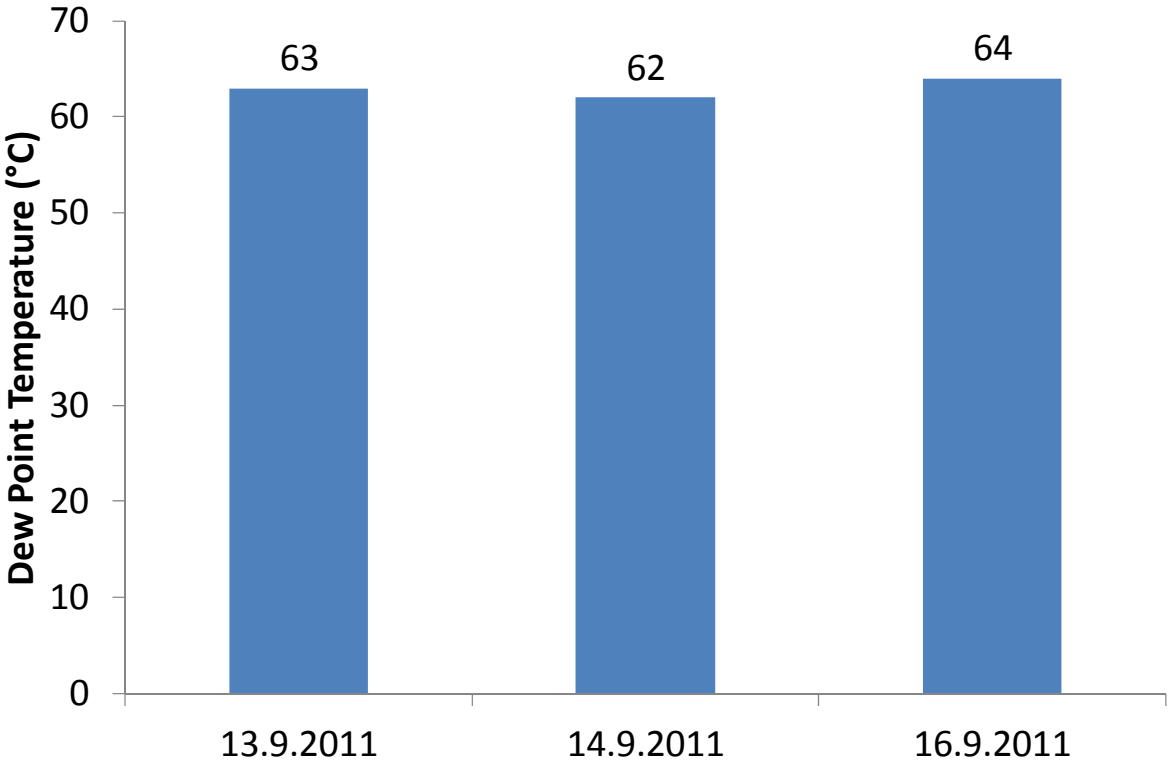
- Controlled condensation
  - Gas passed through a cooled line to condense H_2SO_4
  - 85 °C chosen for condensing temperature
  - Only used at Heinola



Rauma

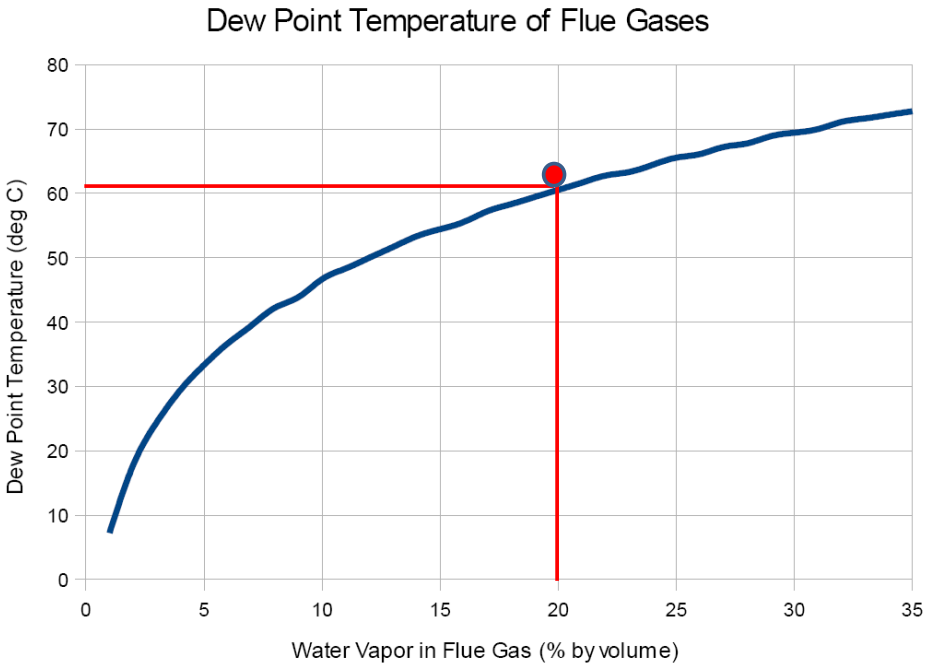
Sampling Dates: 13,14-16.9.2011

Rauma Dew Point Measurements

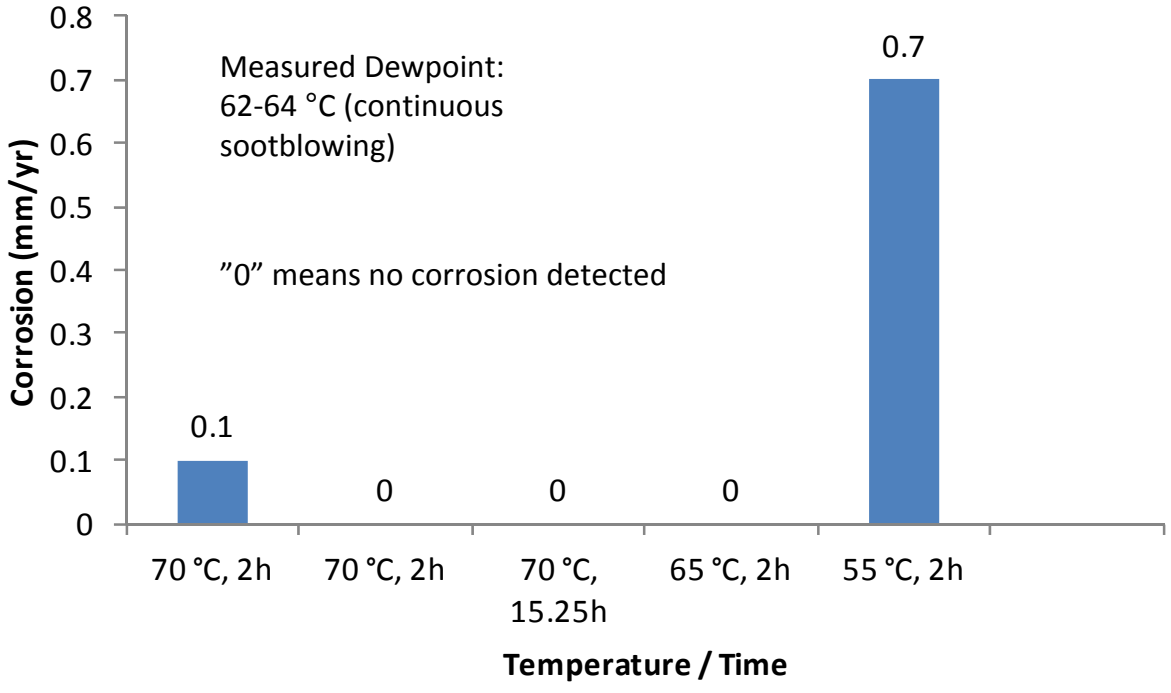


Dew Point

● = measured dew point



Rauma: Corrosion Probe Results



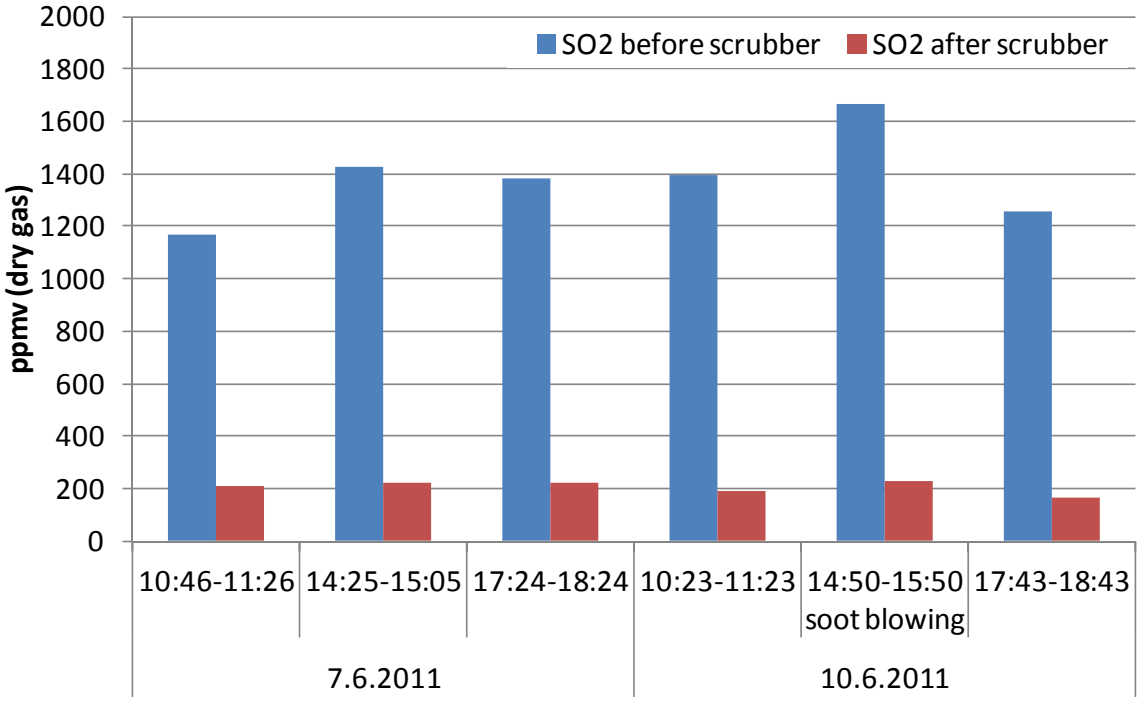
Rauma: SO_2 & H_2SO_4

- Mill operated at:
  - Normal load
  - Reduced load with oil added
- No SO_2 detected at any condition
- No H_2SO_4 detected at any condition

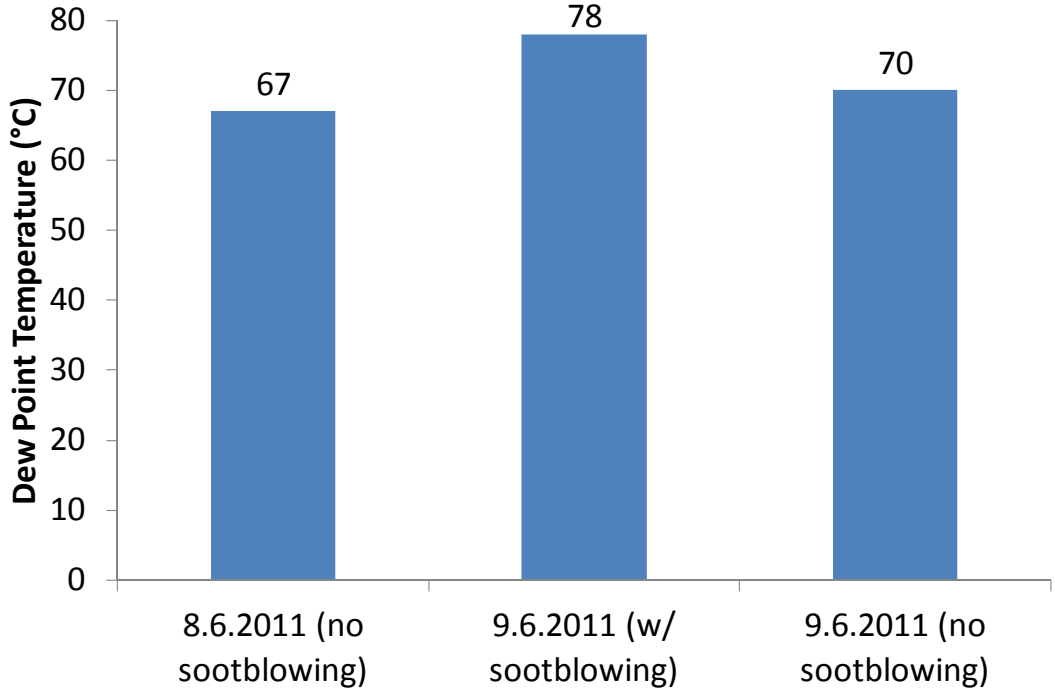
Heinola

Sampling Dates: 7-10.6.2011

Heinola: SO_2 Before and After Scrubber

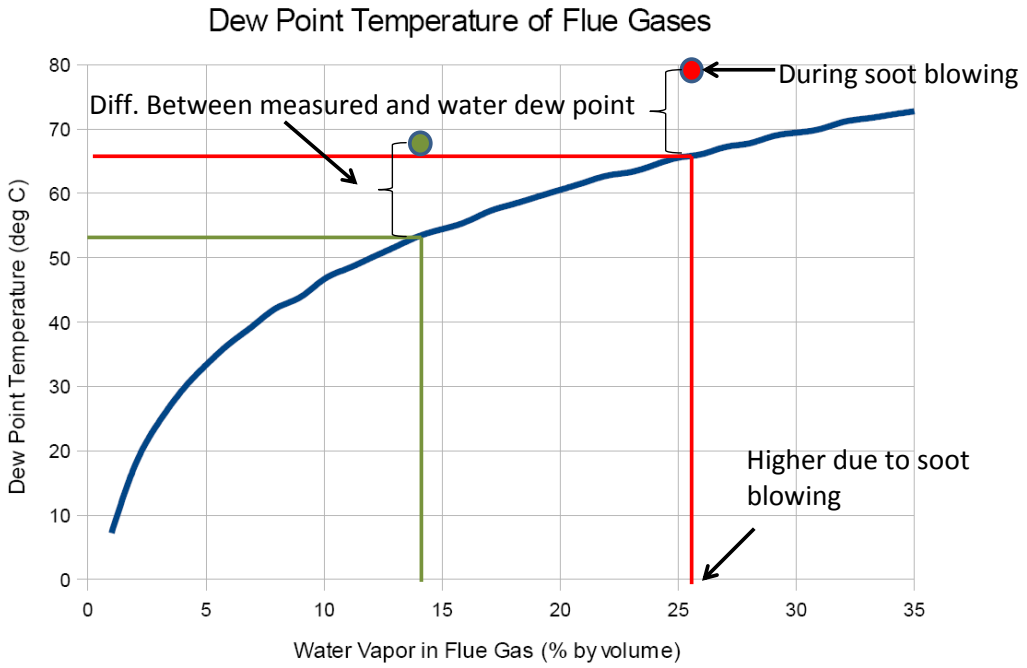


Heinola: Dew Point Measurements (from dew point analyzer)

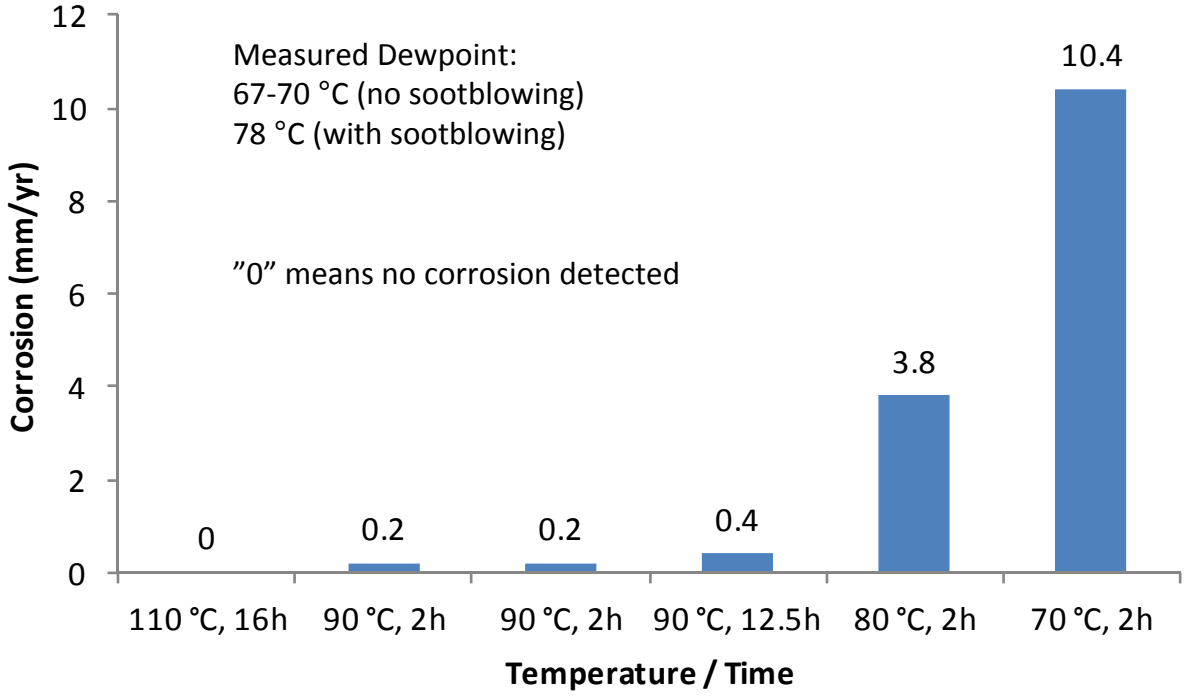


Heinola: Dew Point

= measured dew point



Heinola: Corrosion Probe Results



Heinola: H_2SO_4

- Salt method
  - < 1 ppm
- Controlled condensation (85 °C)
  - 1-4 ppm
- Dewpoint less than 80 °C which means no sulfuric acid

Conclusions

- Dewpoint
  - Acid dewpoint was not found at either mill
  - Water dewpoint was measured in Rauma
  - Elevated dewpoint found at Heinola, but not acid dewpoint
- H_2SO_4
  - Isopropanol method was not applicable
  - Salt method appears to work well
  - H_2SO_4/SO_3 theory needs further clarification

Conclusions

- Corrosion
  - At Rauma corrosion started below 65 °C (dewpoint was 62-64 °C)
  - At Heinola, corrosion started at 80-90 °C (slightly higher than the dewpoint)

IMPROVING HEAT RECOVERY IN BIOMASS-FIRED BOILER PROJECT PRESENTATION

Doug Singbeil
FPInnovations

Improving Heat Recovery In Biomass-Fired Boilers

James Keiser, ORNL
Doug Singbeil, FPInnovations
Sandy Sharp, SharpConsultant

FPInnovations, SharpConsultant, Georgia Institute of Technology, and University of Tennessee-Knoxville

SkyRec

Oct 20, 2011

Project Partners

- Åbo Akademi University (conducting relevant research) participant
- Andritz Oy (boiler manufacturer) cost sharing partner
- Babcock & Wilcox (boiler manufacturer) cost sharing partner
- Catalyst Paper (boiler operator) cost sharing partner – host for corrosion probe
- Chalmers University (conducting relevant research) participant
- Domtar Corporation (boiler operator) cost sharing partner
- E.ON Engineering (utility company/boiler operator) cost sharing partner
- FM Global (insurance company) cost sharing partner
- FPInnovations (co-investigator) participant and cost sharing partner
- Foster Wheeler (boiler manufacturer) cost sharing partner
- Georgia Institute of Technology (co-investigator) participant and cost sharing partner
- Haynes International (tube manufacturer) cost sharing partner
- Howe Sound Pulp and Paper (boiler operator) cost sharing partner – host for corrosion probe
- International Paper (boiler operator) cost sharing partner
- Mead Westvaco (boiler operator) cost sharing partner – host for corrosion probe
- Outokumpu (alloy manufacturer) cost sharing partner
- Rolled Alloys (tube manufacturer) cost sharing partner
- Sandvik Materials Technology (tube manufacturer) cost sharing partner
- SharpConsultant (co-investigator) participant
- Southern Company (utility co/boiler operator) cost sharing partner – host for corrosion probe
- Special Metals (tube manufacturer) cost sharing partner
- Thyssen Krupp VDM (alloy manufacturer) cost sharing partner
- University of Tennessee-Knoxville (conducting relevant research) participant
- University of Toronto (conducting relevant research) participant
- Vattenfall Power Consultant (utility company/boiler operator) cost sharing partner
- Weyerhaeuser Company (boiler operator) cost sharing partner

Project Objective

Background: Superheater steam temperatures in biomass-burning boilers have been limited due to corrosion of tube materials.

Objective: Identify alternate superheater tube materials and/or alternate superheater designs or operating procedures that will permit a 100 C° increase in superheater steam temperatures

Desired outcome: Operation of biomass-fired boilers at 100 C° higher steam temperatures will permit more efficient use of these fuels with the opportunity for a significant reduction in use of fossil fuels and in production of greenhouse gases

Technical Approach

The project is divided into five tasks:

- Conduct critical review of technology status
- Quantify financial benefits of increased superheater temperatures
- Conduct laboratory corrosion studies in environments simulating superheater conditions in biomass-fired boilers
- Measure corrosion rates of alternate materials in superheater environments below, at, and above the deposit melting point temperatures
- Prepare report summarizing project results

Project Management - Budget

Funding Status

Budget Category	Approved Budget	Funds Received	Expenditures through May, 2011
Personnel	726K		353.0K
Travel and Supplies	97K		95.0K
Capital			
Subcontracts	747K		341.5K
Total ORNL	1,570K	1,570K	789.5K
Industrial Partner Cost Share	805.8K		141.0K *
Total Project	2,376K		930.5K

* Cost share contributions through March 2011

	2010	2011	2012	TOTAL
Proposed funding	552K	530K	488K	1,570K
Actual funding	1,570K			

Accomplishments And Findings (Task 1)

Conduct critical review of technology status

•Discussions held with US project participants

•Visits made to learn about European biomass corrosion research and boiler technologies

• Prepared final report "*Superheater Corrosion in Biomass Boilers: today's science and technology*" (96 pages, 249 refs.)

•Two summary papers prepared:
- Tappi PEERS Conference 2011
- •NACE International CORROSION/2012

Conclusions from Task 1

- Opportunities exist to increase SH steam temps in biomass boilers and still avoid corrosion and/or fouling
  - 7 boiler design modifications address some aspects
  - 3 fuel modifications
- Most severe corrosion caused by alkali metal chlorides that remove otherwise-protective Cr_2O_3
- No coherent theory of alloying that provides predictive understanding of effects of biomass ash deposits
- Number of best practices for laboratory/field testing identified and incorporated into our research program

Accomplishments And Findings (Task 2)

Quantify financial benefits of increased superheater tube temperatures

- Suitable Rankine Cycle calculator identified
- Subcontract in place to use it to calculate financial benefits of higher superheater temperatures in biomass-fuelled boilers
- Partners will define at least 3 base-case boilers
  - Recovery boiler base-case specified and preliminary calculations complete
- Initial calculations will:
  - identify critical input parameters
  - express benefits as $/ft, $/ton and GHGs
- More refined calculations will examine most critical issues

Accomplishments And Findings (Task 3)

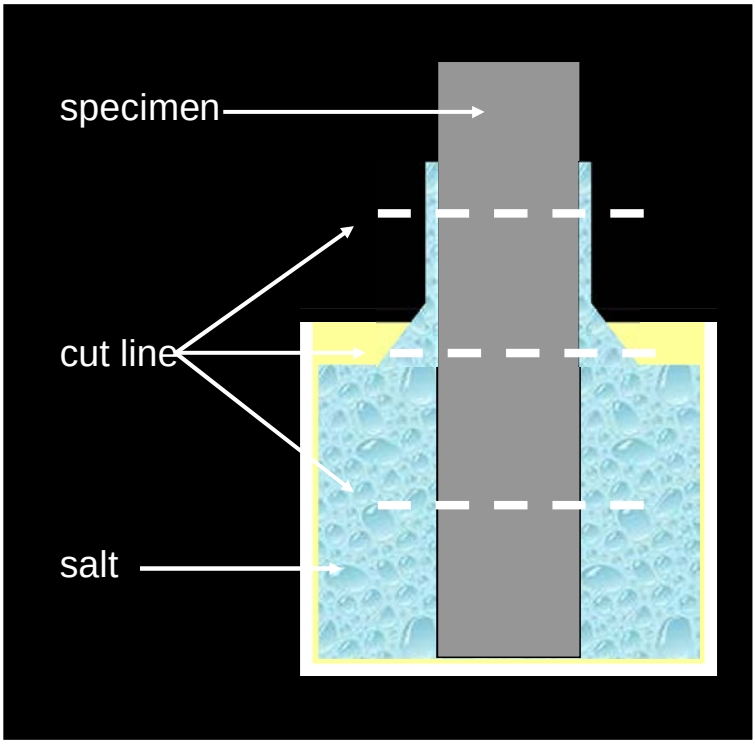
Conduct laboratory corrosion studies in environments simulating superheater conditions in biomass-fired boilers

- Specimen geometry and configuration selected after extensive consultation and internal testing
- Alloys to be used in the test program have been chosen
- All materials for coupons have been received and machining completed on most of the alloys
- Experimental procedure and test matrix have been determined
- 100 and 200 hr tests in recovery boilers salts at 510 C and 625 C have been completed

Four furnaces are available for tests

- Horizontal tube furnaces with 7.6 cm OD tubes
- Gas flow rates of ~ 200 sccm (lineal velocity of 5 cm/sec)
- Simulated flue gases used: 5% O_2, 10% CO_2, 20% H_2O
- Cylindrical specimens will be used; positioned vertically in pots
- Specimens 25 mm long; 5 mm dia; surface finish Ra 0.4-1.6 micron

Specimen design chosen for versatility, ease of manufacture from wall of tube material and analysis options

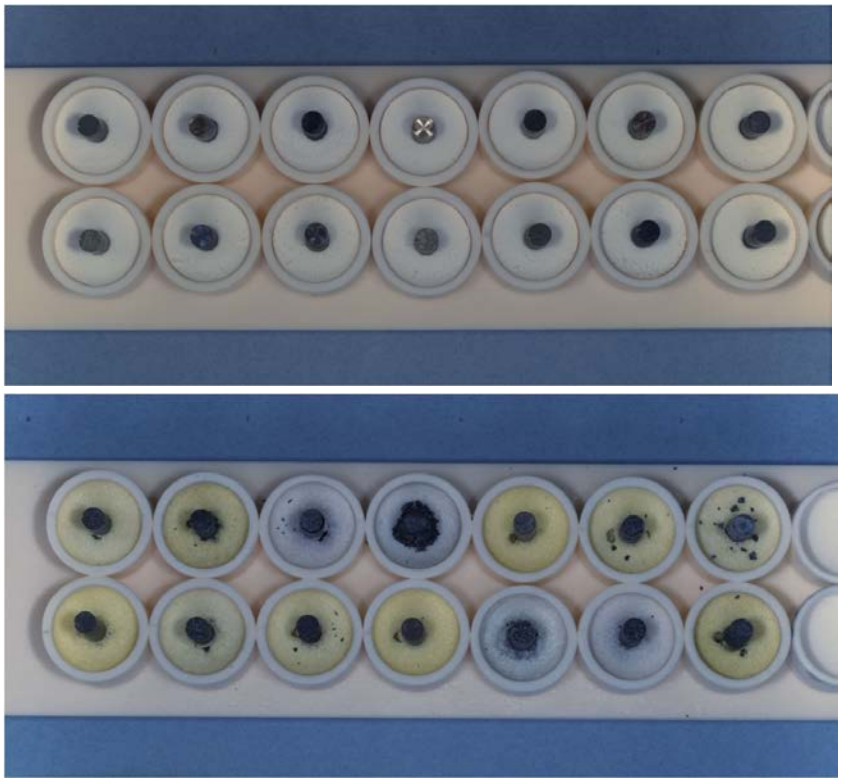


- Amenable to statistical analysis of depth of penetration (Cranfield)
- No issues with edges and corners
- Same design can be used to look at coatings
- Allows investigation of corrosion under salt, at interface, and in gas
- Tests confirmed that the chosen coupon configuration gives simultaneous information about corrosion in gas phase, at the gas/salt interface, and beneath a layer of salt.

Alloys chosen for laboratory program

	Fe	Ni	Cr	Mo	Co	Al
31OH	Bal	19	24	0.1		0.03
HR120	Bal	37	25	0.3		0.07
HR214	4	Bal	16	<0.1		4.3
HR160	0.3	Bal	28	<0.05	31	
San 28	Bal	30	27	3.3		
602CA	10	62	25			2.3
Esshete 1250	Bal	9.5	15	1.0		
A690	9	63	28			
AC-66	Bal	32	27			0.01
A33	32	31	33	1.5		
A59	0.6	60	23	16		0.3

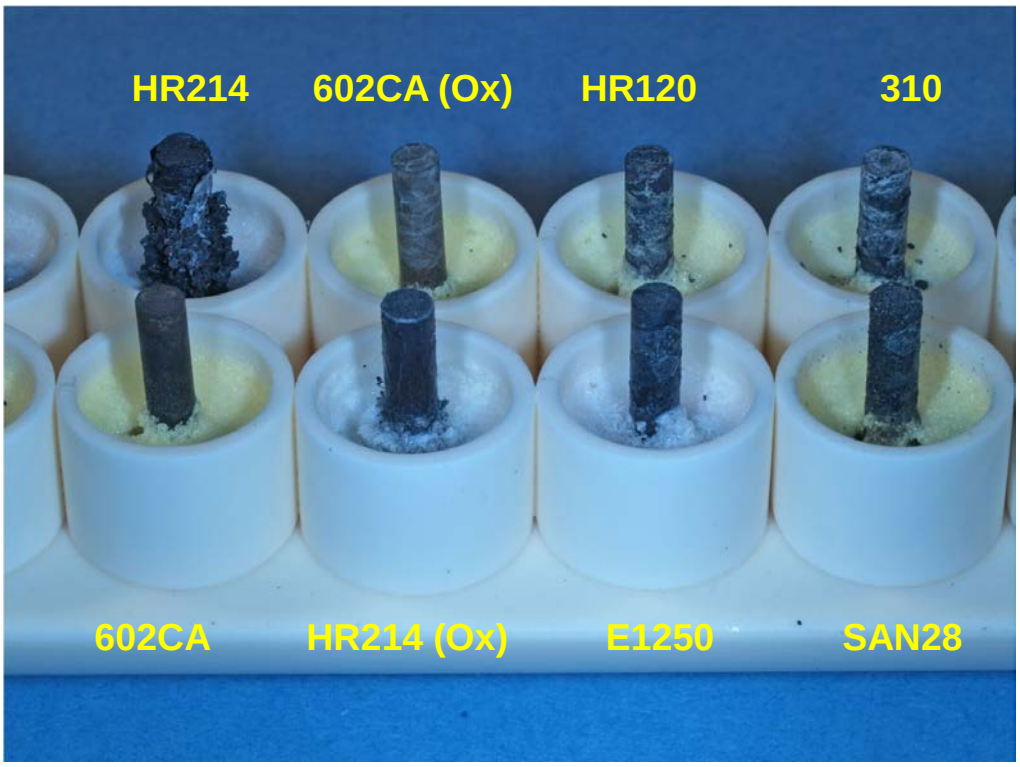
200 hours (salt FMT 524°C) NaCl, KCl, Na_2CO_3, and Na_2SO_4



510°C

625°C

Closer view of specimens as removed from the furnace



Task 4

- Objective of this task is to measure corrosion rates of alternate alloys in superheater environments
- Nine candidate alloys were selected for the corrosion probes by the three co-investigators with input from project partners
- Four exposure sites were identified that represented several extreme conditions

Task 4 – Corrosion Probe Features

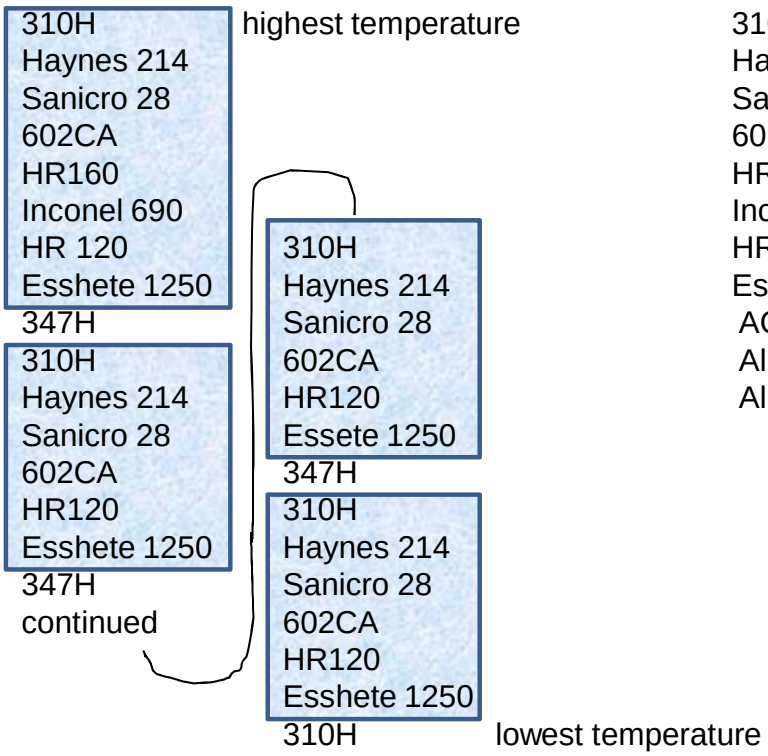
- Corrosion probes have 30 alloy samples each two inches long
- Thermocouples that are attached to 24 of the samples measure the temperature on the surface of the samples (alternating between top and bottom of samples)
- Corrosion probes are air cooled
- The air flow is varied on the basis of the temperature measured by a selected thermocouple
- Each probe will be exposed at least 2000 hours

Task 4 – Corrosion Probe Alloys

- Alloys selected included conventional stainless steels, nickel-base alloys and alumina forming alloys
- Six selected alloys are repeated four times with the intent one set is about 100 Celsius degrees above the maximum superheater temperature in that boiler
- The other alloy sets are at progressively lower temperatures

Alloy arrangement on probes

Corrosion Probe Sample Arrangement



Alloys For Laboratory Corrosion Studies

310H
Haynes 214
Sanicro 28
602CA
HR160
Inconel 690
HR120
Esshete 1250
AC-66
Alloy 33
Alloy 59

Task 4 – Selected Exposure Sites

- Covington, Virginia, in a recovery boiler processing black liquor derived primarily from hard wood – high potassium content
- Gadsden, Alabama, in a power boiler that co-fires biomass and coal – sulfur and chloride content
- Crofton, British Columbia, in a hog fuel boiler that primarily burns seawater floated logs – high chloride content
- Port Mellon, British Columbia, in a hog fuel boiler that burns a combination of beetle-killed pine, seawater floated logs and demolition waste – elevated chloride, possible lead and zinc content

Probe And Instrument Box In MWV Boiler

Task 4 – Exposure Status

- Deposit sample probe and a corrosion probe have been exposed in the Covington boiler
- Deposit sample probes have been exposed and corrosion probes are currently being exposed in the Crofton and Port Mellon biomass boilers
- A corrosion probe is currently being exposed in the Gadsden co-fired power boiler

Probe for Crofton biomass boiler

Task 4 – Samples From Covington Probe Are Currently Being Examined

Task 5 – Communicate Results

- Brief monthly reports are submitted to the Department of Energy
- Quarterly reports are prepared for the DoE and distributed to project partners
- Annual project review meetings are being held – the next is scheduled for November 29th in Oak Ridge
- A report summarizing the project's accomplishments will be prepared

FIELD TESTS OF SUPERHEATER MATERIALS

Martti Mäkipää / Markku Orjala
VTT

Business from technology

SKYREC - Seminar

Material exposures in Joutseno Recovery Boiler

Sokos Hotel President 20.10.2010

Martti Mäkipää, Janne Kärki and Markku Orjala
VTT

Objective of the work

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

Materials selected for the study were 347H, AISI310, HR11N, SAN28, Super 625 and SAN69. See slide 3 for compositional details. Two material samples in the form of rings having a wall thickness of about from 2.7 mm to 2.9 mm were prepared from each material. Wall thickness of each sample was measured using a gauge for various directions.

Full scale material exposures were carried out in Joutseno RB by September-October 2010. Two identical cooled probes, Probe 1 and Probe 2, six different material samples mounted in each in each were exposed in the boiler for a time of one month (600h) close to opposite walls between II and III superheater at the level 10, about one 1 meter below the sootblower, see Slide Nos. 4 and 5 farther on.

Nominal material temperatures on the exposed side of each probe were 530^{o}C and 570^{o}C. Concurrent SH III material temperature values*) were nominally less than 495^{o}C

**) Material temperature data supplied by boiler operator personnel; data nomination "10MIN:93TI0124.18…124.20"*

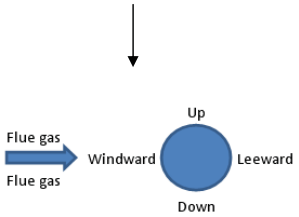
Materials

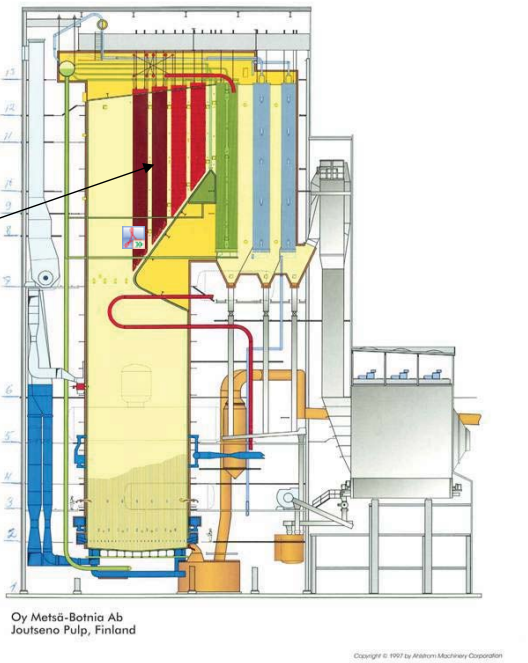
The materials to be studied were selected as 347H, AISI310, HR11N, SAN28, Super 625 and SAN69, the nominal composition of each being as follows:

	SAN28	HR11N	Super 625	SAN 69	AISI 310	347H
C	<0.02	<0.03	<0.03	<0.02	<0.08	<0.08
Si	<0.7	<0.6	<0.5	<0.5	<1.5	<0.75
Cr	26.0-28.0	27-30	20-23	30	24-26	17.0-20.0
Mn	<2.0	<2.0	<0.5	<2.0	<2.0	
Fe	Bal.	Bal.	15-20	10	Bal.	Bal.
Ni	29.5-32.5	38-42	50min	60	19.0-22.0	9.0-13.0
Cu	0.6-1.4					
Nb	(0.32-1.0)					
Mo	3.0-4.0	0.5-1.5	8.0-10.0			

The boiler

Probes between II and III Superheater wer inserted through openings at opposite sidewalls lovated at the Level 10 ½ as shown in the next slide.





Probe 1 ready for insertion through an inlet located about one meter below the sootblower at level 10 ½ , between 2nd and 3rd Superheter

The course of material exposure

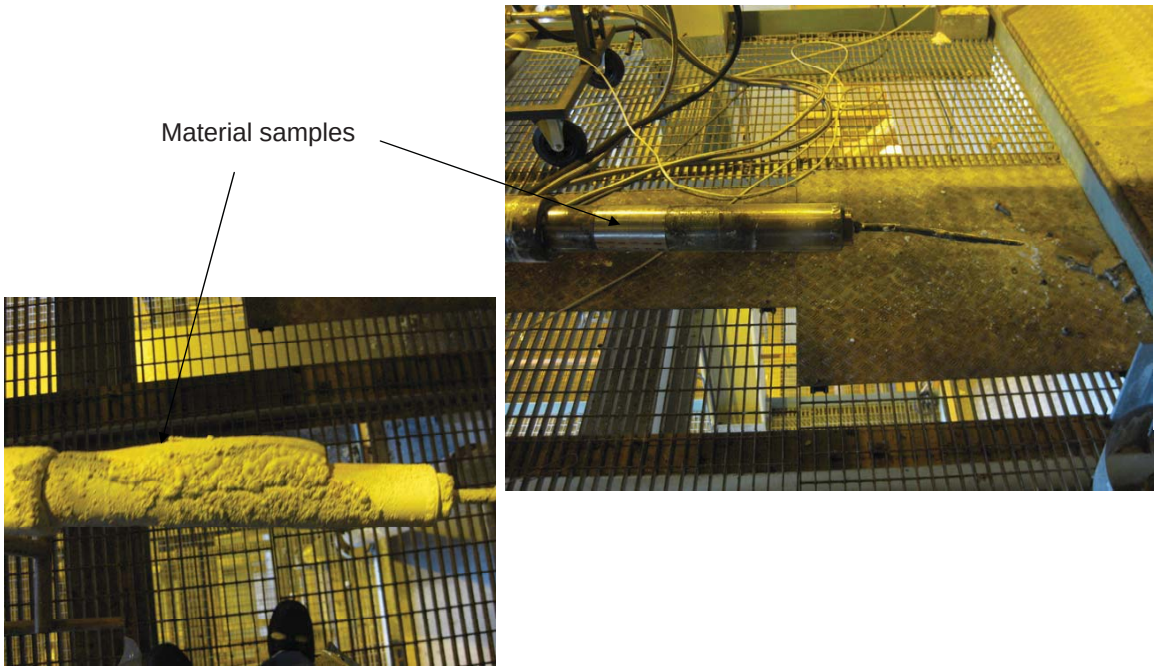
Air- and water-cooled probes used imitate the behaviour of superheater tubes. The surface temperatures of the probes vary depending on the direction of the flue gas flow. The windward temperature is maintained constant by adjusting the cooling rate and the temperatures on other sides change when deposits are formed.

In this particular case, hard deposit acting as an insulator did rapidly form on the flue gas flow side causing that the material temperature on other locations did rise (up to 590°C for few hours).

This problem was corrected by changing the regulating thermocouple from the windward side to the up side (accordingly by 90 degrees).

Material falling from the roof etc. did harm some of the samples. Samples with marked deformation were as follows. Probe 1: SAN 69, AISI 310, 347H; Probe 2: Super 625, AISI 310; wall thickness measurements for these samples were thus of no use.

The lead of the probe as shown before and after the boiler exposure



Post-exposure characterisation of the samples

Post-exposure the rings were mounted on site in resin, taken to laboratory and prepared to metallographic cross sections using ethanol as grinding medium.

Material wall thicknesses of the metallographic cross sections were measured from 8 positions (0, 45, 90,135,180, 225, 270 and 316 degrees from the windward position (0 degrees)) using an optical method. Measuring values thus obtained were compared internally and to pre-exposure measuring values.

Metallographic cross sections were characterised using optical microscope, or after coating with thin carbon film, using an environmental scanning microscope “FEI XL 30 ESEM” equipped with an analysator “Thermoscience” and “Noran System 7” calculation program.

The material sample series having suffered relatively less from deformations was chosen for ESEM-studies, i.e., the series exposed in Probe 2.

Post-exposure characterisation of the samples (continued)

Carbon, independent of its presence in the raw data, has been therefore left out from quantitative elemental composition calculations.

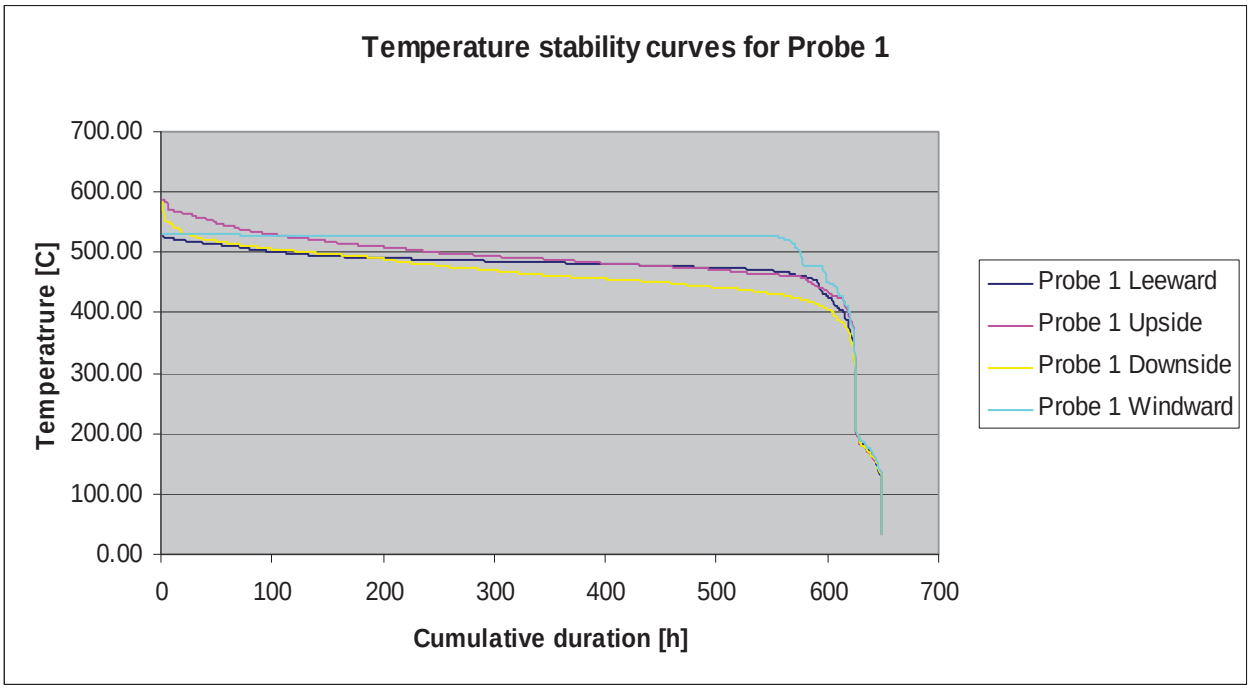
It is notified that the elements Mo and S are difficult to differentiate from each other due to the similar behaviour. A compound specimen MoS2 was analysed. According to the repeated quantitative elemental analysis performed the specimen did contain 66.65 and 66.28 at-% S and 33.35 and 33.72 at- % Mo, i.e., very close to the theoretic values for a strictly stochiometric composition MoS_2.

In spite of this finding one may still dispute the relative quantitative percentages for Mo and S in various metal analyses presented below.

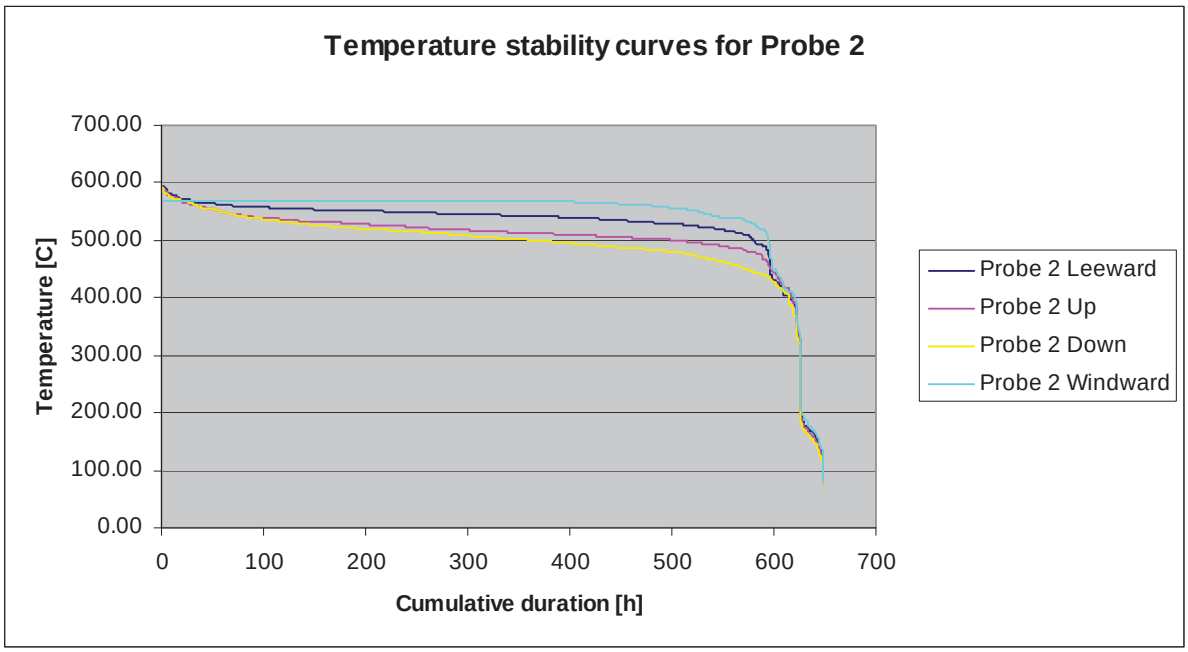
Elemental composition of deposits as well as those of oxide scales, corrosion products, and residual metal phases were analysed at various positions. Analytical results (areal and point analyses) were used for predictive calculations using thermochemical database and calculation tool “FactSage 6.1”.

Results: Material temperature measurement data

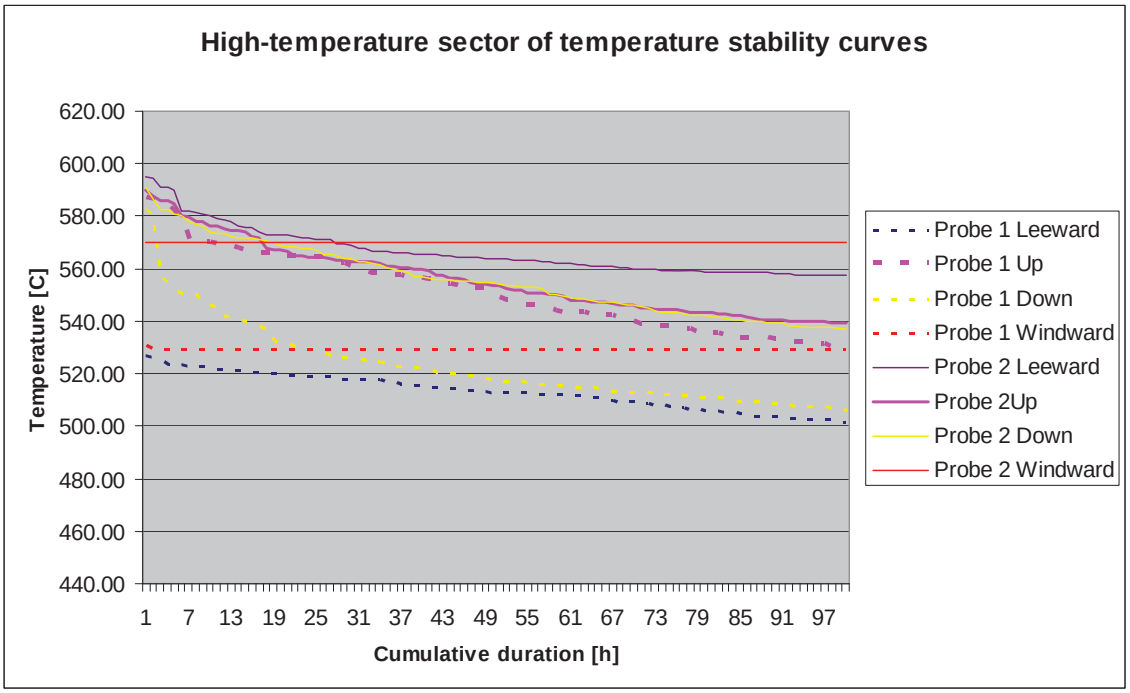
Probe tests: Temperature stability of Probe 1



Probe tests: Temperature stability of Probe 2



Probe tests: High-temperature range of temperature stability curves



Charasteristic material temperature data for various directions in Probe 1 and Probe 2

Temperature:	Average	Median	Maximum	Minimum
Position:	°C	°C	°C	°C
P1 Leeward	487	484	527	402
P2 Leeward	542	545	595	397
P1 Up	499	491	587	422
P2 Up	519	515	590	390
P1 Down	473	466	582	375
P2 Down	507	505	591	368
P1 Windward	526	529	531	436
P2 Windward	562	569	570	417

Results: Sample characterisation

Results of wall thickness measurements on various directions:

Δ = post exposure value (optical) – pre-exposure value (gauge)

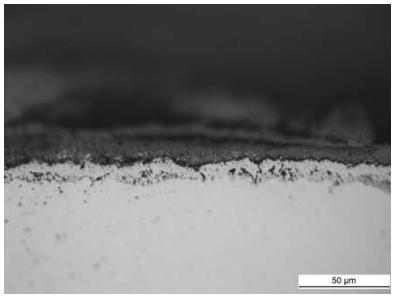
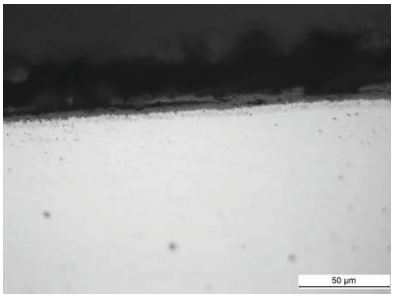
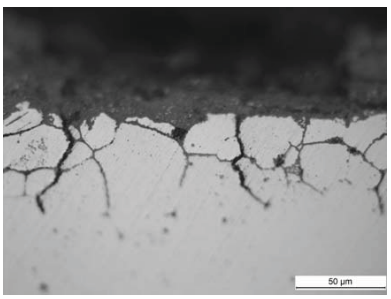
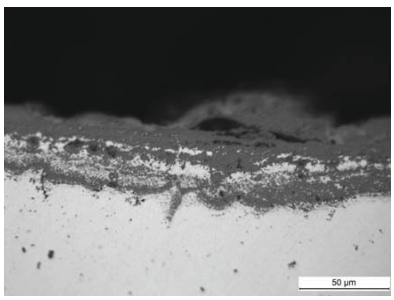
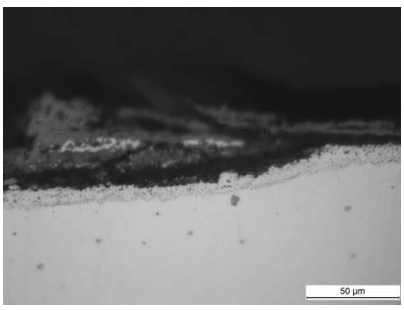
Δ [mm]	Probe 1				Probe 2				
Location	*SAN28*	*HR11N*	*Super 625*	*Mean*	*SAN28*	*Super 625*	*SAN 69*	*347H*	*Mean*
Windward (0)	*0.002*	*-0.058*	*-0.055*	***-0.037***	*0.030*	*-0.002*	*-0.017*	*0.009*	**0.005**
Up (90)	*0.015*	*-0.014*	*0.044*	***0.015***	*-0.007*	*0.008*	*-0.031*	*-0.005*	***-0.009***
Leeward (180)	*0.002*	*0.031*	*-0.022*	***0.004***	*-0.033*	*0.017*	*0.001*	*0.041*	***0.006***
Down (270)	*0.036*	*-0.060*	*0.013*	***-0.004***	*0.003*	*0.000*	*-0.007*	*0.105*	***0.025***
Mean	***0.014***	***-0.025***	***-0.005***	***-0.005***	***-0.002***	***0.006***	***-0.014***	***0.038***	***0.001***

The difference-values vary in a random manner independently of the measuring position and the ring material. Wall thickness measuring values are considered as useless for the corrosion evaluations here.

Optical microscopy of the less-harmed material samples among those exposed in Probe 1

- **347H** material surface cross section on the Windward position appeared as little affected besides oxide growth outwards whereas on the Leeward position material had suffered from general corrosion and additionally of internal attack along open grain boundaries down to the depth of about 75 µm from the current metal surface
- In the case of **SAN 28** there was found internally penetrated (de-alloyed) zone and oxide scale growths on the Windward and Leeward position. Apparent metal loss totalled about 30 µm and 75 µm on the Windward and Leeward position, respectively
- In the case of ***Super 625*** the corrosion attack mode was similar to that in the case of SAN 28, but less in extent, Total metal loss, however, depended much of exact location examined. Apparent metal loss at the cross section locating exactly on the Windward position (0 degrees) was found to be less than 10 µm whereas at locations situated about +/- 30 degrees sideways apparent metal loss was about 25 µm or more. Note that the maximum material temperature at Up and Down positions was close to **590ºC**.

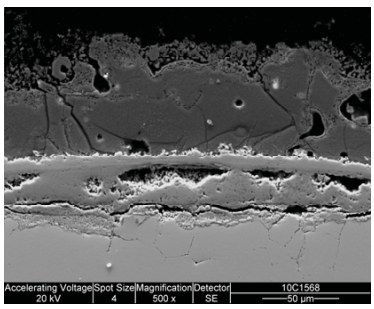
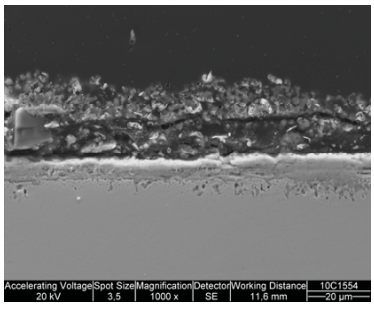
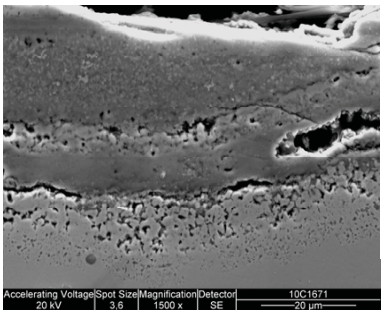
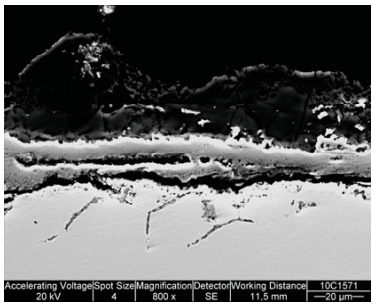
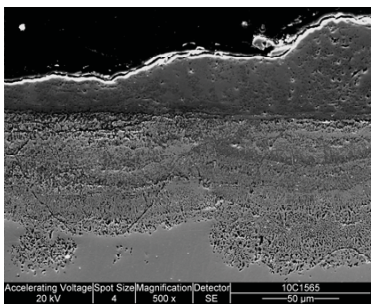
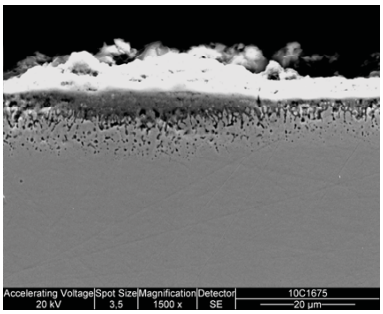
Cross sectional views of some samples exposed in Probe 1

	347H	SAN28	Super 625
Windward: 527ºC (reference position)			
Leeward: 484ºC (median) 527ºC (maximum)			

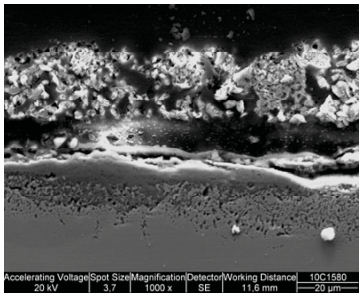
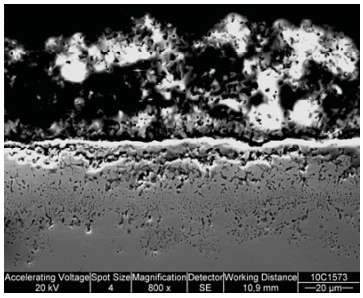
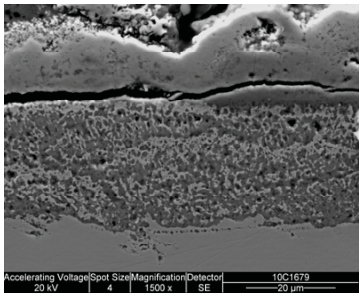
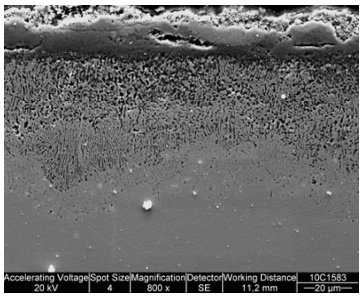
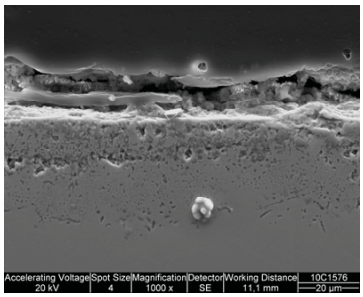
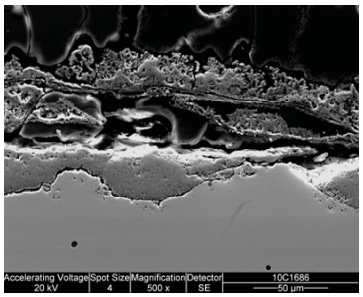
ESEM characterisation of the six material samples exposed in Probe 2

- In the case of 347H grain boundary attack, de-alloying of superficial metal grains and chloride enhanced oxide scale growth are the governing modes of accelerated corrosion.
- Some chloride is very typically found in the areal quantitative analyses of the corrosion products. Point analyses of attacked grain boundaries did, or did sometimes not, reveal sulphur and/or chloride in addition to oxygen. (The conventional analytical limit here is 0.1 wt-% for S and Cl)
- Other five samples made of high-chromium steels and nickel alloys had suffered from internal sulphidation and/or oxidation attack. Oxygen or oxygen and sulphur were found as abundant in various de-alloyed zones impoverished in respect of chromium and enriched in respect of nickel and iron.
- The content of chloride was in general low as compared to oxygen and sulphur. However, few localised enrichments consisting of nickel and chromium chlorides did contain up to 30 % wt-% Cl.

Cross sectional views of some samples exposed in Probe 2

	347H	SAN28	Super 625
Windward: 563°C (reference position)			
Leeward: 545°C (median) 595°C (maximum)			

Cross sectional views of some samples exposed in Probe 2

	HR11N	SAN65	AISI 310
Windward: 563°C (reference position)			
Leeward: 545°C (median) 595°C (maximum)			

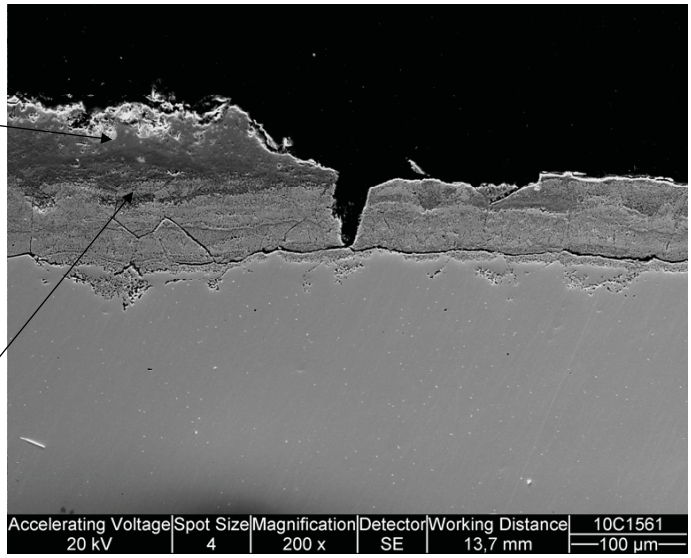
SAN 28, Leeward-side (172 degrees), T_{mean} 544°C, T_{max} 595°C

Quantitative Results for: S2-1, Analysis 59

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	47.36	+/- 0.38	60.48	+/- 0.48
Na	26.80	+/- 0.14	23.82	+/- 0.12
S	20.40	+/- 0.10	13.00	+/- 0.07
Cl	0.35	+/- 0.05	0.20	+/- 0.03
K	3.94	+/- 0.06	2.06	+/- 0.03
Cr	0.48	+/- 0.07	0.19	+/- 0.03
Mn	0.29	+/- 0.05	0.11	+/- 0.02
Fe	0.39	+/- 0.05	0.14	+/- 0.02
Total	100.00		100.00	

Quantitative Results for: S2-1, Analysis 60

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	21.80	+/- 1.46	46.69	+/- 3.12
Na	5.24	+/- 0.14	7.81	+/- 0.21
Al	0.13	+/- 0.03	0.16	+/- 0.03
Si	0.14	+/- 0.02	0.18	+/- 0.03
S	1.09	+/- 0.02	1.16	+/- 0.03
K	0.37	+/- 0.02	0.32	+/- 0.02
Cr	7.05	+/- 0.11	4.65	+/- 0.07
Mn	12.14	+/- 0.20	7.57	+/- 0.13
Fe	45.78	+/- 0.29	28.08	+/- 0.18
Cu	6.26	+/- 0.24	3.38	+/- 0.13
Total	100.00		100.00	



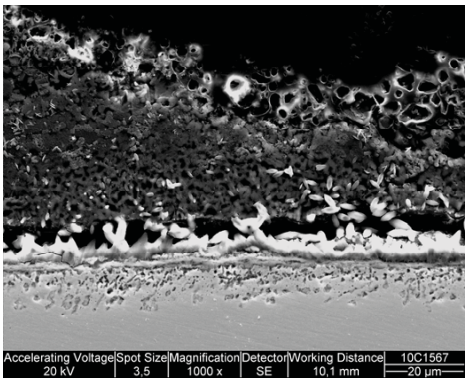
:

SAN 28, Leeward-side, (”down”, 232 degrees)

T_{mean} 544°C, T_{max} 595°C

Quantitative Results for: S2-1, analysis 68
Deposit (Fig. 1567, 315-degrees, ”Down”, 2µm dense oxide, internal attack 10 µm)

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	41.21	+/- 0.73	53.72	+/- 0.96
Na	33.54	+/- 0.17	30.43	+/- 0.15
Mg	0.38	+/- 0.04	0.33	+/- 0.03
S	21.05	+/- 0.11	13.70	+/- 0.07
K	2.28	+/- 0.03	1.21	+/- 0.02
Cr	1.11	+/- 0.05	0.44	+/- 0.02
Mn	0.18	+/- 0.06	0.07	+/- 0.02
Fe	0.25	+/- 0.06	0.09	+/- 0.02
Total	100.00		100.00	



No Cl found in deposit analysis made at a proximate location

Quantitative Results for: S2-1, analysis 66
Deposit (232-degrees, Windward ”down”, metal loss ~ 0.1 mm)

Element	Weight %	Weight % Error	Atom %	Atom % Error
O	40.52	+/- 0.89	53.81	+/- 1.18
Na	29.38	+/- 0.16	27.15	+/- 0.14
S	23.72	+/- 0.13	15.72	+/- 0.08
Cl	0.61	+/- 0.03	0.36	+/- 0.02
K	4.39	+/- 0.05	2.39	+/- 0.03
Cr	1.21	+/- 0.10	0.50	+/- 0.04
Fe	0.18	+/- 0.06	0.07	+/- 0.02
Total	100.00		100.00	

Results of ESEM imaging: total metal loss

Table: Total metal losses) at various positions estimated for various material samples exposed in Probe 2 for 600 h.*

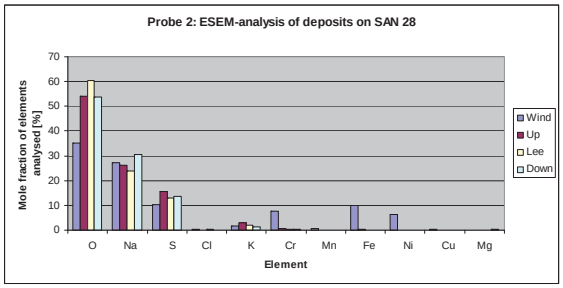
Material	Lee	Up	Down	Wind	Mean
	[mm]	[mm]	[mm]	[mm]	[mm]
SAN28	0.11	0.04	0.01	0.01	0.043
HR11N	0.08	0.05	0.01	0.025	0.041
Super 625	0.015	0.025	0.005	0.05	0.024
SAN 69	0.05	0.06	0.04	0.05	0.05
AISI 310	0.04	0.09	0.005	0.03	0.041
347H	0.05	0.08	0.02	0.1	0.061
Mean	0.06	0.06	0.01	0.04	0.043

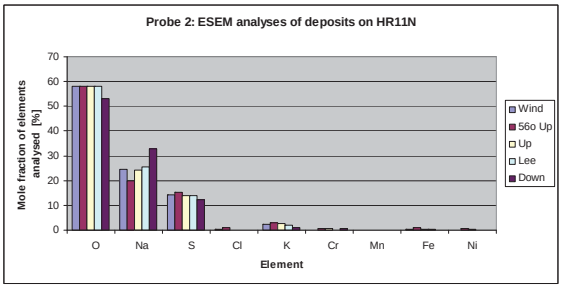
**)Total metal loss corresponds to the sum of internal attack (de-alloying, internal oxidation and/or sulphidation) and oxide scale measured under ESEM.*

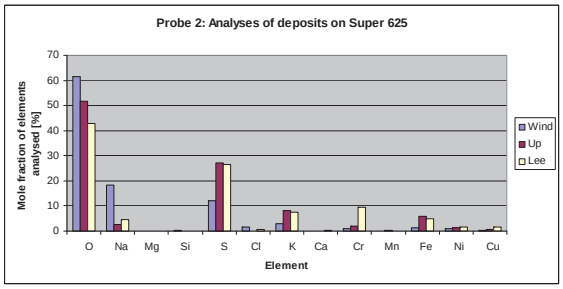
ESEM characterisation of the deposits found on the six material samples exposed in Probe 2

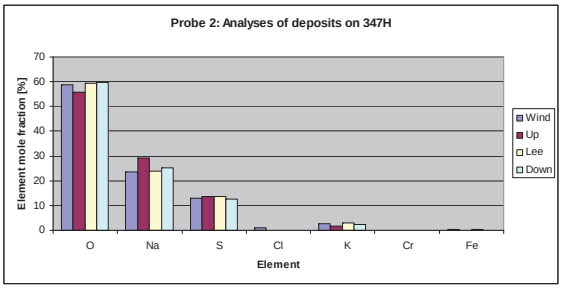
- In the areal analyses of deposits, oxygen, sodium, and sulphur, lesser, lesser, variable amounts of potassium, and some small amounts of chloride (range from < 0.1 wt-% Cl to about 1 wt-% Cl) and some of chromium, iron and nickel was found.
- In the case of high nickel alloys point analyses indicated that the mass fraction of chlorine in metal-near deposits/corrosion products may locally rise up to 10 or 25 wt-% Cl. (Generalized note: The low vapour pressure of $NiCl_2$ favours molten transition metal chloride mixture phases instead of chloride evaporation.)
- Carbon, even if indicated in the raw data, was purposely omitted from the calculated quantitative analysis. As discussed in more detail elsewhere, significant amounts of carbonate may have been actually present in the deposits.

Probe 2: ESEM analyses of deposit cross sections (areal analyses, carbon omitted)

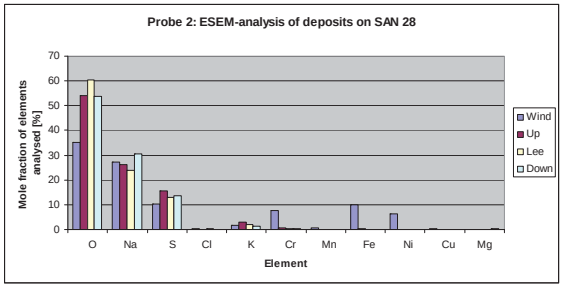


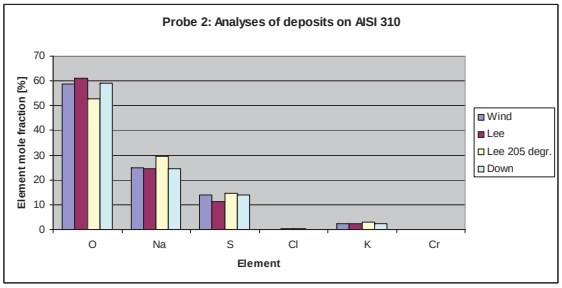


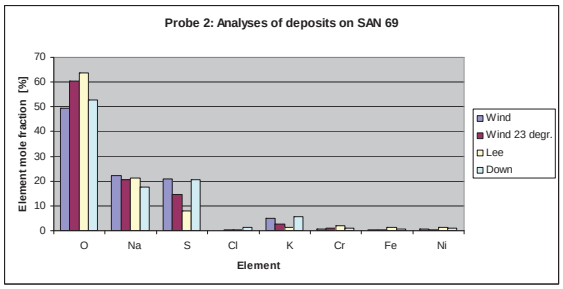


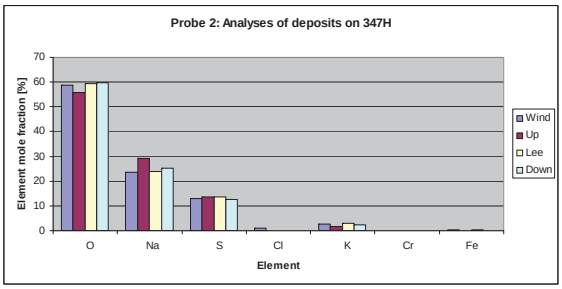


Probe 2: ESEM analyses of deposit cross sections (areal analyses, carbon omitted)





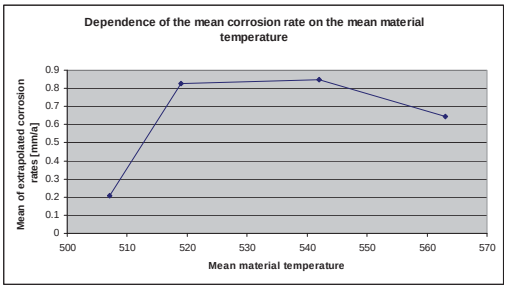




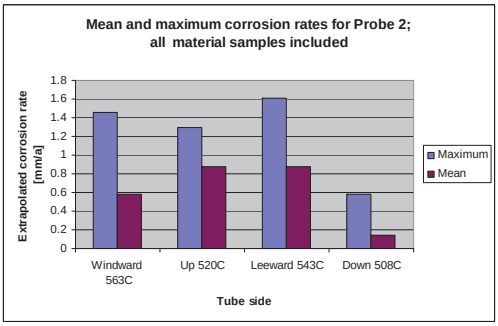
Discussion

- Temperature dependence of the corrosion rate
- Materials ranking according to mean and maximum corrosion rates; effect of alloying highly with chromium?
- Comparison of the results with available full-scale material exposure data
- The role of carbonate in the deposits? Equilibrium calculations modeling chemical interactions amongst superheater deposits of Joutseno RB-type and materials tested; prediction model for long-term behavior?
- Materials ranking ?

Temperature dependence of the corrosion rate

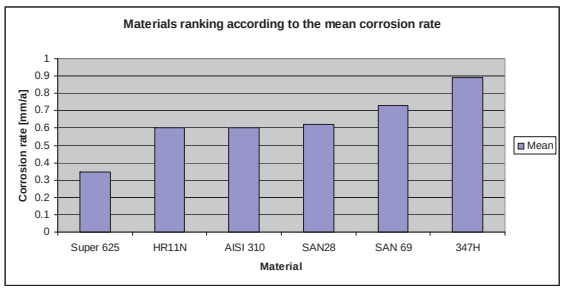


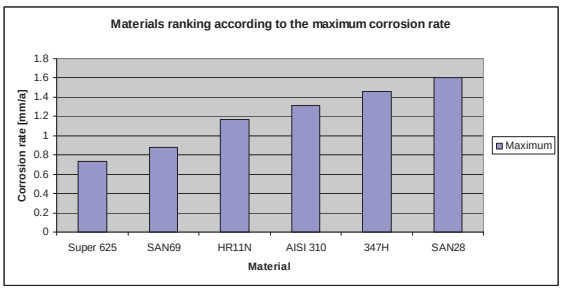
The mean of extrapolated metal loss rates dependend step-wise on the mean material temperature.

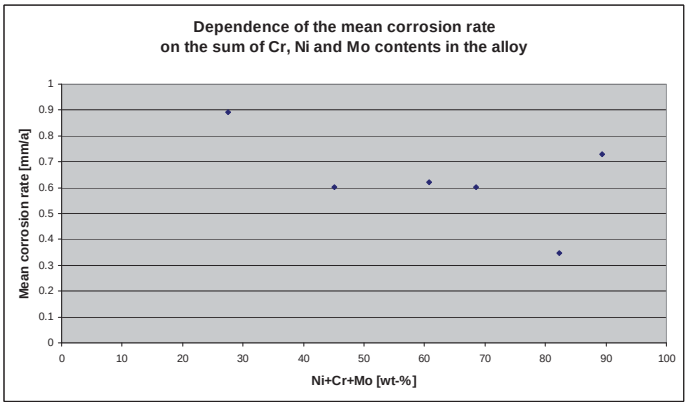


Maximum metal loss rate may be unacceptably high even at the lower end of the material temperature range in this study

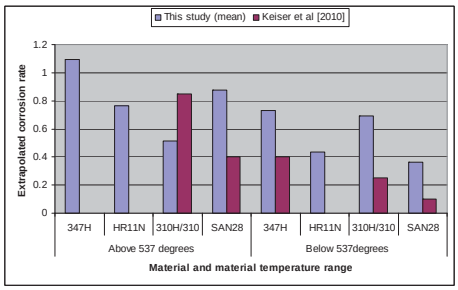
Schematic presentations of materials ranking based on the metal loss observed expressed in units [mm/a]. (Note that the test time is 600 h).

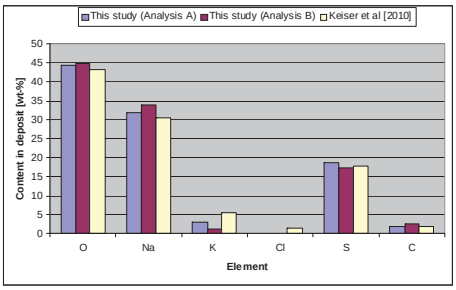






Comparison to recent full scale material exposure data in this study (600 h) and in the study of Keiser et al 2010 (1000 h)





Extrapolated corrosion rate for the same type high chromium alloys materials is found to be lower after the exposure time of 1000 h (Keiser et al (2010) as compared to that of 600 h (this study).

Related deposit chemistries are shown as well. The values of carbon content referred to have been estimated by stoichiometry. First melting temperature (FMT) value were calculated for comparative using FactSage 6.1 in both cases:

Analysis A; FMT ~ 560°C
Analysis B; FMT ~ 580°C
Keiser et al (2010); FMT ~ 537°C (as re-calculated using FactSage 6.1)

The role of carbonate in the deposits?

Under alkali sulfate-alkali chloride-alkali carbonate melt exposures heavy material wastage is observed for highly with chromium alloyed steels an alloys at locations proximate to the melt-air interface, where oxygen potential is high favoring basic fluxing of chromium and iron[1,2].

Rate of (localized) metal loss of high-chromium steels and alloys may then reach, or even exceed, corrosion rate of low alloy and lower grade stainless steels[1,2]. In the presence of KCl and CO_2 the role of chloride rich melts as compared to that of chloride evaporation and/or “active oxidation” is emphasized in the corrosion mechanism[3].

Type 625 nickel alloys, and certain austenitic stainless steels alloyed highly with chromium but moderately with nickel seem to perform best[2].

Carbonate content of deposits in Joutseno boiler superheater area has been investigated in the past[4,5]. These works are recommended for use in further evaluations of the present study.

Ref. 1: Superheater Tube Corrosion in Changing Operation Conditions of Recovery Boilers, Martti Mäkipää, Maria Oksa and Lasse Koivisto, Paper NACE 01424-01-T-5H.

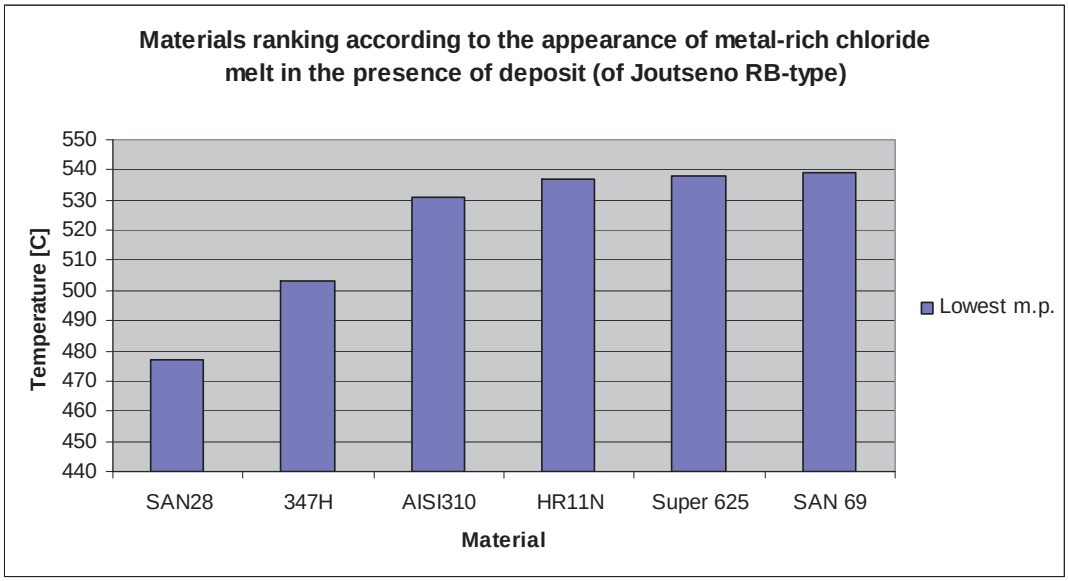
Ref. 2: M. Mäkipää, David J. Baxter, S. Sroda, M. Oksa, Laboratory Testing for Evaluation of Steels and Alloys Used in Superheater Area of Boilers for Biomass-Based Fuels, Journal Materials Science Forum (Volumes 461 - 464), Volume High Temperature Corrosion and Protection of Materials 6, Pages 989-998

Ref. 3: David Baxter, Thomas Malkow and Martti Makipää, The Effect of Salt Composition on the Chlorine Corrosion of Low Alloy Steels, Paper Number 01186, CORROSION 2001, March 11 - 16, 2001 , Houston, Tx, NACE International 2001.

Ref. 4. Wm. James. Frederick Jr., Esa K. Vakkilainen, Sintering and Structure Development in Alkali Metal Salt Deposits Formed in Kraft Recovery Boilers, Energy & Fuels 2003, 17, 1501-1509

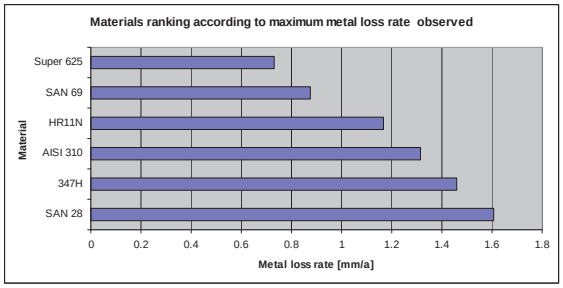
Ref. 5: Wm. James. Frederick Jr., Esa K. Vakkilainen, The Conditions for Boiler Bank Plugging by Submicrometer Sodium Salt (Fume) Particles in Kraft Recovery Boilers, Energy & Fuels 2004, 18, 795-803

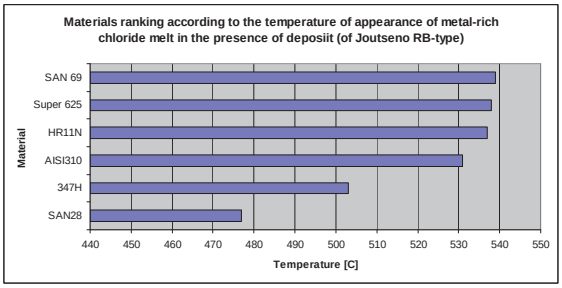
Material ranking according to FactSage 6.1 predictions; Exposure to a BLRB SH-deposit with ~ 0.5 % chloride, and carbonate



*) Lowest m.p. refers to that of transition metal-rich corrosion products as calculated. Melting relationships of the deposit itself are irrelevant here.

Material arranged in the ranking order where the role of pitting resistance is emphasized





Corrosion mechanistic considerations

Laboratory corrosion test atmosphere of ambient air can be considered as preliminary relevant for the case of high-solids firing of soft wood where SO_2 content of flue gases before ESP of less than 1 ppm have been reported.

Pitting resistance of various high-chromium alloys (e.g., Super 625, SAN 28, AC66) is rather good when exposed to alkali sulphate-alkali chloride melt in laboratory under an air atmosphere. In short term (65 h) alkali sulfate – chloride - carbonate melt exposures applying half-immersed specimens made of steels mentioned above enhanced localised corrosion was observed post-exposure at locations proximate to the melt-air interface. In that location a thin molten salt film present and continuously replenished from the melt pool. The oxygen potential of the molten salt film is obviously high favouring basic fluxing of chromium and iron.

Rate of localized metal loss of high-chromium steels and alloys may then reach, or even exceed, corrosion rate of low alloy and lower grade stainless steels. In the presence of KCl and CO_2 the role of chloride rich melts as compared to that of active oxidation is emphasized in the corrosion mechanism.

Then, type 625 nickel alloys, and certain austenitic stainless steels alloyed highly with chromium but moderately with nickel seem to perform best. The role of molybdenum (and that of niobium) in the type 625 alloys is considered, preliminary, as beneficial but as intrinsic very complex at the same time.

Corrosion mechanistic considerations (continued)

An interesting result of equilibrium calculations performed was that any chlorine that is present at low partial pressures of both chlorine and oxygen is apt to retain in the metal preferably as $CrCl_2$ with extremely low vapour pressure*). Important amounts of gaseous nickel chloride $NiCl_2(g)$ and that of gaseous copper species $(CuCl)_3(g)$ in particular were predicted to be present even the conditions mentioned above.

Copper originating from the corroding alloy itself (as SAN 28) or from external sources (liquor, soot blowing steam, corroding materials) may in theory be involved in transport of chlorine species within the corrosion scale and subscale volumes of the corroding high-chromium, high-nickel alloys. Analytical data for Super 625 and SAN 69 specimens exposed in this study indicate that some copper contamination had occurred; copper contamination during specimen handling and preparation is a possible but highly accidental source of copper.

*)Volatile ternary Cr-O-Cl species are known to exist but their role in the chlorine transport within the metal or in the oxide scale is not well understood. (See for more details: G. Fraissler et al. / Chemical Engineering and Processing 48 (2009) 152–164

Summary and conclusions

Full scale material exposures were carried out in Joutseno RB by September-October 2010. 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 and 570 ^{o}C. The boiler operated at 80% dry solids firing mode using softwood liquor with some 0.1 chlorine as fuel.

-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 performed 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).

Summary and conclusions (continued)

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 ^{o}C, peaking for short time up to 590^{o}C.

Taking in regard the temperature sensitivity of the corrosion phenomena in question and the statistical nature of the extent of localised corrosion in place and time 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 open literature

Concluding remarks and recommendations for future work

The basic view taken in this study emphasizing the role of formation of complex melts with contents of various transition metals is basically in accordance with the recent understanding of alkali chloride-alkali sulphate enhanced deposit corrosion of high-alloy steels in boilers.

Localised corrosion attack of highly with chromium alloyed materials is considered, however, to be of statistical nature in the recovery boiler superheater area. Long-term progression of localised corrosion of high-alloy steels and nickel alloys can not be evaluated based on known behaviour of low-alloy steels and lower grade austenitic steels showing enhanced scale growth mainly.

In continued tests efforts to apply statistical methods developed for predictive analysis of hot corrosion test data on larger data sets of corrosion depth measuring values are strongly recommended.

VTT creates business from technology

References

CORROSION TESTS OF SUPERHEATER MATERIALS IN REDUCING CONDITIONS

Dorota Bankiewicz
Åbo Akademi

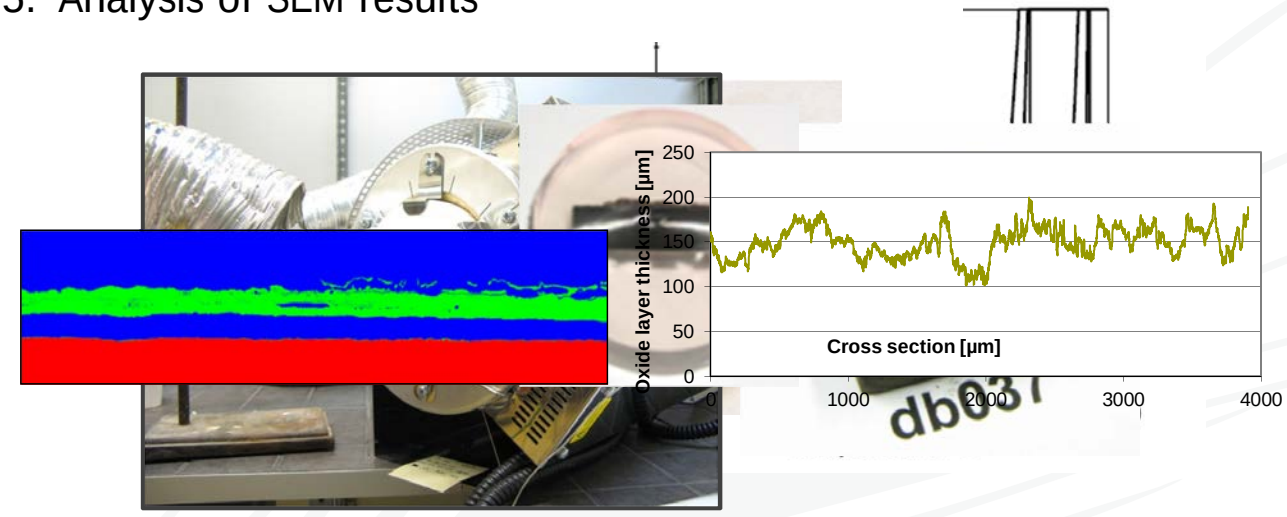
Corrosion tests of superheater materials in reducing conditions – Part 2

Skyrec seminar

October 21st, 2011

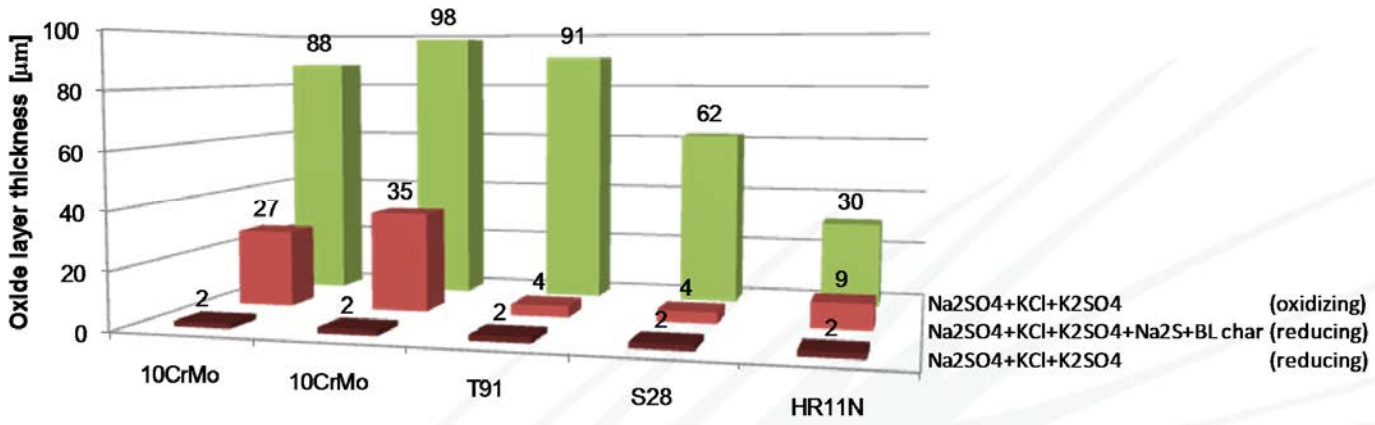
Laboratory method for HT corrosion tests

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



Skyrec II - trial test

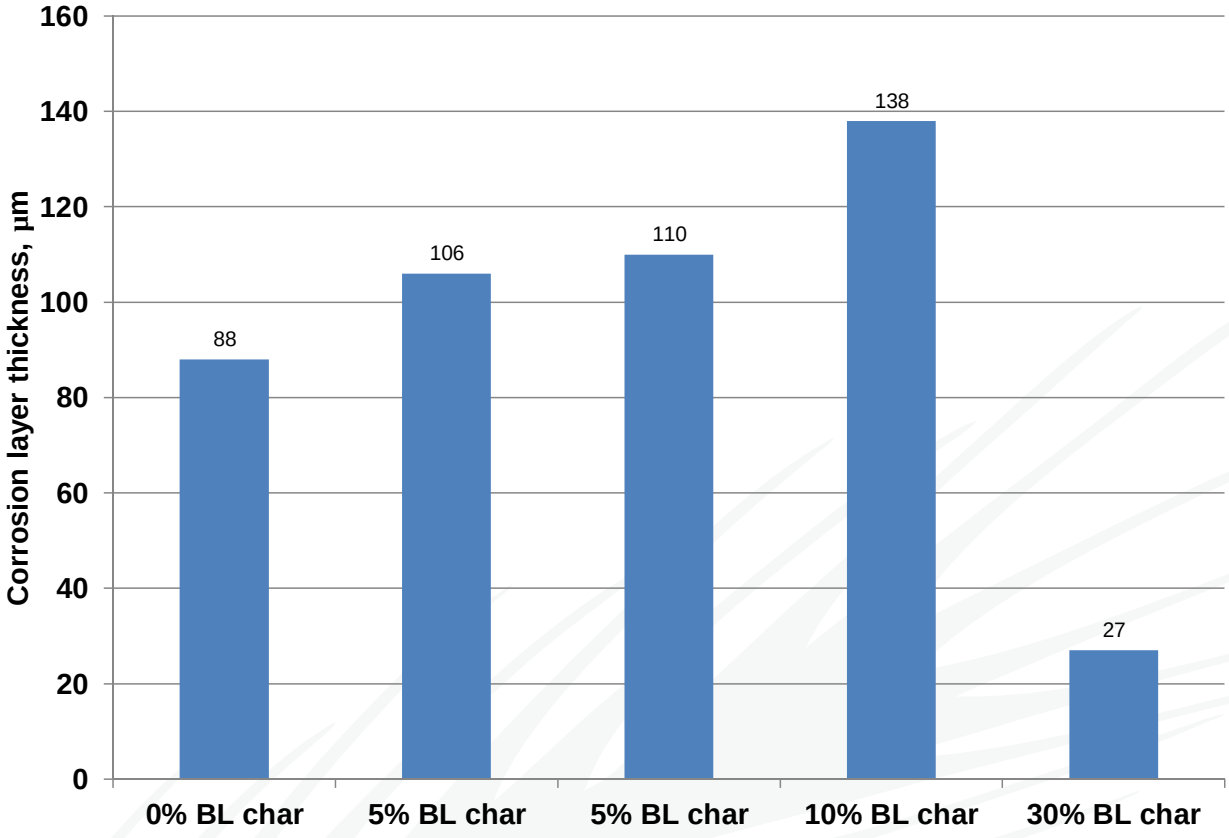
Reducing vs. Oxidising conditions at 550 °C.
Exposures with Salt 10 and 10r50+BL char



Skyrec II - Testing of wood char effect

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

Results - BL char effect - oxide layer thickness



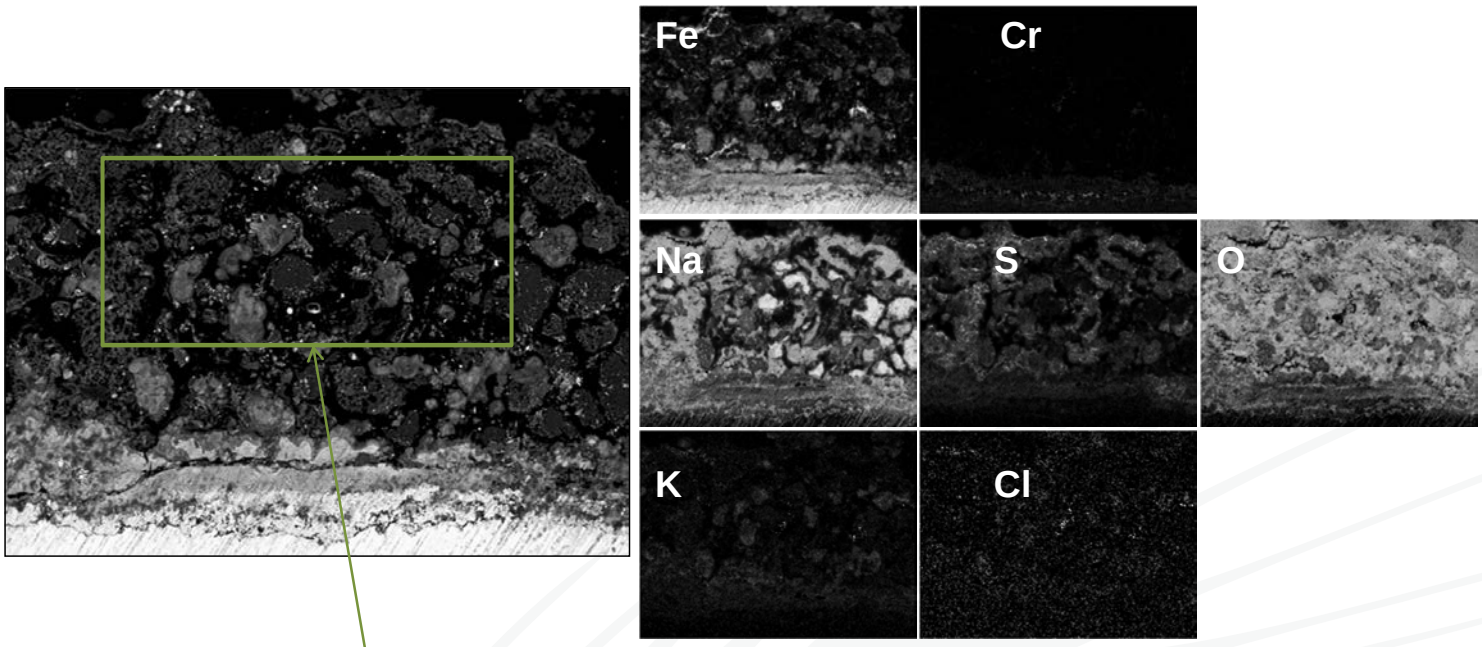
Results – digital pics of the samples after test

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

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

Results – x-ray maps

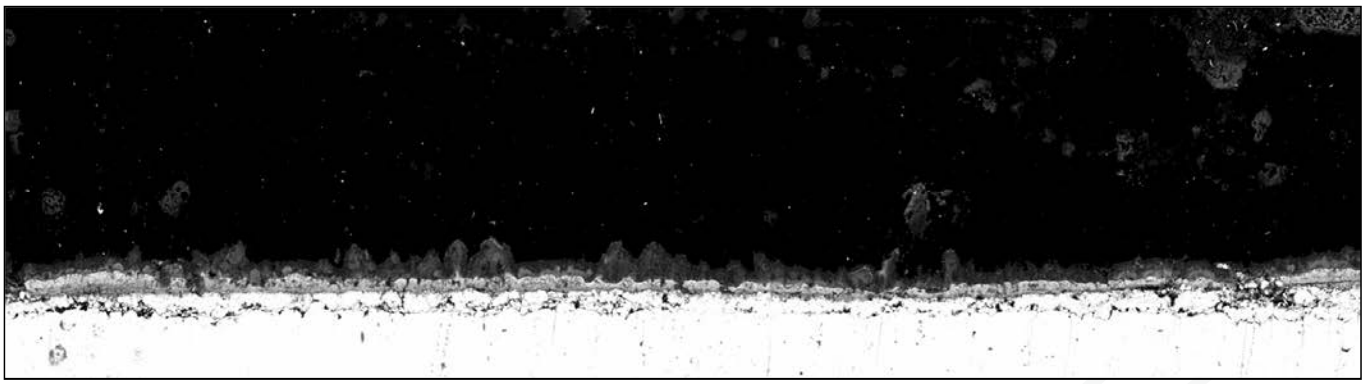
(Na_2S+Na_2SO_4+K_2SO_4+KCl, no BL char)

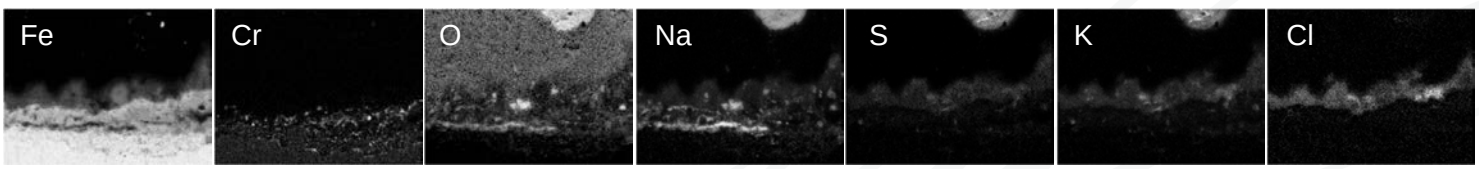


"Separate" salt particles

Results – x-ray maps

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





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

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

Remarks

- in all cases the corrosion rates were significant

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

- BL char additions (5 and 10%) caused increased material degradation with visibly consumed material. Internal oxide + material degradation occurred
(outer corrosion products > higher oxidation thanks to the oxygen from the BL char?!)

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

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

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

I. When no BL char was added, the separate salt particles were visible
II. When BL char was added, the salt looked more molten like on the SEM pics, also the salt cake was heavily swollen and brittle after taking out from the oven, surrounded with black soot like powder

Skyrec II - project

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

Temperatures: 525°C, 565°C

Salts:

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

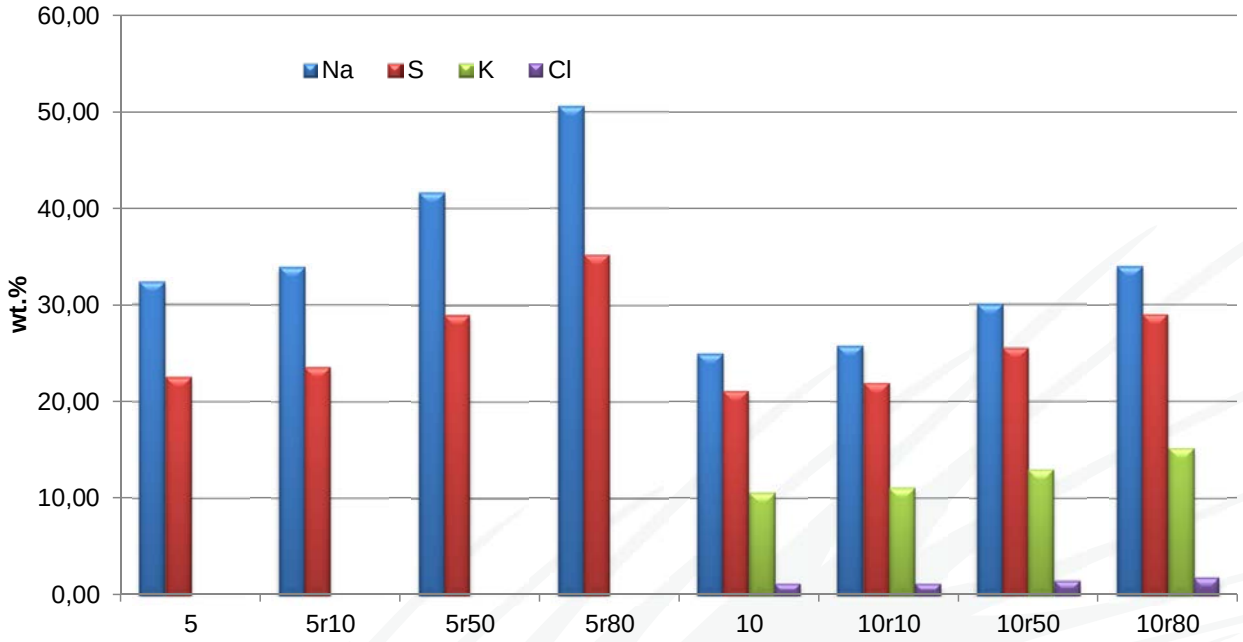
* very little melt, a lot starts to form at 730 °C

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

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

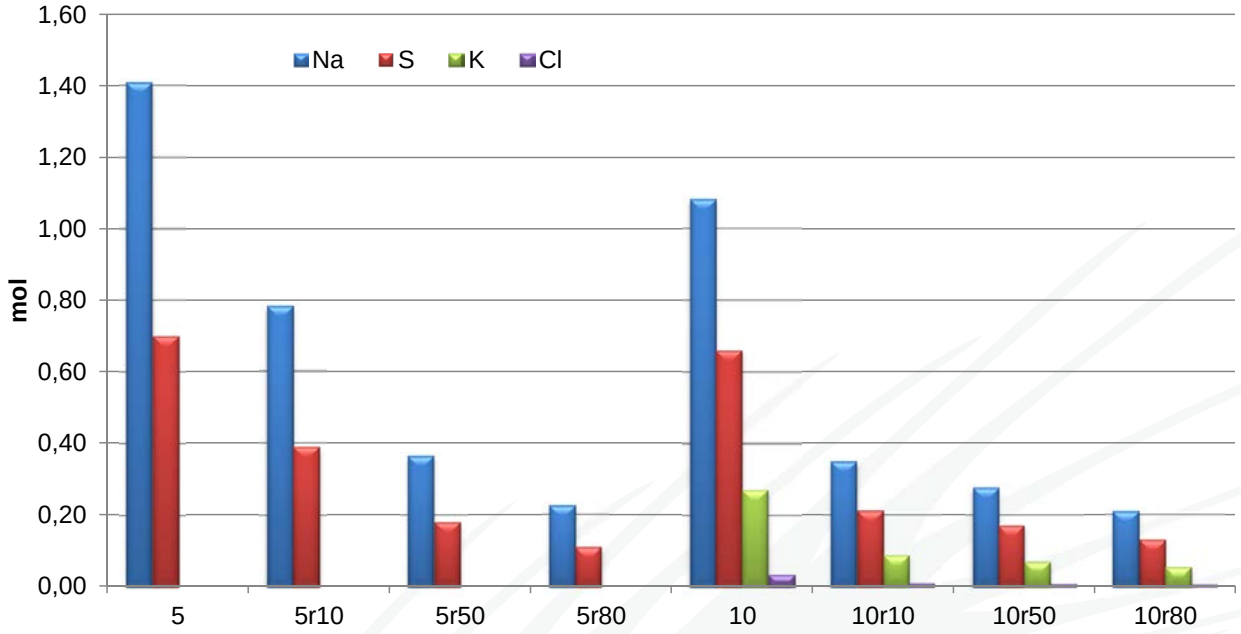
Skyrec II - project

Elemental composition of salts, wt%

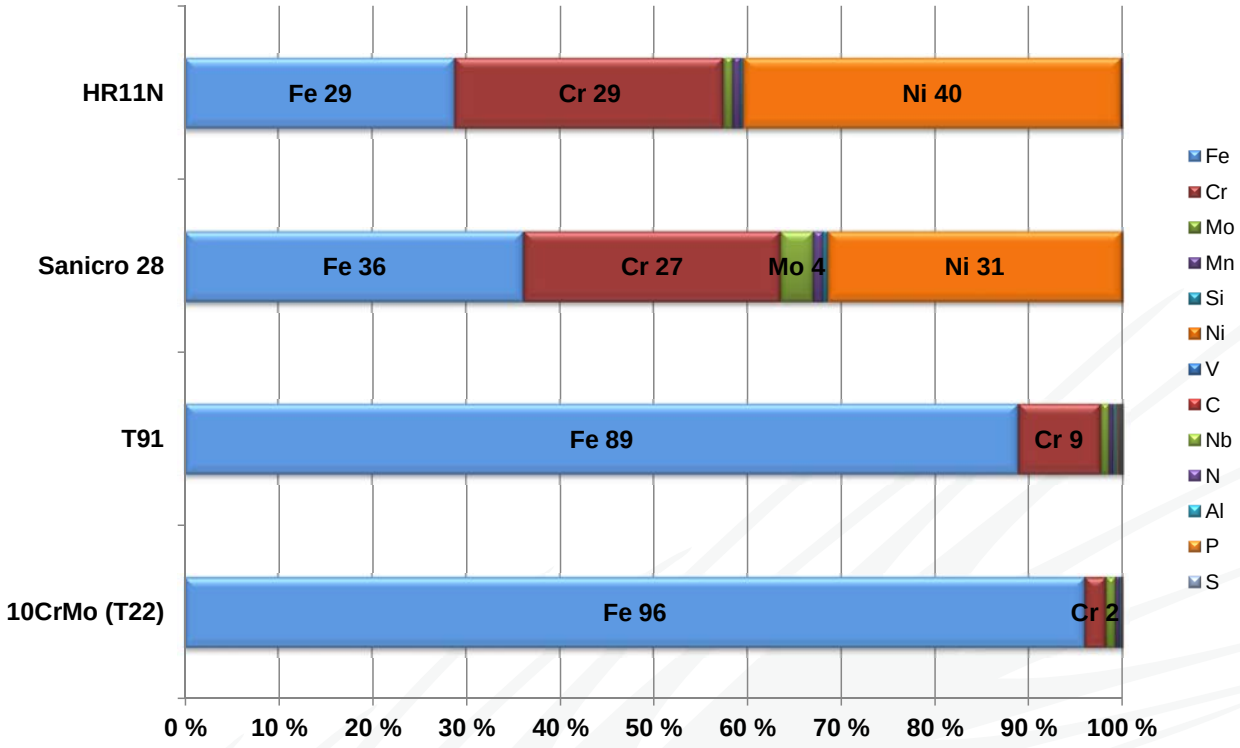


Skyrec II - project

Elemental composition of salts, mol



Skyrec II - tested steels composition



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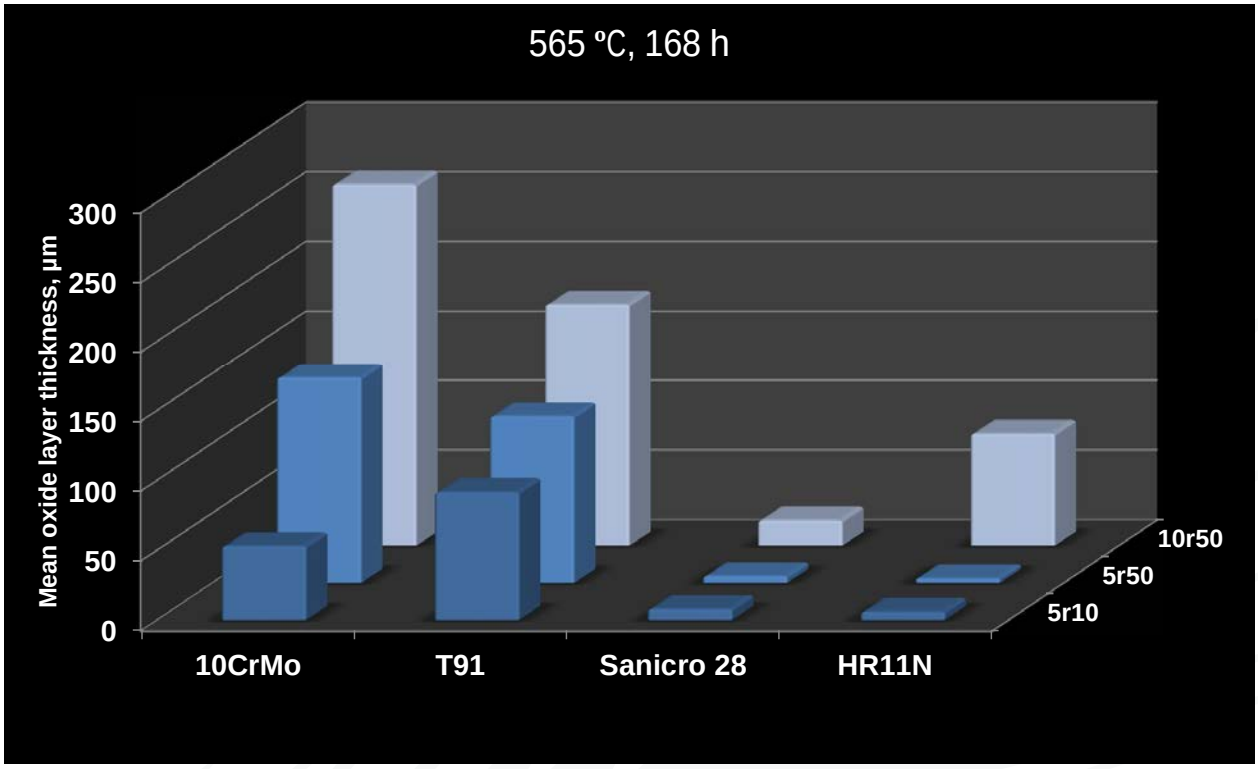
Skyrec II – tests matrix

Temperatures	Steel	Salt	Status
525, 565	10CrMo	10r10	SEM
525, 565	T91	10r10	SEM
525, 565	10CrMo	10r10	SEM
525, 565	HR11N	10r10	SEM
525, 565	Sanicro 28	10r10	SEM
565	T91	10r50	174
565	HR11N	10r50	38
565	Sanicro 28	10r50	18
565	10CrMo	10r50	260
565	HR11N	10r50	80
525, 565	T91	10r80	October
525, 565	10CrMo	10r80	October
525, 565	Sanicro 28	10r80	October
525, 565	HR11N	10r80	October
525, 565	T91	10r80	October
565	10CrMo	5r10	15
565	T91	5r10	92
565	Sanicro 28	5r10	8
565	HR11N	5r10	6
565	10CrMo	5r10	53
565	HR11N	5r50	2
565	10CrMo	5r50	147
565	Sanicro 28	5r50	5
565	HR11N	5r50	3
565	T91	5r50	119
525, 565	T91	5r80	SEM
525, 565	10CrMo	5r80	SEM
525, 565	Sanicro 28	5r80	SEM
525, 565	HR11N	5r80	SEM
525, 565	T91	5r80	SEM

Skyrec II – results



Skyrec II – remarks

- First results show that increase of Na_2S in the salt mixture (5r10 vs. 5r50) enhances slightly corrosion on low alloy steels (10CrMo and T91)
- S28 and HR11N showed quite good resistance to 5r10 and 5r50 salts – corrosion < 10 µm
- Low alloy materials (10CrMo and T91) corroded badly in all three tested salts: 5r10, 5r50 and 10r50
- Salt 10r50 caused extreme degradation to 10CrMo, T91 and HR11N
- S28 performed best out of tested materials (relatively low corrosion with 5r salts but already significant with 10r50)
- Salt 10r50 caused swelling of the salts+corrosion products
- Swelling was not observed after exposures with 5r salts

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FINNISH RECOVERY BOILER COMMITTEE

Skyrec II – To be done

- Corrosion tests to be finished (3 more runs)
- Detailed analysis of all the samples from Skyrec II
- Final reporting (date to be decided)

Skyrec II – To be done

- Corrosion tests to be finished (4 more runs)
- Detailed analysis of all the samples from Skyrec II
- Final reporting (date to be decided)
- Corroded samples will be reported in a printed version of the report
- All the results (SEM/EDX) will be delivered on the CD

FIELD TESTS OF FURNACE MATERIALS

Timo Karjunen, Boildec Oy
Pekka Pohjanne, VTT

IN SITU TESTING OF COMPOUND MATERIALS

Timo Karjunen
Boildec Oy

Pekka Pohjanne
VTT Technical Research Centre of Finland

Background

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

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. 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.

Experimental setup

The test materials are carbon steel (P265GH), 3R12 (AISI 304L), 3RE28 (AISI 310S), 3XRE28 (Sanicro 4C54), Sanicro 28, Sanicro 38 (mod. UNSN08825), Sanicro 67 (Alloy 690), HR11N and Super 625. Material compositions are shown in Figure 1.

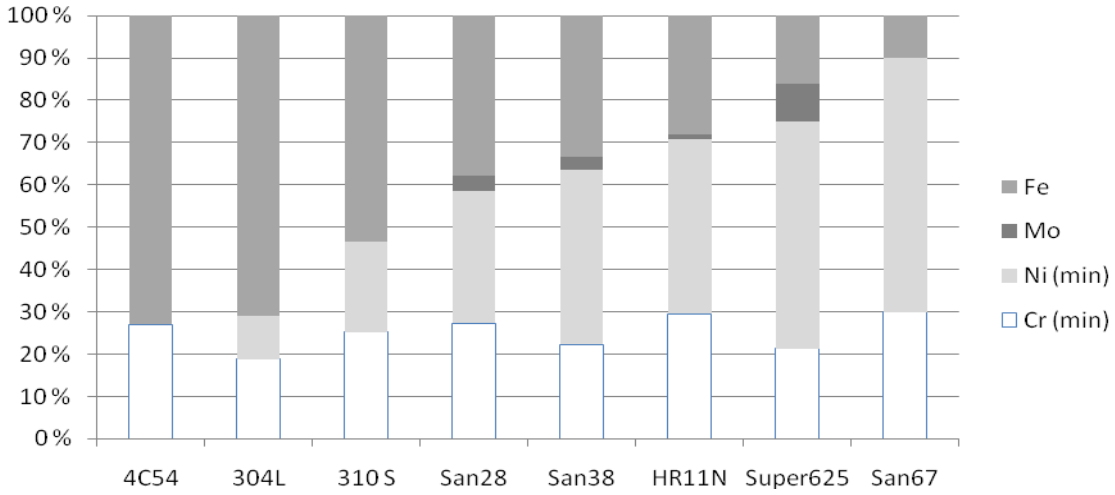


Figure 1. Chemical compostion of the materials used in the experiments.

The test matrix is shown in Table 1. 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). 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 the materials were tested in as received condition, whereas in tests No.4 and 5 the outer and inner surfaces were machined and hand grinded/polished prior assembly to the probe. The grinding and polishing was performed to improve the accuracy of wall thickness measurements. For metallographic analysis one cross-section per sample (Z = 15 mm) was prepared and analysed with scanning electron microscope (SEM). The composition of oxide layers was determined with energy dispersive spectroscopy (EDS).

Table 1. Test matrix.

No	Materials	Duration
1	3R12(AISI 304L), 3RE28(AISI 310S), Sanicro28, Sanicro38	1000 h
2	3R12(AISI 304L), 3XRE28, HR11N, Sanicro67,	1000 h
3	3R12(AISI 304L), HR11N, Sanicro38, Super625	1000 h
4	3R12(AISI 304L), carbon steel (P265GH), Sanicro67, Super625	2700 h
5	3R12(AISI 304L), Sanicro28, HR11N, Sanicro38	> 1000 h (on-going)

The experimental setup consists of natural circulation circuit (Figure 2), which includes steam generator in which the test materials are placed (Figure 3). 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 2. Experimental setup before installation into liquor gun opening.

The circuit is instrumented with measurements for heat transfer liquid and test sample inner surface temperatures and system pressure. Typical measurement data are shown in Figure 4.

Also test material temperatures in centre point were measured, and the initial plan was to use these measurements for tuning the circuit pressure so that the material temperatures would be the same in every test. For that reason, the circuit pressure was lowered in the tests 2 and 3 from that of test 1. However, this resulted in a 35 – 50 % reduction on 3R12 (AISI 304L) corrosion rate, and thus it was concluded that the thermocouples

placed inside test materials did not provide accurate information. Consequently, subsequent tests were decided to carry out at the same pressure as test No 1.

Figure 3. Steam generator front wall with tested materials

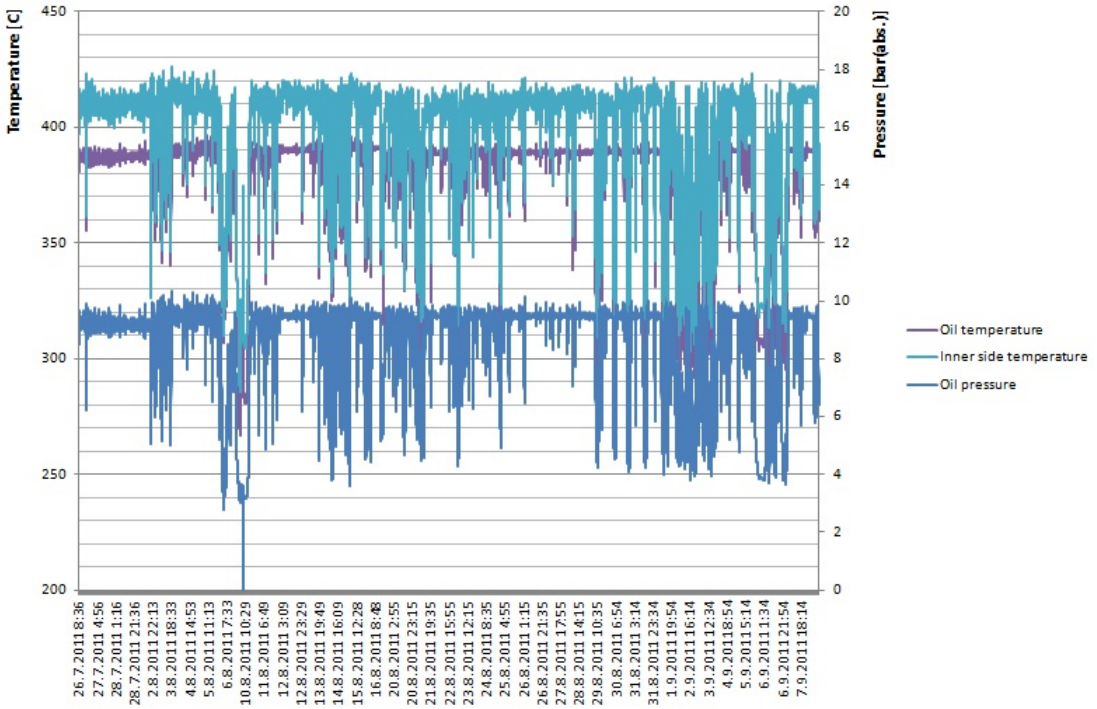


Figure 4. Test material inner surface temperature, heat transfer liquid temperature and circuit pressure in on-going test no 5.

Typically circuit pressure was close to set point more than 80 % of the time. However, there were frequent fluctuations in pressure, and hence in temperatures, downwards. These were caused by temporary showers of black liquor pouring on the steam generator placed in liquor gun opening.

Similar fluctuations have also been seen in the earlier experiments, and in some cases the steam generator was covered with black liquor acting as a heat sink so long that the circuit pressure dropped below atmospheric. Once black liquor shower ends and the steam generator is again exposed to high heat flux, heat transfer liquid at these low pressures may sometimes evaporate vigorously resulting in heat transfer crisis and, consequently, test material temperature surge. These surges are now eliminated by keeping the circuit pressurized by heating it with electrical heaters during the periods when circuit pressure is temporarily low.

Results and discussion

The test temperatures and durations of the probe tests No.1-4 are summarised in Table 2. The probes worked as planned, and the temperatures were quite stable throughout the tests, allowing comparison between the test periods.

*Table 2. T*est temperatures and durations

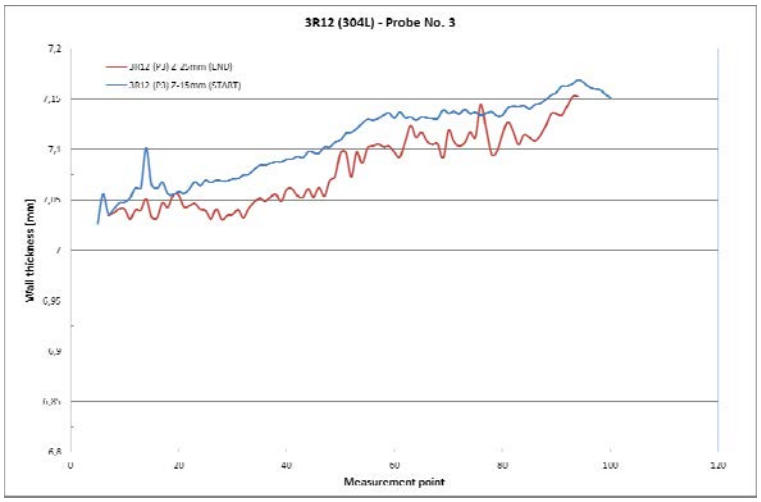
Test No	Test duration [h]		Effective temperature
	Total	Effective[A)]	
1	1006	906 (pressure over 9 bar)	ca. 440°C
2	1023	744 (pressure over 8 bar)	ca. 440°C
3	1250	750 (pressure over 7 bar)	ca. 430°C
4	2700	2154 (pressure over 9 bar)	ca. 440°C

[A)]Used in corrosion rate calculations

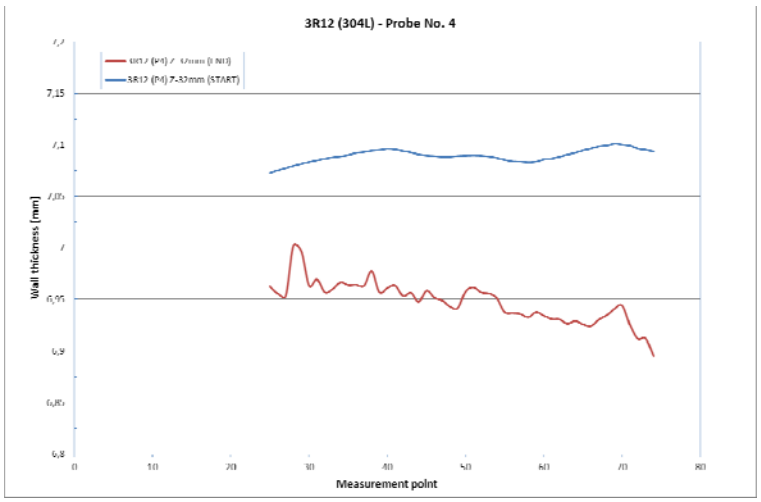
Examples from the wall thickness measurement results are shown in Figures 5 and 6. The measurement data from 3R12 (AISI 304L) sample, with as received surface, is more scattered than the data from specimen with polished surface. Polishing together with longer exposure time improves the accuracy, which is required when evaluating highly alloyed materials.

Figures 7 and 8 show the results of the corrosion rate calculations made on the basis of the wall thickness measurements. The average corrosion rates are calculated on the basis of average wall thickness loss at the specimen apex (ca. 35…50 points/30…45° angle at apex). The maximum corrosion rates are calculated from the wall thinning curved derived from the wall thickness measurements. 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 result, especially to the maximum corrosion rates calculated from the tests No. 1-3, where the materials were tested in as received condition.

Highest corrosion rates, ca. 4 mm/a, were measured for the carbon steel as expected. The traditional composite tube material 3R12 (AISI 304L) had the second highest corrosion rates, order of 0.5 mm/a. From the currently used alternative materials, Sanicro 38 performed somewhat better than the HR11N in the 1000 h tests. This is checked in the on-going long-term test No.5, where both materials are placed in the same probe. The 3RE28 (AISI 310S) and Sanicro 28, with high chromium content, performed at least as well as Sanicro 38 and HR11N. The Sanicro 28 is included in the last long-term test together with Sanicro 38 and HR11N, which will provide valuable comparable information from their performance. According to the wall thickness measurements the corrosion rate of the Sanicro 67 nickel base alloy is lowest from the studied alloys. The other nickel base alloy Super 625 has been behaved anomalously. Its resistance was good in the long term test No.4, whereas it suffered from intense corrosion in Test No.3, in which the temperature was the lowest.



a)



b)

Figure 5. Wall thickness profiles from 3R12(304L) specimens before and after exposure a) in as received condition (Probe No.3) and b) as polished (Probe No.4).

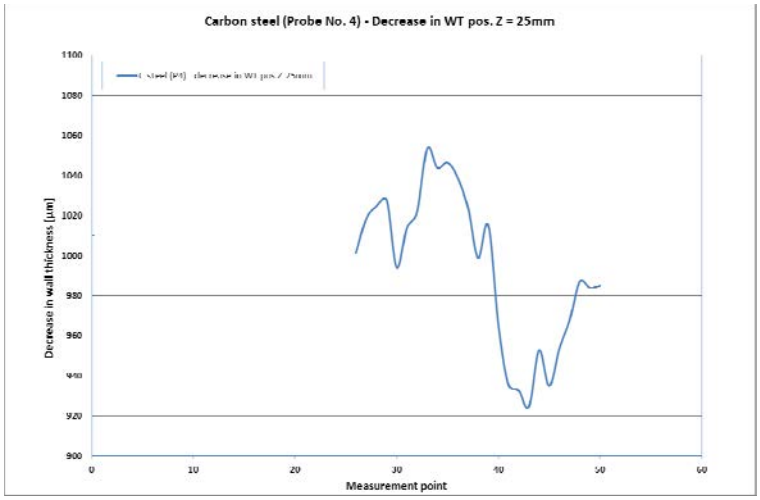
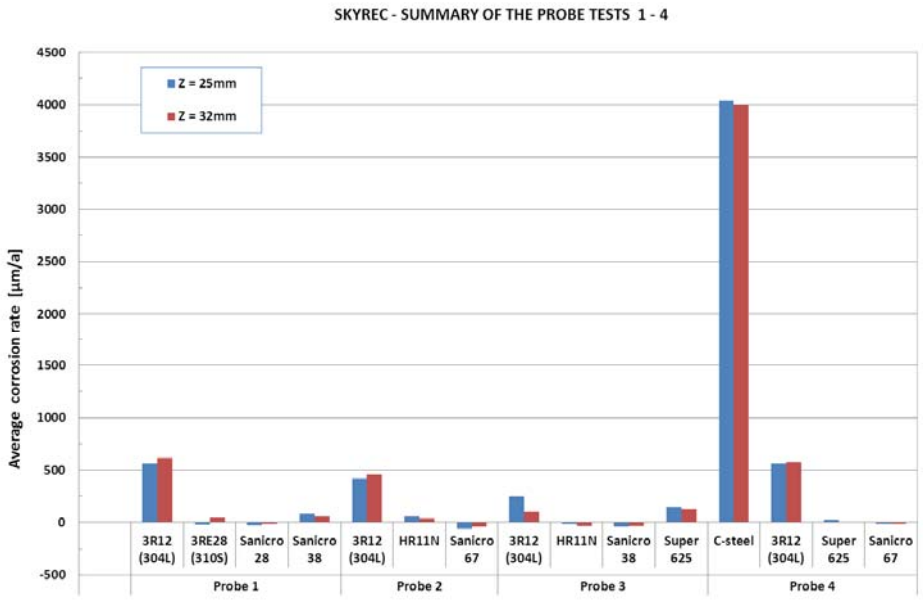
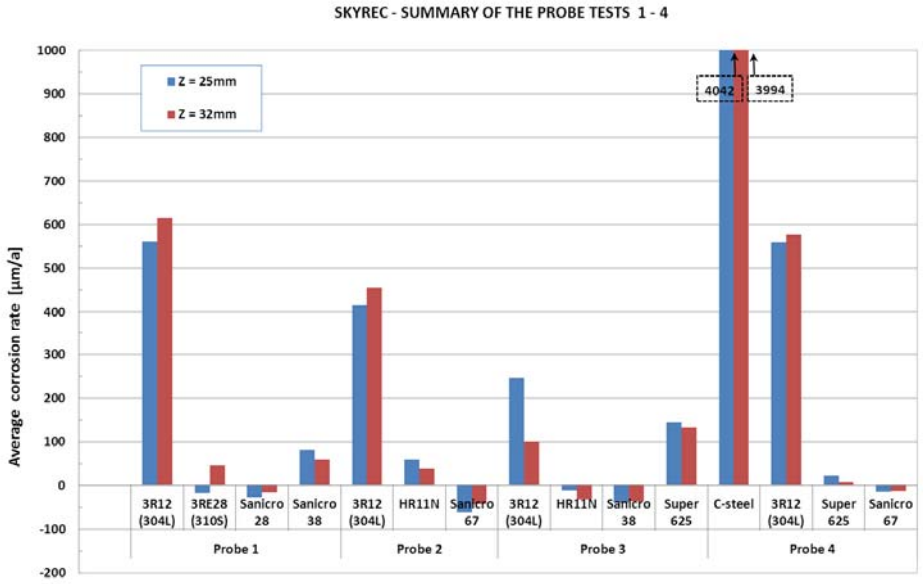


Figure 6. Wall thinning curve of the C-steel sample after 2700 h exposure (Probe 4). The data is derived from the wall thickness measurements performed before and after the exposure.

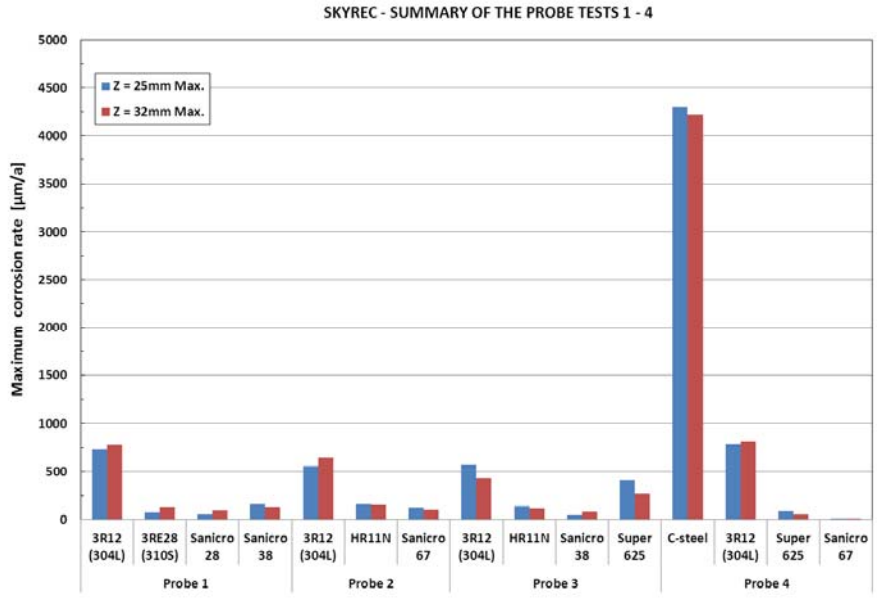


a)

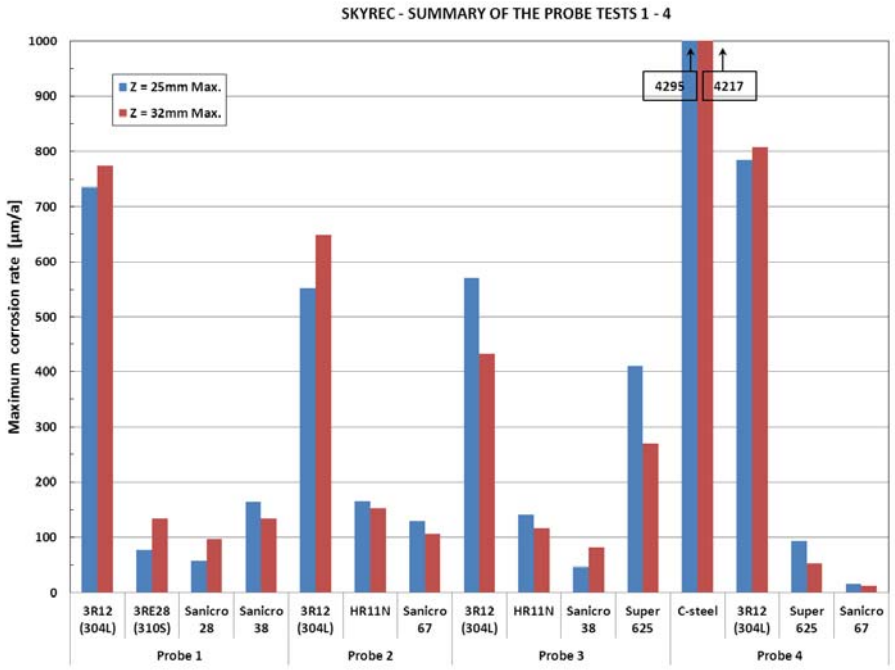


b)

Figure 7. a) Average corrosion rates of the test materials and b) close-up from the Fig. 7a.



a)

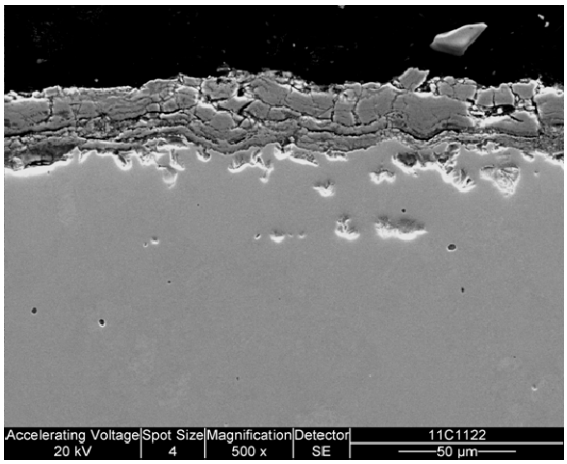


b)

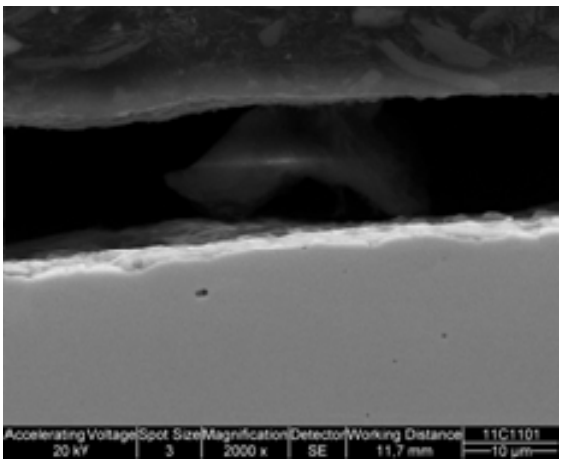
Figure 8. a) Maximum corrosion rates of the test materials and b) close-up from the Fig. 8a.

After the tests the samples were examined with SEM/EDS to determine the type of the corrosion attack and the composition of oxide layers and scales. SEM examination showed that all materials had suffered from general thinning. Examples from SEM investigation sand EDS analysis are shown in Figures 9 – 11. The carbon steel showed scale thickness of about 25 µm after 2700 h exposure and it contained equal amounts of oxygen and sulphur. The layers formed on stainless steels, high nickel and nickel base alloys were thin ca.5 µm, except on the Super 625 where ca. 10 µm thick peeling like scale was observed, Figure 11a.

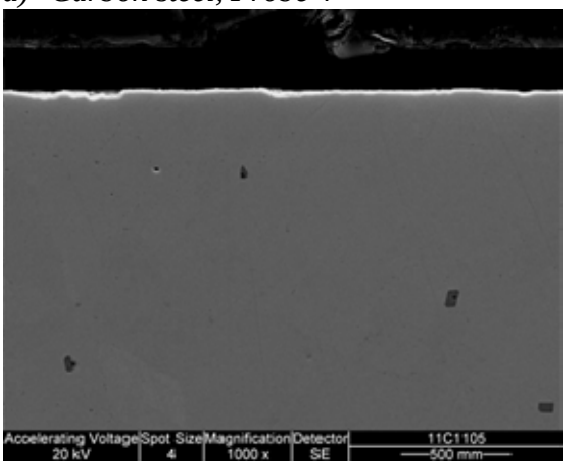
According to the first results the layers on 3R12 (AISI 304L), 3RE28 (AISI 310S), Sanicro 28 and Sanicro 38 (mod. UNSN08825) are depleted in iron and nickel and enriched in chromium. The layers on Sanicro 67 are depleted iron and nickel but no Cr enrichment was observed. The outermost layers on the HR11N and Super 625 are different; they are depleted in iron, nickel, molybdenum and chromium. Reference analysis made from unexposed reference samples showed that the depleted/enriched layers are formed during exposure and do not originate from the specimen manufacturing process. The EDS analysis will be continued in near future to obtain more results to verify the first observations.



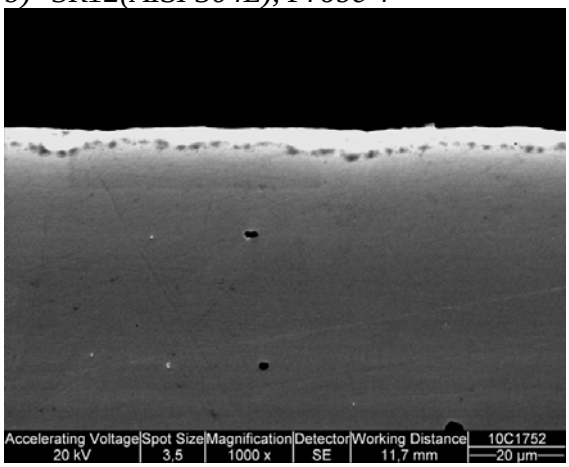
a) *Carbon steel, Probe 4*



b) *3R12(AISI 304L), Probe 4*

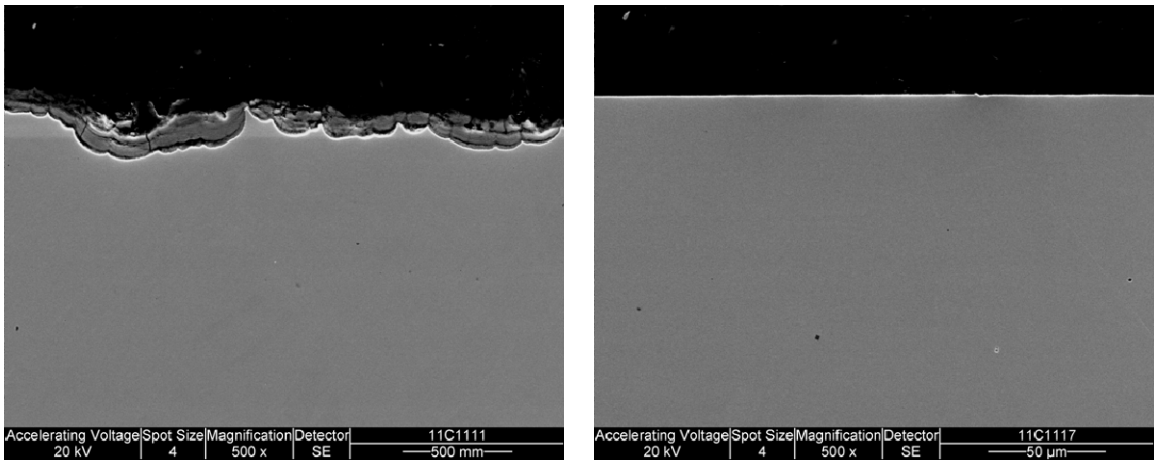


c) *Sanicro 67, Probe 4*



d) *Sanicro 38, Probe 3*

Figure 9. a) Uniform thinning and oxide layers formed on Carbon steel, b) and c) thinning and thin white continuous oxide layer on 3R12(AISI 304L) and Sanicro 67 after 2700 h exposure and c) on Sanicro 38 after 1250 h exposure..



a) Super 625, Probe 4 *b) Super 625, unexposed reference*

Figure 10. a) Uneven surface and oxide layers formed on Super 625 after 2700 h exposure and b) Unexposed Super 625 reference sample, where no compositional changes were observed on thin light outer layer.

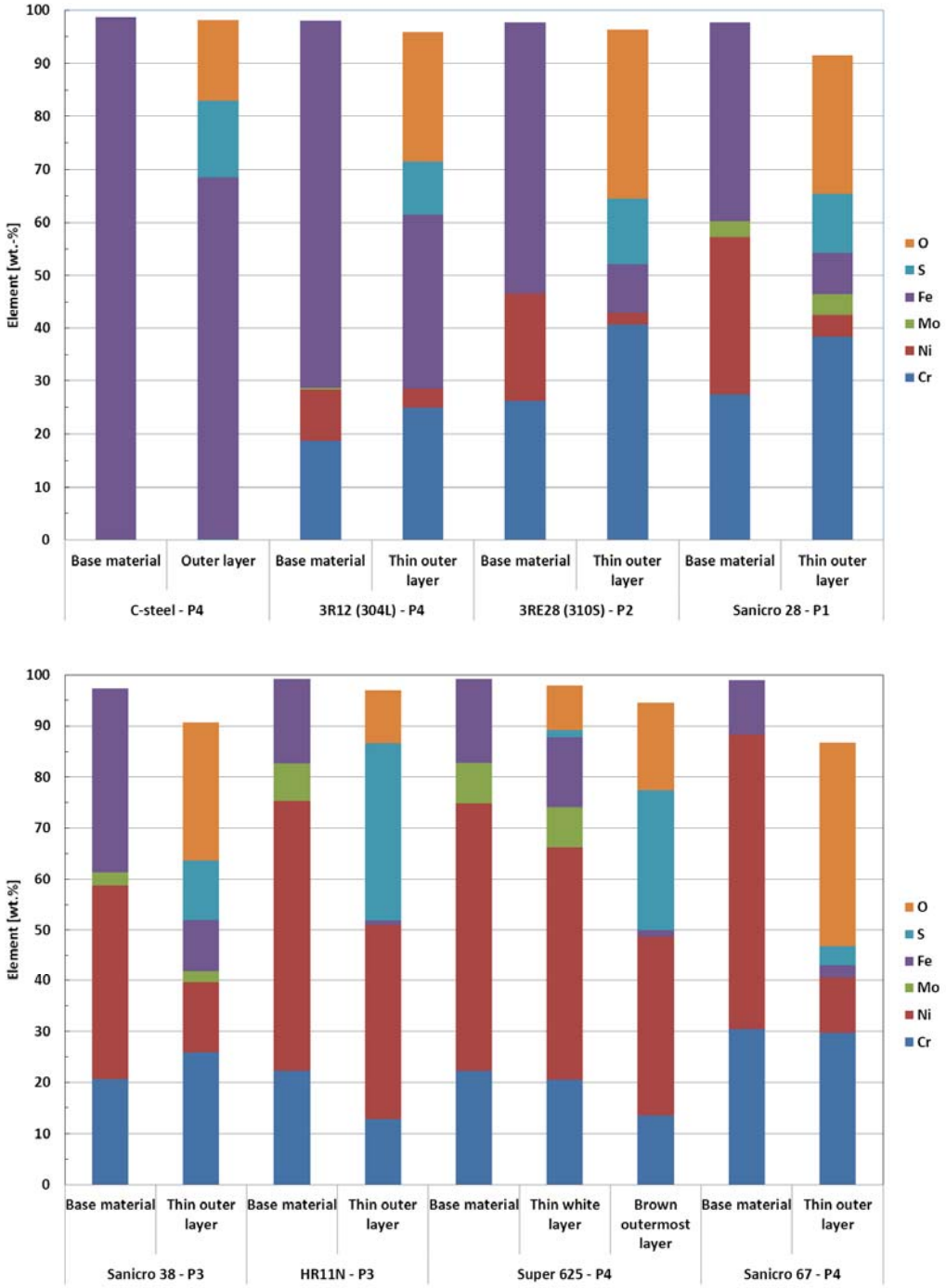


Figure 11. Examples of EDS analysis performed for the test materials after exposure. Note: Quantitative results, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

Conclusions

The study has shown that the probe consisting of a natural circulation circuit, with steam generator where the test materials are placed operates reliably in the demanding conditions existing in the recovery boiler lower furnace.

Results so far have shown that the carbon steel corrodes at extremely high rate (4 mm/a) at the temperature of 440 °C. Also the 3R12 (AISI 304L) composite tube material corrodes in such high rate (ca. 0.5 mm/a) that it can't be safely used in the lower furnace. The resistance of the Sanicro38 (mod. UNS N08825) and HR11N is about three times better than that of the3R12 (AISI 304L). The 3RE28 (AISI 310S) and Sanicro 28, have performed well, their resistance has been equal or even slightly better than that of the Sanicro 38 and HR11N in the short terms tests. The corrosion rate of the Sanicro 67 high chromium nickel base alloy is lowest from the studied alloys. The results of the Super 625 are contradicting, it suffered from intense corrosion in short term test but its' performance was good in the last long term test.

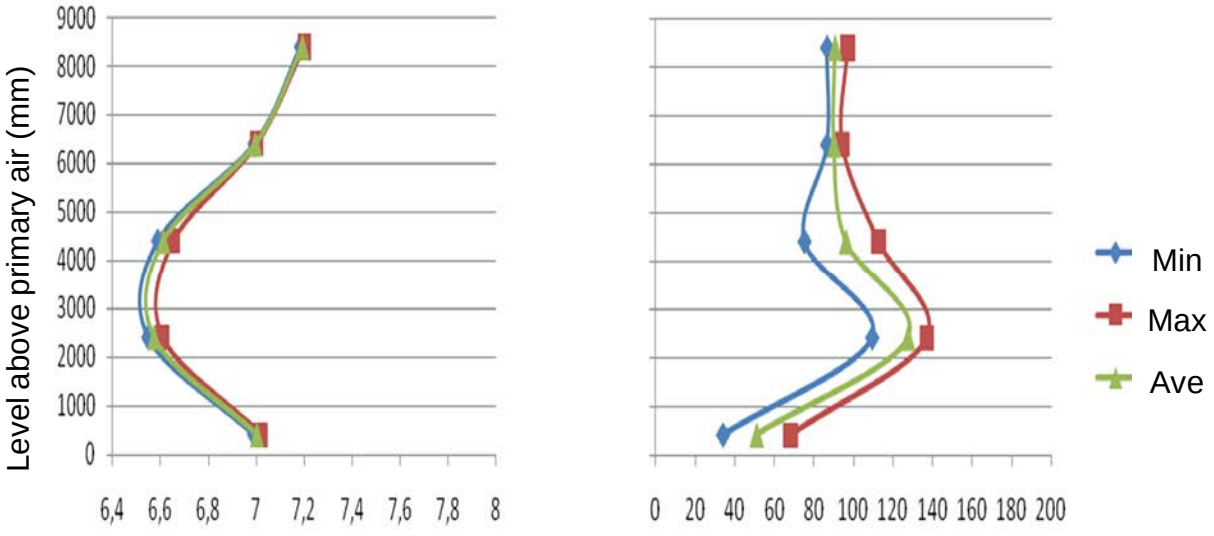
The results support the presumption that the conventional 3R12 (AISI 304L) composite tube material can't be safely used in the future high pressure recovery boilers, where material temperatures are expected to rise to level of 400…440 °C. If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers. The performance of the Sanicro 38 and HR11N was satisfactory in 1000 h tests, but their long term performance needs to be verified with longer tests, and preferably also at lower temperature (400 °C). The new material group which looks promising is the high chromium alloys 3RE28 (AISI 310S) and Sanicro 28, their long term performance should be verified in the future. In current tests the corrosion resistance of the Super 625 has been lower than that of the other highly alloyed materials, thus more and longer tests are needed to verify its performance.

FIELD TESTS OF FURNACE MATERIALS

SKYREC-SEMINAR 2011
Sokos Hotel Presidentti Oct. 20th, 2011

Timo Karjunen, Boildec Oy
Pekka Pohjanne, VTT

Cladding corrosion in current recovery boilers

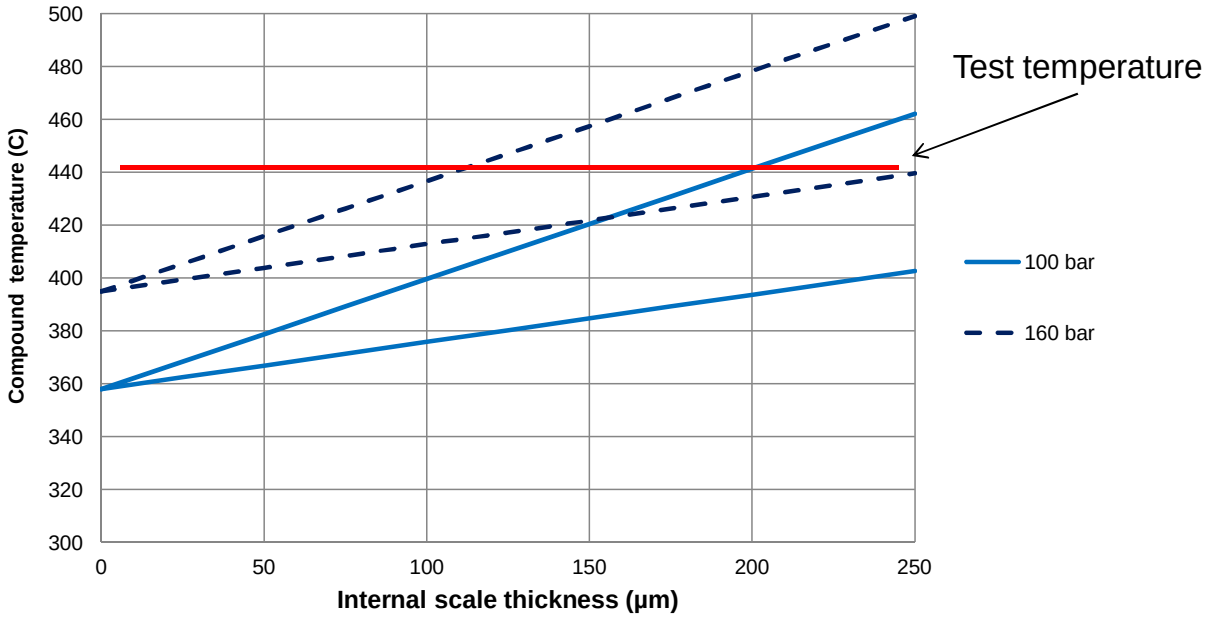


Wall thickness (mm)

Internal scale thickness (µm)

Cladding material 304L (3R12)

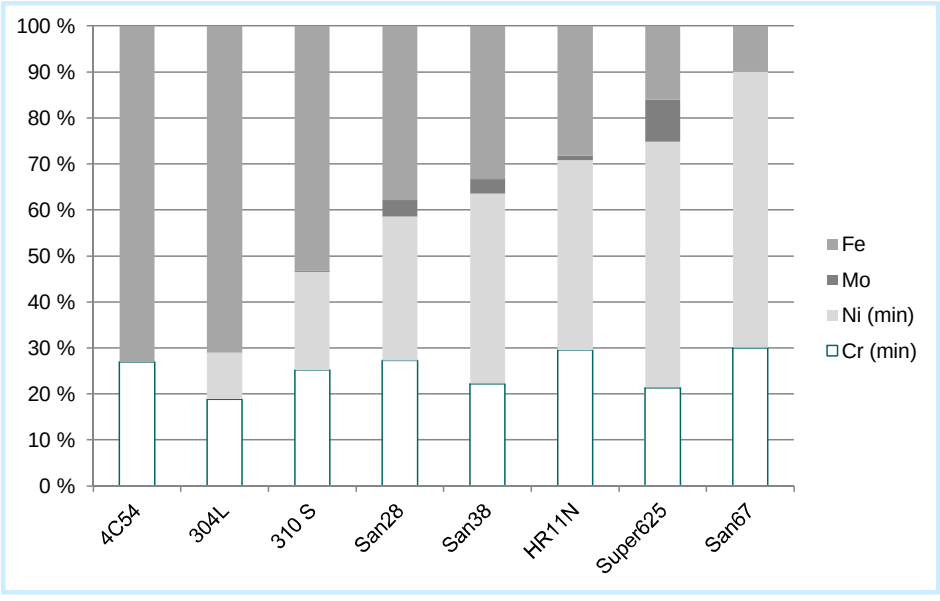
Wall tube cladding temperatures in current and high-pressure recovery boilers



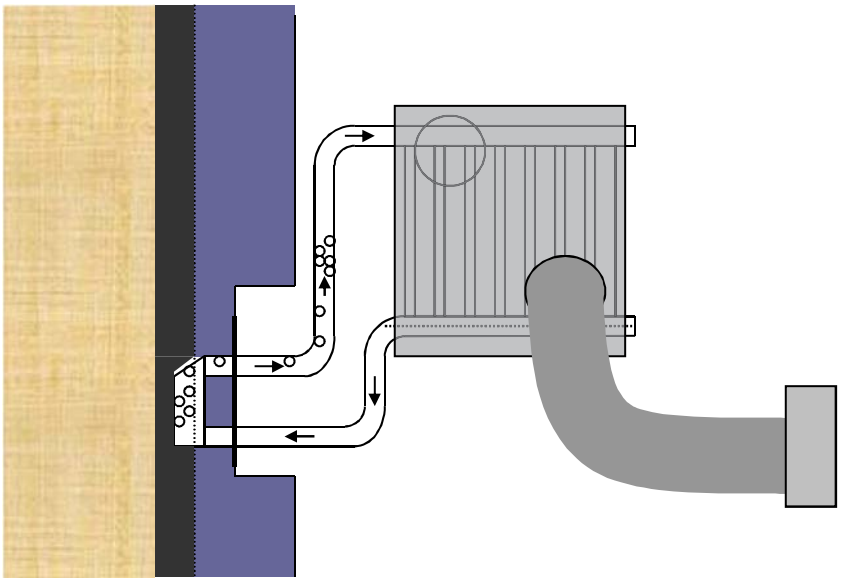
TEST MATERIALS

Selected by SKYREC Steering committee

- Carbon steel (P265GH), 3R12 (AISI 304L), 3RE28 (AISI 310S), 3XRE28 (Sanicro 4C54), Sanicro 28, Sanicro 38 (mod. UNSN08825), Sanicro 67 (Alloy 690), HR11N and Super 625.



PROBE & EXPERIMENTAL SETUP



- Natural circulation circuit, which includes steam generator containing the test materials, is placed in liquor gun opening
- Heat transfer liquid has the same saturation temperature at 6 bar as water at 170 bar (352°C). Test were carried out in 8,5 - 9,5 bar (saturation temperature 382 – 390°C)

PROBE & EXPERIMENTAL SETUP

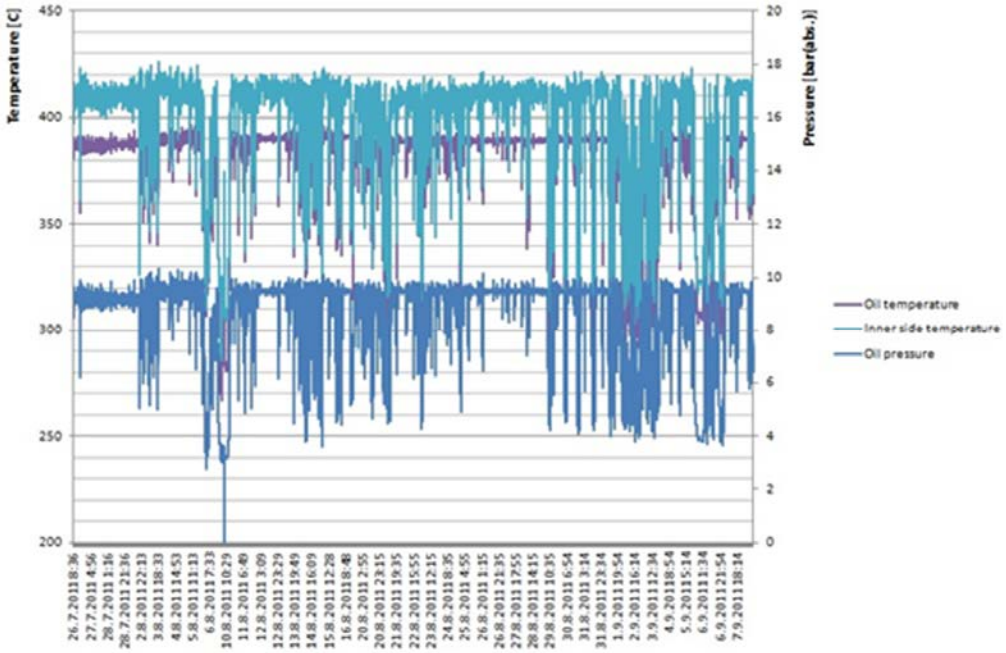
- Diphenyl oxide heat transfer liquid → Moderate pressure
- Air flow control to keep circuit pressure constant
- Electrical heaters to keep the circuit pressurized to avoid heat transfer crisis and test material temperature surges
- Measurements for heat transfer liquid and test sample inner surface temperatures and system pressure

Probe before installation into liquor gun opening (MB Joutseno)

TEST MATRIX

Test No.	Materials	Duration
1	3R12(AISI 304L), 3RE28(AISI 310S), Sanicro28, Sanicro38	1000 h
2	3R12(AISI 304L), 3XRE28, HR11N, Sanicro67,	1000 h
3	3R12(AISI 304L), HR11N, Sanicro38, Super625	1000 h
4	3R12(AISI 304L), carbon steel (P265GH), Sanicro67, Super625	2700 h
5	3R12(AISI 304L), Sanicro28, HR11N, Sanicro38	> 1000 h (on-going)

Temperature and circuit pressure in on-going test No. 5



✓ The probe has worked as planned - The temperatures are quite stable throughout the tests

TEST SUMMARY

Test No.	Test duration [h]		Effective temperature
	Total	Effective[A)]	
1	1006	906 (pressure over 9 bar)	ca. 440°C
2	1023	744 (pressure over 8 bar)	ca. 440°C
3	1250	750 (pressure over 7 bar)	ca. 430°C
4	2700	2154 (pressure over 9 bar)	ca. 440°C

[A)]Used in corrosion rate calculations

Results – Corrosion rates

Corrosion resistance evaluation – Procedures

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

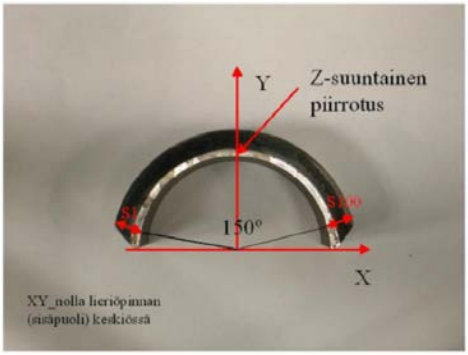
- Thickness profiles at a function of circumference from three locations (axial direction)
  → average & maximum WT loseses

B. Characterisation and corrosion mechanism

- SEM/EDS from metallographic cross sections after/before the profile measurements
- Few analysis also from unexposed reference samples

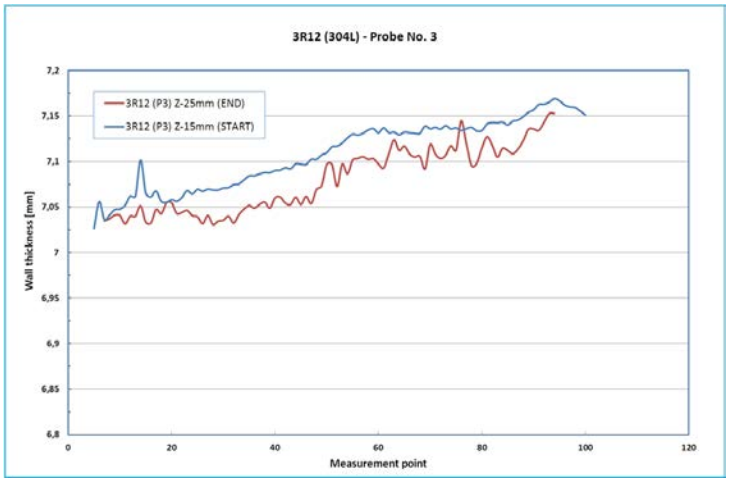
✓ Tests No.1…3 - Materials tested in as received condition

✓ Tests No.4 and 5 - The outer and inner surfaces machined and hand grinded/polished

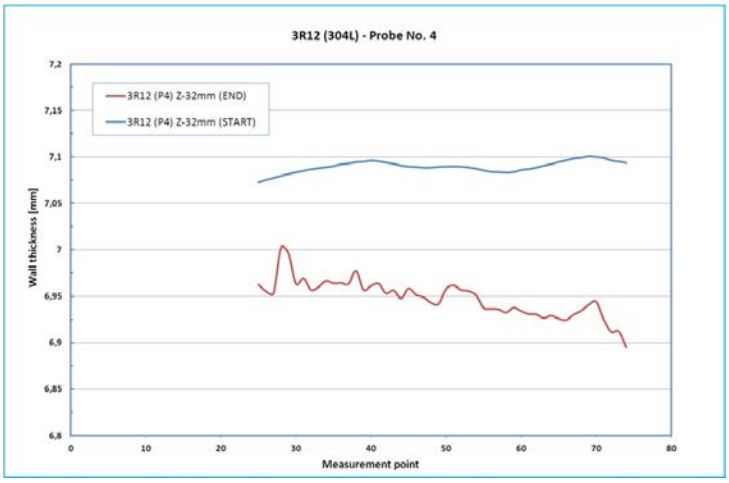


Measurements with coordinate measurement machine

Examples of WT profiles before and after the test

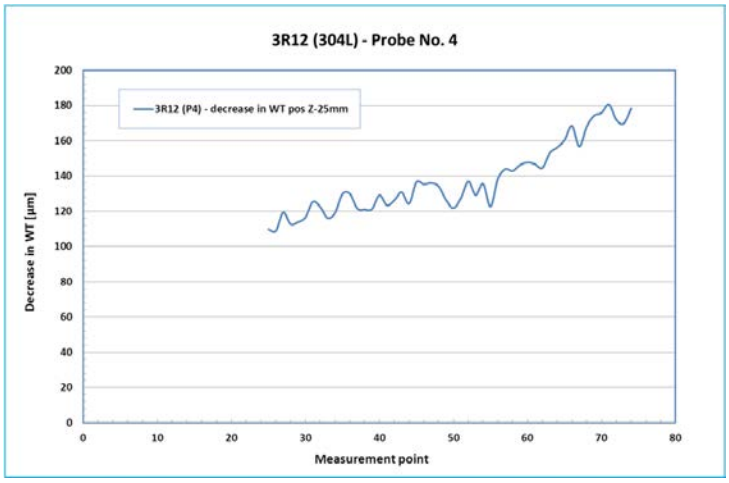


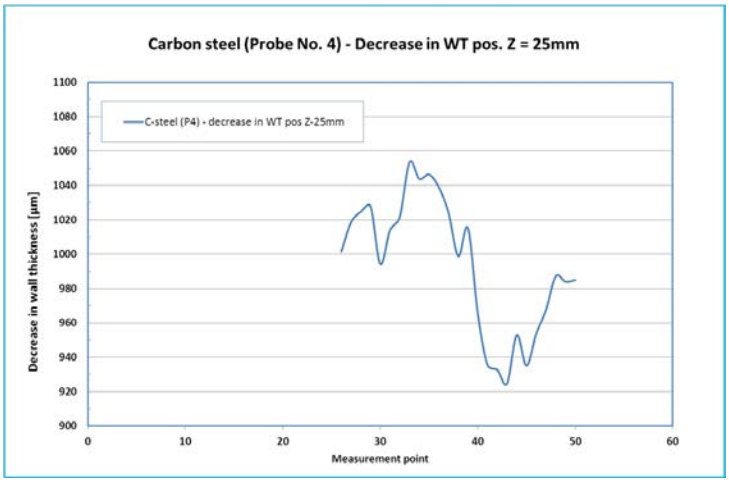
Tested in as received condition,
effective test duration 750 h & temperature 430°C



Outer and inner surfaces machined and hand polished,
effective test duration 2154 h & temperature 440°C

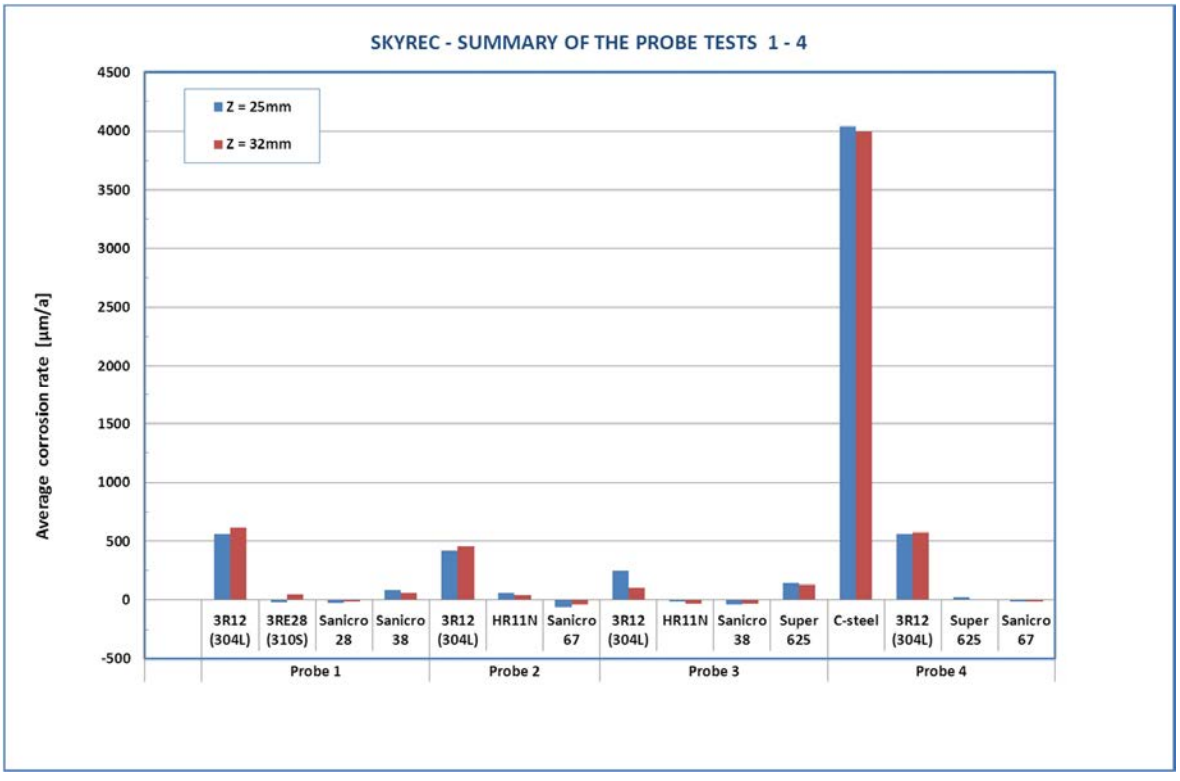
Examples WT thinning curves used for CR calculations



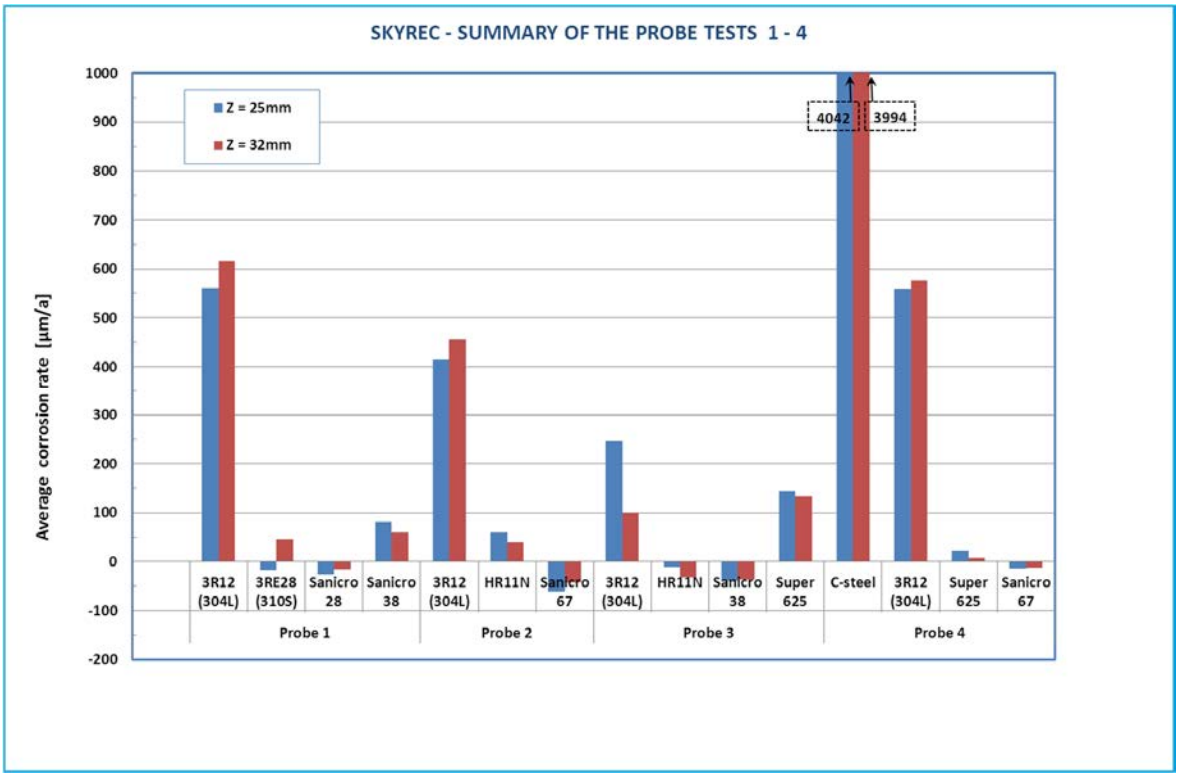


- ***Probe No. 4 – effective test duration 2154 h & temperature 440°C***

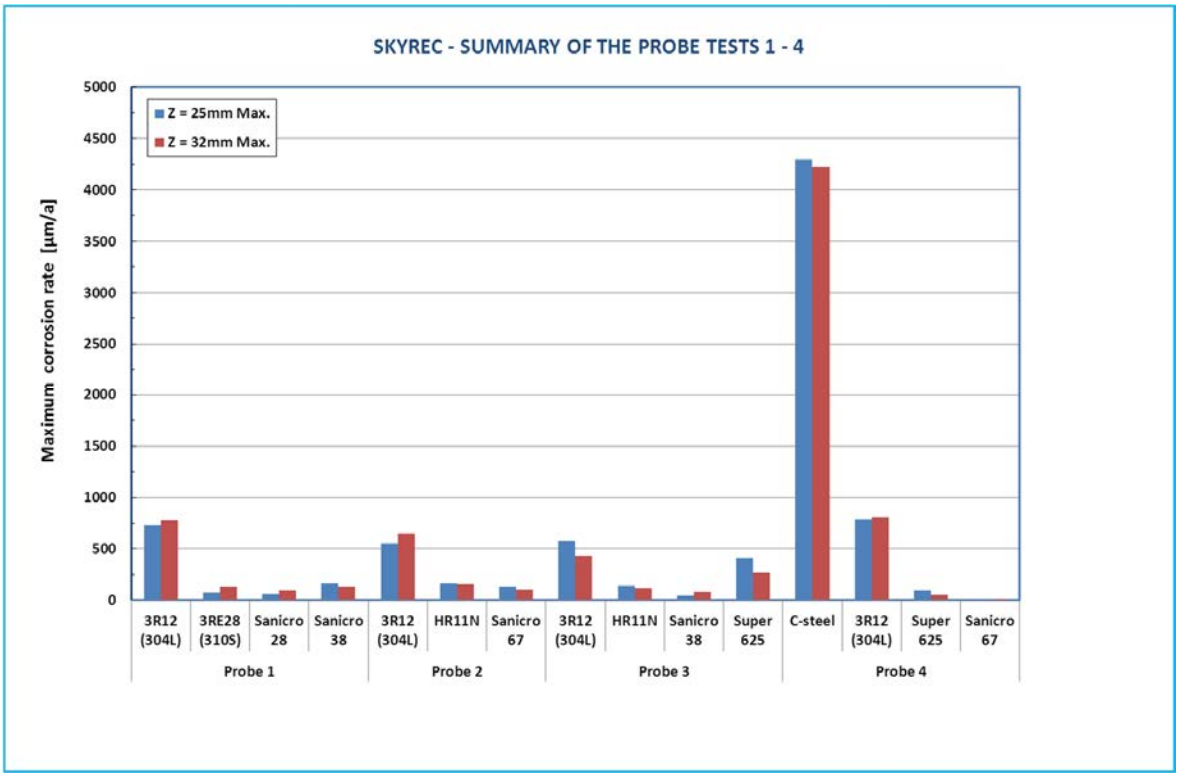
Average CR calculated from the WT profiles



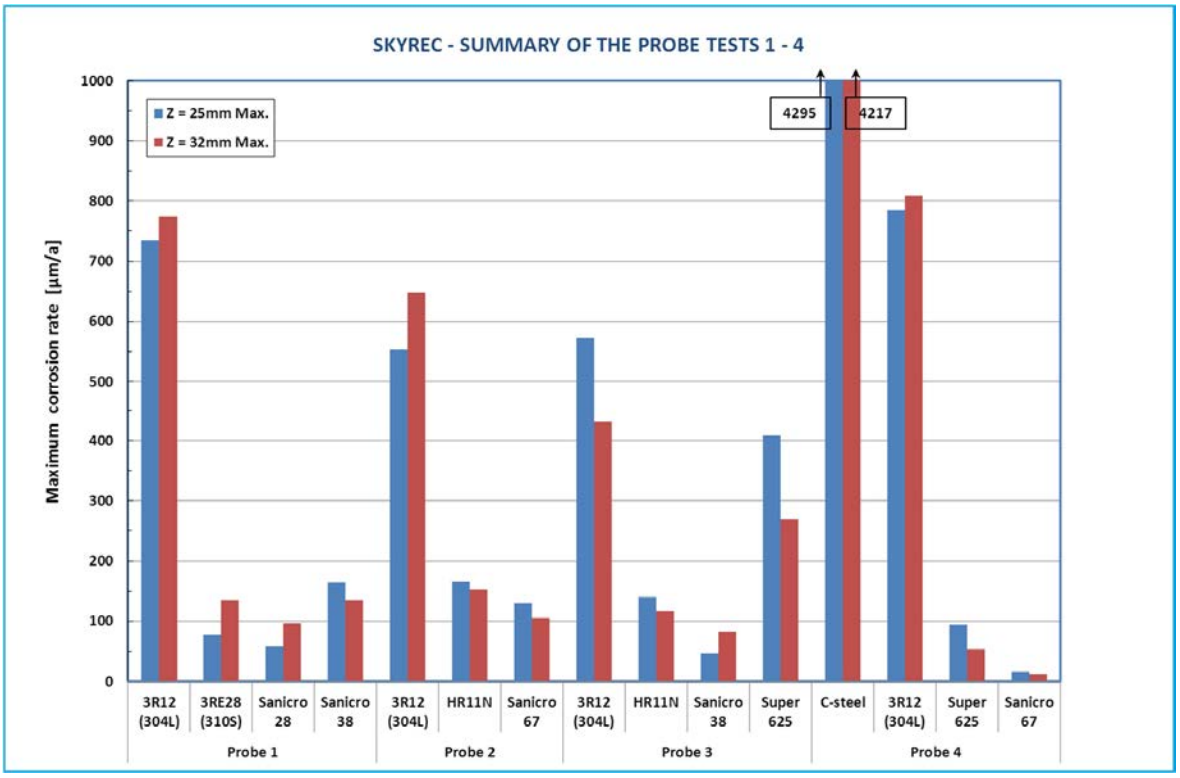
Average CR calculated from the WT profiles



Maximum CR calculated from the WT profiles

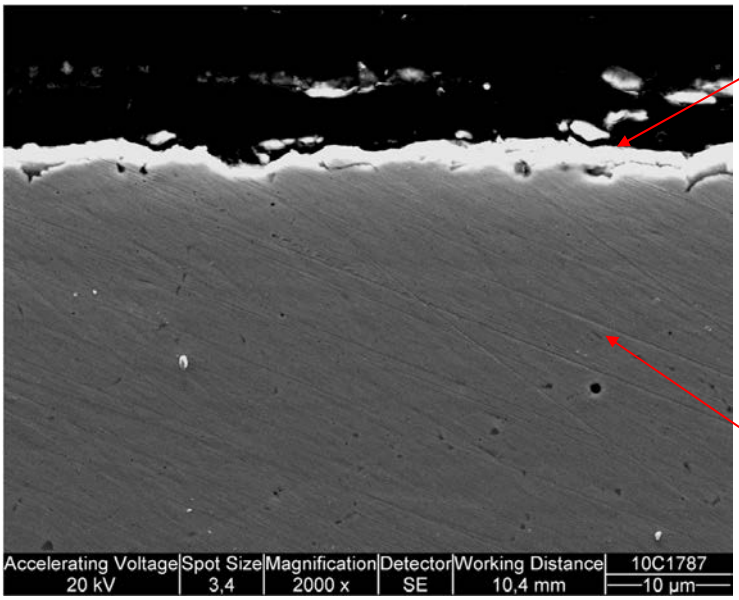


Maximum CR calculated from the WT profiles



Results – Characterisation

First results/observations from last year Dec. 2010



Thin white outer layer

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

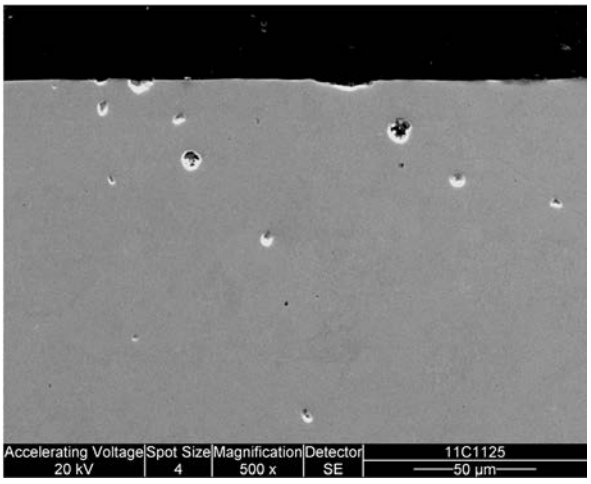
Bulk material

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

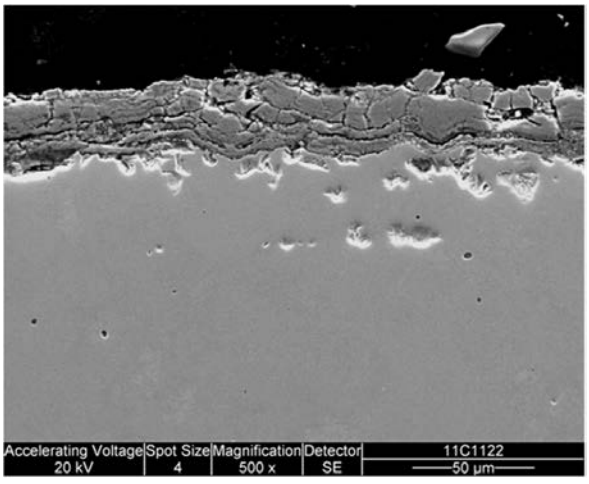
What happens?

- **White outer layer – Low Fe, Ni**

Carbon steel - Probe No. 4



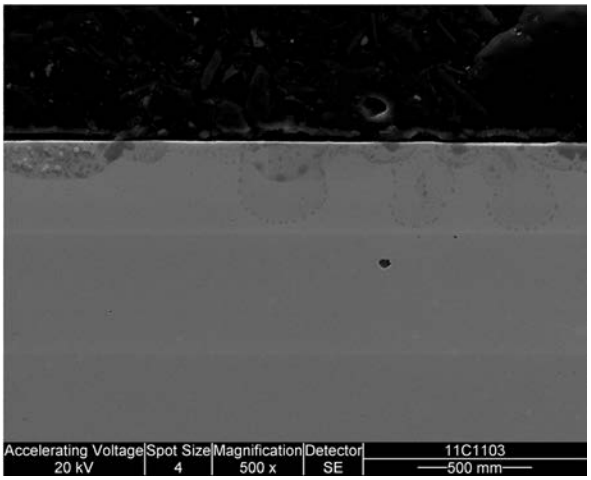
Unexposed reference



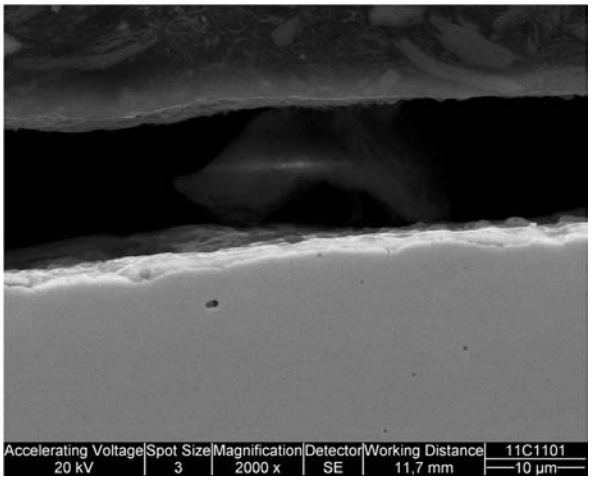
After exposure – effective test duration 2154 h & temperature 440°C

C-steel - P4	Composition wt.-%					
	Cr	Ni	Mo	Fe	S	O
Base material	0,1			98,5		
Outer layer	0,3			68,2	14,4	15,3

3R12 (304L) - Probe No. 4



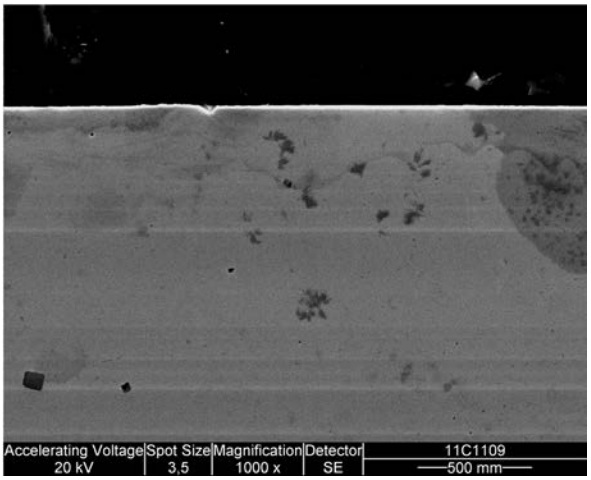
Unexposed reference



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

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

Sanicro 67 - Probe No. 4



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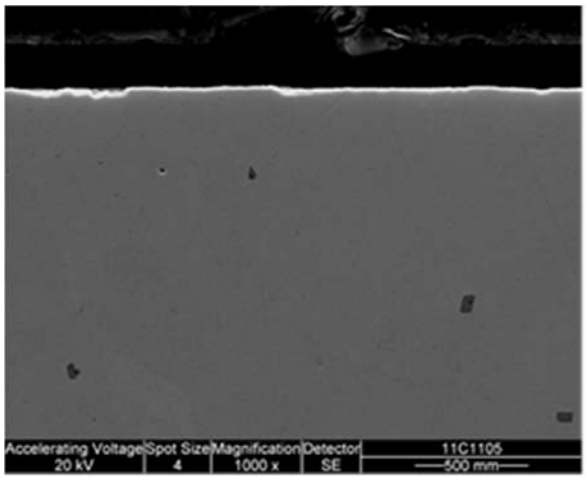
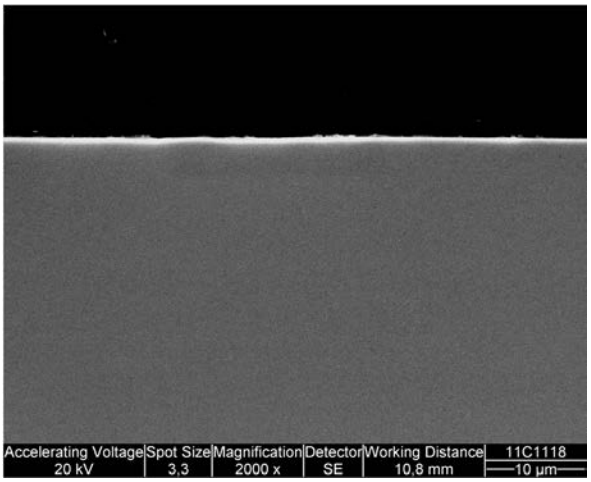


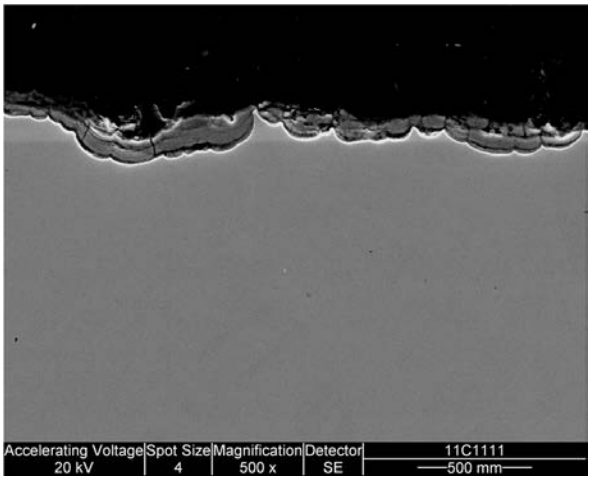
After exposure – effective test duration 2154 h & temperature 440°C

Sanicro 67 - P4	Composition wt.-%					
	Cr	Ni	Mo	Fe	S	O
Base material	30,4	58,1		10,5		
Thin outer layer	29,7	10,7		2,7	3,7	40,0

Super 625 - Probe No. 4



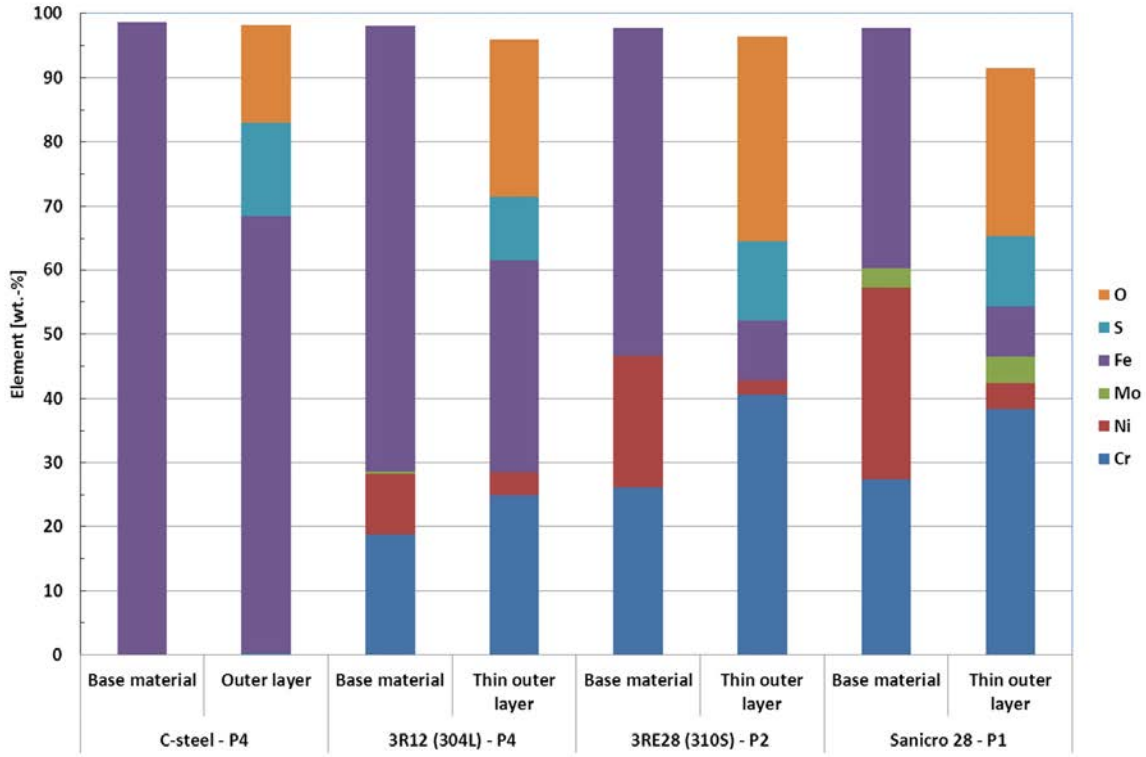
Unexposed reference



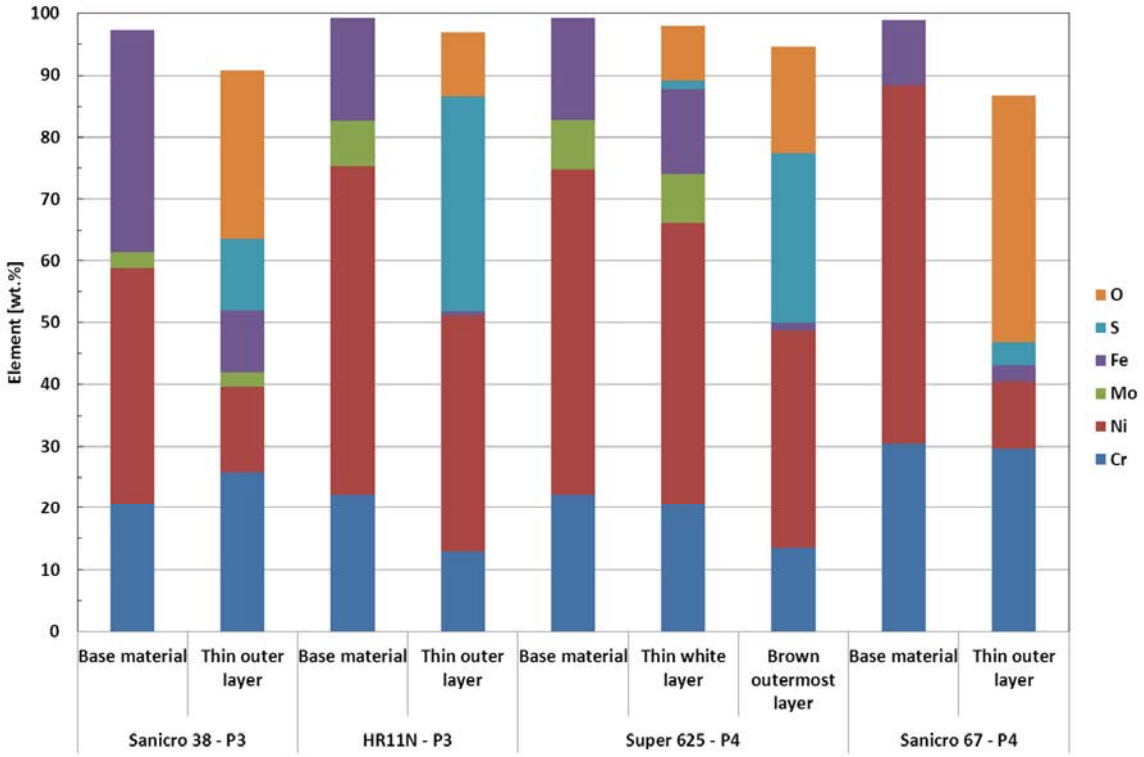
After exposure – effective test duration 2154 h & temperature 440°C

Super 625 - P4	Composition wt.-%					
	Cr	Ni	Mo	Fe	S	O
Base material	22,2	52,7	7,9	16,4		
Thin white layer	20,4	45,9	7,8	13,7	1,4	8,9
Brown outermost layer	13,5	35,1		1,3	27,5	17,2

Characterisation - Summary



Characterisation - Summary



Conclusions

- The probe consisting of a natural circulation circuit, with steam generator where the test materials are placed operates works & gives reproducible results
- Carbon steel corrodes at extremely high rate (4 mm/a) at the temperature of 440 °C.
- The 3R12 (AISI 304L) composite tube material corrodes in such high rate (ca. 0.5 mm/a) that it can't be safely used in the lower furnace
- Sanicro 38 (mod. UNS N08825) and HR11N are ca. three times better than the 3R12 (AISI 304L). *Long term results coming from probe No. 5*
- The high chromium alloys 3RE28 (AISI 310S) and Sanicro 28 are promising, but their long term performance should be verified in the future. *Long term results for Sanicro 28 coming from probe No. 5*
- The corrosion rate of the Sanicro 67 high chromium nickel base alloy is lowest from the studied alloys.
- The corrosion resistance of the Super 625 has been lower than that of the other highly alloyed materials → more and longer tests are needed to verify its performance.

VTT creates business from technology

CERAMICS IN FURNACE

Riku Mattila
Oulu University

Ceramics in the furnace

SKYREC-SEMINAR 2011

Speaker Introduction

Laboratory manager at University of Oulu, laboratory of process metallurgy.1998->

Some relevant studies concerning refractories:

-MSc thesis: refractory material selection to FeCr converter 1994 Outokumpu steel mill Tornio

-Autogenous lining for steel ladle, study Rautaruukki steel mill Raahe 1996

-Black liquor injectors holes areas refractory material 1997-2000 Ahlström

- Cyclone separator material study 2001 Foster wheeler

-R.A. Mattila, J.P. Vatanen and J.J. Härkki. Chemical wearing mechanism of refractory materials in a steel ladle slag line. Scandinavian journal of metallurgy (Denmark), vol.31, no.4, pp.241-245, Aug. 2002.

- Refractory study for lime mud reburning kiln Ahlström 1998,Andritz 2008,2010,2011

Definitions in this research

- Furnace= Soda recovery boiler
- Ceramics=Soda recovery boilers manhole and black liquor injectors holes areas refractory material
- Plant trials place = Stora Enso's Oulu Mill

Previous research

- Laboratory scale was used
- Chemical attack, Sodium components NaCO3,Na2S, cup test
- Chemical attack, rotary drum test
- SEM/EDS,microstructure analysis
- Thermal shock tests
- 1997-2000
- Importance of preparation and installation is vital
- =>the best material available

Previous study

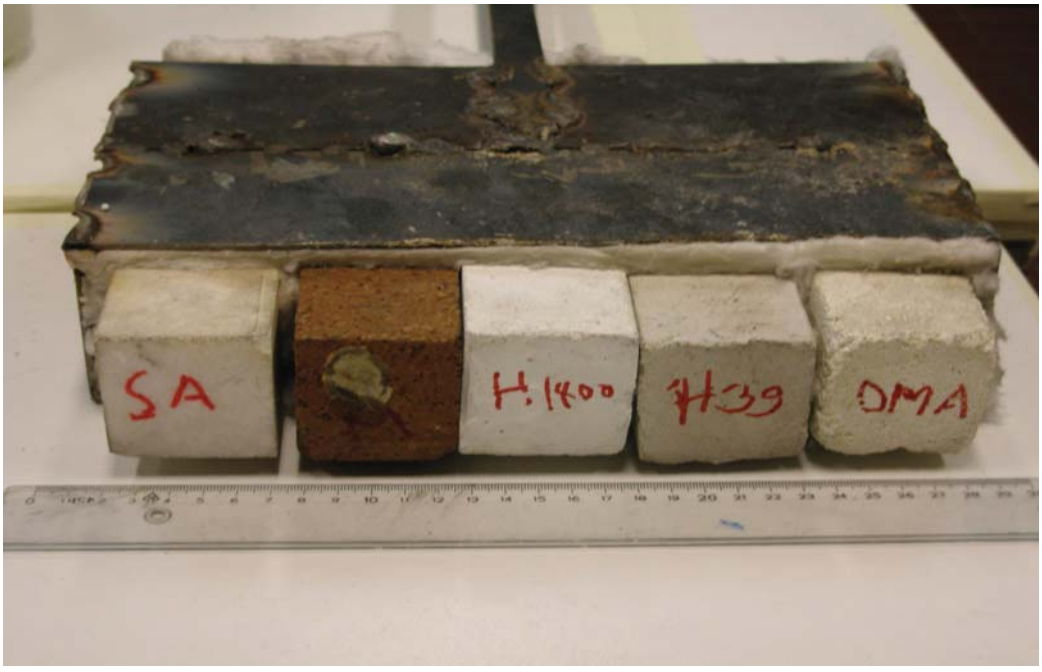
- New material literary study 2005
- =>Zirconium oxide and magnesia-alumina spinel might have potential
- =>Plant trial includes gas effect
- Short plant trial 2005
- => selection of promising materials for longer plant trials

Study plan and materials

- Mehod developed in 2010
- Testing via Injection port
- Refractory steel frame support for ceramic testing materials
- Two frames in different sides of the furnace
- => preliminary tests 2010
- => best materials Hassle D39A lc castable and MgO-iron brick
- => homemade castables were not strong enough mecanically

Test pieces

Test frame

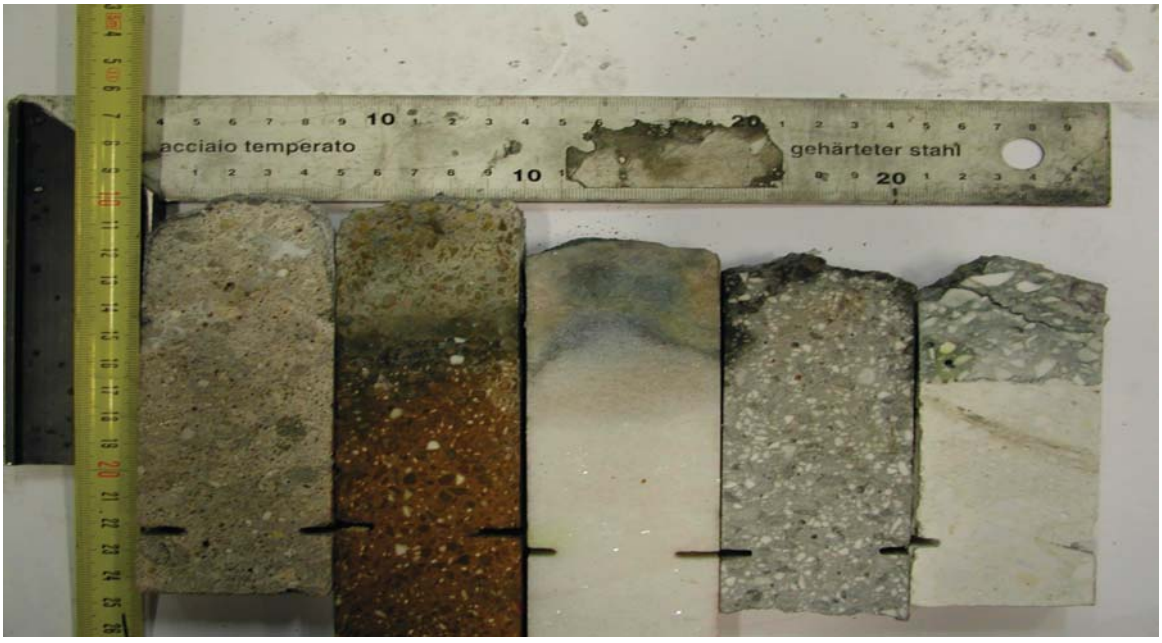


After 7 days, ZrO2 castable broke off

After 7 days, homemade castable spinel broke off

Results 2010

Frame position	Test material	Wear off
1	Hassle D39A	8 mm
2	Betker spinel forming castable	18 mm
3	*Forsterite* (Mg2SiO4) castable	45 mm
4	ZrO2 castable, broke off	60 mm
5	Ankoflo spinel forming castable	20 mm
A1	Hassle D39A	9 mm
A2	Dense Al2O3	15 mm
A3	MgO-iron brick	9 mm
A4	CeO2 included castable	42 mm
A5	Ready made spinel castable, broke off	50 mm



Results 2010

Findings 2010

- Castables need to be stronger but fewer sement
- Wear off is similar this time in different sides of the furnace
- Dense materials were quite good

Improvement to next trial

- Market search for harder ZrO2 castable failed, there was none
- Trying to improve spinel and other castables bonding to be more chemically resistant by nanospinel failed because, nanospinel manufacturing failed due to laboratory accident
- Decided to use best from 1st test and some new Hassle castable

Second test 2011

Second test 2011

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

Dense material wear off by thermal shock

Best material?

- Dense materials like bricks and dense Al_2O_3 form cracks easily so Wear off numbers are a bit missleading
- Wear off is 10 times more on the other side of the furnace, if compared Hassle D39A

Findings

- Best material Hassle D39A castable is already in use
- ZrO_2 castable could have the potential, but they lacking manufacturers
- Full spinel castable, the same applies to these
- $MgO*Cr_2O_3$ brick potential?
- Some more preliminary laboratory test need to be made before next plant trial to ensure quality and potential against Hassle castable

Thank You !

Questions ?

TOC REMOVAL METHODS AND WATER QUALITY RECOMMENDATION

Maija Vidqvist
Teollisuuden Vesi Oy

Teollisuuden Vesi

TOC removal methods and water quality recommendation

Maija Vidqvist
Teollisuuden Vesi Oy

Teollisuuden Vesi

TOC removal methods and water quality recommendation

- Air preheater leakages
- Water quality recommendation
- Measurements
  - A, 108 t/h (1959)
  - B, 504 t/h (1996)
  - C, 144 t/h (2004)
- TOC removal methods

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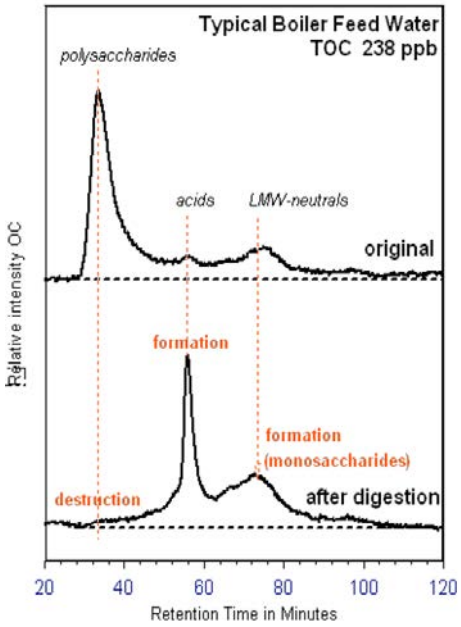
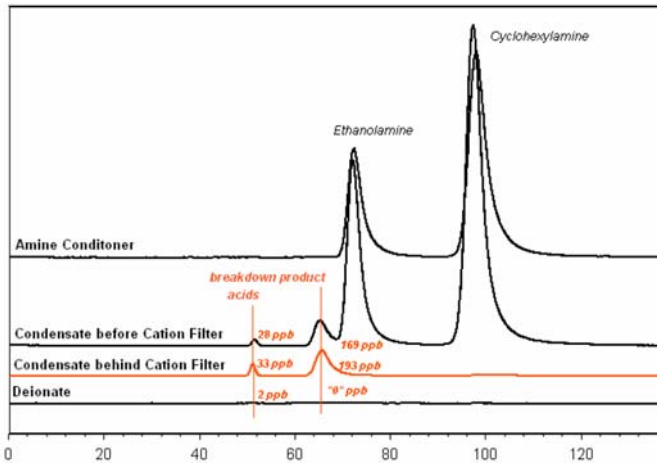
Organics in the steam cycle





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Source: Doc-Labor S. Huber

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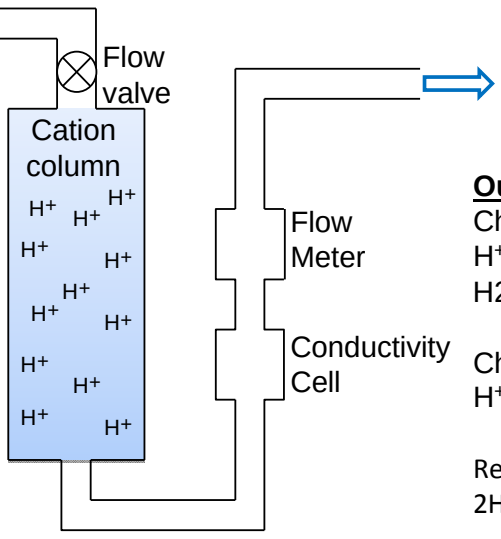
Acid conductivity vs. direct conductivity



Inlet
Neutral Salts
$Na^+ + Cl^-$ 2.2 µS/ppm
$2Na^+ + SO_4^{2-}$ 2.1 µS/ppm

Alkaline
$NH_4^+ + OH^-$ 6.6 µS/ppm
(Ammonia in Water)

Acid
$2H^+ + CO_3^{-2}$ 5 µS/ppm
(Carbon Dioxide in Water)

Outlet
Changes to Acid
$H^+ + Cl^-$ 11.7 µS/ppm
$H2^+ + SO_4^{-2}$ 8.8 µS/ppm

Changes to Water
$H^+ + OH^-$ 0.055 µS/ppm

Remains Unchanged
$2H^+ + CO_3^{-2}$ 5 µS/ppm

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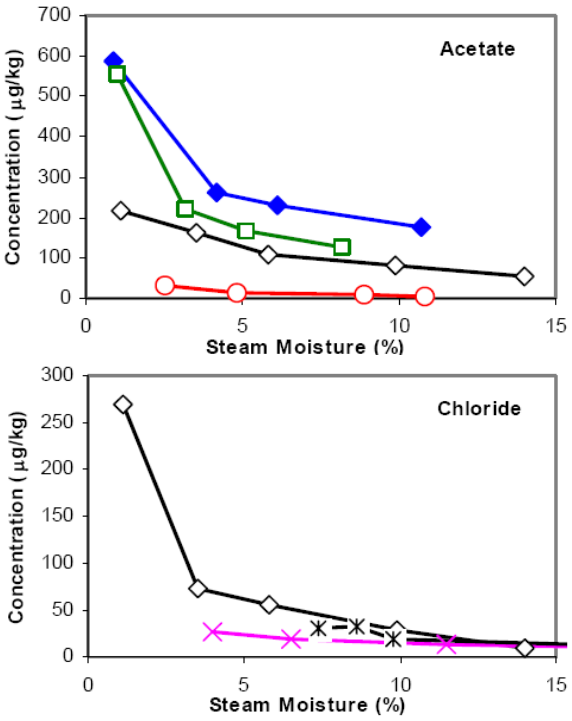
TOC in the water-steam cycle

- Increases cation conductivity
- Decreases (first) condensate pH
- Increases risk for corrosion
- Increases the consumption of the chemicals
- Makes it difficult to follow water quality and changes



Source: Svoboda R., *Investigations into the Composition of Water Phase in Steam Turbines*

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Boiler and steam water quality recommendations

- Based on VGB and EPRI guide lines
- Optimized chemistry only attained with inorganic chemistry
- First set of values published (what we know) for organic volatile chemicals
- No values given for filming amines
- Action limits
- 8,5 MPa, 11 MPa and 16 Mpa
- With and without Cu-metals
- Na_3PO_4
- Recovery boilers

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Optimised vs. acceptable water chemistry

	Optimised water chemistry	Acceptable water chemistry	
		inorganic	Organic
Feed water	Ammonia (O)	Ammonia + Hydrazine (R)	Ammonia/ETA + Hydrazine/organic scavenger
Boiler water	Na_3PO_4 Low content	Na_3PO_4 High content	Na_3PO_4 High content
Condensate treatment	100 % ion exchange	Softener/ Mechanical filter	Softener/ Mechanical filter
Cu-alloys	No	Yes	Yes
Probability on air leakages	Unsubstantial	Substantial	Substantial

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Make-up water quality

Make-up water quality before make-up water tank		
Conductivity	mS/m	≤ 0,008
SiO_2	µg/kg	≤ 5
Na	µg/kg	≤ 3
Cl	µg/kg	≤ 3
SO_4	µg/kg	≤ 3
TOC	µg/kg	< 200
Fe (total)	µg/kg	≤ 5

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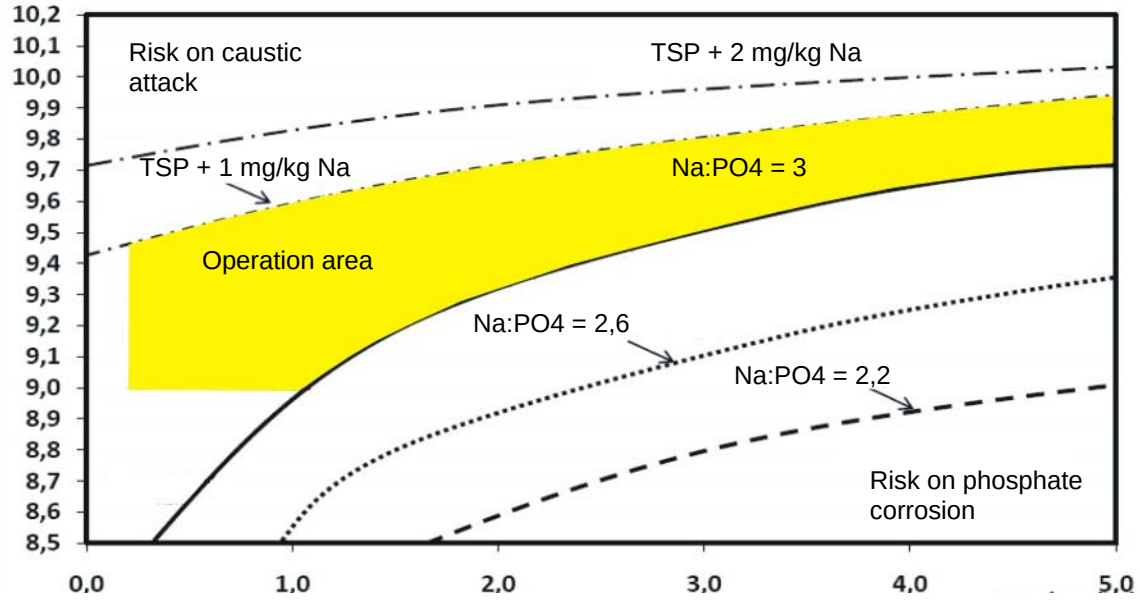
Phosphate Chemistry/Operation area



TSP = Trisodiumphosphate

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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	

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Action levels

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.

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Action levels

Action level or range	Characterisation	Responsibility for action	Action during operation	Action during 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.

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

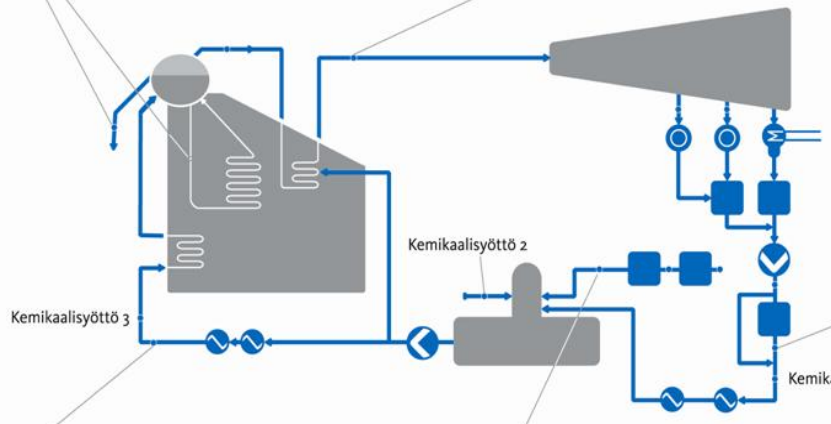
Recommendations for water quality, 16 MPa, drum boiler/inorganic chemistry, no Cu-metals

Kattilavesi

Parametri	O	TR1	TR2	TR3	*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	TR1	TR2	TR3	*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	TR1	TR2	TR3	*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	TR1	TR2	TR3	*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

Teollisuuden Vesi

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

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

Kattilavesi

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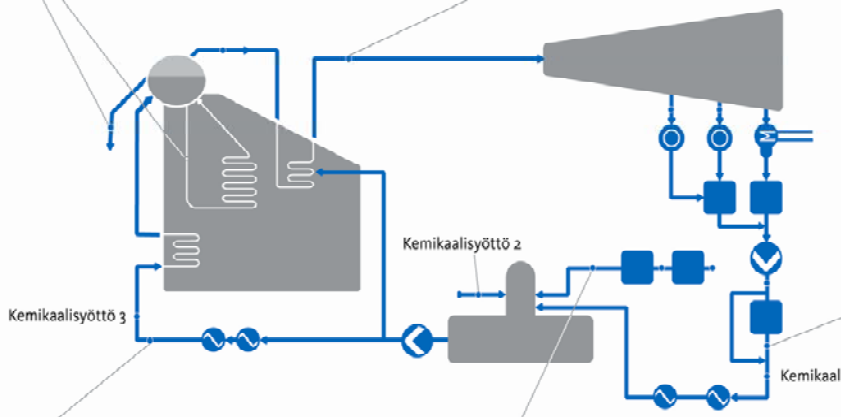
Suora johtokyky mS/m	<1,0	<1,5	2	3	a, c
SiO_2 ppb	kts. kuvaaja 9				b
Na ppb	kts. kuvaaja 10				b, c
Cl	kts. kuvaaja 11				b
SO_4	kts. kuvaaja 12				b, d
Cu ppb	<3	3	-	-	b, d
Fe ppb	<5	5	-	-	b, d
PO_4	≤1,75	≤2,25	-	-	b, c

Tulistettu höyry

Parametri	O	TR1	TR2	TR3	*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	0,05	0,1	0,12	a, c
SiO_2 ppb	≤5	10	20	40	a, c
Na ppb	≤5	10	20	40	a, c
TOC ppb	<100	500			b, d
Fe ppb	≤5	10	20	-	b, d
Cu					



Lauhde

Parametri	O	TR1	TR2	TR3	*Näytetiedot*
pH	9,3 - 9,6	8,5 - 10,0	-	-	a, c
Kationivaihdettu jk. mS/m	≤0,02	0,08	-	-	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	0,6	-	-	b, d

Syöttövesi

Parametri	O	TR1	TR2	TR3	*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	0,05	0,1	0,12	a, c
Happi ppb	5 - 20	1 - 5	20	50	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	0,6	-	-	b, d

Lisävesi

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

Näytetiedot

Selitys	
a	jatkuvatoiminen mittaus
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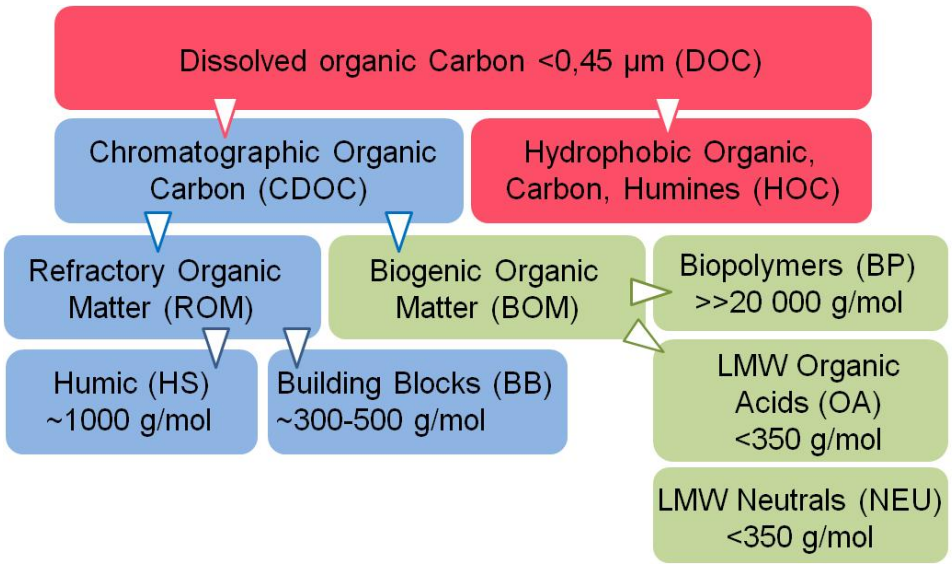
TOC removal methods

- Nature of TOC in the raw water
- Measurements
  - How the present traditional treatment works?
- Removal methods and their efficiency

Teollisuuden Vesi

Organic carbon in raw water



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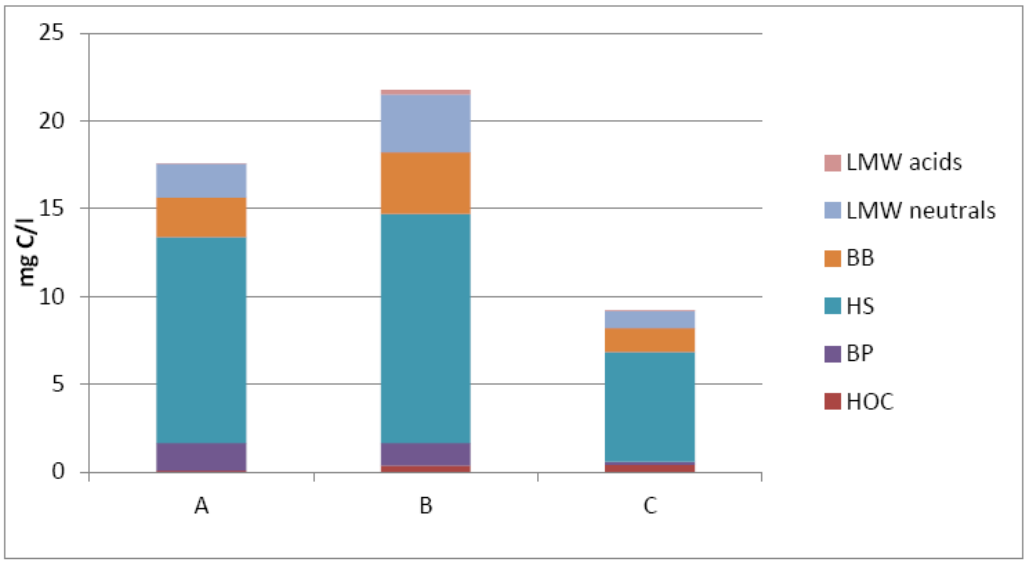
Nature of TOC in the surface water



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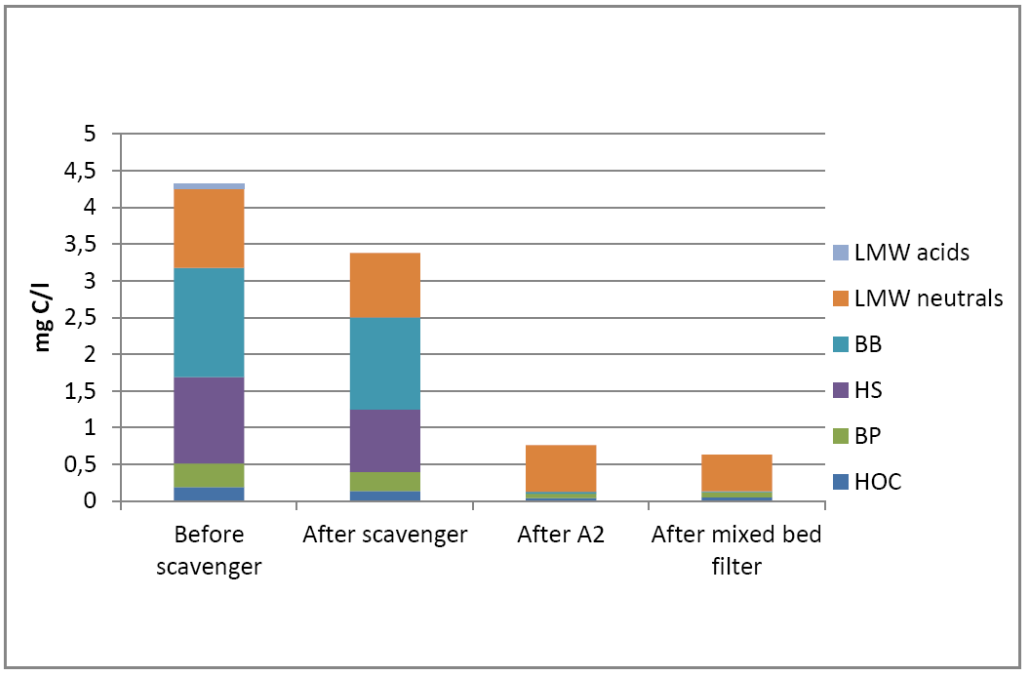
Ion exchange/ TOC removal / Example



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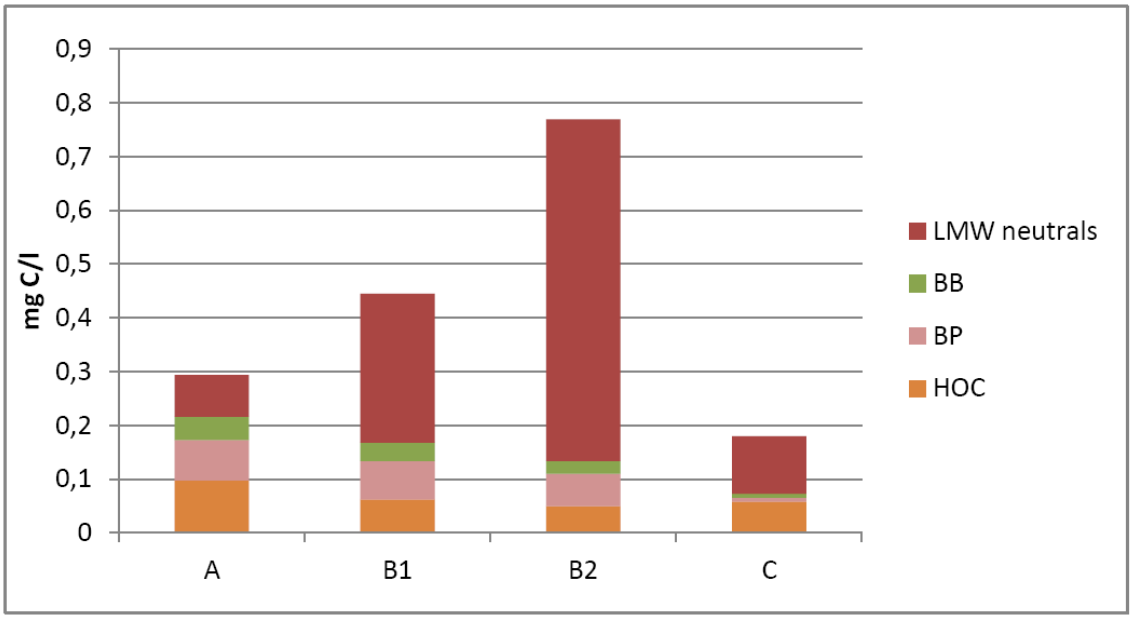
Make-up water quality / Boiler units A, B and C



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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 % > 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

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Removal method	Principle	TOC-reduction rate	Comments and notes
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.

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Conclusions

- TOC nature dependent on time and place
- Know your boiler and turbine limits
- Verify TOC reduction rate and total costs before installation of a new system
- Consider 100 % condensate treatment

Teollisuuden Vesi

Acknowledgements

- Finnish Recovery Boiler Committee
- Steering group
  - Keijo Salmenoja, Andritz
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  - Esa Melin

ACTIVATED CARBON AND UV-TREATMENT IN TOC REMOVAL FIELD TEST

Tero Luukkonen
JP-Analysis

Activated carbon and UV treatment in TOC removal field tests

JP analysis

Main participants in the project

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iP-PRODUKTER
K-D GROUP

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UNIVERSITY of OULU

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HAARLA

Hanovia

JP analysis

Chemviron Carbon

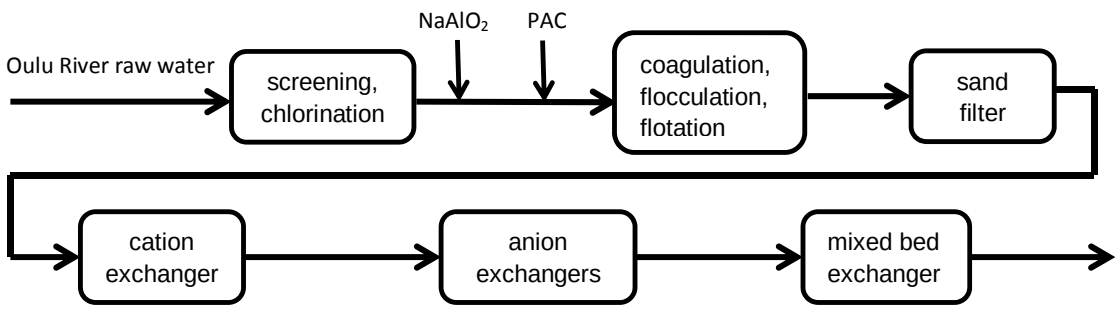
storaenso

Contents

- Active carbon tests
  - TOC reductions
  - Effects on conductivity of water
  - Silica
- UV treatment tests
  - TOC reductions
  - Effects of number of UV lamps, wavelenght, H_2O_2 and TiO_2 catalyst
- LC-OCD measurement results

JP analysis

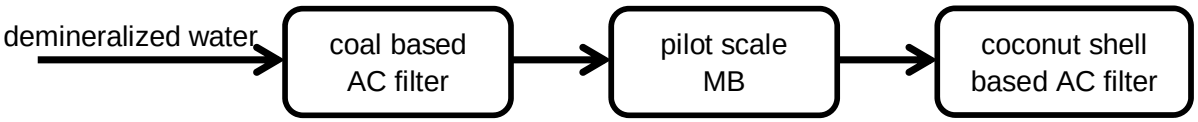
Active carbon tests: experimental set-up



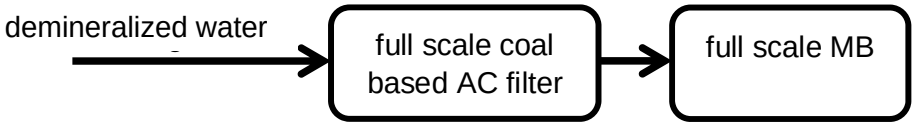
Water treatment process of Stora Enso Oulu mill

JP analysis

Active carbon tests: experimental set-up

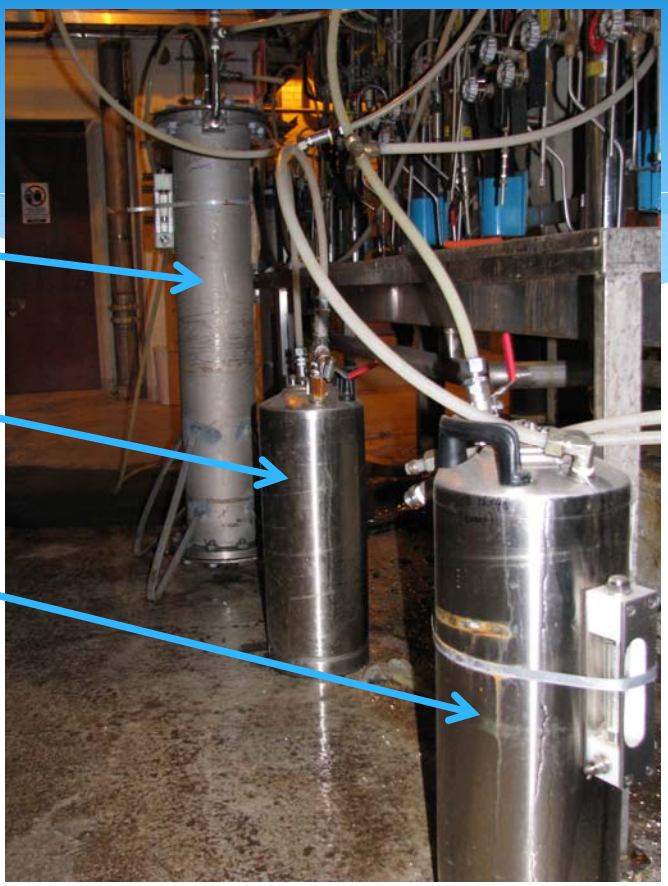


Test scheme of pilot scale AC filters.



Test scheme of full scale AC filters.

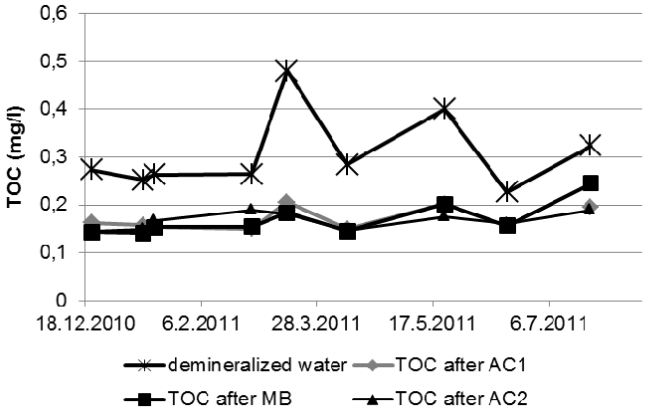
JP analysis



JP analysis

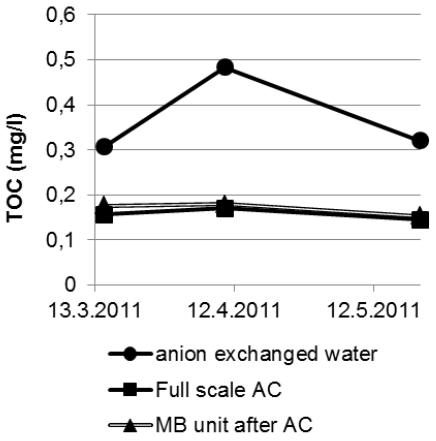
Active carbon: TOC reductions

Pilot scale AC filters



Residual TOC removal 38 – 57 %

Full scale AC filters

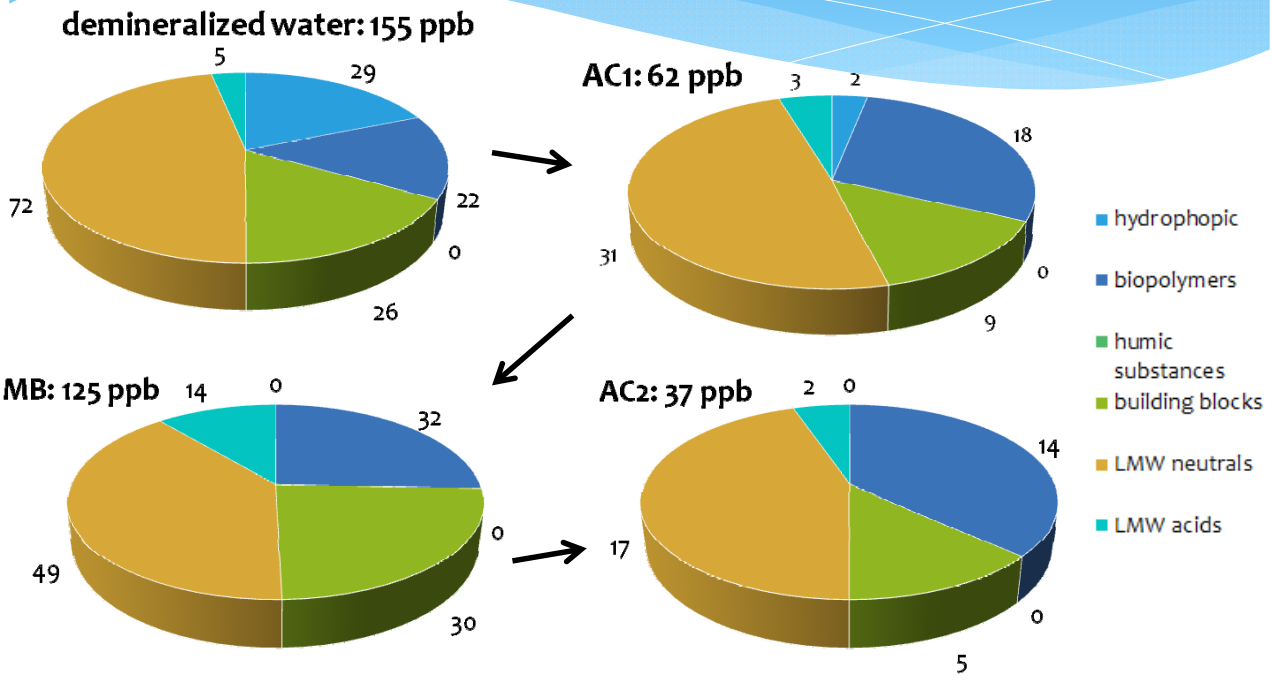


Residual TOC removal 40 – 65 %

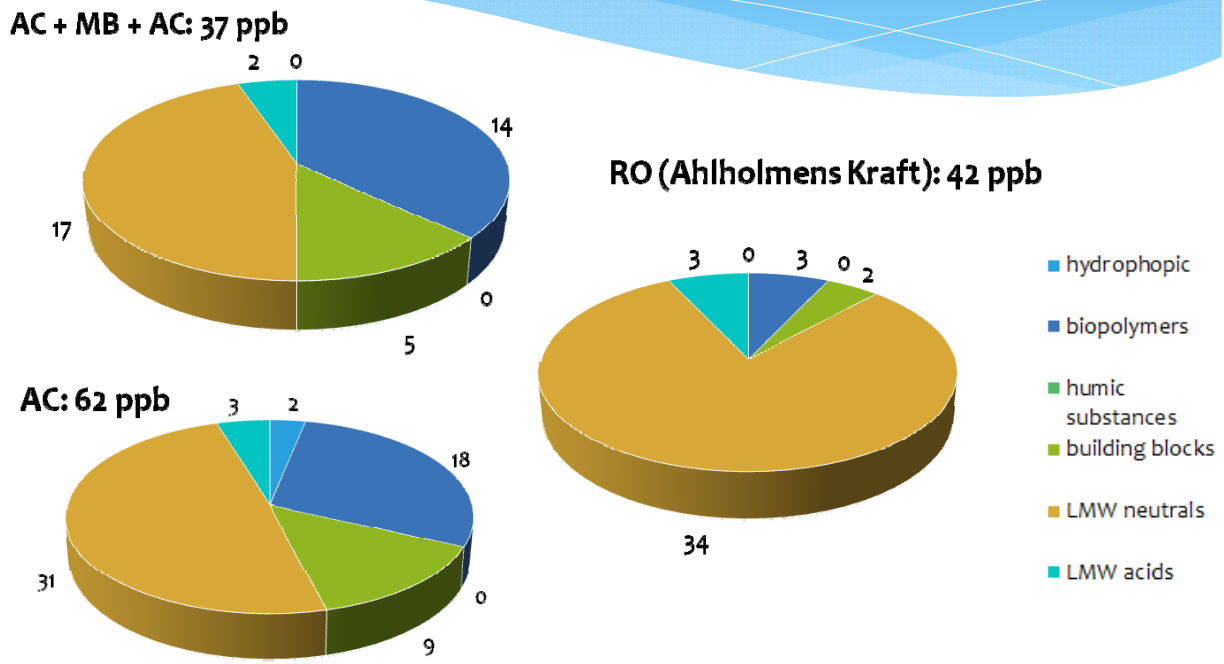
JP analysis

Active carbon: LC-OCD results

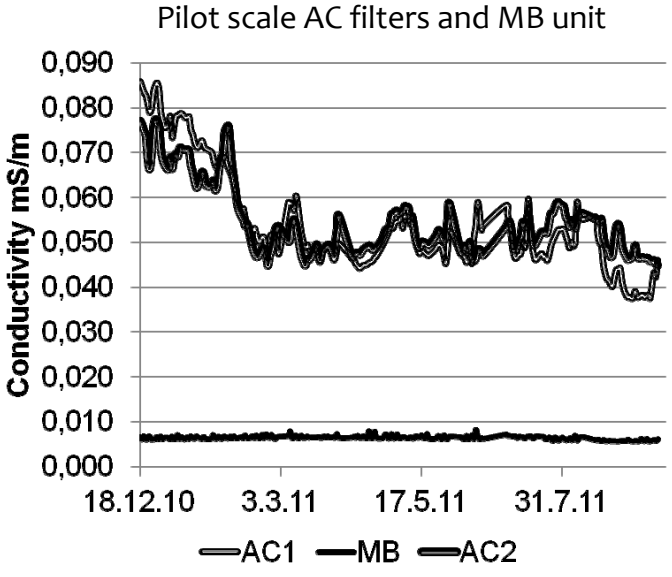
(after ~ 10 months in use)

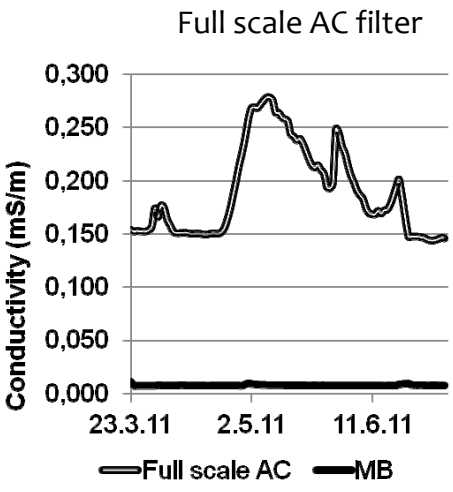


AC vs. RO (LC-OCD)



Active carbon: conductivity





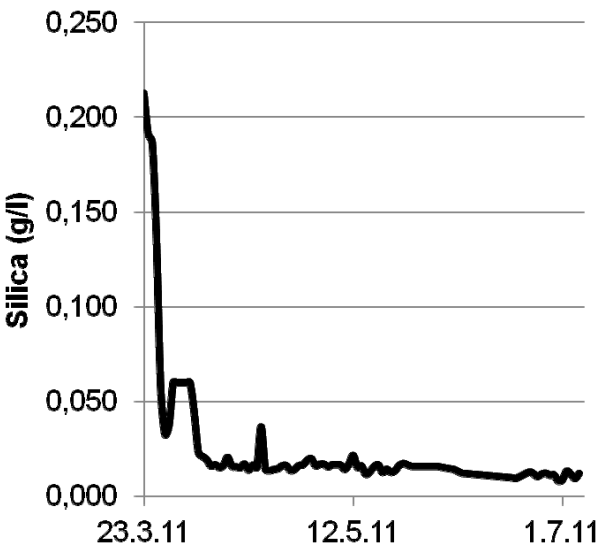
Active carbon: conductivity, some remarks

* MB unit needed after AC to decrease conductivity
* Correlation between TOC removal efficiency and conductivity was a bit unclear (linear R^2 only ~ 0,5)
* Conductivity rise at AC bed was due release of ionized compounds from AC itself – not ionization of TOC
* AC bed was not operating as biological filter because of low nutrient content of water

JP analysis

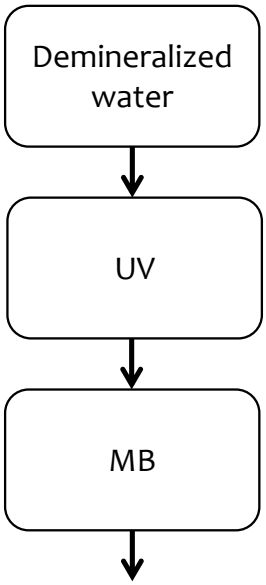
Active carbon: silica

* Silica causes severe scale problems in water-steam cycle
* Measured on-line during full scale test
* New AC bed released silica for ~ 2 weeks
* Silica was removed with subsequent MB



JP analysis

UV treatment: experimental set-up



JP analysis

UV treatment: results

- One chamber: max. 30 % TOC removal
- Four chambers: only 4 % increase in TOC removal

- Effect of TiO_2 catalyst: negligible
- Effect of H_2O_2: ? (experimental set-up failed: plastic piping released organic compounds)

- Effect of wavelenght:
  - Medium pressure lamp (wavelenght peaks at 254 nm and 185 nm): better (30 % TOC removal)
  - Low pressures lamp (wavelengh peak sharply at 185 nm): not that effective

JP analysis

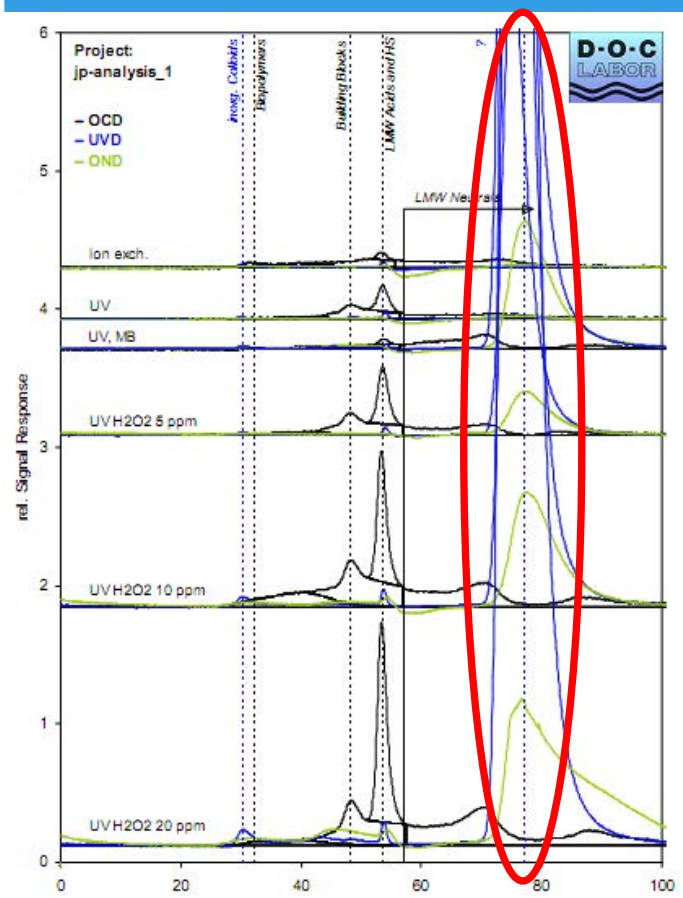
TiO_2 catalyst

* TiO_2 should enhance hydroxyl radical formation
* This type of catalyst (porous net) had no effect

UV treatment: H_2O_2 dosing

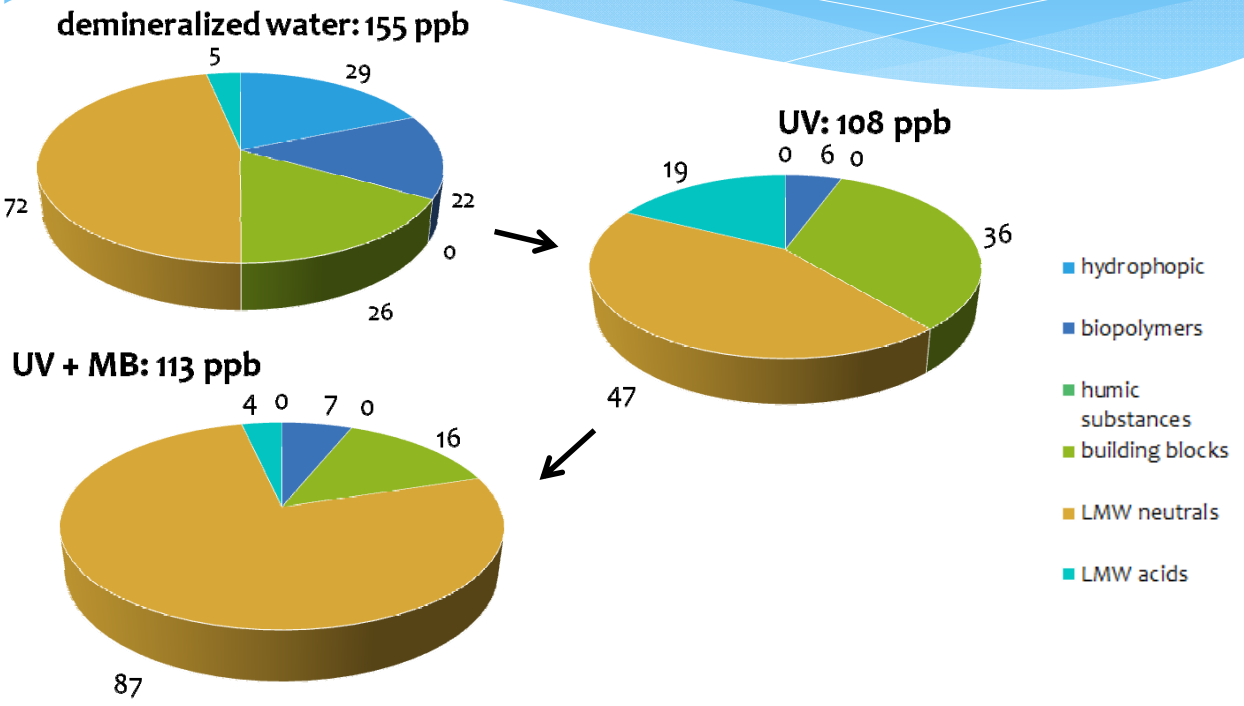
H_2O_2 (35 %), elevated to ~ 40 m from dosing point

Flowmeter



* Unknown peaks in LC-OCD chromatogram which are probably plastic additives

UV treatment: LC-OCD



Conclusions: AC

* Active carbon can remove up to 40 - 60 % of residual organic material (TOC)
* AC bed lifetime before regeneration is at least 10 months
* Subsequent MB is needed to remove elevated conductivity and silica
* AC works fine in full scale

JP analysis

Conclusions: UV

* UV treatment was able to remove up to 30 % of residual TOC
* Removal efficiency did not improve with:
  * Lower wave lenght (more energy)
  * H_2O_2 (oxidant)
  * TiO_2 (catalyst)
  * Number of UV chambers (contact time)
* Possible reason for this: water should be pretreated with e.g. RO (this is normal procedure in microelectronic or pharmaceutical industry water treatment)

JP analysis

Thank you!

Questions, comments

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