Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING 6/2010

TIME December 15th, 2010 10.00 – 16.00

PLACE Pöyry Finland Oy, Vantaa

PARTICIPANTS

Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman
Hidenori Ogawa	Sumitomometal Industries, Ltd. (during items 1-6)
Kaj Nordbäck	Chairman of Finnish Recovery Boiler Association
Keijo Salmenoja	Oy Metsä-Botnia Ab, Rauma
Tommy Sand	Sandvik
Kalle Salmi	Metso Power Oy, Tampere
Mika Paju	Oy Metsä-Botnia Ab, Joutseno

Group members without a right to vote:

Esa Vakkilainen	LUT, project coordinator
Markus Nieminen	Finnish Recovery Boiler Association, secretary
Reijo Hukkanen	Stora Enso Oyj, Fine Paper, Oulu
Olli Talaslahti	Oy Metsä-Botnia Ab, Rauma

Other:

Marja Heinola	Andritz Oy
Kari Haaga	Metso Power
Markku Orjala	VTT
Martti Mäkipää	VTT
Pekka Pohjanne	VTT
Niklas Vähä-Savo	Åbo Akademi
Markus Engblom	Åbo Akademi
Timo Karjunen	Boildec Oy

APPENDICES

1 Project budget 15.12.2010
2 Project budget 15.12.2010 – Chart
3 Project schedule 15.12.2010
4 ÅA, Utilization of pyrolysis gases from the recovery boiler – presentation 15.12.2010
5 ÅA, Utilization of pyrolysis gases from the recovery boiler – draft report 15.12.2010
6 ÅA, Co-firing of black liquor and biomass, part 2 – presentation 26.11.2010
7 ÅA, Co-firing of black liquor and biomass, part 2 – draft report 10.12.2010
8 VTT, Mill tests of superheater materials – presentation 15.12.2010
9 VTT: Analyses of furnace materials – characterisation results from Probes 1,2 and 3, 15.12.2010
10 LUT, Pulp mill optimal steam pressure levels – presentation 15.12.2010
11 LUT, Pulp mill optimal steam pressure levels – draft report 15.12.2010 (in Finnish)
12 Cewic, TOC removal methods, field tests of AC and UV-treatment – draft report 15.12.2010 (In Finnish)
13 TOC removal methods, field tests of AC and UV-treatment, part 2 – offer 14.12.2010 (In Finnish)
14 ÅA, Corrosion tests in reducing conditions, PART II – offer 25.11.2010
15 VTT: Effect of water quality and different chemicals on magnetite layer properties, PART II – offer 27.9.2010 (in Finnish)
16 ÅA, Dew point measurements – offer 8.12.2010

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

1 CALLING MEETING TO ORDER

1.1 Absences

Martti Korkiakoski	Tekes
Lasse Koivisto	Andritz Oy, Varkaus
Timo Peltola	Sandvik, Helsinki
Timo-Pekka Veijonen	Stora Enso Oyj

Tommy Sand was substitute of Sandvik member Timo Peltola.

Hidenori Ogawa replaces Hiroshi Matsuo as Sumitomo's member in the steering committee.

1.2 Agenda

Previously delivered agenda was changed, so that Åbo Akademi projects were presented first then VTT's projects.

1.3 MEMO of the previous meeting (4/2010 and 5/2010)

The memos of the previous meetings were accepted.

From now on the memos will have separate heading for decisions made in the meeting.

2 MEETING DECISIONS

Draft report to be commented before next meeting:

- ÅA, Utilization of pyrolysis gases from the recovery boiler (APPENDIX 5)
- ÅA, Co-firing of black liquor and biomass – laboratory combustion tests, part 2 (APPENDIX 6)
- LUT, Pulp mill optimal steam pressure levels (APPENDIX 11)

Boildec Oy, Field testing of furnace materials

- Materials for test 4: Carbon steel, 304L, Sandvik 67, Super 625
- All samples shall be machined to provide more accurate thickness measurements

Teollisuuden Vesi Oy, FRBC's Water quality recommendation

- Steering committee nominated workgroup for the project: Lasse Koivisto, Andritz, Toni Wahlman, Botnia, Anja Lehikoinen, Metso Power Lauri Mattila, UPM, N.N, Stora Enso

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

- Ordering of the work postponed again to next meeting, when the results of Cewic-project are available

Åbo Akademi, Corrosion tests in reducing conditions – PART II

- Ordering of the work was postponed until offer is revised. Now we have to order part 1 and part 2 to get comparable data. Keijo Salmenoja will contact Åbo Akademi. Decision order or not is made in e-mail meeting in January 2011.

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

- Decision order or not was postponed to e-mail meeting in January 2011.

Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment, part 2

- It was decided to give durability committee permission to order the project, budget 15 000 euro. Reijo Hukkanen will contact Tero Luukkonen to clarify/revise the offer so that there is only items what we want.

Åbo Akademi, Dew point measurements

- Ordering of the work was postponed until the condition of existing dew point analysers is known. Decision is made in e-mail meeting in January 2011.

3 BUDGET

Budget (situation 15.12.2010) is presented in APPENDIX 1 and in APPENDIX 2 as chart.

Ordered work sum is 638 177 eur and reservations/offers 274 800 eur, totally 912 977 eur.

We must order and execute projects for 61 822 eur before June 30th 2011, because TEKES will participate maximum 50 % from 700 000 eur (350 000 eur), but deadline for refund is June 30th 2011. We have extra funding (no refund from TEKES) 105 000 eur, which can be utilized also after 30.6.2011.

4 TIME SCHEDULE

Schedule (situation 15.12.2010) is presented in APPENDIX 3.

Projects should be completed by the end of June 2011 and the final report written by the end of October 2011.

5 FINISHED PROJECTS

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

6 ONGOING PROJECTS

6.1 ÅA, Utilization of pyrolysis gases from the recovery boiler

Objective:
Extracting pyrolysis gas from the lower part of the recovery boiler could possibly be used to replace fossil fuels in the lime kiln. This study will use mass balance and energy balance calculations to study possibilities for extracting pyrolysis gases from the lower part of a recovery boiler. The extracted amount will be assumed to be such that it would cover the need of the lime kiln. In addition to the mass and energy balances, existing CFD calculations of two Kraft recovery boilers will be investigated. The aim of this latter part is to establish typical variation in the gas composition in the lower part of existing boilers as well as to discuss the amount and role of the particulate matter in the lower gas atmosphere.

Status:
Work is done and Markus Engblom from Åbo Akademi presented results, APPENDIX 4.

The following conclusions are made:

- Extraction of gas with a heating value of 3 MJ/kg could be feasible with normal recovery boiler operation.
- Existence of suitable location for gas extraction depends on recovery boiler operation. A high fuel-to-air ratio, for example, close to a furnace wall would be desirable
- Dust load is estimated to be in the range 30-80 g/Nm3
- Factors not included in this study, but which could be relevant to consider include: modifications to recovery boiler operation to maximize gas heating value; gas extraction; and removal of dust from the extracted gas.

Draft report for comments, APPENDIX 5. Comments should be addressed to Markus (maengblo@abo.fi) before next scheduled meeting 15.2.2011.

Schedule:
Final report will be accepted in next meeting 15.2.2011.

6.2 ÅA, Co-firing of black liquor and biomass – laboratory combustion tests, part 2

Objective:
Project consists of two separate works: One consists of droplet combustion tests with wood and lean BL. Second task will focus on better understanding of the behaviour of nitrogen in biosludge. Project was ordered at the steering group in an e-mail meeting 29.1 – 2.2.2010.

Status:
Work is done and Niklas Vähä-Savo, ÅA gave a presentation about project results, APPENDIX 6.

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 lingoboost
- More work – mill & lab needed around bio sludge

Draft report for comments is APPENDIX 7. Comments should be addressed to Niko DeMartini (nmartini@abo.fi) before next scheduled meeting 15.2.2011.

Schedule:
Final report will be accepted in next meeting 15.2.2011.

6.3 VTT, Mill tests of superheater materials

Objective:
Corrosion field tests of superheater tube materials are made with VTT's cooled deposit/corrosion probe in Joutseno recovery boiler. Materials (table below) were chosen in meeting IV, 8th September 2009.

AISI 347	San 67	Alloy 28 (HR21, San 28)	TP310	HR11N	Super 625*

* 50 Ni – 21.5 Cr – 17.5 Fe – 9 Mo

Probe's material temperature set points were verified meeting 15.6: first probe 530 °C and second probe 570 °C. Set points are maximum surface temperatures of windward side.

Status:
Official measurements are started September 16th 2010 and finished week before schedule week 42.

Martti Mäenpää, VTT presented results (APPENDIX 8). The probes and test materials were damaged when salt cakes fell down during boiler shut-down, so corrosion rate cannot be calculated.

Schedule:
Draft report for comments is delivered January 2011.

Comments:
- Report should include information about black liquor properties and boiler data during the measurement.
- Material temperature 510 °C means steam temperature ca. 460-480 °C
- Probes will be mounted through a manhole located on 10.5 floor, nearest sootblower is about 1 m away; no protection is designed against it

6.4 Boildec Oy, Field testing of furnace materials

Objective:

Corrosion field tests of furnace materials are made with Boildec's probe in the Joutseno recovery boiler.

Current schedule and materials:

Test 1: Mar 2 - Apr 15, 2010	Test 2: May 15 - Jun 20, 2010	Test 3: Jul - Aug, 2010	Test 4: Jan - Feb, 2011
AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)
AISI 310S	Sandvik 67	Super 625 (Sumitomo "N")	Carbon steel
Sanicro 38	HR11N = (Sumitomo "R")	HR11N (Sumitomo "R")	Sandvik 67
Sanicro 28	Sandvik 4C54	Sanicro 38	Super 625

Status:
First test was finished successfully April 15th.
Test number 2 completed on June 23rd.
Test number 3 was completed September 6th

Materials for test number 4 were decided:
- Carbon steel
- 304L
- Sandvik 67
- Super 625

Carbon steel was chosen to get visible corrosion. Metso will deliver the carbon steel sample and welding instructions to Timo Karjunen, Boildec Oy.

Joutseno boiler will have scheduled shutdown in week 19, 2011. Test time can be extended if needed, but after 1000h carbon steel sample is inspected for visible corrosion.

All samples will be machined to provide more accurate thickness measurements.

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

Decision
- Materials for test 4: Carbon steel, 304L, Sandvik 67, Super 625.
- All samples will be machined to provide more accurate thickness measurements

6.5 VTT, Analysis of the furnace test materials

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

Status:
Samples from tests 1, 2 and 3 are now analysed. Pekka Pohjanne, VTT gave a presentation about the result so far, see APPENDIX 9.

Conclusions:
- WT measurements from the cross section does not give accurate results
- Thickness profiles with coordinate measurement machine provide useful results
  - Not absolute values but suitable for ranking. Small differences are not significant.
  - Recommendation: Accuracy can be improved by using machined & polished samples (tube or plate)
- Reference corrosion samples from boilers if possible

Schedule:
- Probes 1 – 3: Microscopy for the last specimens (3RE28 and 3XRE28) at the beginning of January 2011
- Probe 4: Samples will be prepared before the Boildec test begins in January 2011 and then analysed after the test is finished

Comments
- Same material, different thickness -> can we repeat 304L test behaviour, tests 1, 2 and 3 had temperature difference

6.6 LUT, Pulp mill optimal steam pressure levels

Background:
When modernizing the existing pulp mill the common question is how to show what the economical pressure level is. Should the mill keep the old level or decrease it?

Objective:
Work has three parts:
Part 1. Collect data steam pressure levels in use and reasons for those levels
Part 2. Calculate the annual average steam balances for both modern and traditional pulp mill of about 600 000 ADt/a. Evaluate investments costs between different pressure levels and affect of various electricity price to the chosen pressure levels. Calculations with/without power boiler and with fine paper integrate.
Part 3. Find out means to increase power to heat ratio in existing pulp mills during mill modernization.

Status:
Part 1. is done

Part 2. is done
Part 3. is almost done

Esa Vakkilainen presented shortly the project results, APPENDIX 10.

Draft report for comments is APPENDIX 11 (in Finnish). Comments should be addressed to Esa (esa.vakkilainen.lut.fi) before next scheduled meeting 15.2.2011.

Schedule:
Final report will be accepted on next meeting 15.2.2011.

Comments:
- cooking pressure requirement

6.7 FRBC's Material recommendation

Objective:
Durability committee suggests updating existing recommendation "Suojaussuositus" from 1997
Following chapters to be updated (author):
- Chapter 1. Recovery boiler materials and weldings (?)
- Chapter 2. Recovery boiler coatings (VTT)
- Chapter 3. Repair of pressure vessels (Metso)
- Chapter 4. Recovery boiler inspections (Inspecta)
- Chapter 5. Recovery boiler incidents (Thesis worker?)

Durability committee propose (meeting August 30th) that there should a separate chapter for recovery boiler incidents, typical incidents in recovery boiler for example: boundary between carbon steel and stainless steel, spray cooling nozzles etc.

Status:
Chapters 2, 3 and 4 are on-going or started in beginning of 2011. For chapter 1, part of the text can be copied from previous projects for example SOTU II. Durability committee will search out thesis worker for chapter 5.

Schedule:
Schedule will be updated in durability committee meeting 2.2.2011.

Comments:
- Coatings chapter should include also welding
- Could the chapter recovery boiler incidents written as a master's thesis?

6.8 Oulun Yliopisto, Ceramic structural materials

Objective:
Project will be executed in two phases in the Oulu mill. Quick (duration two weeks) test with all materials will be done first. Longer test with 3-4

best materials after that and then will be decided which samples microstructure are studied. Microstructure study extra cost 1025 € / sample.

Status:
Quick test number 1 was started 16.2.2010 and ended 2.3.2010, materials made by University of Oulu materials (ZrO2 and Spinel) broke when frame was taken out. Some materials have absorbed smelt chemicals by diffusion.

Quick test will be done again to verify the results:
- Probes uppermost and lowest material are same material (MgO-iron)
- Reference material is MgO-ironmass
- selfmade materials (ZrO2, spinel) should be industrial quality

Durability committee (30th August 2010) proposes following materials to be tested. ZrO2 will be industrial made. The uppermost and lowermost materials are now the same, so two materials from the previous are excluded, Forsterite and CeO2.

Probe 1:	Probe 2:
MgO-iron	MgO-iron
Hassle D39A	Ankoflo
ZrO2	Nanospinel
Betker	Fireclay
MgO-iron	MgO-iron

Schedule:
University (Riku Mattila) informed 14.12.2010 that they have had challenges to produce nanospinel and they could start the test number 2 at 3.1.2011 earliest.

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

Objective:
The idea is to carry out field tests with activated carbon and UV-treatment. Also study of reverse osmosis (RO) as an alternative is included in the work. Investment costs and operating costs are evaluated.

Status:
Tero Luukkonen has send draft report for comments, APPENDIX 12 (In Finnish).

Conclusions:
- RO treatment plant offers from four suppliers are listed
- Recovery boiler make-up water is challenging for RO plant due to high water flow, several parallel plants is needed.
- Cost for RO plant water is below 0,1 €/m3
- Three different sort of activated carbon was tested, two of them (AQUACARB 608C 12X40 or GPC-LF 12X40) seems best (TOC-

reduction ~40%), but differences are insignificant. Availability and price are decisive factors.
- Reason for water conductivity increase during AC tests is still partly unknown. Reason could be conversion of organic carbon to inorganic carbon, but BET-analyses don't support this.
- During the tests active carbon operation was based purely on absorption, not biological activation
- Size distribution measurements show fluctuation in Oulu river organic matter content
- Measured TOC concentrations from Oulu mill water/steam cycle were higher than guidelines allow
- Measured acetate and formate concentrations from Oulu mill water/steam were very low

Mr. Luukkonen changes employer after 15th December 2010 and has send offer for monitoring industrial size activated carbon test and the Hanovia UV-treatment tests, APPENDIX 13.

Next steps:
- Industrial size AC test starts in January, one anion-exchanger is converted to active carbon filter at Oulu mill
- Pilot tests in Pietarsaari in beginning of December
- Hanovia pilot UV-unit is delivered to Oulu mill during January and after that to Pietarsaari mill

Schedule:
This project phase is completed after final report is accepted next steering committee meeting

6.10 Teollisuuden Vesi Oy, FRBC's Water quality recommendation

Steering committee chose Teollisuuden Vesi Oy to write the water quality recommendation in e-mail meeting 2-4th December 2010.

Steering committee has nominated workgroup for the project:

Andritz	Lasse Koivisto
Botnia	Toni Wahlman
Metso	Anja Lehikoinen
UPM	Lauri Mattila
Stora Enso	N.N

Stora Enso's member is not decided yet.

Date for first meeting is preliminary 7th January 2011 at Hirvihaaran kartano, Mäntsälä. First draft version of the recommendation will be ready at end of January 2011.

7 PROPOSALS

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

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

Decicion:
Ordering of the work postponed again to next meeting, when the results of Cewic-project are available.

7.2 Åbo Akademi, Corrosion tests in reducing conditions – PART II

Åbo Akademi's offer, APPENDIX 14.

Background:
This offer is based on earlier results obtained from laboratory tests. These tests were done in a gas containing CO and N2 and additionally active carbon were placed on the synthetic salts. The reason for using active carbon instead of black liquor chars, which are more reducing, was that BL-chars contain chlorine and since one of the tested salts (Salt 5) does not contain any chlorine it was decided not to use the char. However, when looking at the results from these tests is seems that no or only a small reduction (at 600°C) of the sulphate to sulphide was achieved with this test setup.

Objective:
In this offer the tests are planned to be done with BL-char despite the fact that it may contain some chlorine and thus affect the results, at least for the test with Salt 5. The offer contains three parts:

- Part A in which the reducing effect of the BL-char is preliminary tested and a verification of sulphate reduction is to be established
- Part B in which a further mapping of the temperature on the reducing effect is to be done
- Part C is to finalize a similar test matrix as was done in the earlier tests in 2009.

Before starting with Part A, a couple of TGA-tests will be done to establish the reduction temperature of a mixture of NaSO4 and BL-char.

Decision:
Ordering of the work was postponed until offer is revised. Now we have to order part 1 and part 2 to get comparable data. Keijo Salmenoja will contact Åbo Akademi. Decision is made in e-mail meeting in January 2011.

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

VTT's offer, see APPENDIX 15 (In Finnish).

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

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

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

Part 3: The effect of chemicals and decomposition products on magnetite layer formation and properties
- Circulating water circuit
- Autoclave volume smaller than circulating water tank volume -> chemicals decomposition is minimal during the test
- Magnetite layer formation is monitored by EIS (Electrochemical. Impedance Spectroscopy) during 24h test
- After the test magnetite layer is examined with SEM/EDS.

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

Decision:
Ordering of the work was postponed to e-mail meeting in January 2011.

7.4 Others proposals

7.4.1 Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment, part 2

Tero Luukkonen has send offer for monitoring industrial size activated carbon test and the Hanovia UV-treatment tests, APPENDIX 13. Current project status, see chapter 5.9.

Decicion
It was decided to give durability committee permission to order the project, budget 15 000 euro. Reijo Hukkanen will contact Tero Luukkonen to clarify/revise the offer so that there is only items what we want.

7.4.2 Åbo Akademi, Dew point measurements

Åbo Akademi's offer, APPENDIX 16.

Objective:
This is a proposal to make dew point measurements, SO3 measurements and corrosion measurements in two boilers: one Kraft boiler with the possibility of operating with low and high SO2 and O2; and Heinola's NSSC boiler with extremely high SO2 Measurements would be taken behind the ESP, before any scrubber.

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

1. Dew point measurements will be made with a commercial instrument ("Land" etc). The question there is the sensitivity of the electrical signal at the low concentrations of condensing sulphuric acid normally present in kraft boiler flue gases.

2. Corrosion measurements will be made with our air-cooled probes and samples will be analyzed with SEM/EDS. Careful control of the probe temperature will be required. Also open questions relate the exposure time.

3. Flue gas samples will be bubbled through an isopropyl alcohol (IPA) water mixture for capture of SO3 and subsequent analysis of the sulphate ion concentration according to the standard methods for SO3 analysis. The challenge here is to exclude any escape particulate material in the IPA solution. Dust sulphate carryover to the IPA solution will disturb the SO3 analysis.

Decision
Ordering of the work was postponed until the condition of existing dew point analysers is known. Decision is made in e-mail meeting in January 2011.

8 PROJECT IDEAS

9 OTHER ISSUES

9.1 International co-operation

9.1.1 Northern America

ORNL project “improving heat recovery in biomass-fired boilers” has meeting in January 2011.

9.2 Translating project reports into English

Secretary has asked word-versions of the reports that are in Sumitomo’s list, most of them are made by VTT.

One VTT report is still missing:
Yli-Olli, Sanni, Pohjanne, Pekka, Kinnunen, Tuomo. 2006.
Soodakattila tulevaisuudessa II - Materiaalien sulfidoitumiskokeet, sondi-näytteiden analysointi.
Raportti 30.10.2006.

This is the most interesting and should translated first.

10 NEXT MEETINGS (MEETING CALENDAR FOR 2011)

2011 meeting calendar:

- Meeting I: February 15th at 10.00 a.m, Pöyry Finland Oy, Vantaa
- Meeting II: May 5th at 10.00 a.m, Pöyry Finland Oy, Vantaa