Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING 1/2011

TIME February 15th, 2011 10.00 – 15.00

PLACE Pöyry Finland Oy, Vantaa

PARTICIPANTS

Hidenori Ogawa	Sumitomometal Industries, Ltd. (during items 1-6)
Keijo Salmenoja	Oy Metsä-Botnia Ab, Rauma
Timo Peltola	Sandvik, Helsinki
Lasse Koivisto	Andritz Oy, Varkaus

Group members without a right to vote:

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

APPENDICES

1 Project budget 15.2.2011
2 Project schedule 15.2.2011
3 ÅA, Utilization of pyrolysis gases from the recovery boiler – final report 15.12.2010
4 ÅA, Co-firing of black liquor and biomass, part 2 – final report 10.12.2010
5 ÅA, Corrosion tests in reducing conditions, PART II – offer 25.11.2010
6 VTT, Mill tests of superheater materials – draft report 20.1.2011
7 Boildec Oy, Field testing of furnace materials – offer extra tests 25.1.2011
8 VTT, Analysis of the furnace test materials – offer extra tests 11.2.2011
9 Teollisuuden Vesi Oy, Water recommendation - introduction and table of contents 14.1.2011
10 ÅA, Dew point measurements – offer 8.12.2010

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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
Timo-Pekka Veijonen	Stora Enso Oyj
Reijo Hukkanen	Stora Enso Oyj, Fine Paper, Oulu
Olli Talaslahti	Oy Metsä-Botnia Ab, Rauma
Kalle Salmi	Metso Power Oy, Tampere
Mika Paju	Oy Metsä-Botnia Ab, Joutseno
Kaj Nordbäck	Chairman of Finnish Recovery Boiler Association
Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman

Keijo Salmenoja, Botnia was chosen as chairman of this meeting, as Matti Tikka, UPM is absent.

1.2 Agenda

No changes to agenda.

1.3 MEMO of the previous meeting (6/2010)

The memo of the previous meeting was accepted.

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

2 MEETING DECISIONS

Accepted reports:

- ÅA, Utilization of pyrolysis gases from the recovery boiler (APPENDIX 3)
- ÅA, Co-firing of black liquor and biomass – laboratory combustion tests, part 2 (APPENDIX 4)

Åbo Akademi, Corrosion tests in reducing conditions – PART II

- Steering committee decided to order the work (APPENDIX 5), and project will continue if BL char test results look promising.

VTT, Mill tests of superheater materials

- Comments to the draft report should be send to the secretary by the end of February 2011

Boildec Oy, Field testing of furnace materials

- Test 4 is continued over 1000h if visible corrosion is not detected.
- Steering committee decided to order extra tests (number 5).

– Materials for test 5 is decided by e-mail

VTT, Analysis of the furnace test materials
– Steering committee decided to order sample preparation and analyses for extra test (number 5).

LUT, Pulp mill optimal steam pressure levels
– It was decided to collect opinions what is the minimum steam pressure requirement in cooking.
– Also other comments are appreciated: esa.vakkilainen@lut.fi

Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment
– Comments are appreciated: reijo.hukkanen@storaenso.com

Åbo Akademi, Dew point measurements
– Steering committee decided to order the work. Secretary will ask candidates for mill experiment, the boiler should have high sulphidity.

3 BUDGET

Budget (situation 15.2.2011) is presented in APPENDIX 1

Ordered work sum is 653 177 eur and reservations/offers 157 400 eur, totally 810 577 eur.

We must order and execute projects for 46 822 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 15.2.2011) is presented in APPENDIX 2.

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

5 FINISHED PROJECTS

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

6 ONGOING PROJECTS

6.1 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:
Results were presented in previous meeting 15.12.2010 and final report is received, APPENDIX 3. No comments to report.

Decision:
Steering committee accepted the final report.

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:
Results were presented in previous meeting 15.12.2010 and final report is received, APPENDIX 4. No comments to report.

Decision:
Steering committee accepted the final report.

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

Objective:
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 sulfide was achieved with this test setup.

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 re-

duction is to be established, Part B in which a further mapping of the temperature on the reducing effect is to be done, and 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.

Status:
Project was preliminary accepted in e-mail meeting, with following changes to the offer, APPENDIX 5:

- The parts A and B will be combined to Phase 1 (26 400 €)
- Part C will act as an option and can be ordered if so decided/wanted. This part completes the corrosion studies
- If we are willing to order this work, ÅA will test the applicability of the BL char to produce reducing conditions
- If the tests are not promising, the order can be cancelled

ÅA is currently testing NaSO4 => NaS DTA/TGA with black liquor char. If this works they will start the official experiments.

Decision:
Steering committee decided to order the work (APPENDIX 5), and project will continue if BL char test results look promising.

6.4 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:
Results were presented in previous meeting 15.12.2010 and draft report is received, APPENDIX 6.

Comments to the draft report should be send to the secretary by the end of February 2011, so that VTT has enough time to revise the report before next meeting.

Schedule:
Final report is accepted in next meeting May 5th 2011.

Comments:

- Add figure to explain windward, leeward, up and down
- Add boiler figure which shows the position of the probes
- Material compositions missing
- Analysis of corrosion materials
- Results are what they are -> we should be able to explain the results

6.5 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:
Test 4 is current on-going, test time 1000h is fulfilled at the end of May 2011. After 1000h test time carbon steel sample is inspected and if no visible corrosion is detected test time is extended. Joutseno boiler has scheduled shutdown in week 19, 2011.

Question is how to verify the carbon steel corrosion at site and what is the typical corrosion rate for carbon steel?

Secretary has asked offer for extra test, APPENDIX 7.

Decision:
Steering committee decided to order extra test (number 5).

Schedule:
Next test (number 5) starts after test 4 is finished. Secretary will ask the materials suggestion from project participants by e-mail.

Comments:

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

– Corrosion mechanism seems to be dissolution -> VTT would like have reference sample if possible

6.6 VTT, Analysis of the furnace test materials

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

Status:
Preparation of test 4 materials is done.

Analysis of tests 1, 2 and 3 were presented in previous meeting. Results of microscopy for the last specimens (3RE28 and 3XRE28) not yet received. VTT has asked reference samples from boilers tubes if possible.

Secretary has asked offer for extra test, APPENDIX 8.

Schedule:
Preparation of test 5 materials can begin after steering committee has decided the materials. Materials should know at least month before test begins.

6.7 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:
Draft report for comments is received. Master thesis worker returns from Moscow in spring to finalize the work. Comments to the report should be addressed to Esa (esa.vakkilainen@lut.fi)

It was decided to collect opinions what is the minimum steam pressure requirement in cooking.

Schedule:
Final report will be accepted on next meeting 5.5.2011.

6.8 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?)

Status:
Chapters 2, 3 and 4 are on-going. For chapter 1 author is not yet asked. One possible author for chapter 1 is Hannu Hänninen, Aalto University. He is returning from MIT in end of September 2011. Durability committee is searching thesis worker for chapter 5, one candidate is from Varkaus polytechnic.

Schedule:
Recommendation should be ready during year 2011.

6.9 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:
Oulu University have had problems producing nanospinel, durability committee proposes that nanospinel is replaced with Hassle P1800.

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

Schedule:
New test should be started as soon as possible.

6.10 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:
Draft report of phase 1 is received. Comments to the report can send to reijo.hukkanen@storaenso.com

Monitoring of the field tests is continued in phase 2.

Schedule:
Final report will be accepted on next meeting 5.5.2011

6.11 TOC removal methods – field tests of activated carbon, UV-treatment - phase 2

Objective:
Project includes monitoring industrial size activated carbon test and the Hanovia UV-treatment tests.

Status:
Monitoring of active carbon pilot test is on-going. Next step is to start industrial size test with active carbon, one anion-exchanger is converted to active carbon filter.

UV-equipment from Hanovia should be delivered to the mill in the end of February. Waiting for confirmation from Hanovia about the schedule.

Contract is still unclear, is the project accepted as Cewic project or not. The difference is that the budget with Cewic is 15 000 eur, without Cewic about 23 000 eur.

Comments:
- Salmenoja has received offer that from UV-equipment manufacturer that guarantees 50-60% TOC-reduction

6.12 Teollisuuden Vesi Oy, FRBC's Water quality recommendation

Separate workgroup is nominated for this project.

Andritz	Marja Heinola
Botnia	Toni Wahlman
Metso	Arja Lehikoinen
UPM	Toni Orava
Stora Enso	Tero Arvilommi

Status:
Introduction and table of contents is received, APPENDIX 9.

First draft version of the recommendation will be ready at end of February 2011. Next meeting 9th March

Schedule:

Next meeting 9th March

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

Objective:
Increase of recovery boiler steam temperature and pressure will have effect on water chemical 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 next meeting.

7.2.1 Åbo Akademi, Dew point measurements

Åbo Akademi's offer, APPENDIX 10.

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.

Status:
Åbo Akademi has tested the analyzer.

Niko DeMartini message:

It seems to work for the water dew point (we obtained a reasonable number in our test at an oil fired boiler), but we are uncertain if it is sensitive enough for the acid dew point (we did not see one in this trial, but the temperature in the sampling location was high ~340 °C and may have interfered with the measurement).

Since it is not clear that purchasing a new dew point analyzer would improve the sensitivity, we would suggest proceeding with what we have proposed. Since we will also be using a technique to sample and analyze SO3, we believe we can get meaningful information as proposed, though we cannot guarantee that the sample probe will measure the acid dew point. Sampling first at Heinola would help prepare us for the harder Kraft recovery boiler scenario.

Decision:
Steering committee decided to order the work. Secretary will ask candidates for mill experiment, the boiler should have high sulphidity.

7.3 Boildec Oy, Field testing of furnace materials, extra test

Decision:
Steering committee decided to order extra test (number 5), APPENDIX 6.

7.4 VTT, Analysis of the furnace test materials, extra test

Decision:
Steering committee decided to order sample preparation and analyses for extra test (number 5).

7.5 Others proposals

No other proposals.

8 PROJECT IDEAS

No other project ideas.

9 OTHER ISSUES

9.1 Final seminar

Final seminar will be held before or after (next or previous day) to Recovery Boiler Day in the end of October in Helsinki.

9.2 International co-operation

9.2.1 Sweden

Värmeforsk (Jan Storesund) wants to change information with SKYREC-project i.e. furnace material tests. They have on-going work concerning higher steam data of biomass, waste and recovery boilers. Värmeforsk report is completed in about half a year.

Secretary will ask more information about the project before deciding what to do.

9.2.2 Northern America

ORNL project “improving heat recovery in biomass-fired boilers” had meeting in January 2011 and they send us the material.

9.3 Translating project reports into English

Translation of the report is ongoing:
Sulfidation and black liquor coating tests
Mustala, Sanni, Pohjanne, Pekka, Heikinheimo, Liisa, Pankakoski, Pekka and Kinnunen, Tuomo, VTT 10.3.2006.

The goal of the project was to estimate the resistance/behaviour of the chosen boiler steam/superheater tube materials under hydrogen sulphate and hydrogen sulphate + water vapour. Also resistance againts corrosion caused by drying of wet black liquor was tested. Materials: 304L, Sanicro 38, Sanicro 36Mo, Sanicro 65, 4C54 and HR11N.

10 NEXT MEETINGS (MEETING CALENDAR FOR 2011)

2011 meeting calendar:

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

Markus Nieminen