Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING 3/2011

TIME September 5th, 2011 10.00 – 15.00

PLACE Pöyry Finland Oy, Vantaa

PARTICIPANTS

Lasse Koivisto	Andritz Oy, Varkaus
Hidenori Ogawa	Sumitomometal Industries,Ltd.
Timo Peltola	Sandvik, Helsinki
Mika Paju	Oy Metsä-Botnia Ab, Joutseno
Kalle Salmi	Metso Power Oy, Tampere
Keijo Salmenoja	Andritz Oyj, Helsinki
Reijo Hukkanen	Stora Enso Oyj, Fine Paper, Oulu
Keijo Salmenoja	Andritz Oyj

Group members without a right to vote:

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

Other:

Nikolai DeMartini	Åbo Akademi (by phone)
Dorota Bankiewicz	Äbo Akademi

APPENDICES

1 Project budget and schedule 23.9.2011
2 LUT, Pulp mill optimal steam pressure levels – final report 29.7.2011
3 ÅA, Dew point measurements – presentation 4.10.2011
4 ÅA, Corrosion tests in reducing conditions, PART II – presentation 5.10.2011
5 Boildec Oy, Field tests of furnace materials – test No.4 report 7.6.2011
6 Boildec Oy, Field tests of furnace materials – offer test No.5 extension 9.9.2011
7 VTT, Analysis of the furnace test materials – presentation 8.9.2011
8 FRBC material recommendation – chapter 3: Repair of pressure vessels
9 FRBC material recommendation – chapter 4: Recovery boiler inspections
10 Cewic, TOC removal methods – field tests of activated carbon, UV-treatment and RO-treatment – presentation 5.10.2011
11 Teollisuuden Vesi Oy, FRBC's Water quality guidelines – presentation
12 5.10.2011
SKYREC final seminar – final programme

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
Timo-Pekka Veijonen	Stora Enso Oyj
Kaj Nordbäck	Chairman of Finnish Recovery Boiler Association
Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman

1.2 Agenda

No changes to agenda.

1.3 MEMO of the previous meeting (3/2011)

On the memo was one error: Keijo Salmenoja, Andritz is part of the group members.

The memo of the previous meeting was accepted with change.

2 MEETING DECISIONS

LUT, Pulp mill optimal steam pressure levels
- Final report was accepted.

Oulun Yliopisto, Ceramic structural materials
- Final report was accepted

VTT, Mill tests of superheater materials
- Final report was accepted

Åbo Akademi, Corrosion tests in reducing conditions – PART II
- T_0 should be added to the presentation for different salts.

Boildec Oy, Field testing of furnace materials
- Boildec offer of extended test time was accepted.

Material recommendation
- Project will be separate from SKYREC, durability committee continue working with it during normal project work.

Teollisuuden Vesi Oy, FRBC's Water quality guidelines
- Secretary can publish the guidelines after Teollisuuden Vesi Oy has updated durability committee comments.

3 BUDGET

Budget (situation 23.9.2011) is presented in APPENDIX 1

Ordered work sum is currently 756 294,37 €, from which 702 869,37 € is already paid. Project budget is 805 000 € so we have 48 706 € left.

4 TIME SCHEDULE

Schedule (situation 23.5.2011) is presented in APPENDIX 1.

Three projects are still ongoing:
- Åbo Akademi, Dew point measurements
- Åbo Akademi, Corrosion tests in reducing conditions – PART II
- Boildec Oy, Field testing of furnace materials

Dew point and corrosion test projects will be done by the end of year 2011. 5th test of furnace materials will be ready in December 2011, but analysis will done in January 2012.

Final report for TEKES will be 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 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:
Final report was received for comments 27.8.2011, APPENDIX 2.

Report can also be downloaded below address:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/2682c71379a8da80c22577f20051c0c0?OpenDocument

Decicion:
Final report was accepted.

6.1.1 Åbo Akademi, Dew point measurements

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

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

Åbo Akademi's offer:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/982c9bb8c552f1e2c225784500511608?OpenDocument

Status:
Åbo Akademi has done measurements in Heinola (June, week 23) and Rauma (September, week 37).

Niko DeMartini presented the current situation and results by phone, presentation APPENDIX 3.

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

Schedule:
Project results will be presented in the SKYREC seminar on October 20th.
Final report will be ready in December 2011.

Comments:

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

Questions and answers:

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

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

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

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

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

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

Objective:
The goal of the project is to estimate the resistance/behaviour of the chosen boiler steam/superheater tube materials (10CrMo9-10, T91, S28, HR11N)

under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in a reducing atmosphere.

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

In part 2 tests are done with black liquor chars instead of active carbon to establish reducing conditions.

Test plan, Part A:
The corrosion tests will be done with the same base salts as earlier, but with some of the sulphur replaced and added as Na2S. “rx” and “rx” in the salt names refer to that x% of the sulphur is added as Na2S.

1) Temperature: 565°C “Sotu” salts:
- 5r10, 5r50, 5r80, 10r10, 10r50 and 10r80 mixed with 30-wt% BL-char

2) Temperature: 525°C “Sotu” salts:
- 5r80, 10r10 and 10r80 mixed with 30-wt% BL-char

Materials: 10CrMo9-10, T91, Sanicro 28, HR11N
- Total number of samples in Part A: 36 + 9 (repetitions)
- Total number of samples in Part A to SEM: 45

Status:
Dorota Bankiewicz presented current results, APPENDIX 4.

Conclusions so far:
- First results show that increase of Na2S 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

Schedule:
Åbo Akademi has done most of the tests, 4 more runs still to be done. After that detailed analysis of all the samples.

Final report is ready in November.

Dorotha Bankiewicz will also present the results in SKYREC-seminar 20th October.

Comments:
- what is T_0 for different salts.

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:
Final report was received in April 2011.

Report can be downloaded, link:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/d338a1188e114c03c225781700403032?OpenDocument

Decicion:
Final report was accepted.

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

6.4 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 1006 h	Test 2: May 10 - Jun 23, 2010 1023 h	Test 3: Jul 16 - Sep 6, 2010 1250 h	Test 4: Feb 2 - Jun 6, 2011 2700 h	Test 5: Aug 30 - Dec 2011 on-going
AISI 304L	AISI 304L	AISI 304L	AISI 304L	AISI 304L
AISI 310S	Sanicro 67	Super 625	Carbon steel	HR11N
Sanicro 38	HR11N	HR11N	Sanicro 67	Sanicro 38
Sanicro 28	Sandvik 4C54	Sanicro 38	Super 625	Sanicro 28

Status:
Test 4 started February 2nd and ended June 6st, totalling 2700 of which 2154 were effective (probe pressure over 8 bar), test report APPENDIX 5.

Test 5 is currently on-going, according to Pekka Pohjanne, VTT there is Sanicro 28 instead of Sandvik4C54 which is against previous meeting decision.

Boildec has offered continuation of the test 5 from original 1000h APPENDIX 6.

Cost for extending the test for ten weeks is 7080 eur (2880 eur + 420 eur/week).Idea is get same test time as test number 4. The fixed price (2880 eur) includes the dismantlement the probe before boiler shutdown and building it back after to boiler shutdown

The price includes two men, three days (6 h/day, 80 eur/h) work and travels:

- one day for uncool, drain, dismantle the probe and moving it to storage
- one day for moving it from storage and building it up
- one day for vent, heat and adjust the probe

Decision:
Boildec offer of extended test time was accepted.

Comments:

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

6.5 VTT, Analysis of the furnace test materials

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

Status and schedule
VTT has analysed the material samples from test 4, preliminary results, APPENDIX 7.

- Carbon steel has ~lost 1 mm wall thickness
- 304L has lost ~0,15 mm wall thickness
- Super625 and San67 has no corrosion

Optical microscope & SEM/EDS analysis are on-going. Results will be presented in SKYREC-seminar 20th October.

Preparation of test 5 materials are done, analysis will be done when test ends in December.

Comments:

- in presentation 23.11.2010 material Super 625 (Probe 3), there is clear 3 marks in the WT profiles before and after the test graph -> Could VTT put these markings into same position?
- Is 4C54-material in test 5 or not
- Material names, what is 3XRE28?
- Measurement scale (wall thickness measurements) in the presentations should always be same, easier to compare
- Could there be summary slide for all materials

6.6 FRBC's Material recommendation

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

Status
Updating is ongoing:

- Durability committee will update chapter 1 in next meeting 24.11
- VTT offers updating the chapter 2 (coatings) by about 6000 euros
- Durability committee has updated chapter 3 repair of pressure vessels, APPENDIX 8
- Inspecta has updated chapter 4: recovery boiler inspections, APPENDIX 9
- Durability committee will write chapter 5

Decision:

Project will be separate from SKYREC, durability committee continue working with it during normal project work.

Schedule:
1. Recovery boiler materials and weldings (2011)
2. Recovery boiler coatings (2012)
3. Repair of pressure vessels (Done, 2011)
4. Recovery boiler inspections (Done, 2011)
5. Recovery boiler incidents (Durability committee)

Comments:
- Recommendation tells you only what you should take in to consideration, not what material you should choose
- Could the recommendation be updated in parts?
- Durabity committee should discuss what is the main purpose of recommendation, who will use it etc.
- Is it more like a handbook not recommendation?

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

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

Status:
All tests are done, results see APPENDIX 10.

Conclusions:
- Active carbon can remove up to 40 - 60 % of residual organic material (TOC)
- AC bed lifetime before regeneration is at least 10 months
- Subsequent MB is needed to remove elevated conductivity and silica
- AC works fine in full scale
- UV treatment was able to remove up to 30 % of residual TOC
- Removal efficiency did not improve with:
  - Lower wave lenght (more energy)
  - H2O2 (oxidant)
  - TiO2 (catalyst)
  - Number of UV chambers (contact time)

Writing of the final report is ongoing. Tero Luukkonen will present the results in the SKYREC seminar October 20th

6.8 Teollisuuden Vesi Oy, FRBC's Water quality guidelines

Teollisuuden Vesi Oy has done boiler and steam water quality guidelines for FRBC.

Separate workgroup was nominated for this project to comment/discuss the guidelines during work.

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

Status:
Preliminary recommendation has been send to steering committee in the end February 2011. Durability subcommittee has commented the guidelines and we are waiting of Teollisuuden Vesi reply.

You can download the preliminary report:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/6dcb567284207fc7c225787e004e64d7?OpenDocument

Maija Vidqvist from Teollisuuden Vesi Oy will present the guideliness in the SKYREC seminar October 20th, see presentation APPENDIX 11

Summary:
- 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
- Na3PO4
- Recovery boilers

Schedule:
- Guidelines will be published in December 2012

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 degradation and magnetite layer properties. Degradation of alkaline chemicals in over 300 °C has not been studied and effect on magnetite layer in 340 °C is not known.

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.

7.3 Others proposals

No other proposals

8 PROJECT IDEAS

9 OTHER ISSUES

9.1 Final seminar

Final seminar will be held October 20th in Sokos Hotel President, Helsinki. Presentation will be held in English.

Proposed programme, APPENDIX 12

9.1.1 Northern America

Jim Keiser, Oak Ridge National Laboratory cannot come to the SKYREC-seminar. Instead of Jim, Doug Singbeil will present their project: Improving heat recovery in biomass-fired boilers.

9.2 Translating project reports into English

Translation of report is done:
Sulfidation tests
Mustala, Sanni, Pohjanne, Pekka, Heikinheimo, Liisa, Pankakoski, Pekka and Kinnunen, Tuomo, VTT 10.3.2006.

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

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

10 NEXT MEETINGS (MEETING CALENDAR FOR 2011)

2012 meeting calendar:
– Meeting I: 7th February at 10.00 a.m, Pöyry Finland Oy, Vantaa

Markus Nieminen