Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING 2/2011

TIME May 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
Yukitoshi Yamazaki	Sumitomometal Industries,Ltd.

Group members without a right to vote:

Esa Vakkilainen	LUT, project coordinator
Markus Nieminen	Finnish Recovery Boiler Association, secretary
Keijo Salmenoja	Andritz Oyj

APPENDICES

1 Project budget 5.5.2011
2 Project schedule 5.5.2011
3 ÅA, Corrosion tests in reducing conditions, PART II – revised offer 5.5.2011
4 VTT, Mill tests of superheater materials – final report 20.1.2011
5 Boildec Oy, Field testing of furnace materials – test 4 temperatures
6 Oulun Yliopisto, Ceramic structural materials - draft report 2.5.2011
7 FRBC material recommendation – chapter:Recovery boiler inspections (Inspecta)
8 SKYREC final seminar – proposed 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
Reijo Hukkanen	Stora Enso Oyj, Fine Paper, Oulu
Kalle Salmi	Metso Power Oy, Tampere
Kaj Nordbäck	Chairman of Finnish Recovery Boiler Association
Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman
Jukka Mikkonen	Stora Enso Oyj

1.2 Agenda

No changes to agenda.

1.3 MEMO of the previous meeting (2/2011)

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

Åbo Akademi, Corrosion tests in reducing conditions – PART II

- Steering committee decided to order the Part A (APPENDIX 3), see test plan below. Temperatures will be different: 525 °C and 565 °C

VTT, Mill tests of superheater materials

- Comments to the final report should be send to the secretary by 19th May
- Secretary will ask proposal for new test.

Boildec Oy, Field testing of furnace materials

- It was decided to continue the test number 4 to week 22 (April 30th).
- Materials for test 5 were decided

FRBC Material recommendation

- Durability committee should discuss the purpose of the recommendation, do we need it

3 BUDGET

Budget (situation 5.5.2011) is presented in APPENDIX 1

Ordered work sum is currently 738 477,37 €, from which 494 327,37 € is already paid and 244 150,00 € will be invoiced 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 5.5.2011) is presented in APPENDIX 2.

Most of the projects are 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 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 was received 15.12.2011:
http://www.soodakattilayhdistys.fi/apps/soodakattilayhdistys/download.nsf/11d6a3ccd3209b4cc2257784003c4a58/2682c71379a8da80c22577f20051c0c0?OpenDocument

Comments on minimum steam pressure requirement in cooking/bleaching and other should be addressed to Esa (esa.vakkilainen@lut.fi). Esa has received already 5 comments on pressure requirements question.

Schedule:
Master thesis worker returns from Moscow in spring to finalize the work during summer 2011. Final report will be presented on next meeting 5.10.2011.

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 are preparing the measurements, see test plan below.
Secretary will contact to the mills and discuss about the test plan.

One week dew point measurement with high SO2 in Rauma seems not possible in environmental and boiler fouling point of view

Schedule:
Heinola at least once in May (SO2/SO3 + dewpoint measurements) and once in June (corrosion measurements).

Rauma would be run in August/September. We will want to take SO2/SO3 + dewpoint measurements at Rauma in May to give us a frame of reference for August/June.

Test plan:
Test plan (Heinola):
- 1-2 days in Heinola for dew point and SO2/SO3 measurements in the stack.
- Collecting of liquor, esp ash samples and process data at the same time.
- ~2 weeks for analyzing and validating results
- 1 week for corrosion measurements with air cooled probes in stack

Test plan (Rauma):

- 1 week normal operation
  - 1st day dew point measurement and SO2/SO3 measurement in the stack.
  - Days 2-5 corrosion measurements (economizer region)
- 1 week operation with high SO2 levels
  - 1 day dew point measurement and SO2/SO3 measurement in the stack.
  - Days 2-5 for corrosion measurements with air cooled probes in stack

Dew point measurement:

- 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.
- Åbo Akademi has tested the instrument in oil fired boiler -> works with water dew point, open question still is it sensitive enough for the acid dew point?

Corrosion measurement:

- Corrosion measurement is done with an air cooled probe with detachable metal rings and samples will be analyzed with SEM/EDS.
- Exposure times from ~2h-48h.
- Careful control of the probe temperature will be required. Also open questions relate the exposure time.

Analysis:

- 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.

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

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 were are 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.

Status:
Åbo Akademi has tested the reducing effect of the BL-char and a verificate that sulphate reduction is established, see results APPENDIX 3. Tests have been performed in the DTA/TGA to investigate the reduction of Na2SO4 in the presence of BL-char and N2 with and without CO.

The results showed that at the relevant corrosion test temperatures (< 600°C) no actual reduction took place (APPENDIX 3, Attachment 1). Also one corrosion test in the tube furnace was made at 550°C in 5% CO + N2, with Salt 10, where about half of the sulphur in the salt was replaced by Na2S (Salt 10r). This test showed clearly an increased corrosion on the 10CrMo9 material. This test is presented in APPENDIX 3, Attachment 2.

Decision:
Steering committee decided to order the Part A (APPENDIX 3), see test plan below. Temperatures will be different: 525 °C and 565 °C

Schedule:
Part A: the report is ready in October 2011

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

Price A: 30 700 € + VAT

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:
SKYREC jory has commented the preliminary report received in February. Now VTT has send (2.5.2011) revised report, APPENDIX 4.

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

Comments to the revised report should send to markku.orjala@vtt.fi or to the secretary by April 19th.

Decicion:
Secretary will ask proposal for new test.

Schedule:
Final report is accepted in next meeting October 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

6.4 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: Feb - May, 2011	Test 5: Aug - Oct, 2011
AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)
AISI 310S	Sanicro 67	Super 625 (Sumitomo "N")	Carbon steel	HR11N (Sumitomo "R")
Sanicro 38	HR11N (Sumitomo "R")	HR11N (Sumitomo "R")	Sanicro 67	Sanicro 38
Sanicro 28	Sandvik 4C54	Sanicro 38	Super 625 (Sumitomo "N")	Sandvik 4C54

Status:
Test 4 is ongoing and originally was planned to end April 9th, but Joutseno mill has postponed their shutdown to the beginning of June, so it was decided to continue the test to week 22 (April 30th).

Probes thermocouples broke 15.3, but lasted almost six week, data APPENDIX 5. Inner side and oil temperature thermocouples are still working.

Carbon steel sample thickness was measured after 800 hours with ultrasound.
Result was 5,20 +/-0,05 mm. Beginning:
Z -15mm 5,499 5,474 5,504

Z -25mm	5,501	5,487	5,504
Z -32mm	5,500	5,493	5,506

so 0,3 mm has been lost.

Decision:
It was decided to continue the test to week 22 (April 30th).

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 will analyse the material samples from test 4 after it is ended. They try to do analyses before the summer holidays.

Preparation of test 5 materials can begin; test will start after the summer holiday in august.

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?
- 4C54

6.6 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 decided to replace the nanospinel with Hassle P1800.

New two week test started 4.4.2011 and ended 18.4.2011, results APPENDIX 6.

Probe 1:	Probe 2:
Fireclay	Fireclay
MgO-iron	MgO-iron
Hassle P1800	Hassle P1800
Hassle D39A	Hassle D39A
homemade spinel	homemade spinel

Conclusion is that “old” materials still better than new ones.

Schedule:
Durability committee will accept the report on their next meeting.

6.7 FRBC’s Material recommendation

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

1. Updating is ongoing, chapters 2-4. One possible author for chapter 1 is Hannu Hänninen, Aalto University. He is returning from MIT in end of September 2011.

2. VTT offers updating the coatings chapter by about 6000 euros.

3. Secretary has discussed with Petri Lähdekorpi, Metso about the repair of pressure vessels-chapter. Some of information can be found in TUKES guides:
http://www.tukes.fi/Tiedostot/painelaitteet/esitteet_ja_oppaat/painelaite-kunnossapito-opas.pdf
http://www.tukes.fi/Tiedostot/painelaitteet/esitteet_ja_oppaat/painelaiteopas.pdf

4. Inspecta has updated the inspection part, chapter for comments, APPENDIX 7.

Polytechnic Varkaus offers to do the recovery boiler incidents-chapter by about 10 000 euros. It would be a thesis.

Decision:
Durability committee should discuss the purpose of the recommendation, do we need it

Schedule:
Most of the work is done during 2011.

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?

6.8 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:
Industrial size activated carbon test are ongoing. Surprising results was that activate carbon releases silicate despite it should be one of the purest in the market.

UV-tests started in week 14, no results yet received.

6.9 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:
Preliminary recommendation has been send to workgroup in the end February. Workgroup has commented the recommendation in meeting 9.3.2011

Schedule:
- Next meeting is scheduled 26.5.
- Recommendation is send to committee members for comments in the beginning of June.

– After comments recommendation will be finished in the beginning of September.

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

8.1.1 VTT, Mill tests of superheater materials, part 2

Secretary will ask proposal for part 2 from VTT

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 8

9.1.1 Northern America

Jim Keiser, Oak Ridge National Laboratory is coming to the SKYREC-seminar to present their project: Improving heat recovery in biomass-fired boilers

9.2 Translating project reports into English

Translation of the report is ongoing:
Sulfidation 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 III: 5th October at 10.00 a.m, Pöyry Finland Oy, Vantaa

Markus Nieminen