

Finnish Recovery Boiler Committee

SKYREC STEERING COMMITTEE MEETING XII

TIME September 15th, 2010 10.00 – 16.00

PLACE Pöyry Finland Oy, Vantaa

PARTICIPANTS

Matti Tikka	UPM-Kymmene Oyj, Kymi, chairman
Lasse Koivisto	Andritz Oy, Varkaus
Hiroshi Matsuo	Sumitomometal Industries, Ltd. (during items 1-7)
Timo-Pekka Veijonen	Stora Enso Oyj
Keijo Salmenoja	Oy Metsä-Botnia Ab, Rauma
Kenneth Blomqvist	Sandvik

Group members without a right to vote:

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

Other:

Maija Vidqvist	Teollisuuden Vesi Oy (during items 7.1 -7.2)
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APPENDICES

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| I | Project budget 13.9.2010 |
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| X | OY/Cewic, TOC removal methods – field tests of activated carbon and UV-treatment – meeting with Hanovia Ltd. 25.8.2010 |
| XI | Teollisuuden Vesi Oy, TOC removal methods and their applicability in make-up water treatment – summary report 11.8.2010 |
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DISTRIBUTION

Steering committee and their substitutes
Durability Sub Committee, Black Liquor Sub Committee
Board of the FRBC
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1 CALLING MEETING TO ORDER

1.1 Absences

Kaj Nordbäck	Chairman of Finnish Recovery Boiler Association
Martti Korkiakoski	Tekes
Olli Talaslahti	Oy Metsä-Botnia Ab, Rauma
Reijo Hukkanen	Stora Enso Oyj, Fine Paper, Oulu
Kalle Salmi	Metso Power Oy, Tampere
Timo Peltola	Sandvik, Helsinki
Mika Paju	Oy Metsä-Botnia Ab, Joutseno

Kenneth Blomqvist, Sandvik was deputizing for Timo Peltola, Sandvik on this meeting.

Hiroshi Matsuo, Sumitomo is moving to Japan, he inform his successor later.

2 MEMO OF THE PREVIOUS MEETING (3/2010)

The memo of the previous meeting was accepted.

3 BUDGET

Budget (situation 13.9.2010) is presented in APPENDIX I and in APPENDIX II as chart.

Ordered work sum is 608 620 eur and reservations 114 000 eur, totally 720 620 eur. TEKES will participate maximum 50 % from 700 000 eur (350 000 eur), so budget looks ok if all reservations are materialized.

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 13.9.2010) is presented in APPENDIX III.

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

Both field test projects (furnace and superheater material) are behind schedule. Furnace material tests (Boildec Oy) are going on, but superheater materials tests (VTT) are not started yet. Superheater material test is currently the most critical item.

5 FINISHED PROJECTS

5.1 LUT, Once-through and reheater recovery boiler - concept studies

5.2 Åbo Akademi, Laboratory tests of superheater material

5.3 Teollisuuden Vesi Oy, TOC removal methods and their applicability in make-up water treatment

5.4 Oulun Yliopisto, Reduction of TOC from recovery boiler make-up water

6 ONGOING PROJECTS

6.1 LUT, Pulp mill optimal steam pressure levels (WP1, S2)

Background:

When modernizing the existing pulp mill the question is how to show what is the economical pressure level. 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.

Schedule:

Project is completed by the end of November 2010.

Status:

Aapo Hiltunen, LUT will carry out the work as his master's thesis. Black liquor sub-committee will supervise the project. Work will be done in English but reported also in Finnish.

Part 1. is done. LUT will contact mills if more information is needed.

Part 2. Aapo has calculated investment cost of different cases and currently analysing results. Results will be presented at next meeting in December.

Different investment cost cases:

- install 3.5 bar pressure level alongside with existing 5 bar.
- decrease sootblowing steam pressure
- increase low pressure steam pipe

Calculate 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.

- modern about 600 000 ADt/a pulp mill
- traditional about 600 000 ADt/a pulp mill
- modern pulp mill + bark boiler
- traditional pulp mill + bark boiler
- modern pulp mill + fine paper mill
- traditional pulp mill + fine paper mill
- modern pulp mill + bark boiler + fine paper mill
- traditional pulp mill + bark boiler + fine paper mill

6.2 ÅÅ, 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.

Schedule:

Work will be finished by 31.12.2010 and reported at a common meeting and as a presentation handout.

Status:

Work will be started during September 2010.

6.3 Åbo Akademi, 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 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.

Schedule:

Original project schedule was by the end of September 2010, now it is October 2010.

Status:

Niko DeMartini's report:

We should be wrapping up the laboratory work by the end of September provided we get some analytical results soon, so we are planning on being able to present results in October.

6.4 VTT, Mill tests of superheater materials, (WP2, T3)

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*
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* 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.

Schedule:

Original schedule for the measurements were autumn 2009. Everything has been ready since spring 2010, only manpower is missing from VTT.

VTT has confirmed that test will start in week 37, September 13th 2010. First there will be a 2 day testrun, and official measurement will start September 16th 2010.

Status:

Official measurements are started September 16th.

Comments:

- Are we interested in testing materials on present steam temperatures or future steam temperatures?
- Material temperature 510 °C means steam temperature ca. 460-480 °C
- If our target steam temperature is 540 °C, material temperatures should be 570 °C and 590 °C
- In material temperatures 550 °C and 570 °C, there is a certain percentage molten phase in the deposits

- 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.

6.5 FRBC's Material recommendation (WP3, P1)

Objective:

Durability committee suggests updating existing recommendation "Suojaussuositus" from 1997.

Following chapters to be updated (possible author):

- Recovery boiler materials and weldings (Sandvik?)
- Recovery boiler coatings (VTT)
- Pressure vessel repairs (Metso)
- Recovery boiler inspections (Inspecta)

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.

Schedule:

Writing is not timetabled yet, chapter recovery boiler materials and weldings cannot start until material test are finished.

Status:

Nothing to report

Comments:

- Coatings chapter should include also welding
- Could the chapter 5: recovery boiler incidents be special work/candidate thesis?

6.6 Oulun Yliopisto, Ceramic structural materials (WP3, P2)

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.

Schedule:

Project is completed tentatively by the end of May 2010, it is now behind the schedule. Test number 1 (quick test) will be done again, to verify the results after Oulu's recovery boiler is running smoothly currently sulphidity is low. Project should be completed by the end of year 2010.

Status:

Quick test 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.

Test number 1 (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

University (Riku Mattila) proposed that the spinel could be nanospinel, which melting point is 900 C; making it takes some time, weeks.

Durability committee (30th August) 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:

MgO-iron
Hassle D39A
ZrO₂
Betker
MgO-iron

Probe 2:

MgO-iron
Ankoflo
Nanospinel
Fireclay
MgO-iron

Comments from steering committee meeting March 17th:

- what is the total material lost, now only the height is measured
 - OY: all has same surface 50x50mm
- Has hardness changed?
 - OY: only with ZrO₂, which broke when probe was taken out
- what is the effective material lost, colour change area included if hardness is changed.
 - OY: to be calculated
- frame has probably hindered the penetration and protected the samples
 - OY: probably, but is the same situation for all materials

Comments from durability committee meeting May 6th:

- probes uppermost and lowest material should be the same material
- quality of selfmade materials = industrial quality?

- could the reference material be MgO-ironmass.

6.7 Boildec Oy, Field testing of furnace materials (WP3, P3)

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: Nov - Dec, 2010
AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)	AISI 304L (reference material)
AISI 310S	Sandvik 67	Super 625 (Sumitomo "N")	?
Sanicro 38	HR11N (Sumitomo "R")	HR 11N (Sumitomo "R")	?
Sanicro 28	Sandvik 4C54	Sanicro 38	?

Status:

Tests are about a year behind the original schedule due to problems with probe temperature control. Now problems have been solved and tests are going on.

First test was finished successfully April 15th. Test number 2 completed on June 23rd. From both tests we have reports.

Test number 3 was completed September 6th, report APPENDIX IV.

Test number 4 is planned to be reference run.

Timo Karjunen, Boildec Oy is invited to next meeting to present/discuss project.

Comments:

- temperature measurements reliability
- all tubes look undamaged, no corrosion seen -> extend test time?

6.8 VTT, Analysis of the furnace test materials (WP3, P3)

Objective:

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

Status:

Pekka Pohjanne has sent a analyse report of test number 1 and 2, APPENDIX V in Finnish, APPENDIX VI in English.

Analyses of test number 1 have been done again, but results can't be totally trusted. The accuracy of cross-section thickness measurement is not suffi-

cient because tubes have already dents and too much wall thickness variation. These cause alignment challenge because measurements should be taken from exact same points as before the test. In addition inclination errors are possible.

Analyses of test number 2 have same challenges.

The thickness profile of the samples will be measured week 36 at MIKES (Centre for Metrology and Accreditation). This should be possible because sample surfaces are clean, no corrosion products, which could weaken the measurement accuracy. A thickness profile measurement gives more data and improves result reliability when alignment etc. problems decrease.

Pekka Pohjanne, VTT is invited to next meeting to present/discuss project.

Comments

- Before starting test number 4, we wait results from MIKES
- Could the tube surfaces machined/grinded before testing.

6.9 VTT, Effect of water quality and different chemicals on magnetite layer properties (WP4, V3)

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.

Chosen amines to be tested:

- cyclohexylamine
- 2-amino-2-methyl-1-propanol
- morpholine
- ammonium as reference

Schedule:

Previous work is completed, VTT will make offer about further research.

Status:

Mikko Vepsäläinen, VTT gave a presentation about the project results in previous meeting June 15th and in durability committee meeting on August 30th. Results and proposed further research, APPENDIX VII.

Further research:

Part 1: Chemical decomposition products

- Static autoclave
- Chemical concentration higher than previous test

- Qualitative and quantitative analyses of the chemical decomposition products in water and steam

Part 2: 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
- Amines and/or decomposition products are added to the water circuit, magnetite layer properties are monitored by electrochemical measurements

Comments:

- Could the part 2 made in operating boiler -> sample valve
- What are the qualitative/quantitative analyse methods?
- More detailed proposal needed, test plan, conditions

Comments on durability committee meeting August 30th:

- Decomposition products should be analysed before any statement can be said about chemical decomposition
- How is resistance and durability of the magnetite layer measured
- Autoclave test where water flow is 1 m/s or higher, 12 hour long measurement
- Water/steam flow at recovery boiler tube can be at top water 3,5 m/s steam 6 m/s. Bottom of the tube, water 0,5 – 1,9 m/s.

Comments on steering committee meeting June 15th:

- Magnetite layer's elemental composition should be checked, now only thickness was measured
 - After meeting VTT analysed the samples, magnetite layers contains iron and oxygen, with mole ratio 3:4 -> magnetite. Also there were small amounts of carbon and aluminium.
- How magnetite layer has developed, large particles in the surface
- Decomposition products not measured, should be possible with gas chromatograph
- SEM image from pure metal samples
- Flow inside the autoclave unknown, how well does the boiler tube simulate?

6.10 OY/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.

Schedule:

Tentative schedule is June – September 2010. Secretary will check the current schedule.

Status:

Tero Luukkonen has send presentation about project status; see APPENDIX VIII (in Finnish)

Active carbon:

- Same active carbon bed during February 24th – June 28th, TOC-reduction (~20%) much lower than in 2009 test (~ over 50%)
- Active carbon bed was renewed June 28th, but TOC-reduction efficiency (~40%) is not as good as in 2009 test.
- Different filter locations are tested, currently before mixed-bed filter
- Used active carbon from Oulu water supply plant was added on August 12th, water conductivity increased after filter -> carbon was impure
- Still to be done:
 - BET-analyses from the carbon
 - Size distribution from the water samples
 - Ion chromatography -> asetate and formiate concentrations
 - LC-OCD (Huber): characterise and quantify organic compounds in water

UV-treatment:

- Hanovia Ltd. is interested co-operation, see memo August 25th on APPENDIX IX (in Finnish)
- discussion going on about delivering pilot unit to Oulu mill

RO-treatment:

- Inquiries of pilot plants has been made, Prominent and HOH has pilot plant in a trailer.

6.11 Teollisuuden Vesi Oy, TOC removal methods and their applicability in make-up water treatment

Report was accepted in meeting March 17th.

Maija Vidqvist, Teollisuuden Vesi Oy has written more detailed summary, see APPENDIX X (in Finnish)

Steering committee requested that table 1. TOC reduction processes would be done in English.

7 PROPOSALS

7.1 FRBC's Water quality recommendation, (WP4, V1)

Status:

Durability committee is preparing the table of contents for water quality recommendation.

Secretary has sent it to below listed companies for tendering:

- Boildec (received)
- Teollisuuden Vesi Oy (received)
- Pöyry
- VTT

Maija Vidqvist, Teollisuuden Vesi Oy was invited to this meeting to discuss water quality recommendation and other water projects.

Teollisuuden Vesi Oy proposes to establish workgroup (4-6 members from FRBC) for writing the water recommendation. There would be 5 meeting with different topics:

- Standard values
- Continuous measurements vs. laboratory measurements, operating instructions what do when value exceeds the limit
- TOC and organic and inorganic chemicals
- Chemical cleaning and forming of magnetite protection, different water treatment processes
- Final meeting

Teollisuuden Vesi would introduce the meeting topics and write memos. Also other experts can be invited to the meetings.

Discussion summary:

- Raw water quality defines the most suitable process to produce make-up water for recovery boiler -> not just one alternative
- Important measurements from raw water:
 - salinity/conductivity
 - humus
 - TOC
- Reverse osmosis (RO) is best, but needs efficient preliminary treatment
- Nano filtering (NF) can use lake/river water, no need for flocculation/flotation
- UV-treatments operation costs can be high depending on lamp duration and price.
- UV-treatment can be added to existing process, RO/NF need changes on the process.
- Condensate quality is also important, some fractions can contain lot of TOC

Teollisuuden Vesi would revise the offer:

- preliminary recommendation text (ISO-standard and Värmeforsk-report) is written by Teollisuuden Vesi and send to the workgroup before meetings
- After meetings revised text is send to the FRBC members for comments
- Comments are collected and recommendation text revised again

Schedule:

Decision of the recommendation writer is done in the beginning of October. We are still waiting offers from VTT and Pöyry.

Actual work could begin January 2011 at earliest.

Comments:

- Water quality recommendation should include practices what to analyse and how often and also operating instructions what to do when a value exceeds the limit.

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

Teollisuuden Vesi Oy offers a work (APPENDIX XI) where the investment costs and operating costs of different TOC removal methods (reverse osmosis, UV-treatment, nano filtering, active carbon filterin) 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 to next meeting, when the results of Cewic- project are available.

7.3 Others proposals

No other proposals.

8 PROJECT IDEAS

8.1 Åbo Akademi, Laboratory tests of superheater materials

The following optional test is suggested by Åbo Akademi:

1. To increase the amount of active C/sample and mix it well with the salt
2. To increase the test temperature in order to attain a stronger reduction of Na₂SO₄ to Na₂S
 - a. 610, 620, 630, 640, 650°C (active C as a reducing agent)
 - b. heat up the samples to e.g. 630°C, keep it there for a certain certain time to achieve a sulphate reduction and then decrease the temperature

to the test temperature. However, this treatment may influence the materials differently, and may in some cases give unclear results

3. To create reducing conditions by different methods:

- a. BL-char on the salt
- b. BL-char/salt mixture

Option 3 was already considered in this work, however, since BL-char contains chlorine and it is known that the corrosion can be very sensitive to the amounts of Cl it was decided to use active carbon as the reducing agent.

Part 3 would be interesting to do, Keijo Salmenoja will discuss with Mikko Hupa, ÅA.

Comments:

- repeatability of tests is questionable, no constant results
- what are the laboratory conditions that we want, in real superheater there is oxygen present.

9 OTHER ISSUES

9.1 International co-operation

9.1.1 Sweden

Niko DeMartini has been discussing with Niclas Berglin and Rikard Wadsborn from Innventia and Mikael from ÅF about co-operation:

Co-operation with Sweden/Innventia won't go forward. Värmeteknik, who Innventia were looking for funding from, is unable to fund them at this moment. Innventia expect to apply for funding in November or then in March depending on the group they will seek funding from. Then any collaboration from Åbo Akademi side would be part of a separate project.

9.1.2 Northern America

Jim Keiser, ORNL visited Åbo Akademi and had discussion about collaboration opportunities between the SKYREC and ORNL project "improving heat recovery in biomass-fired boilers"

The APPENDIX XII contains the quarterly report on our project "Improving Heat Recovery In Biomass-Fired Boilers" for the April 1 through June 30 quarter of this fiscal year

9.2 Translating project reports into English

Secretary has received list from Sumitomo what report should be translated and found translator which should be qualified to translate SOTU reports. The rate is 1,7 – 2,0 €/per translated line.



Secretary has asked word-versions of the reports that are in Sumitomo's list, most of them are made by VTT. Only one report is still missing, which is the most interesting and should translated first.

Also another translator found, discussion is going on.

10 NEXT MEETINGS (MEETING CALENDAR FOR 2010)

2010 meeting calendar:

- Meeting VI: December 15th at 10.00 a.m, Pöyry Finland Oy, Vantaa