Suomen Soodakattilayhdistys ry

LIPEÄTYÖRYHMÄN KOKOUS 4/2017

AIKA 21.11.2017 klo 14.00 – 15.30

PAIKKA Skype

LÄSNÄ

Timo Saarinen	Metsä Fibre Oy, Rauma, PJ
Sami Metiäinen	Pöyry Finland Oy, Kouvola
Emil Vainio	Åbo Akademi, Turku
Aino Vettenranta	Valmet Technologies Oy, Tampere
Klaus Niemelä	VTT, Espoo
Markus Engblom	Åbo Akademi, Turku
Esa Vakkilainen	Lappeenrannan teknillinen yliopisto
Antti Tikkanen	Pöyry Finland Oy, Vantaa, siht.

LIITE 1	ÅA, Understanding Low Temperature Corrosion in BL Combustion, Phase 3 - Final Report 24.8.2017
LIITE 2	Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport, ÅA–tarjous 11/2017

JAKELU
Julkaisu: Soodakattilayhdistyksen kotisivulla
Tiedote: Hallitus Yhdyshenkilöt Lipeätyöryhmä
Sihteeristö

1 POISSAOLOILMOITUKSET

Kokoukseen olivat estyneet osallistumasta:

Toni Orava	UPM Kymmene Oyj, Kuusankoski
Jorma Torniainen	Labtium Oy, Espoo
Nikolai DeMartini	Åbo Akademi, Turku
Tuuli Oljakka	Andritz Oy, Helsinki
Jouni Hiltunen	Stora Enso Oyj, Varkaus

2 ASIALISTA

Asialista hyväksyttiin muutoksitta.

3 EDELLISEN KOKOUKSEN PÖYTÄKIRJA

Edellisen kokouksen pöytäkirjan käsittely siirrettiin seuraavaan kokoukseen.

4 VALMISTUNEET PROJEKTIT

4.1 Understanding low temperature corrosion in BL combustion – Phase 3, Åbo Akademi

Projekti on jatkotyö saman sarjan aiemmille osille: Phase 1 ja Phase 2.

Tausta:
Projektin aiemmissa osissa on selvinnyt, ettei rikkihapolle löydy kastepistettä soodakattiloissa ja alin mahdollinen savukaasujen lämpötila määräytyy teräspinnoilla korroosiota aiheuttavien suolojen hygroskooppisen luonteen mukaan. Oleellinen huomio on, ettei muilla suoloilla kuin puhtaalla $NaHSO_4$:llä todettu tapahtuvan korroosiota 110 °C lämpötilassa (kokeissa materiaalin ja kaasun lämpötila on sama).

Työn tavoite:
Työn tarkoitus on saada varmistus toisen osan saaduille tuloksille (24 tunnin kokeet) suorittamalla 1000 tunnin koe. Oletus on, että matalalämpötilakorroosio ilmenee nopeasti eli 24 tunnin kokeiden tulokset vastaavat 1000 tunnin koe tuloksia.

Tilanne:
Työn loppuraportti (Liite 1) saatiin Åbo Akademista elokuun lopulla ja lähetettiin ennen kokousta työryhmälle kommentoitavaksi. Jo ennen kokousta esitettiin tekijöille tarkentavia kysymyksiä ja näitä sekä muita kommentteja käytiin läpi kokouksessa. Työn tärkeimmät lopputulokset olivat:

- 22 tunnin altistuskokeen perusteella todettiin että 16Mo3/5 –materiaali on vähemmän altis tuhkassa olevien suolojen kastepistekorroosiolle kuin ST45.8 –materiaali.
- 22 tunnin kokeen perusteella 1000 tunnin kokeeseen valittiin Pietarsaaren soodakattilasta peräisin oleva tuhkanäyte. 1000 tunnin kokeessa näyteuunissa oli molempia ym. materiaaleja yksi kappale kolmessa eri lämpötilavyöhykkeessä (120 °C, 105 °C ja 101 °C).

- Yksikään koemateriaali ei osoittanut merkkejä korroosiosta 1000 tunnin altistuskokeen jäljiltä

Edellisessä kokouksessa työryhmä antoi kommentteja raportista ja esitti, että Kestoisuustyöryhmältä kysytään käytännön kokemuksia aiheeseen liittyen. Kestoisuustyöryhmä ei ehtinyt kokouksessaan käsitellä aihetta, joten sihteeri lähetti sähköpostilla pyynnön KTR:n jäsenille kertoa lyhyesti käytännön kokemuksista matalalämpötilakorroosioon liittyen. Kommentteja kerätään marraskuun loppuun asti, jonka jälkeen Emil Vainio koostaa niistä lyhyen katsauksen raporttiin.

Päätös:
Sihteeri kerää kommentit Kestoisuustyöryhmältä, välittää ne raportin laatijalle joulukuun alussa ja raportin päivityksen jälkeen lähettää raportin työryhmälle viimeistä hyväksyntää varten. Lopullinen hyväksyntä raportista tehdään sähköpostitse työryhmän kesken.

5 KÄYNNISSÄ OLEVAT PROJEKTIT

5.1 Black Liquor Evaporation Book, ÅA

Tausta:
Kirjan tarkoituksena on perehdyttää nuoria insinöörejä mustalipeän haihdutukseen sellutehtaalla sekä tarjota yksityiskohtaista tietoa mustalipeän ominaisuuksista sekä haihduttamon likaantumisesta. Kirjaa voidaan käyttää pohjatietona tieteelliselle tutkimukselle kuin myös haihduttamon yleisten ja likaantumisongelmien selvittämiseen.
Kirjan kirjoittajia ovat Jim Fredrick ja Nikolai DeMartini. SKY:n osuus kirjan kuluista kattaa DeMartinin osuuden.

Tilanne/Aikataulu:
Työryhmä sai kommentoitavaksi uusimman version kirjasta lokakuussa. Kokouksessa työryhmällä oli mahdollisuus lyhyesti vielä kertoa kommenteistaan ja huomioista. Sihteeri lähettää saadut kommentit kirjan kirjoittajalle.

Päätös:
Työryhmä edellyttää kirjan valmistuvan vuoden 2017 aikana.

6 PROJEKTIEHDOTUKSET

6.1 Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport, ÅA

Tausta ja tavoite:
Työn tarkoituksena on tutkia ja saada tietoa soodakattilan tulistinten likakerroksen rakenteesta ja kemiasta, mistä on hyötyä teollisuudelle tulistinalueen korroosion ymmärtämisessä. Laboratoriotutkimusten perusteella on voitu päätellä, että likakerrokseen muodostuu lämpötilagradientti, joka aiheuttaa alkalikloridien siirtymistä kohti tulistinputken ”kylmempää” pintaa. Aihetta ei ole juurikaan tutkittu soodakattiloilla.

Tilanne:
Työryhmä sai päivitetyn tarjouksen projektista ja siinä työ oli jaettu kahteen osaprojektiin (7000€ ja 30 000€). Tarjous löytyy liitteestä 2.

Ensimmäinen osaprojekti on jatkoa esiselvitykselle, jonka ÅA on toteuttanut Rauman tehtaan kanssa. Ensimmäisessä osassa kehitetään näytteenottoproseduuria ja pyritään tekemään siitä mahdollisimman toimiva. Tavoitteena on kasvattaa näytteenottoajan pituus 20 minuutista yhteen viikkoon.

Projektin toisessa osassa tavoitteena on kasvattaa näytteenottoaikaa vielä pidemmäksi esimerkiksi tuhanteen tuntiin. Toisessa osassa käsiteltäisiin aihetta myös paljon syvällisemmin teorian kannalta, kun taas ensimmäinen osa on käytännölistä pohjatyötä toista osaa varten. Projektin toinen osa toteutettaisiin mahdollisesti diplomityönä.

Päätös:
Työryhmä päätti esittää ensimmäisen osaprojektin toteuttamista yhdistyksen hallitukselle. Työryhmän mielestä aihe itsessään on kiinostava ja jälkimmäiseen osaan eteneminen ei ole mahdollista ilman ensimmäistä osaa. Ensimmäisessä osaprojektissa kehitetään myös näytteenottolaitteistoa, minkä työryhmä koki mielenkiintoiseksi ja näki sen olevan yleishyödyllistä tutkimusta tulevaisuuden kannalta.

6.2 Biolietteen polton vaikutukset soodakattilassa ja lipeälinjalla

Tausta ja tavoite:
Biolietettä on poltettu monella tehtaalla ja siitä on erilaisia kokemuksia. Ongelmia syntyy prosessiin kuulumattomien aineiden rikastuessa lipeäkiertoon, mihin vaikuttaa mm. onko tehdas integraatti vai ei. Yksittäisten kokemusten perusteella ongelmia on havaittu sekä kaustistamolla että haihduttamolla.

Julkista tietoa polttokokemuksista ei kuitenkaan ole. Sen sijaan laboratorioanalyysejä biolietteen poltosta on Åbo Akademin tutkimuksesta (Ammonia formation and recovery in a kraft pulp mill and fate of biosludge nitrogen, SKY 5/2012). Soodakattilayhdistyksen ulkopuolella biolietteen polttoa on selvitetty ainakin vuonna 2006 Niko Metsämuuronen diplomityössä (LUT/Ene) "Sellutehtaan lietteiden termokemiallinen prosessointi”.

Työn tulisi vastata seuraaviin kysymyksiin:
- nouseeko lipeän typpipitoisuus ja edelleen NOx-päästöt?
- mitä lietteen polttaminen käytännön operoinnin kannalta tarkoittaa? Tuleeko kiertoja avata? Aiheuttaako likaantumista?
- mitkä ovat kustannukset tehtaalle?
- miten mädätetty bioliete eroaa mädättämättömästä?

Toteutus:
Eri toteutustapoja pohdittiin työryhmän kesken. Työryhmä esitti työn teettämistä diplomityönä tai pro gradu –tutkielmana, jonka kirjallisuusosuudessa käsiteltäisiin tähänastinen tutkimus ja kokeellisessa osassa voisi esimerkiksi tehdä lipeän ja lietteen yhteispolttoa. Tätä on aiemmin tehty mm. Åbo Akademissa. Työryhmä haluaa muistuttaa, että työtä tehdessä on tärkeää suhtautua aiheeseen kriittisesti ja löytää syyt miksi lietteen polttoa ei laajamittaisesti harjoiteta, eikä lähtökohtaisesti hakea vain polton positiivisia puolia.

Toinen, hieman laajemman aiheen vaihtoehto olisi päivittää raportti 3/2004 (Mustalipeän polttomenetelmät Suomen soodakattiloissa) nykypäivään ja käsitellä biolietteen polttoa raportissa.

Kokouksessa keskusteltiin työn toteutusvaihtoehdoista ja todettiin, että aiheen käsittely olisi suotuisampaa tehdä erillisenä työnä eikä osana raportin päivitystä.

Päätös:
Työryhmän mielestä työn sisältö, toteutuskonsepti ja mahdollinen toteuttaja on mietitty, minkä lisäksi aihe on muutenkin tärkeä ja mielenkiintoinen. Työryhmä päätyi kuitenkin jättämään työn seuraavalle vuodelle.

6.3 Soodakattilan ja talteenottokierron vierasainetaseet

Tausta ja tavoite:
Soodakattilayhdistys on kysynyt palautteessa jäsenistöltään heitä kiinnostavia tutkimusaiheita ja usein on tullut esiin vierasaineaiheet. Yhdistys on vuonna 2007 teettänyt diplomityön aiheella Soodakattiloiden raskasmetallitaseet, jonka kokeellisessa osassa on tehty taseet talteenottokierron EU12 –raskasmetalleille sekä natriumille, rikille, kloorille, kaliumille ja kalsiumille.

Toteutus:
Tavoitteena olisi päivittää tai toistaa työ sillä painotuksella, että tutkittaisiin erityisesti niitä alkuaineita (esim. Na, S, Cl, K, Ca, P, Mg, Al), joiden tiedetään aiheuttavan ongelmia talteenottokiertoprosessissa. Lisäksi työn avulla voisi valmistautua tulevaisuuteen ja kartoittaa näytteistä myös fluoria ja elohopeaa, sillä näiden mittaamista vaaditaan suurten polttolaitosten (LCP) BREFissä ja on mahdollista että tulevaisuudessa myös mittausvaatimus ulotetaan soodakattiloihinkin.

Projekti olisi mahdollista toteuttaa diplomityönä ja työryhmän mielestä luontevin paikka on Åbo Akademi, sillä he toteuttivat aiemmankin tutkimuksen vuonna 2007. Analyysit tulee kuitenkin suorittaa ulkopuolisella laboratoriolla.

Tilanne:
Työryhmä piti työn aihetta ajankohtaisena ja yleisesti kiinnostavana, joten Åbo Akademin Markus Engblomilta pyydettiin tarjous työhön liittyen. Tarjouksen saatuaan työryhmä päättää lopullisesti viedäänkö toteutusehdotus hallitukselle hyväksyttäväksi.

7 MUIDEN TYÖRYHMIEN KUULUMISET

Muiden työryhmien kuulumiset päätettiin jättää seuraavaan kertaan.

8 MUUT ASIAT

Sihteeri muistutti tulevasta Konemestaripäivästä.

9 SEURAAVA KOKOUS

Seuraava kokous sovittiin pidettäväksi Skypen välityksellä 16.1.2018 alkaen klo 13:00.

Vakuudeksi

Antti Tikkanen

LIITE 1

ÅA, Understanding Low Temperature Corrosion in BL Combustion, Phase 3 - Final Report 24.8.2017

Final Report - Understanding Low Temperature Corrosion in BL Combustion – Phase 3

Nikolai DeMartini, Emil Vainio
22 September 2017

Summary & Conclusions

Five precipitator ashes were obtained and analyzed by SEM-EDX. Of these five, three (Pietarsaari, Orange TX, Heinola) were used in 22h tests in which 100mg of ash was placed on a polished 2cmx2cm coupon of 16Mo3/5 and at temperatures of 60 °C to 110 °C. The gas used in this work was air containing 25 vol% H_2O. The three ashes tested were chosen to provide a high carbonate ash (Pietarsaari) an ash with some bisulfate (Heinola) and an ash from a low solids recovery boiler which has low to no Na_2CO_3 (Orange, TX). Based on these short-term tests, conditions were chosen for the 1000h test. One of the key conclusions of the 22h tests was the 16Mo3/5 is less susceptible to dew point corrosion under hygroscopic salts than ST45.8.

Figure 1. Sample holder used in the 1000h test. Note the thermocouples above the steel coupons. The samples at 120 °C are at the far left, the 100 °C samples are at the far right and the 105 °C samples are the samples in between.

For the 1000h test, the sample holder was modified to provide 3 temperatures and to hold 6 steel coupons (3 of 16Mo3/5 and 3 of ST45.8), Figure 1. The back element in the tube furnace was disconnected, which meant that there were different temperatures at different positions in the furnace. In this way, it was possible to get three different temperatures in one furnace run. The temperatures selected were 120 °C, 105 °C and 101 °C. The temperatures were measured by thermocouples positioned above the samples. The concentration of water was 25 vol-%. The 1000h test was run with the precipitator ash from Pietarsaari. The ash composition was (33.2% Na, 3.7% K, 44.6% SO_4, 0.7% Cl, 17.8% CO_3) based on SEM-EDX for Na, K, S, and Cl and CO_3 by balance.

The samples (unwashed and washed) after the 1000h test are shown in Figure 2. No corrosion was seen in any of the samples at any of the temperatures. We had seen in earlier tests with 1 precipitator ash [Holmblad, 2015; DeMartini, 2015] that no corrosion occurred after 24h in 27% H_2O at 100 °C. For the other ash tested in that study, there was very slight corrosion visible at 100 °C. These earlier results indicated that 100 °C is close to the borderline of corrosion, but none was seen in these tests. The other important observation is that these results are consistent with the 22h tests. This combined with the earlier study supports the idea that short tests 4-22h can be used to screen conditions. The results also indicate that steel temperatures of 100 to 110 °C should be possible without corrosion in 25 vol-% H_2O. The 22h tests results indicate that there is not a very big difference for boilers firing low solids black liquor (low carbonate, possibly some bisulfate) with those firing high solids black liquor (high carbonate). Thus significant additional thermal energy can be recovered from both modern and older recovery boilers.

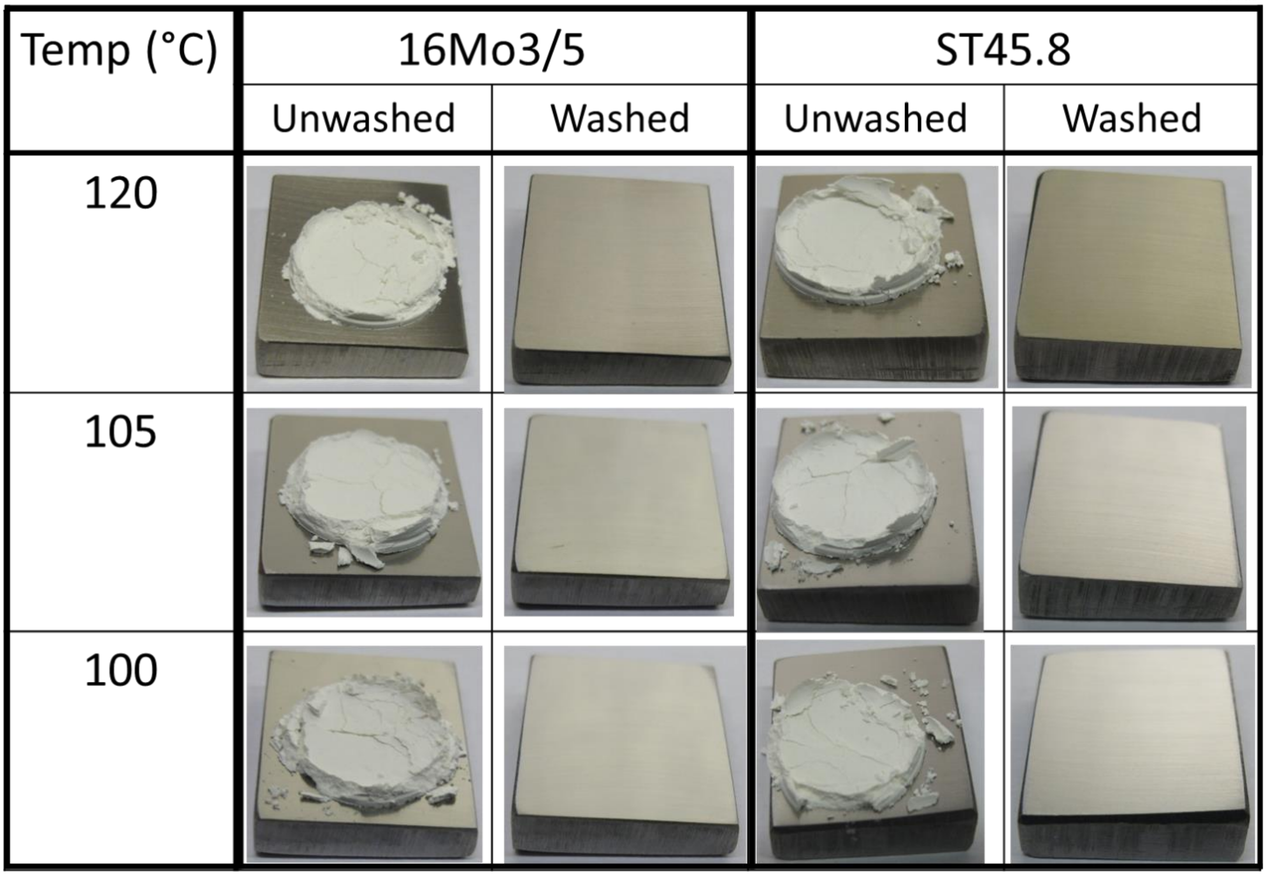


Figure 2. Samples after the 1000h test, both unwashed and washed.

Experimental

Precipitator Ashes

Precipitator ash samples were obtained from 5 mills and analyzed by SEM-EDX and titration, Table 1. For the high carbonate ash, the carbonate numbers from both a charge balance and titration agree reasonably well. The Heinola and Oragne, TX samples probably contain some carbonate as well as some bisulfate. The charge balance based on the Na, K, S, Cl analysis by SEM-EDX would indicate there is some carbonate present. However, SEM-EDX does not analyze H. Thus, the cation concentration could be higher so there must be some carbonate present. The 9.5 pH of the Orange, TX sample is only slightly alkaline indicating the presence of bisulfate. The Heinola sample is slightly on the acidic side indicating the presence of bisulfate and carbonate. The ash from Pietarsaari had the highest carbonate content based on the mass balance using the SEM-EDX results for Na, K, S and Cl. Three of the ashes Pietarsaari, Heinola and Orange, TX) and pure sodium sulfate were used in corrosion tests using 16Mo3. Sodium sulfate was also tested on ST45.8 to repeat the results of Holmblad [2015].

Table 2. Composition of ashes tested using SEM-EDX and titration. [a]CO_3 determined by charge balance in the SEM-EDX results. [b]CO_3 determined by titration.

	Na wt-%	K wt-%	SO_4 wt-%	Cl wt-%	CO_3 [a] wt-%	CO_3 [b] wt-%	pH	S/(Na_2+K_2) mol frac
Pietasaari	33.2 %	3.7 %	44.6 %	0.7 %	17.8 %	14.1 %	11.353	0.60
Heinola	31.5 %	2.9 %	59.3 %	0.0 %	6.3 %	0	6.2	0.85
Orange, TX	32.1 %	1.8 %	60.8 %	0.4 %	5.0 %	0	9.5	0.88
Kymi	30.9 %	5.2 %	52.0 %	0.3 %	11.6 %	10.2 %	11.4	0.73
Rauma	31.7 %	4.2 %	51.9 %	0.7 %	11.6 %	11.5 %	11.4	0.73

22h runs

The three ashes chosen for the 22h tests were Pietarsaari, Heinola and Orange, TX. Pietarsaari was chosen as a high carbonate ash representing a modern recovery boiler firing high solids black liquor. The Orange, TX mill precipitator ash was chosen as an ash from an older boiler firing low solids black liquor. The Heinola precipitator ash was chosen as an ash with some bisulfate in it. Both sodium carbonate and bisulfate were found to be more hygroscopic than sodium sulfate [Holmblad, 2015] and so it was of interest to see if these ashes, which represented both ends of the extreme in terms of alkalinity, behaved differently.

For the corrosion experiments, we used a similar experimental approach as used by Henri Holmblad [2015] in our earlier dew point corrosion work, Figures 3 & 4. The modification, is that the last heating element in the tube furnace was disconnected to create a temperature gradient from the front to the back of the furnace. For the 22h runs, steel samples were placed in the front and back of a ceramic sample holder, Figure 5. The sample holder was positioned to give a temperature that was 15 °C lower for the back sample when compared to the front sample. In each of these runs, the same steel (16Mo/3 or ST45.8) was used in the front and back with the same salt, so the only variable was the temperature. The vol-% H_2O in all of the runs at 25 vol-%. The 16Mo3/5 was the recommended steel for these experiments. However, this steel showed less susceptibility to dew-point corrosion than the ST45.8 had in our earlier studies. For this reason, some runs were also carried out with ST45.8. The 22h experiments run are given in Table 3.

Table 3. Samples and temperatures run for the 22h tests.

Ash	Steel	Temperature (°C)	
Pietarsaari	16Mo3/5	110	95
Pietarsaari	16Mo3/5	105	90
Pietarsaari	16Mo3/5	90	75
Pietarsaari	16Mo3/5	75	60
Heinola	16Mo3/5	110	95
Heinola	16Mo3/5	105	90
Heinola	16Mo3/5	90	75
Orange, TX	16Mo3/5	110	95
Orange, TX	St45.8	110	95
Orange, TX	16Mo3/5	90	75
Na2SO4	16Mo3/5	90	75
Na2SO4	St45.8	90	75

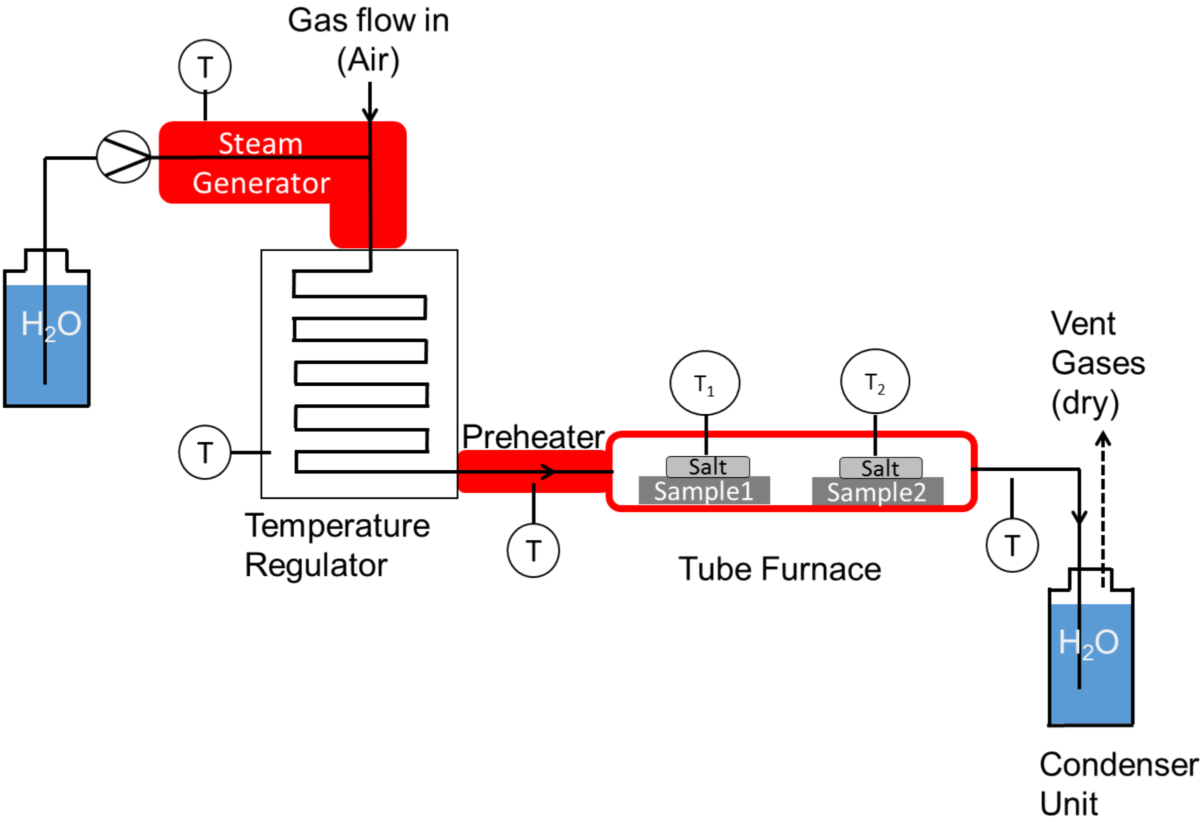


Figure 3. Diagram of the experimental set-up.

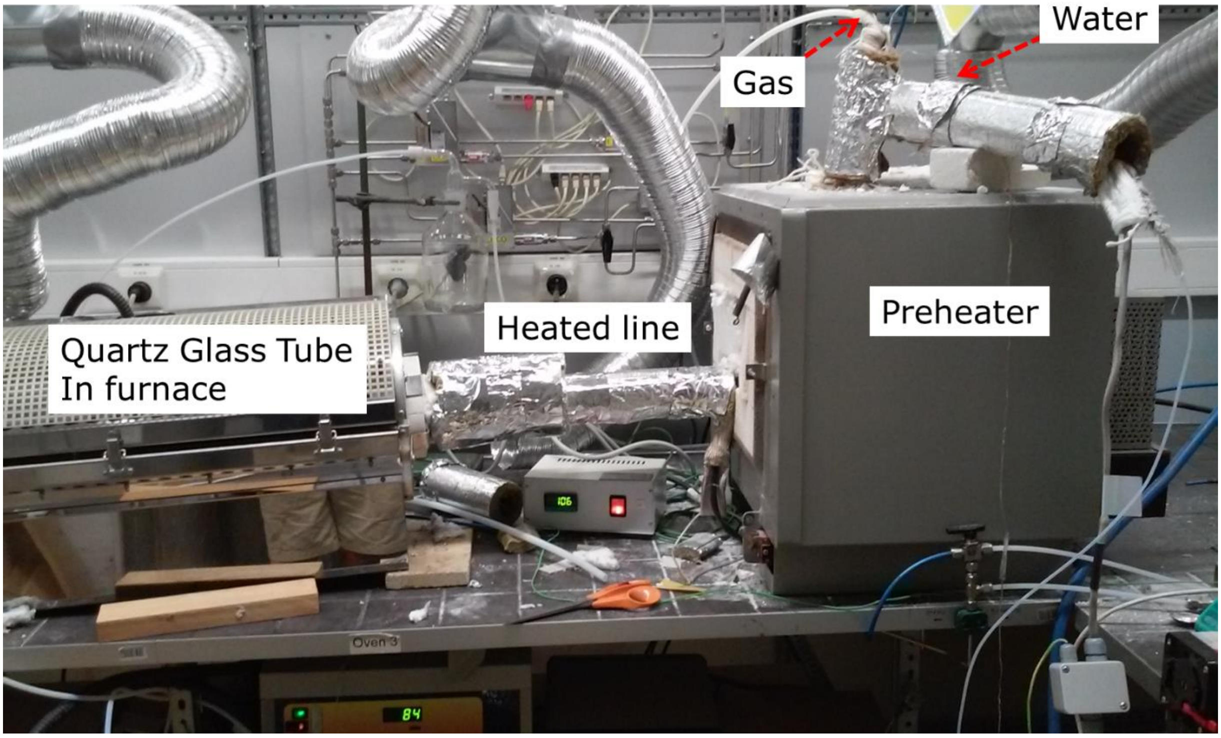


Figure 3. Tube furnace used in this work.

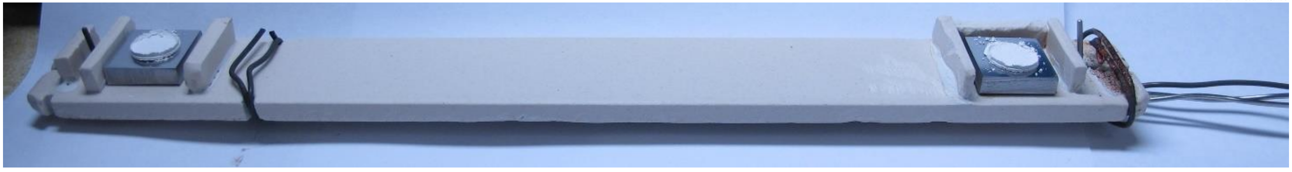


Figure 5. Sample holder used in the 22h tests.

1000h run

For the 1000h test, the sample holder was modified to provide 3 temperatures and to hold 6 steel coupons (3 of 16Mo3/5 and 3 of ST45.8), Figure 6. In this way, it was possible to get three different temperatures in one furnace run. The highest temperature selected were 120 °C and the gradient resulted in temperatures of 105 °C and 101 °C for the samples at the cooler end. The concentration of water was 25 vol-%. The 1000h test was run with the precipitator ash from Pietarsaari. This ash was chosen as it was reasonably representative of Finnish recovery boiler ashes. Also, the 22h tests indicated that there was not a significant difference in the behavior of the different ashes.

Figure 6. Sample holder used in the 1000h test. Note the thermocouples above the steel coupons. The samples at 120 °C are at the far left, the 100 °C samples are at the far right and the 105 °C samples are the samples in between.

Results & Discussion

22h runs

In our most recent project on this topic for SKY we found that 100-110 °C was the safe temperature for low temperature corrosion of ST45.8 steel [Holmblad, 2015]. The first experiments were carried out between 95 and 110 °C using 16Mo3/5 with the three ashes. Corrosion was expected at 95 °C based on the earlier results with ST 45.8. However, no corrosion was seen on the 16Mo3/5 for any of the three ashes. The temperature was lowered in subsequent runs. For the Pietarsaari and Heinola ashes, corrosion was first seen at 75 °C, Figure 7. For the Orange TX, ash corrosion was not seen at the lowest temperature tested (75 °C). Tests were run with Na_2SO_4 with both ST45.8 and 16Mo3/5 to see if the lack of corrosion was due to the steel. As can be seen in Figure 8, no corrosion was seen under Na_2SO_4 for the 16Mo3/5 sample, but corrosion was visible on the ST45.8 at 75 °C. We also ran some experiments with both steels under the precipitator ash from Orange, TX, Figure 9. Corrosion was seen on the ST45 at 95 °C, but not on the 16Mo3. No corrosion was seen on either steel at 110 °C. These results indicate that 16Mo3/5 is less susceptible to dew point corrosion than ST45.8.

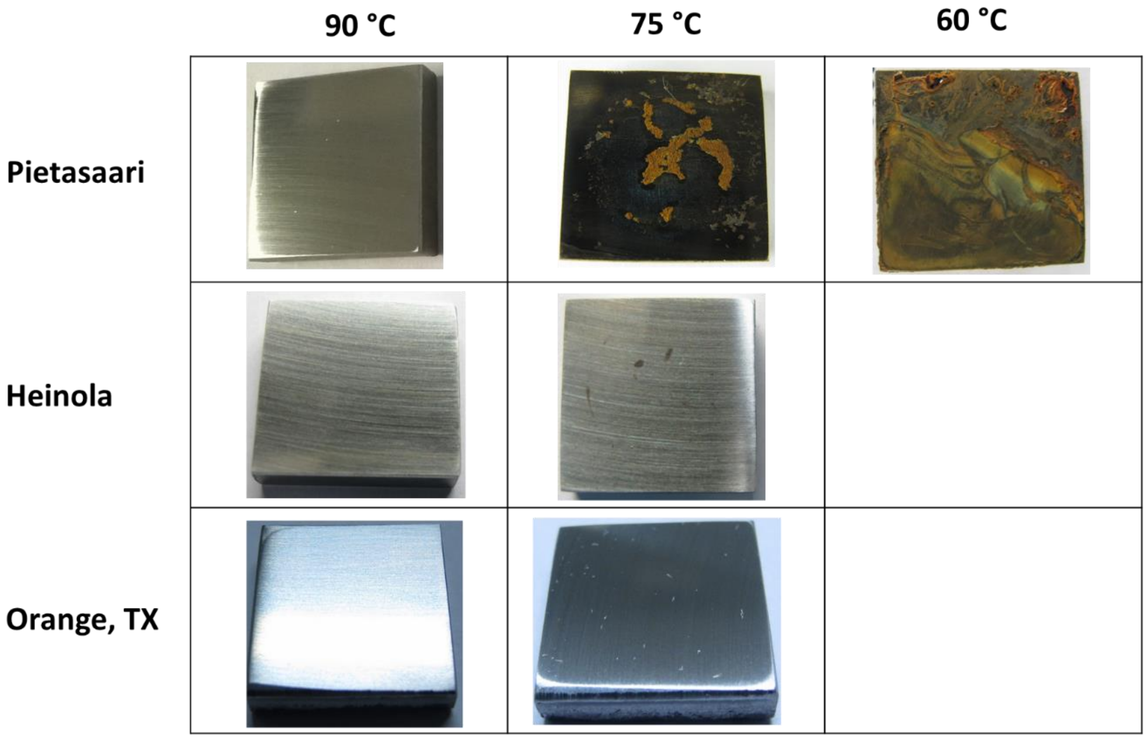


Figure 7. Corrosion results for 16Mo3/5 under Pietasaari, Heinola and Orange, TX ashes, Temperatures 60, 75 and 90 °C.

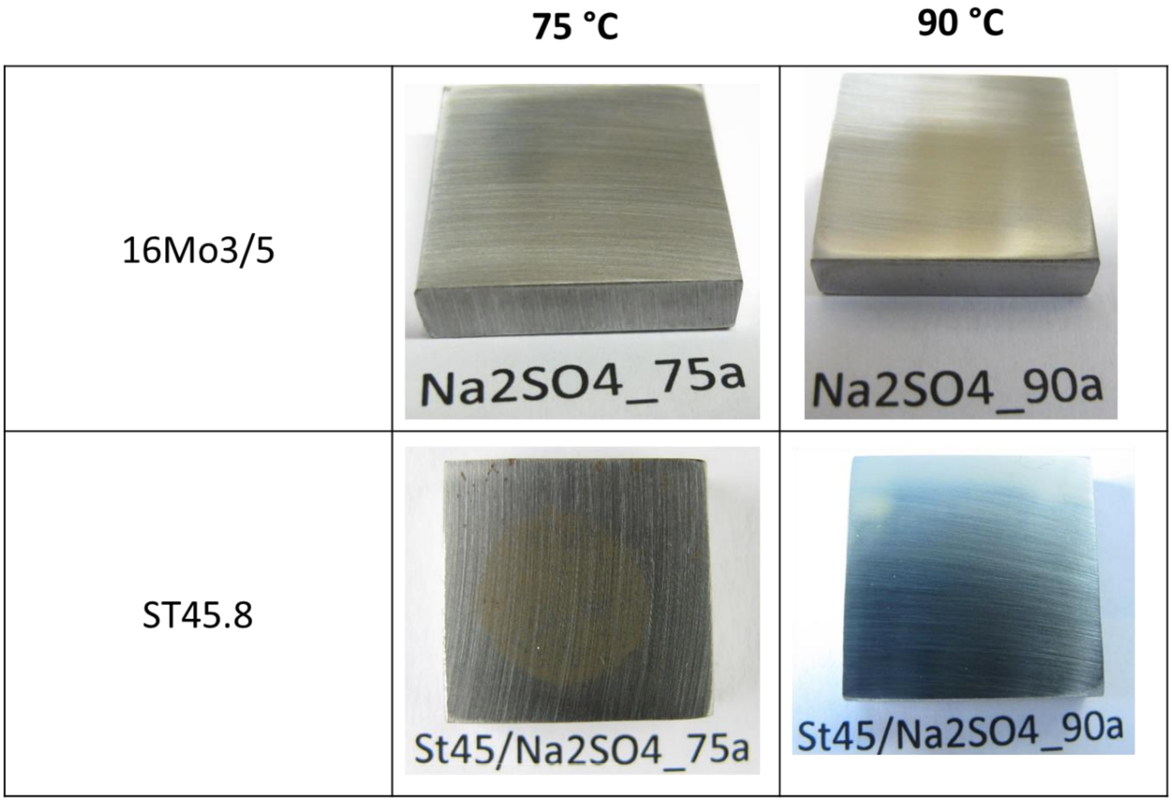


Figure 8. Corrosion results for 16Mo3/5 and ST45.8 at 75 and 90 °C under Na_2SO_4 in 25 vol-% H_2O in air.

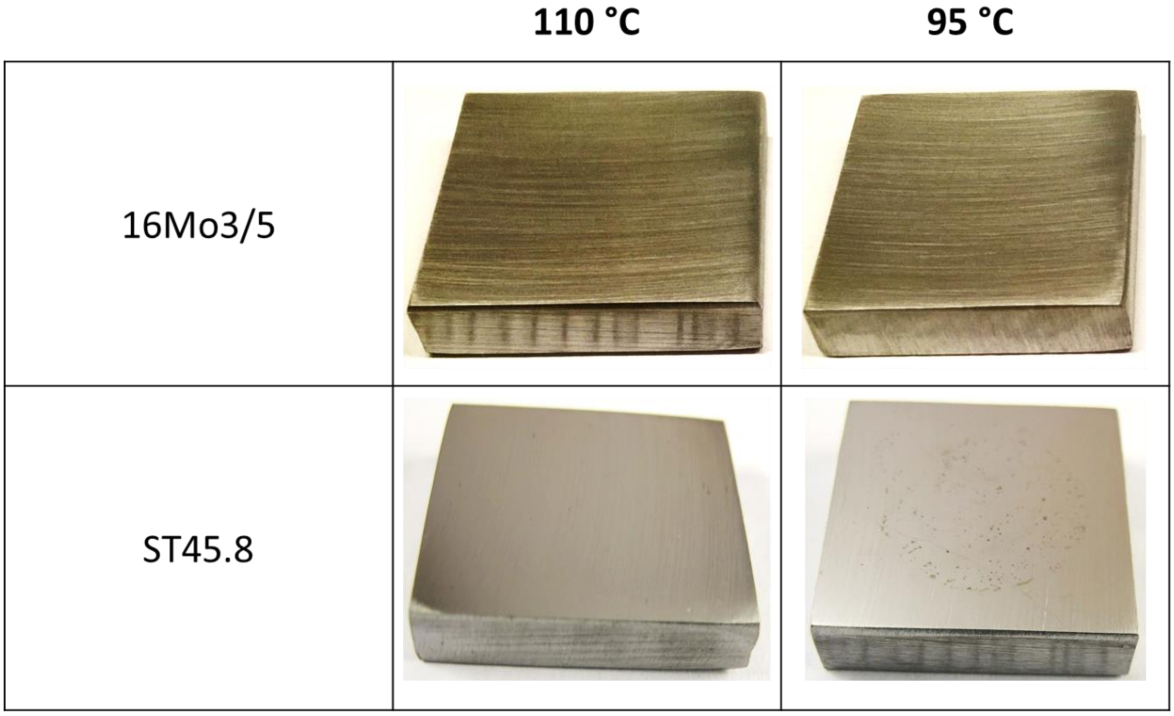


Figure 9. Corrosion results for 16Mo3/5 and ST45.8 at 95 and 110 °C under the Orange, TX precipitator ash in 25 vol-% H_2O in air.

1000h run

The thermocouple measurements for the 1000h run are shown in Figure 10. There was a very small change in temperature just after 650h. This occurred when an electrician momentarily cut the electricity. We had a remote alarm and it was caught and the electricity was put on within about 15 minutes. The small drop in temperature did not affect the results, since the water feed was also shut down for the short period.

The coupons with and without the precipitator ash after the 1000h test are shown in Figure 11. There was no clear sign of water absorption in any of the samples and no corrosion was observed. These results are consistent with an earlier 24h tests with another precipitator ash [Holmblad, 2015] in which no corrosion was seen after 24h at 100 °C in 27 vol-% H_2O. The 1000h test results indicate that shorter tests 4-22h are sufficient for screening steels/ashes. The results also indicate that steel temperatures of 100 to 110 °C should be possible without corrosion in 25 vol-% H_2O. Combined with the 22h tests, the results indicate that there is not a very big difference for boilers firing low solids black liquor (low carbonate, possibly some bisulfate) with those firing high solids black liquor (high carbonate). It should be possible to recover a significant amount of thermal energy from the flue gases of both modern and older recovery boilers.

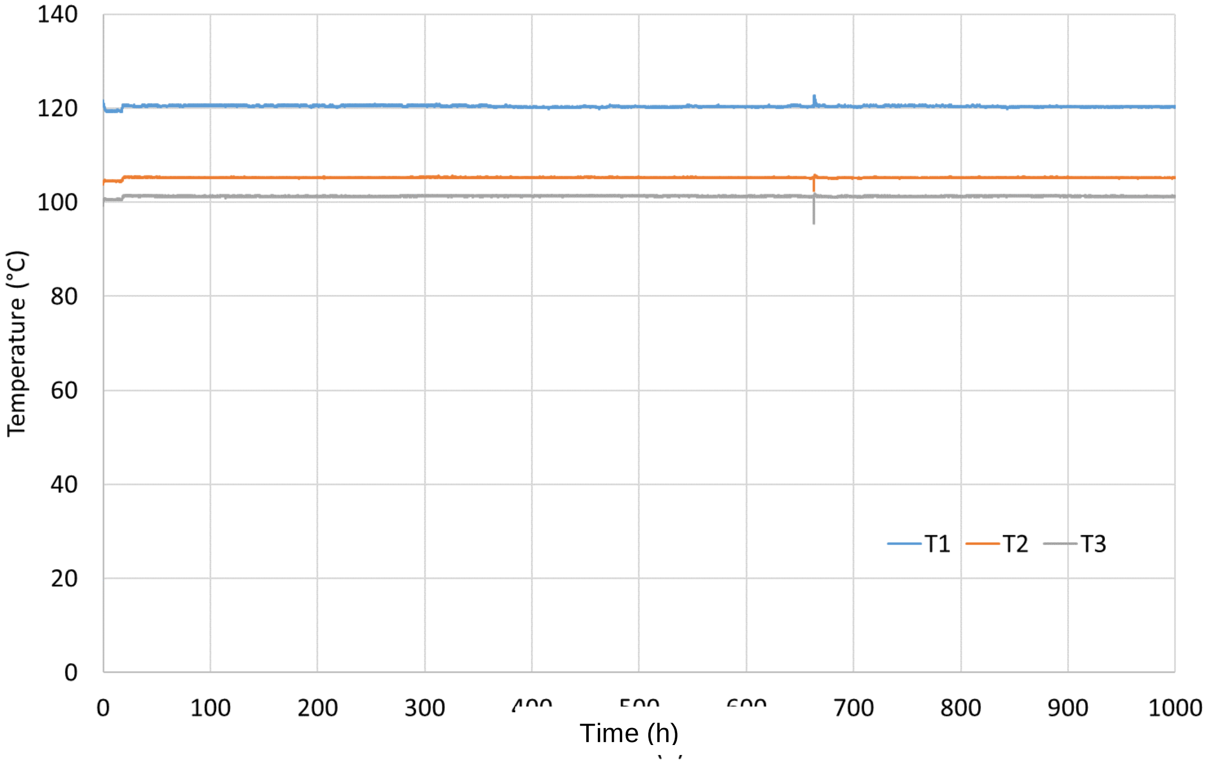


Figure 10. Thermocouple measurements at the 3 steel coupon positions.

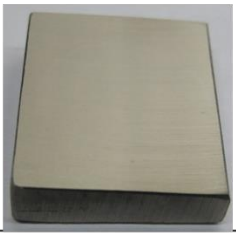
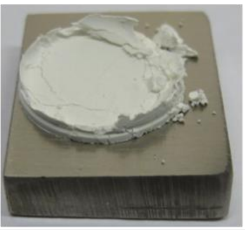
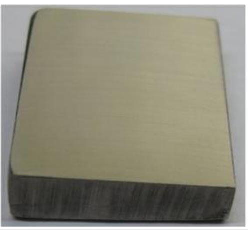
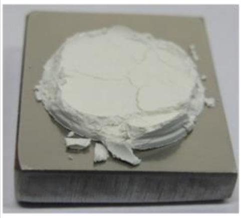
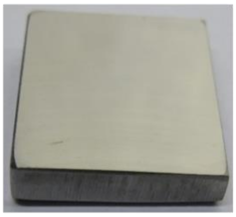
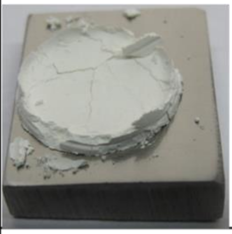
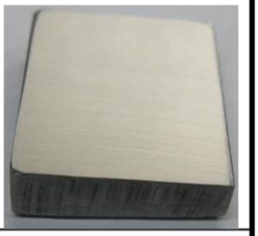
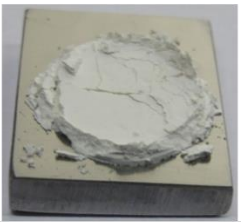
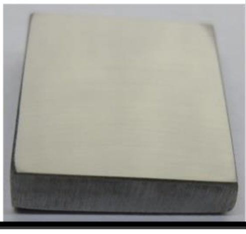
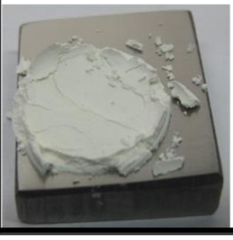
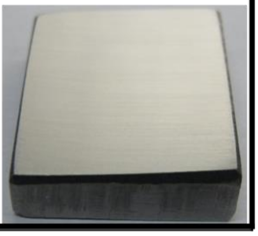
Temp (°C)	16Mo3/5		ST45.8	
	Unwashed	Washed	Unwashed	Washed
120				
105				
100				

Figure 11. Samples after the 1000h test, both unwashed and washed.

General Discussion

Corrosion probe studies and SO_3/H_2SO_4 measurements in part 1 of the low-temperature corrosion project showed that there is no acid dew point in kraft recovery boilers. Furthermore, the measurements at Heinola, where there was high SO_2, indicate that even in a high SO_2 environment, no acid dew point exists in the flue gases. This is because SO_3 is very reactive towards alkaline ash. In kraft recovery boilers, SO_3 and H_2SO_4 reacts with Na_2CO_3 to form sulfates (Reactions 1 and 2). In the furnace, SO_3 may also react with gaseous NaOH to form Na_2SO_4 (Reaction 3).

$$Na_2CO_3(s) + H_2SO_4(g) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(g) \quad (1)$$

$$Na_2CO_3(s) + SO_3(g) \rightarrow Na_2SO_4(s) + CO_2(g) \quad (2)$$

$$2NaOH(g) + SO_3(g) \rightarrow Na_2SO_4(s) + H_2O(g) \quad (3)$$

Corrosive acidic sodium bisulfates may also form in sulfite boilers and in kraft boilers with a high ratio of S/Na in the black liquor and low solids firing. Sodium bisulfate is formed in the presence of H_2SO_4 reacting with Na_2SO_4 according to Reaction 4. Sodium bisulfate forms a sticky deposit with a low melting temperature, 185°C (DeMartini 2017), and it has shown to be very corrosive also at lower temperatures.

$$Na_2SO_4(s) + H_2SO_4(g) \rightarrow 2NaHSO_4(s,l) \quad (4)$$

The water dew point is normally 50-60ºC and does not normally cause corrosion in recovery boilers, except if there are cold areas caused by e.g. air leakage. The dew point of hydrochloric acid (HCl) is about the same as for water vapour and does not cause corrosion in normal operation. However, hygroscopic salts absorb moisture from the flue gas to form a wet deposit at much higher temperatures than the pure water dew point. The phenomenon when a salt or salt mixture absorb enough water to totally dissolve is called deliquescence. Salts will start to absorb water at a temperature above the deliquescence temperature. Some salts are more hygroscopic than others, and usually a mixture of salts is more hygroscopic than individual salts. For example, Na_2CO_3 and Na_2SO_4 are mildly hygroscopic, whereas $NaHSO_4$ is very hygroscopic. Thus, the hygroscopicity of an ash deposit depends on ash composition. For example, for the low carbonate ash Orange, TX, corrosion was seen for ST45.8 at a temperature of 95ºC and water vapour concentration of 25 vol%. It has to be noted that a higher water vapour concentration would lead to corrosion at higher material temperature. This may occur near sootblowers where the water vapour concentration may locally be high. Once a deposit absorbs moisture and becomes wet, it requires a higher temperature to dry than the deliquescence temperature.

Corrosion may also be initiated during down-time of a boiler. Deposits in the boiler might absorb humidity from the air and cause corrosion. It is thus important to completely wash away the salts during the shut down. Corrosion products, e.g. $FeCl_2$, may accelerate the corrosion due to its very hygroscopic nature. This would require further research.

The effect of acidic gases with a low dew point temperature (HCl) may have an effect on the corrosion rate of a wet deposit, because some HCl may be absorbed in the deposit. This would require more research to understand the effect of gases absorbing in wet deposit.

References

DeMartini, N.; Vainio, E.; Holmblad, H.; Hupa, M. Understanding low temperature corrosion in Kraft Recovery Boilers – Implications for Increased Energy Recovery. 2016 TAPPI PEERS Conference. Sept 25-28, Jacksonville, FL (2016)

Holmblad, H., Low temperature corrosion in black liquor recovery boilers due to hygroscopic salts. MSc. Thesis, Åbo Akademi University, Turku, Finland (2015).

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Appendix

Table 4. Composition of ashes based on the SEM-EDX results and calculated first melting point of the ashes assuming all sulfur as sodium sulfate. T_0 for Heinola ash is not shown due to uncertainties in the amount of bisulfate. Note, the Orange, TX ash may also contain some bisulfate and the result should be interpreted with caution.

	Na wt%	K wt%	SO_4 wt%	Cl wt%	CO_3 wt%	T_0
Pietarsaari	33.2	3.7	44.6	0.7	17.8	537
Orange, TX	32.1	1.8	60.8	0.4	5.0	590
Kymi	30.9	5.2	52.0	0.3	11.6	534
Rauma	31.7	4.2	51.9	0.7	11.6	545

LIITE 2

Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport, ÅA–tarjous 11/2017

Johan Gadolin
Process Chemistry Centre

ÅBO AKADEMI
UNIVERSITY

Proposal: Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport

November 2017
Markus Engblom, Daniel Lindberg, Leena Hupa

Executive summary

The work described in this proposal aims for better understanding of changes in morphology and chemistry during aging of recovery boiler deposits. Laboratory, pilot, and industrial scale data so far suggests that recovery boiler deposit chemistry and morphology change over time. The understanding so far is that alkali chloride transport can occur within deposits, resulting in densification of the deposit and chloride enrichment within the deposit and also at the deposit-steel interface. These changes can have practical implications for deposit removability and corrosion of the superheater material. However, systematic studies into recovery boiler deposit aging is lacking.

The objective of this work is to systematically establish how deposit morphology and chemistry depend on deposit formation and aging, especially on the aging processes connected to the deposit temperature gradient. Ultimately this new information can help the industry manage corrosion in the superheater region of recovery boilers and power boilers.

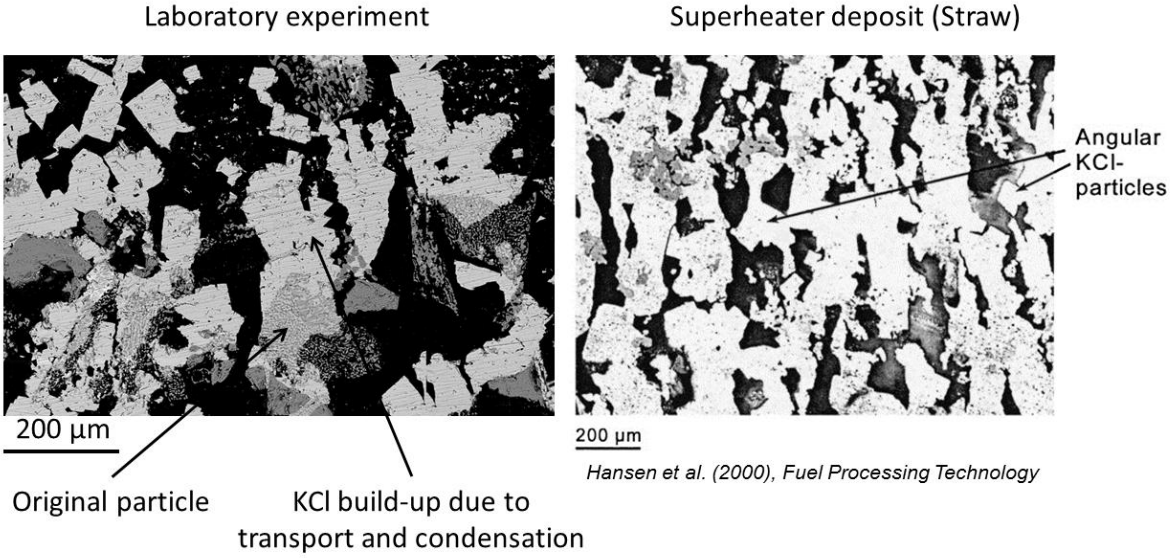
In the proposed work, deposits of different age will be collected from a recovery boiler using air-cooled probes, followed by detailed SEM/EDX analysis of the deposit cross sections. Comparison of the deposit SEM/EDX data will be made to identify time-dependent changes in deposit chemical composition and morphology (e.g. porosity). Mathematical modeling will be utilized to further analyse the experimental data, e.g. by calculations of characteristic temperatures (T_0, T_{15}, T_{70}, T_{100}) for the deposit of different age.

Acknowledging the challenge associated with the deposit collection process over longer time periods, pre-studies into sample collection have been carried out at the Metsä Fibre Rauma recovery boiler. Boiler deposit collection has so far been tested for a relatively short time of 20 minutes. In addition to the Rauma deposit, samples collected from two other recovery boilers have been analysed using SEM for the purpose of obtaining data of the chemical composition as function of position along the deposit cross section, from the steel surface to the outer surface of the deposit. Currently we have developed a functioning process for deposit collection and analysis. We also have collaborated with Rauma for a new design for the probe to be used in longer sampling. The prototype is being constructed.

The work proposed here is divided into two stages. Stage one (7 000 euro) is a continuation of the pre-study, with the objective of obtaining enough practical experience of the deposit collection that a more comprehensive study can be carried out. In the first stage, the sampling time will be extended from 20 minutes to one week. The main purpose of stage one is to provide practical experience in longer sampling times and identification of possible areas of further development needed in the sampling process. Stage one is also expected to provide a good basis for SKY in making a decision to proceed to stage two or not, and a more detailed plan for the work to be done in stage two.. Stage two would be a more comprehensive study, and could be carried out as a master thesis work (30 000 euro), in which sampling times will be extended e.g. to 1000 hours.

Background

Experiments carried out in the laboratory at Åbo Akademi University with granular salts have shown alkali chloride transport to occur within the deposit when a temperature gradient is present over the deposit. The practical implication of this is that Cl is transported towards the cooler heat transfer surface, resulting in enrichment of Cl at the heat transfer surface. Figure 1 presents a SEM image of the deposit cross section, showing alkali chloride build-up within the deposit. Figure 1 also shows a SEM cross section of a deposit collected from a boiler firing straw. The intra-deposit build-up of potassium chloride in the straw deposit visually resembles the build-up in the laboratory deposit, indicating that the alkali chloride transport occurs also in boiler environment.



Hansen et al. (2000), Fuel Processing Technology

Figure 1. *SEM/EDX deposit cross section images from laboratory experiments and boiler deposits showing localized build-up of KCl within deposits due to temperature gradient induced transport.*

Alkali chloride transport within deposits has also been studied in pilot/bench scale using synthetic salts relevant for recovery boilers. Figure 2 presents SEM cross sections of deposits collected from an entrained flow reactor. In the images, signs of alkali chloride transport and build-up are seen after a relatively short time of only 1.5 hours.

More recently, Costa et al. report differences in the chemical composition of a recovery boiler deposit, when comparing the deposit tube side vs the deposit flue gas side. The deposit of Costa et al. was taken directly from a superheater tube. Figure 3 presents a photograph and chemical composition of the Costa et al deposit.

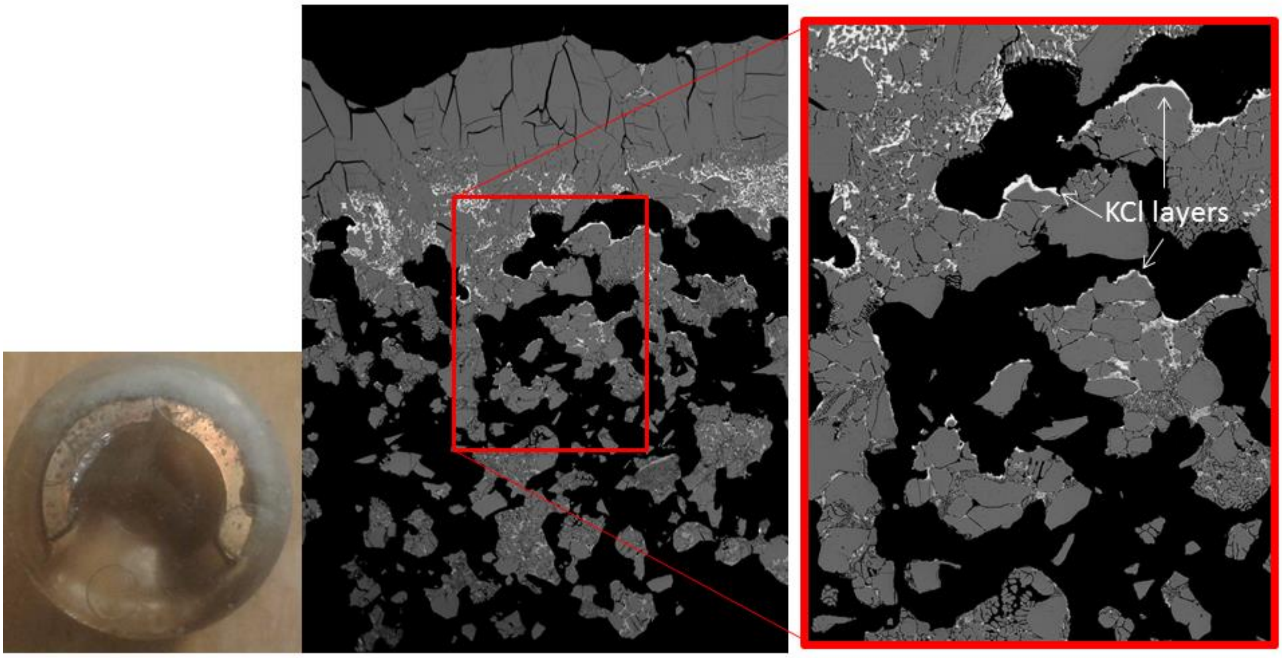


Figure 2. *Photograph (left) and SEM/EDX deposit cross section images (right) from entrained flow reactor experiments showing localized build-up of KCl within a KCl/K_2SO_4 deposit due to temperature gradient induced transport after only 1.5 hours exposure (unpublished research, Niemi 2016).*

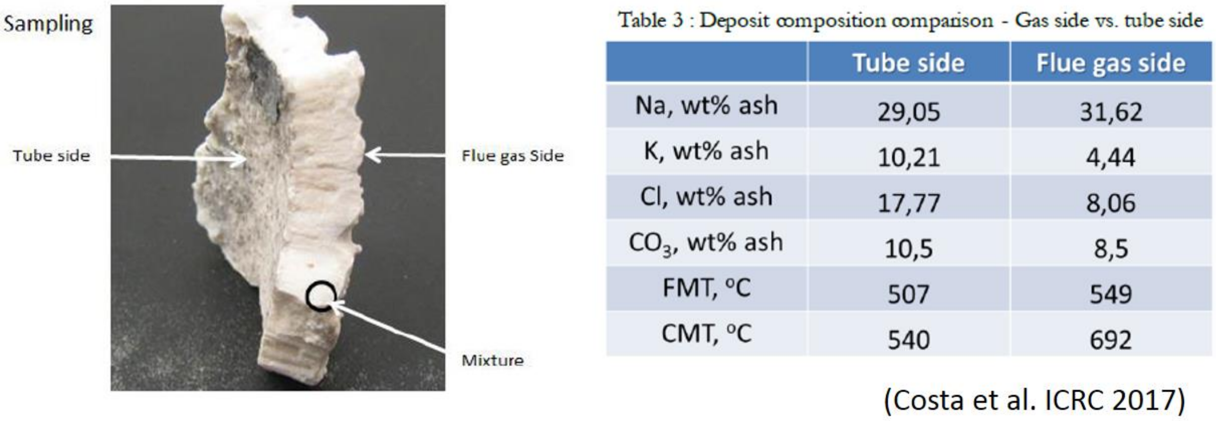


Table 3 : Deposit composition comparison - Gas side vs. tube side

	Tube side	Flue gas side
Na, wt% ash	29,05	31,62
K, wt% ash	10,21	4,44
Cl, wt% ash	17,77	8,06
CO_3, wt% ash	10,5	8,5
FMT, ºC	507	549
CMT, ºC	540	692

(Costa et al. ICRC 2017)

Figure 3. *Photograph of recovery boiler deposit collected from a superheater tube and analysis of the deposit composition on tube side and flue gas side showing chloride enrichment on tube side and consequent lowering of first melting temperature (FMT, T_0) and complete melting temperature (CMT, T_{100}) estimated using thermodynamic modeling (Costa et al., 2017)*

In our pre-study, deposit sampling was tested at the Rauma mill recovery boiler. Due to limited time, only one deposit sample was collected, over a time period of 20 minutes. In addition to the Rauma sample, two other deposit sample cross sections were analysed using SEM. Figure 4 presents a Cl map from one of the deposits, as well as corresponding Cl profile and characteristic melting temperature profiles calculated using thermodynamic modeling. The pre-study showed that deposit sampling is technically possible, although care needs to be taken in handling the deposit so it does not accidentally detach from the probe before the deposit+sampling probe metal ring is sealed by casting into epoxy. However, it was also noted that deposit collection can be done by intentionally removing the deposit from the probe before casting it into epoxy, such as in the case in the deposit in Figure 4.

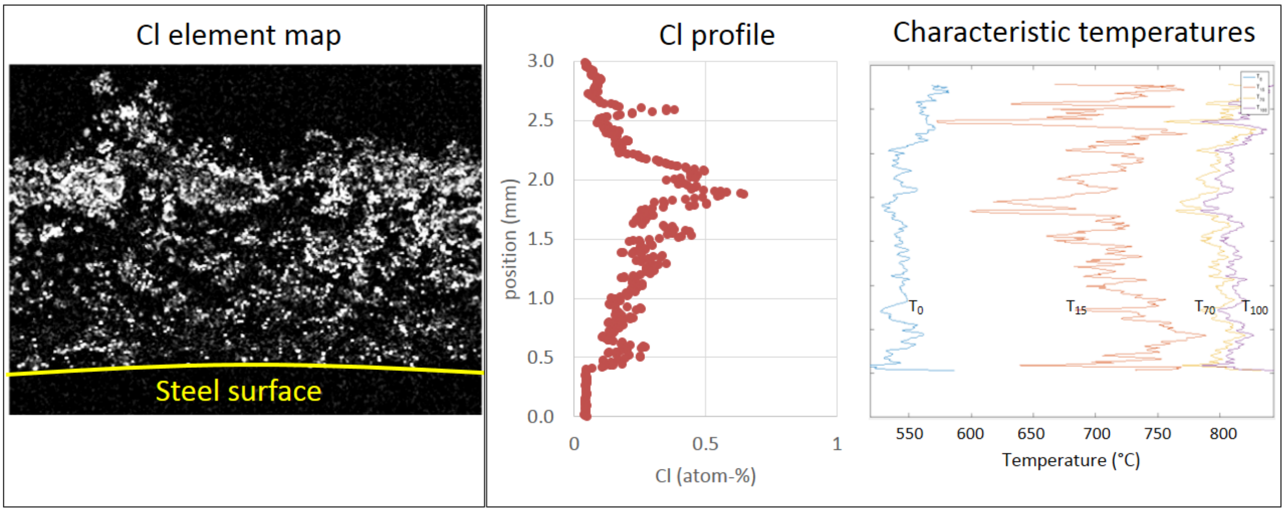


Figure 4. *On left: Deposit SEM Cl element map; on right: deposit average Cl profile and calculated deposit characteristic melting temperature profiles as function of position through the deposit.*

We are currently in the processes of designing and constructing a new probe for deposit collection. This is done in collaboration with the Rauma mill. Figure 5 presents schematic drawings of the new probe construction and probe attachment when placed into the boiler for measurements. The main difference from the probe used earlier to the new construction is that the earlier probe construction was more complicated and thus more expensive. The new construction is planned to be a simple pipe, through which cooling air is blown into the boiler. In the earlier construction, a sample ring is located in the probe tip and the ring is removed after sample collection. In addition, there were two concentric pipes, with the cooling air returning to the base of the probe, located outside the boiler. The new construction will allow us to directly cast the probe tip with deposit attached into epoxy. This removes the additional step of the earlier design in which the steel sampling ring is first removed from the probe and then the ring with deposit is cast into epoxy; this additional step having been identified as a potential step where the deposit may accidentally detach from the probe ring. Other modifications of the new design include a larger hole through which the probe with deposit is removed from the boiler, as well as addition of an arm with which the probe will be more securely fixed in place during deposit collection. We are also looking into possibilities how to remotely keep an eye on the probe temperature control.

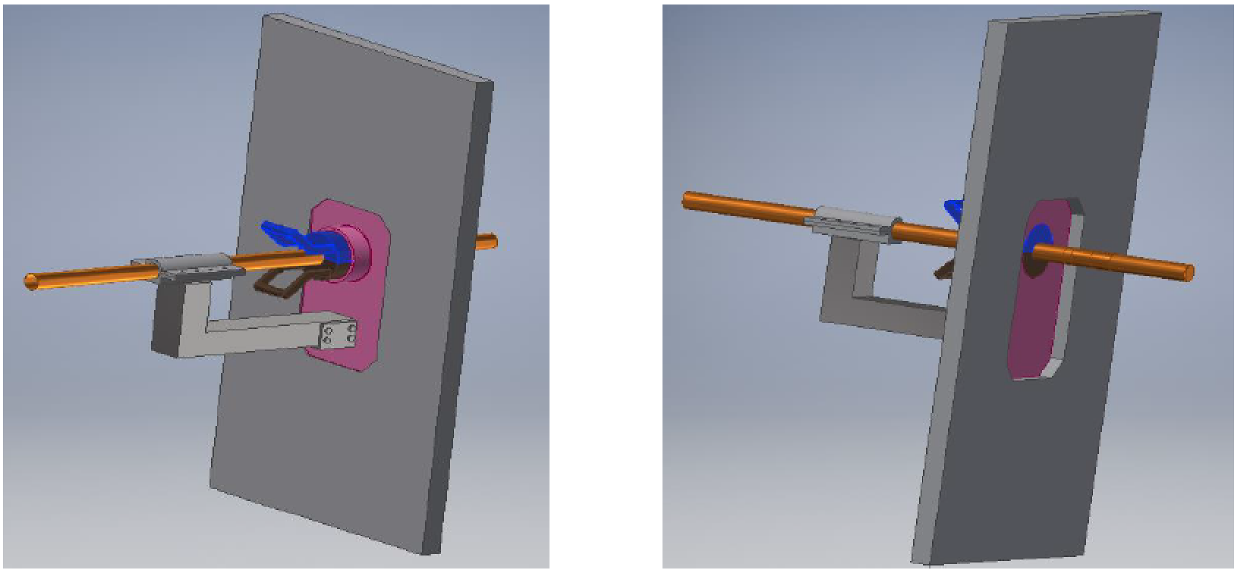


Figure 5. *Schematic pictures of the new probe design; on left: seen from outside the boiler; on right: seen from inside the boiler. Solid bodies (blue and brown) with handles are sealings in the shape of half-cylinder, which serve then purpose of stopping dust build-up in the hole during deposit collection. The sealings are removed when probe is taken out from the boiler.*

Taken together, the data so far from laboratory, pilot, and industrial scale, suggests that recovery boiler deposit chemistry and morphology change over time. The understanding so far is that alkali chloride transport can occur within deposits, resulting in densification of the deposit and chloride enrichment within the deposit and also at the deposit-steel interface. These changes can have practical implications for deposit removability and corrosion. However, systematic studies into recovery boiler deposit aging is lacking.

Objective

The objective of this work is to begin to establish how deposit morphology and chemistry depend on deposit formation and aging, especially on the aging processes connected to the deposit temperature gradient. Ultimately this new information can help the industry manage corrosion in the superheater region of recovery boilers and power boilers.

Description of work

The main activities of the proposed work would consist of deposit sampling at a Kraft recovery boiler and detailed analysis of deposit cross sections using SEM/EDX. The sampling campaign is planned to be carried out in co-operation with one or several of the industrial partners in SKY. The pre-study has been carried out at the Metsä Fibre Rauma mill, and the mill currently is positive to continuing with stage one outline in this proposal. This proposal deals with funding to cover the Åbo Akademi part of the sampling campaign and deposit SEM/EDX and supporting analyses.

The work proposed here is divided into two stages. Stage one is a continuation of the pre-study, with the objective of obtaining enough practical experience of the deposit collection that a more comprehensive study can be carried out. In the first stage, the new probe construction will be tested and the sampling time will be extended from 20 minutes to one/two weeks. The exact sampling times may need to be refined based on discussion with the mill, but currently we (ÅA) would be interested in obtaining samples over time periods of 2 hours, 24 hours, and one or two weeks. Doing these measurements is expected to provide practical experience of collecting deposits over time periods where sootblowers are not in operation (2 hours) as well as time periods where the process is running as in normal operation and the probe is inside the boiler for a considerably longer time period than so far tested.

Stage two would be a more comprehensive study, and could be carried out as a master thesis work, in which sampling times will be extended e.g. to 1000 hours. A more detailed plan of the work in stage two would be done based on stage one results.

Schedule

The work in stage one is expected to be completed during the first half of 2018.
Stage two work is expected to require 6-9 months (MSc thesis duration is planned as 6 months).
Stage two could start during the second half of 2018, and be completed by spring/summer 2019.
Stage two is understood to be conditional on the decision to be made by SKY to proceed or not to proceed based on stage one results.

Cost

The amount applied for stage one is 7 000 euro (+VAT).
The amount applied for stage two is 30 000 euro (+VAT).