LIITE 1

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

Johan Gadolin Process Chemistry Centre

Åbo Akademi University

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

Nikolai DeMartini, Emil Vainio

24 August 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.

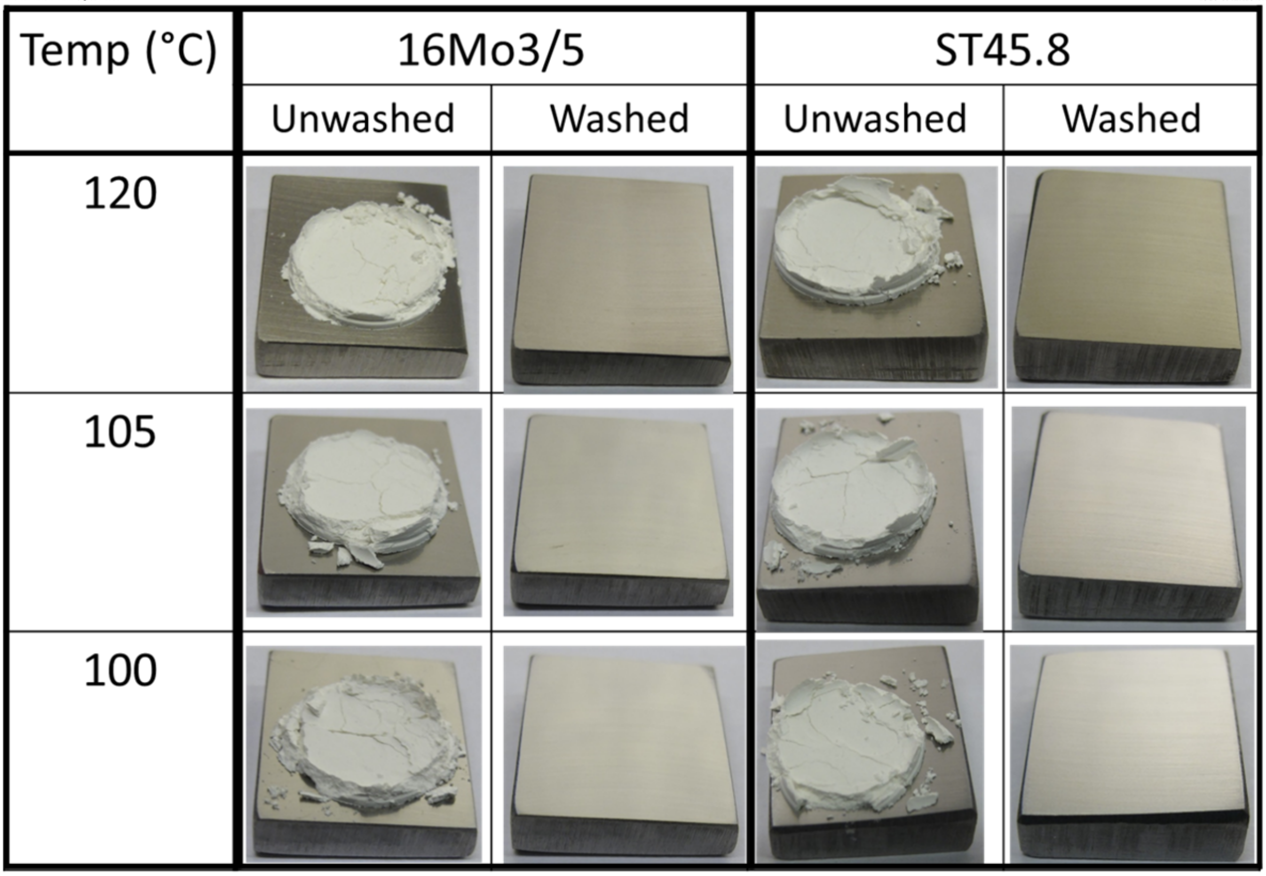


Figure 2. Samples after the 1000h test, both unwashed and washed.

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

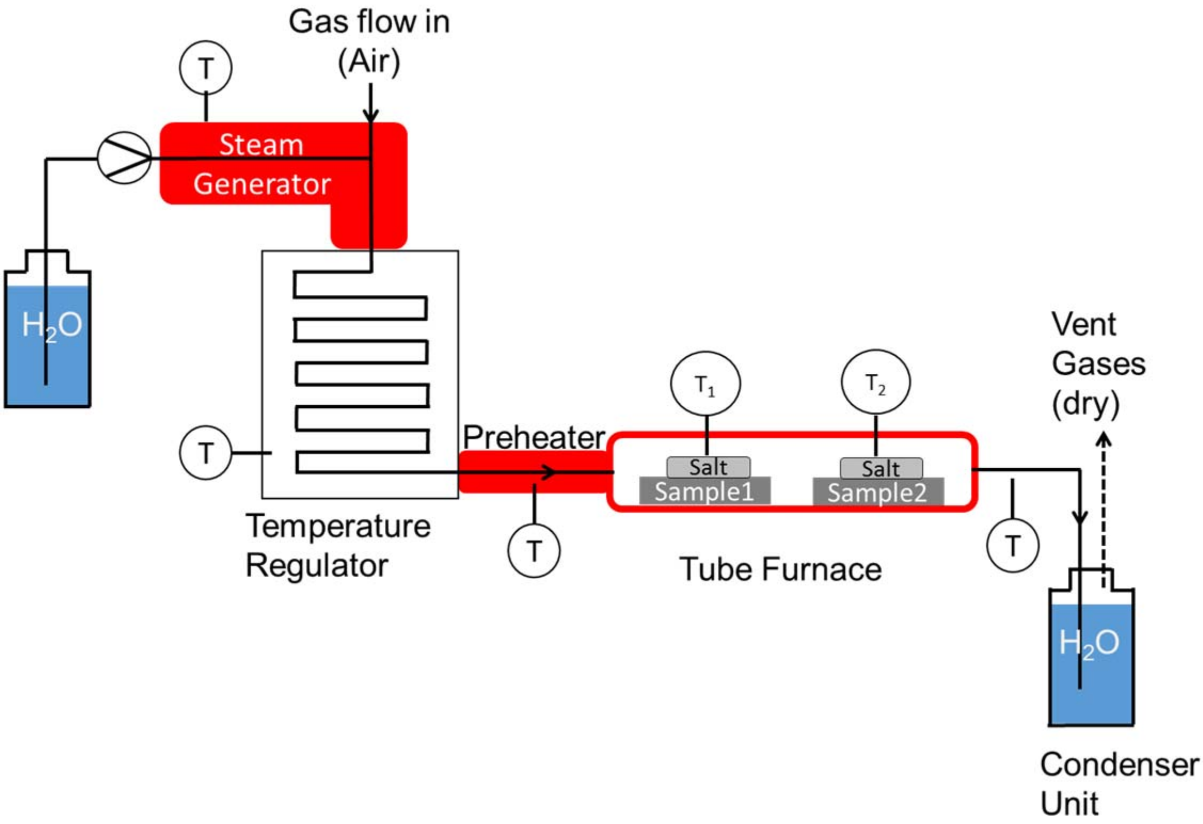


Figure 3. Diagram of the experimental set-up.

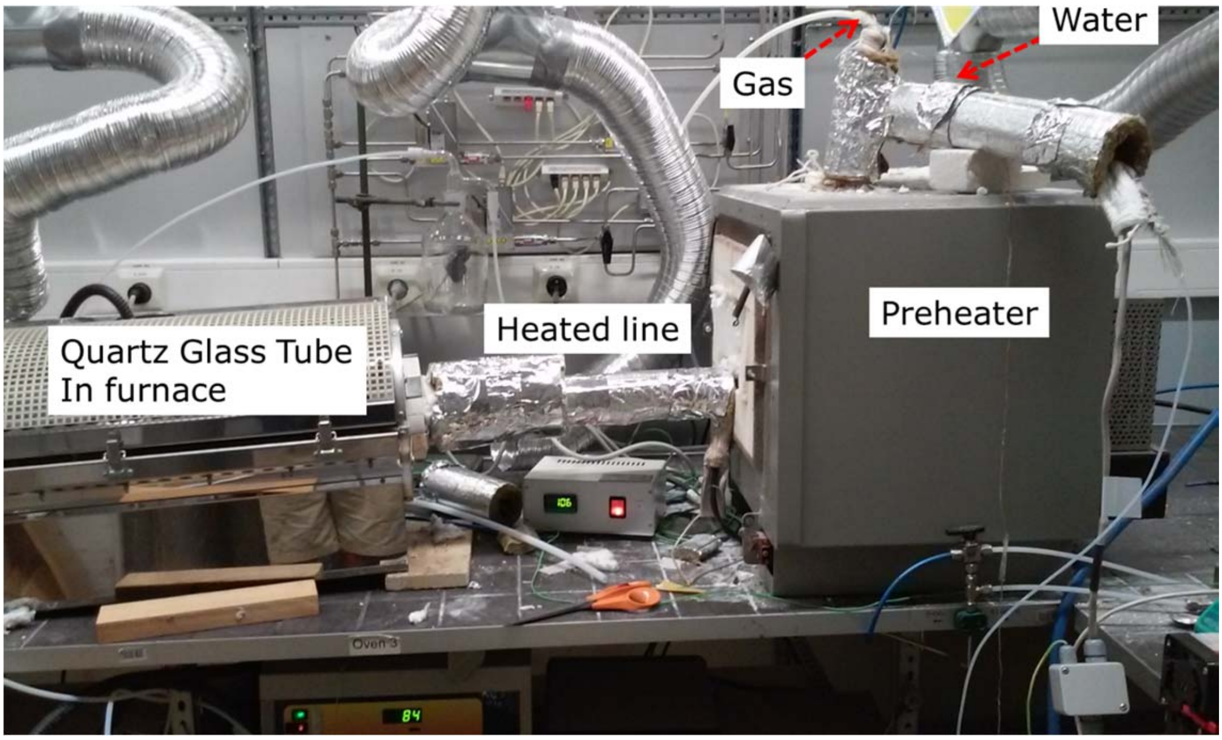


Figure 3. Tube furnace used in this work.

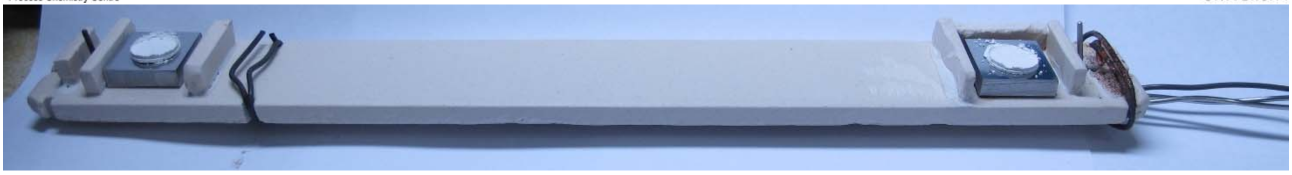


Figure 5. Sample holder used in the 22h tests.

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.

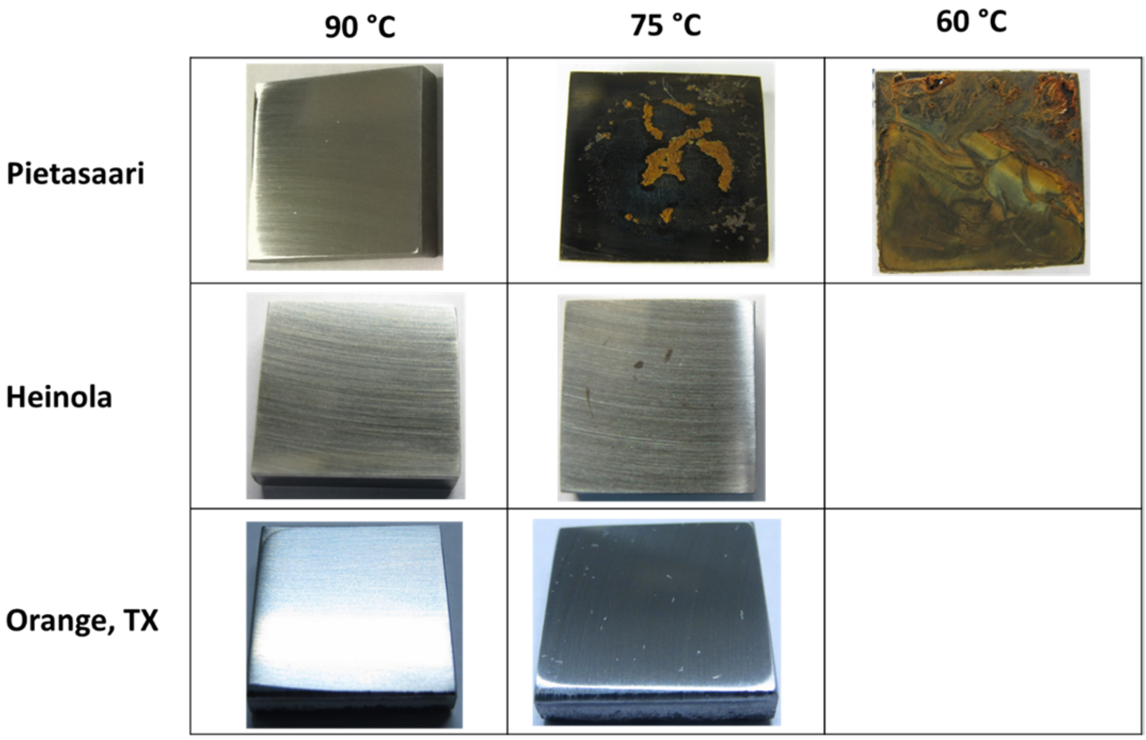


Figure 7. Corrosion results for 16Mo3/5 under Pietasaari, Heinola and Orange, TX ashes, Temperatures 60, 75 and 90 °C.

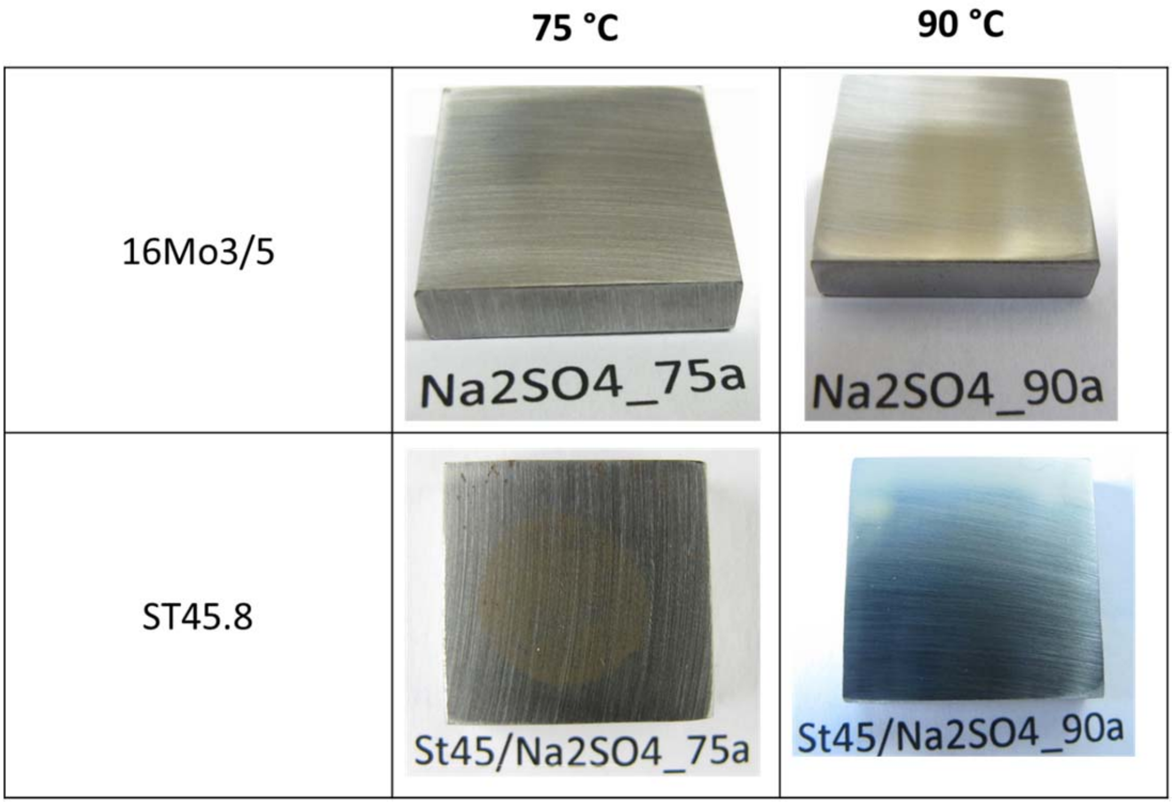


Figure 8. Corrosion results for 16Mo3/5 and ST45.8 at 75 and 90 °C under Na_2SO_4 in 25 vol-% H_2O in air.

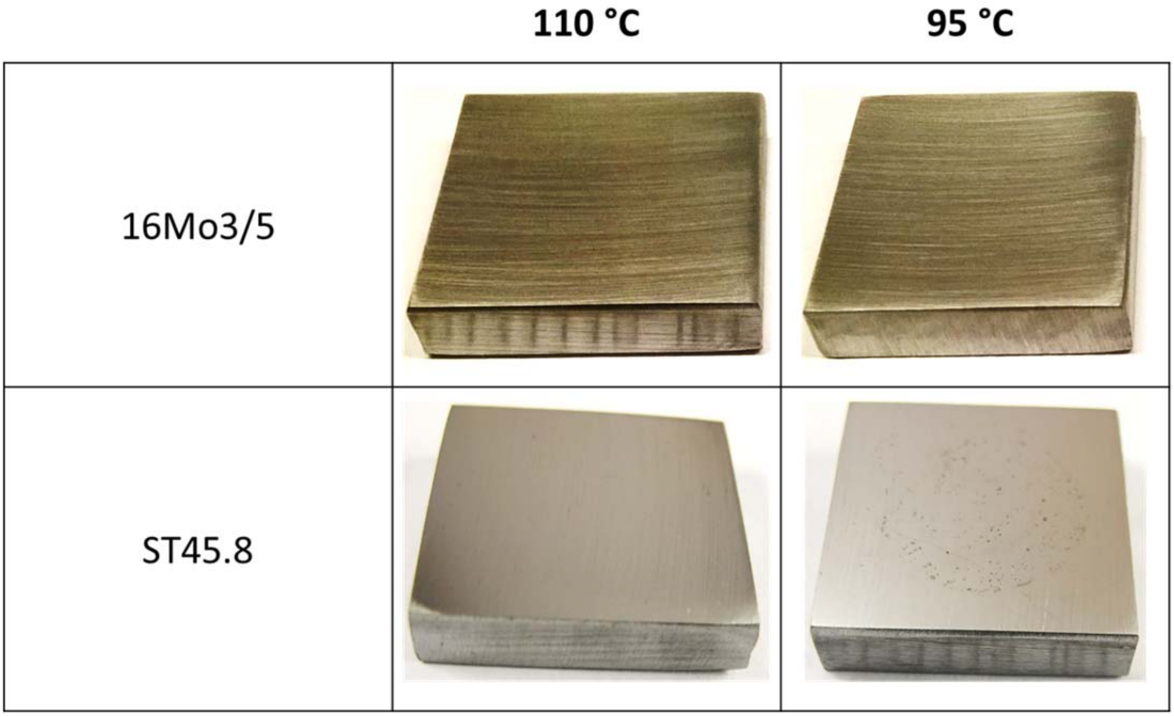


Figure 9. Corrosion results for 16Mo3/5 and ST45.8 at 95 and 110 °C under the Orange, TX precipitator ash in 25 vol-% H_2O in air.

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.

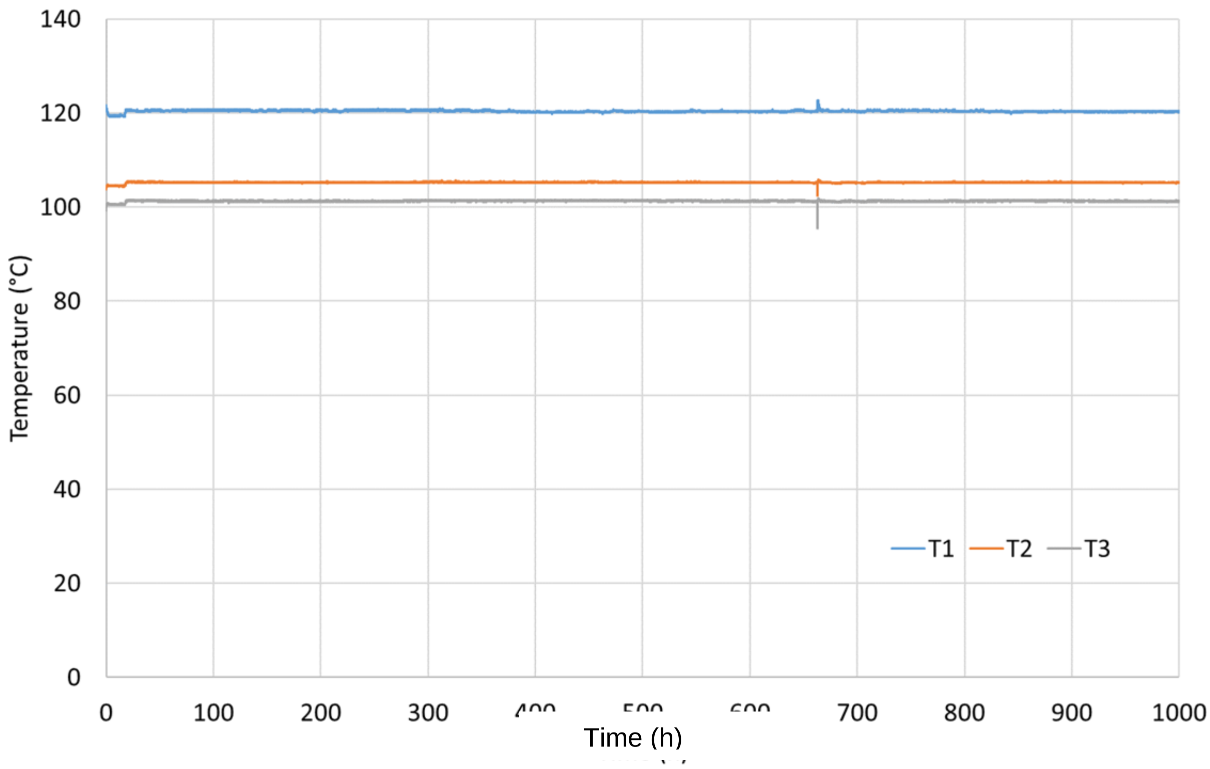


Figure 10. Thermocouple measurements at the 3 steel coupon positions.

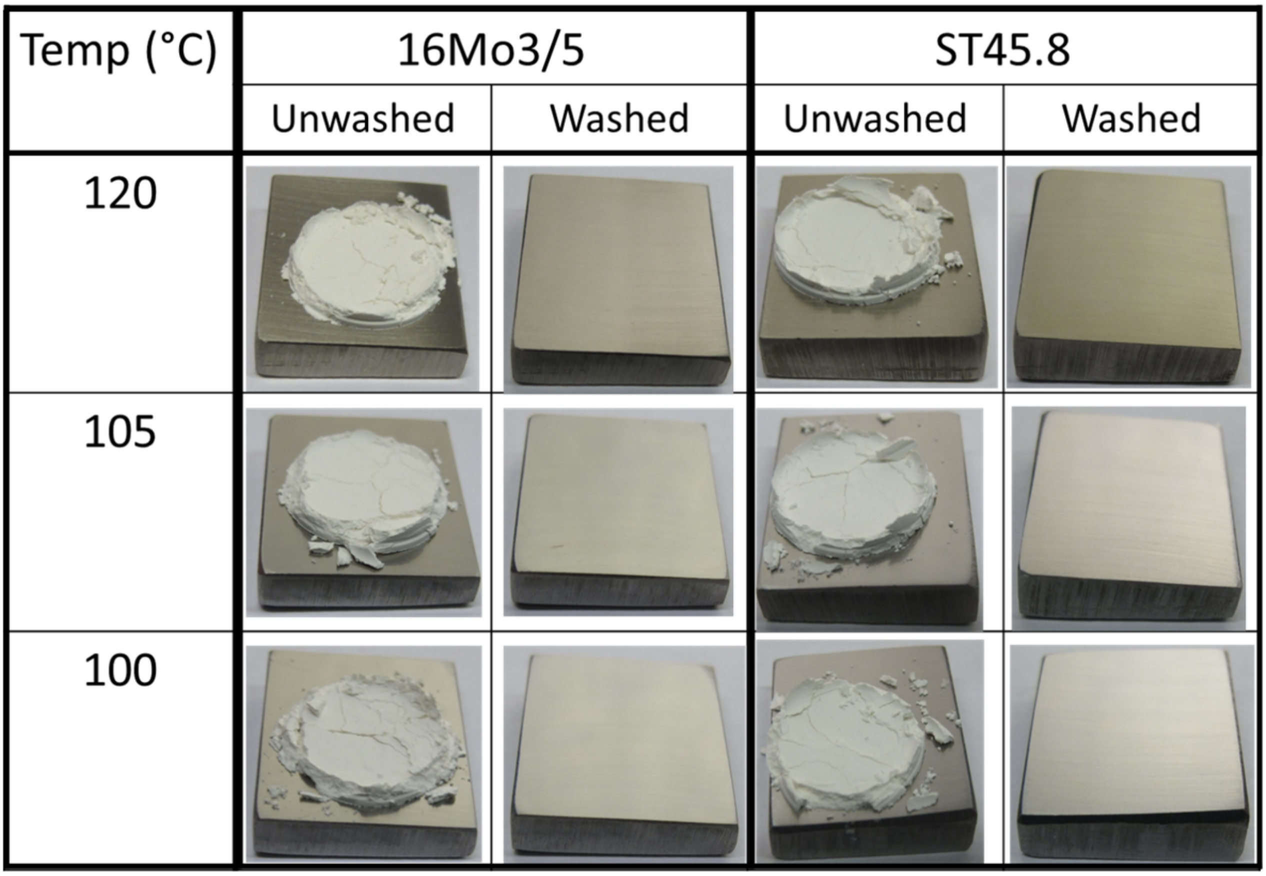


Figure 11. Samples after the 1000h test, both unwashed and washed.

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).

LIITE 2

ÅA, Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport –projektiehdotus 7.9.2017

Johan Gadolin PROCESS CHEMISTRY CENTRE

Åbo Akademi University

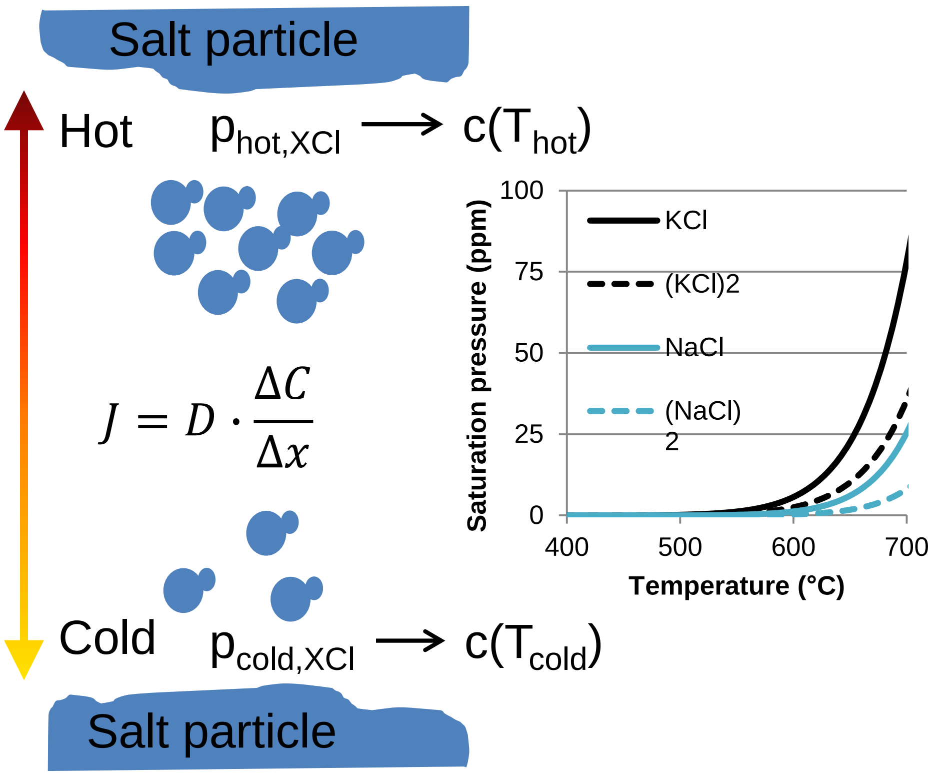
Intradeposit changes with time due to temperature gradient – Deposit Sampling Pre-Study

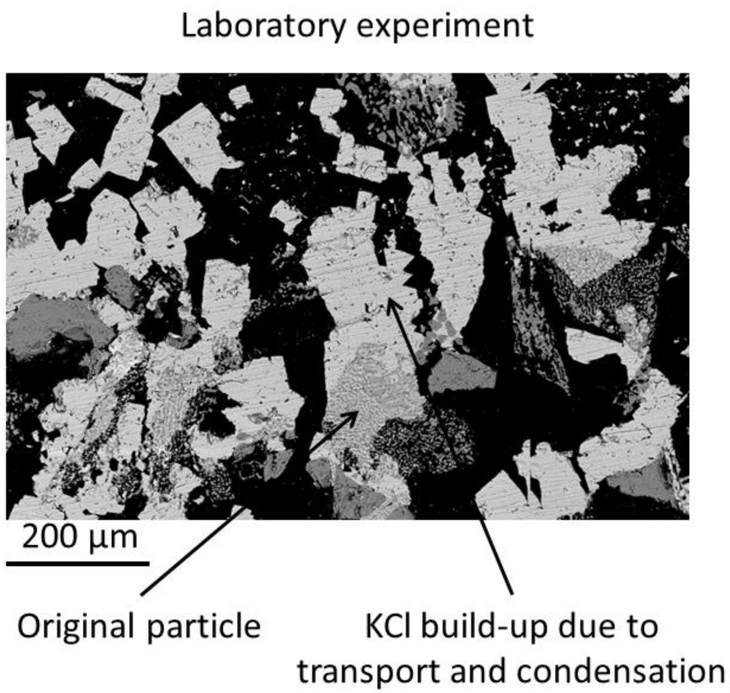
Markus Engblom

LTR meeting 7.9.2017

Background

- Intradeposit alkali chloride transport
  - Changes deposit chemistry and morphology with time

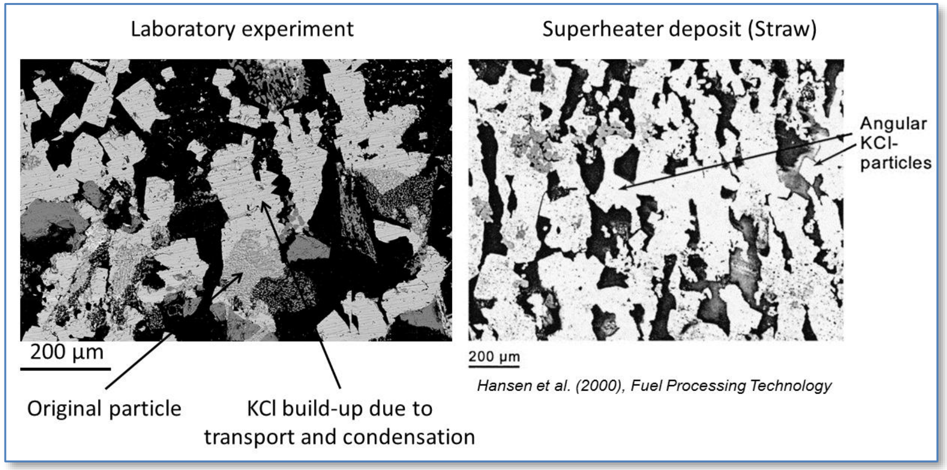




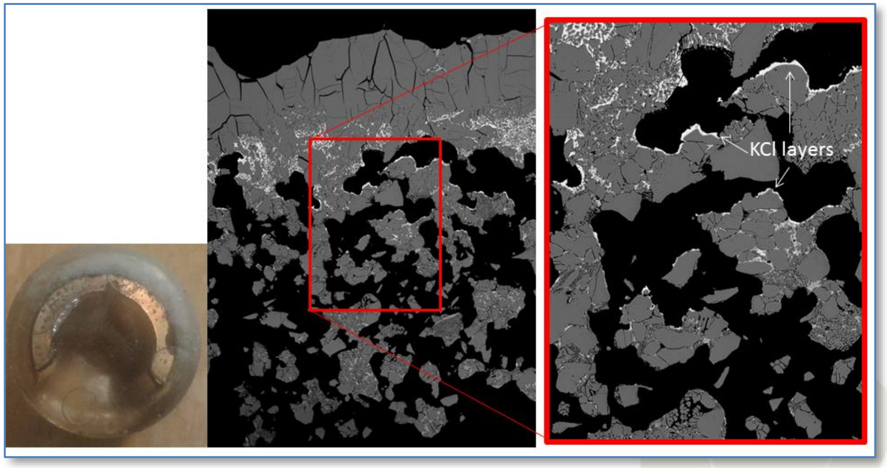
Background

- Intradeposit alkali chloride transport
- **Lab data exists – but limited data from mills**
- **Pre-study to see if possible to obtain mill-samples and how to analyse their cross sections for profiles**

Laboratory gradient furnace & boiler



Bench scale - Entrained flow reactor



Mill samples

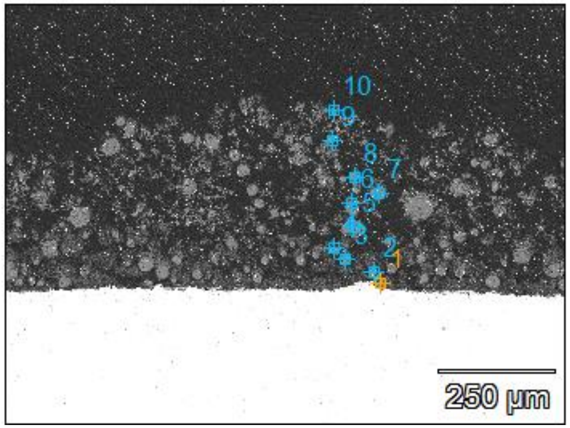
- Campaign at Rauma mill (15 min)
  - Probe 450°C with removable ring – deposit attached
  - After tertiary SH, close to roof, 660 °C
  - SEM: no Cl detected

- Deposit from Finnish mill (~2 hours)
  - Probe 300 °C with removable ring – deposit attached
  - Before BB
  - SEM: no Cl detected

- Deposit from Swedish mill (~2 hours)
  - Carryover probe 450 °C – deposit detached
  - Primary SH
  - SEM: Cl detected and cross section further analysed

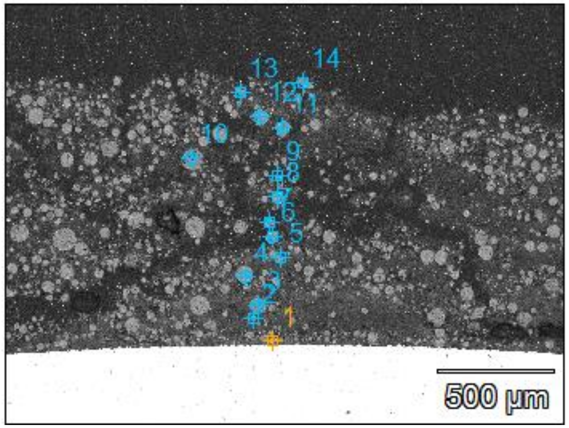
SEM analysis

Rauma



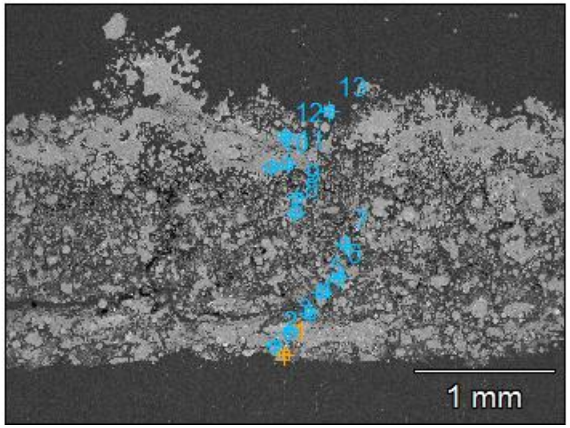
- No Cl detected

Finnish mill



- No Cl detected

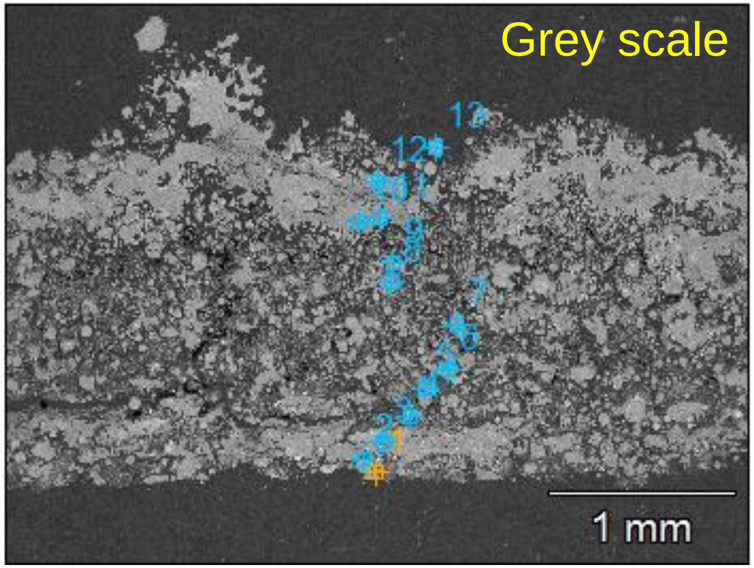
Swedish mill

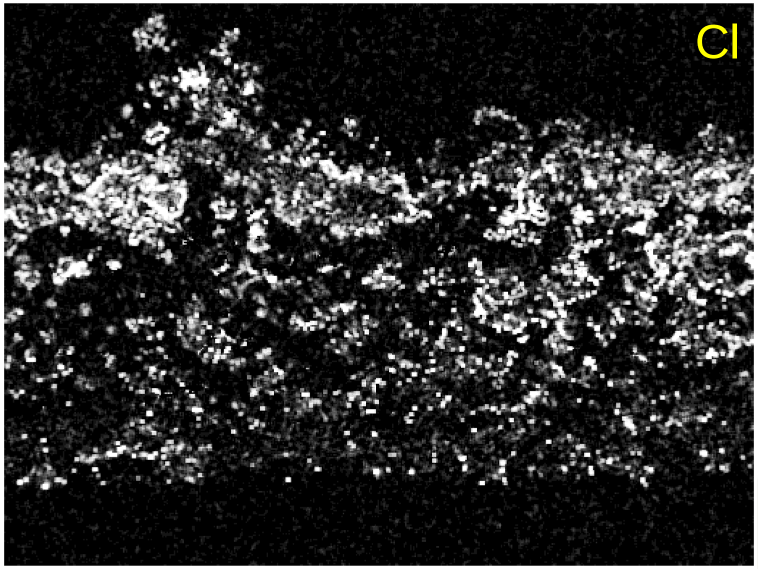


- On average 0.5-0.8 wt-% Cl
- SEM images further analysed for profiles of Cl and other elements

SEM analysis

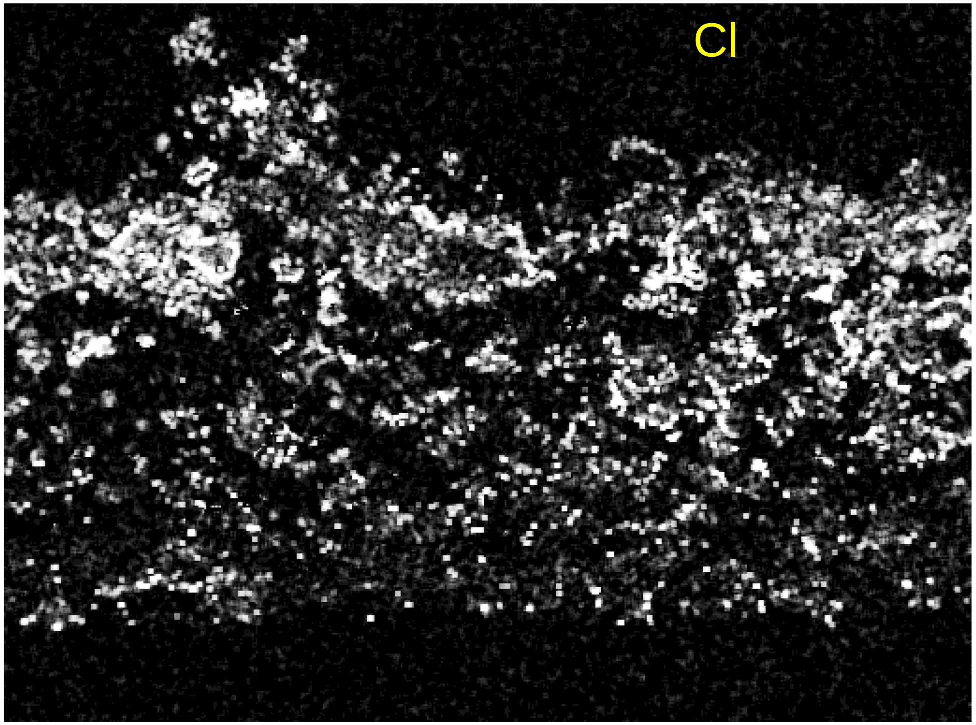
- Traditional: Spot and line analysis
- Tested: Horizontal averages from elemental x-ray maps

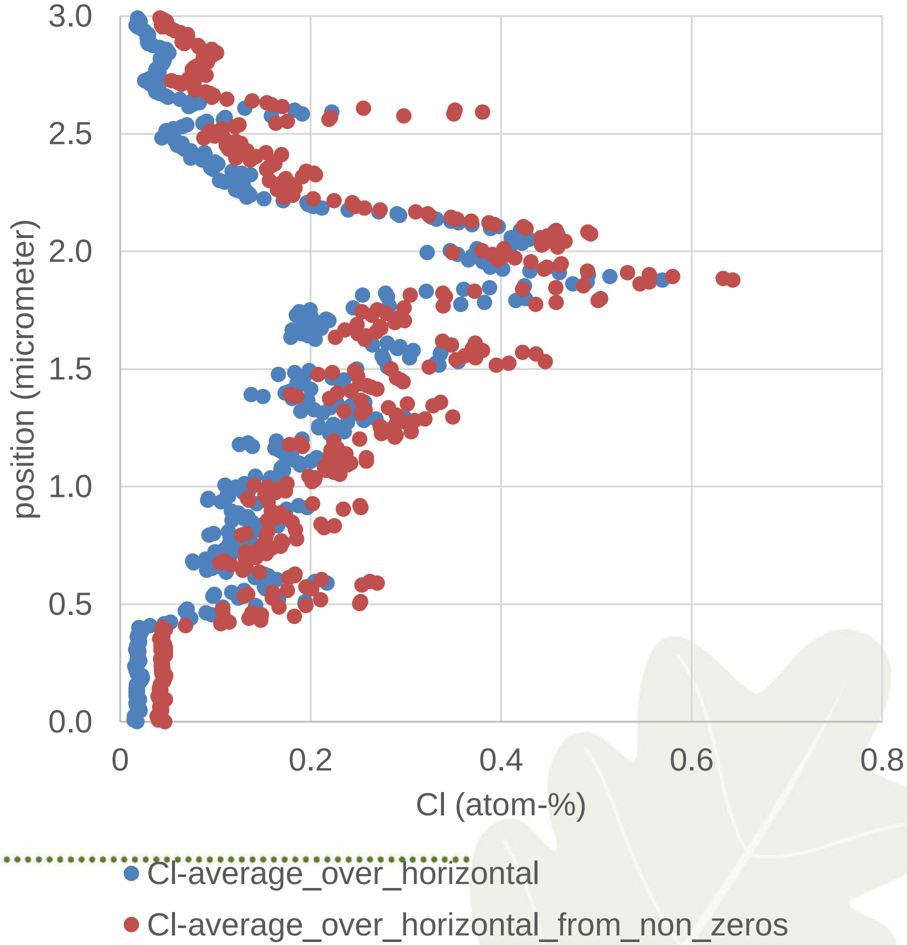




SEM analysis

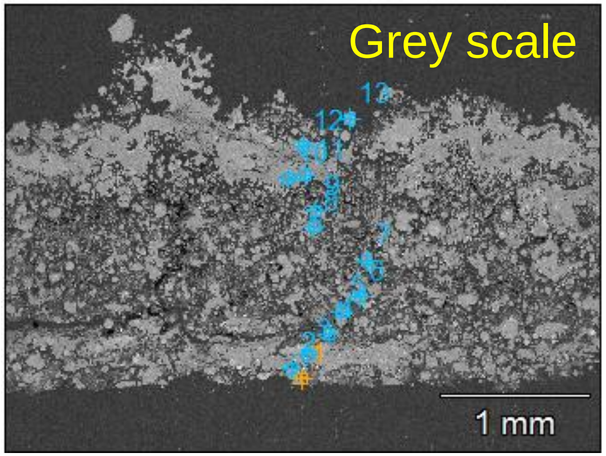
- Horizontal averages from elemental x-ray maps

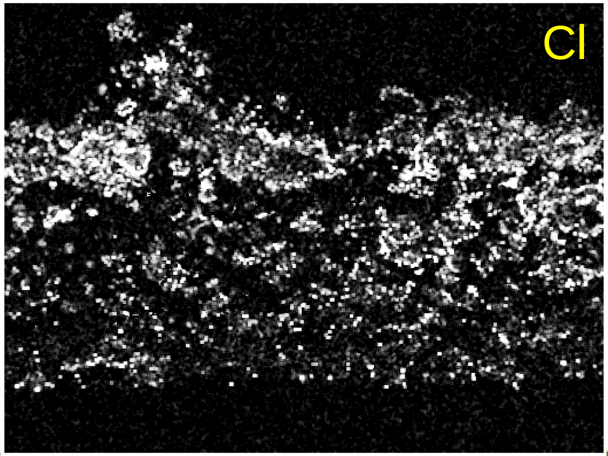


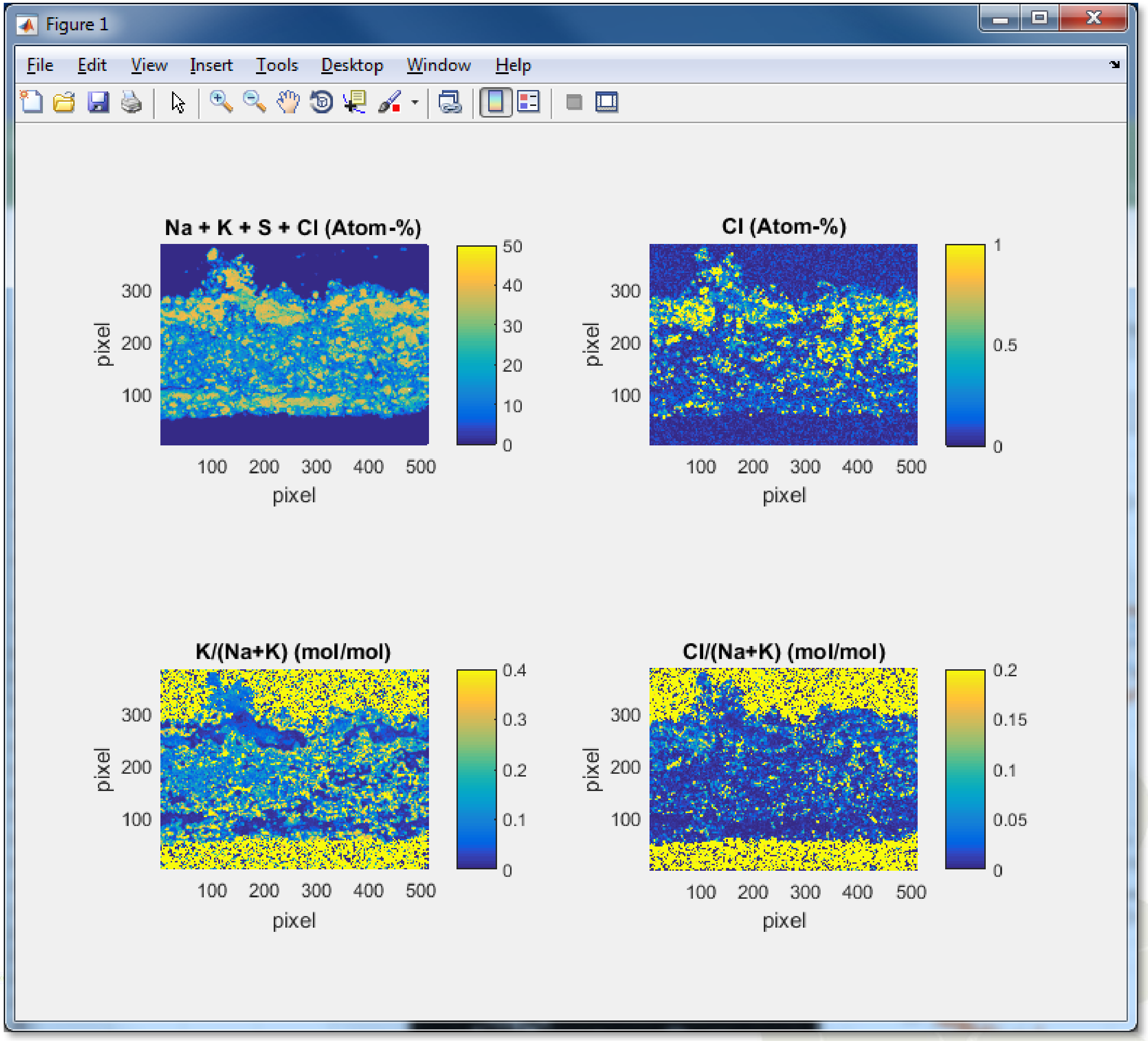


SEM analysis

- Room for method refinement – which pixels contain relevant information?







Conclusions

- Short time (≤ 2 hours) deposit sampling and analysis for the purpose of better understanding deposit aging appears possible

- Corrosion probes have been used in 1 month / 1000 h experiments in RB
  - Corrosion rate determined from ring mass loss – deposit has been irrelevant

- Question remains if it is possible to obtain deposit samples on rings after longer exposure times than tested so far
  - Plugging of probe opening
  - ...

How to proceed?

- Continue method development/testing
  - Goal: to obtain deposit samples from longer runs than so far, say a few days or a one week
  - A ”small” project with SKY

- Is there interest from SKY side to finance a MSc thesis
  - Sampling, analysis method refinement, analysis of results
  - Starting earliest 2018

LIITE 3

Muiden työryhmien kuulumiset

Muiden työryhmien kuulumiset

Projekti	KTR: Hitsauspinnoitettujen putkien käyttö soodakattiloissa, VTT
Tavoite	Selvittää hitsauspinnoitettujen putkien käytettävyyttä / soveltuvuutta soodakattiloihin
Tekijä	VTT
Kustannus (bud. / tot.)	12 000 eur / 12 000 eur (+alv) (kirjallisuustutkimus) 8 000 eur / 9700 eur (+alv) (karakterisointitutkimus) 52 500 eur / - eur (+alv) (vanhennuskokeet)
Tilanne / Aikataulu	1. Kirjallisuuskatsaus valmistui 5/2016 2. Karakterisointitutkimus valmistui 01/2017 (KMP esitys) 3. Vanhennuskokeet käynnissä -> lämpötila 650 C tehty 4. Jännityskorroosiokokeet (mahdollinen jatkoprojekti) Kolmelta toimittajalta (Uhlig, AZZ/WSI, Areva Uddcomb) saatu 625, 825 ja 309 pinnoitettuja putkia • Referenssiputkina San38/San28/304L kompound • Vanhennuskokeet tehdään kolmessa eri lämpötilassa (600, 650, 700 C) ja kolmella eri pitoajalla (10, 100, 1000 h)

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	KTR: Selvitys sularännien toiminnasta vaihtelevalla kuormalla
Tavoite	Selvitetään lämpövuon (sulavirtauksen/lämpötilojen vaihtelu) vaikutusta sularännien vaurioitumiseen Pyritään löytämään syitä miksi sularännit eivät kestä edes 12 kuukautta
Tekijä	LUT, Eetu Rantanen / Esa Vakkilainen
Kustannus (bud. / tot.)	12 000 eur / - eur (+alv)
Tilanne / Aikataulu	• Työ aloitettu keväällä 2017 • Tehtailta pyydetty dataa jäähdytysvesivirtauksista ja sitä kautta laskettu lämpötehon muutoksia -> riittävä määrä isoja muutoksia -> säröily • Sunilassa tehty/tehdään lämpökameramittauksia • Halukkaat tehtaat edelleen voivat osallistua lähettämällä DCS dataa

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	KTR: Sularännisuositus
Tavoite	1. Kerättiin tietoa tapahtuneista vaurioista ja niiden syistä kyselyn avulla 2. Tehty SKY:n suositus BRLBAC:n ohjeen pohjalta
Tekijä	KTR
Kustannus (bud. / tot.)	2 000 eur / 5 000 eur (+alv)
Tilanne / Aikataulu	25.01.17 Ohjeen esittely vauriokeskustelussa 22.03.17 Ohje päivitetty keskustelun perusteella 05.04.17 KTR kokouksessa lisäykset tekstiin 28.09.17 KTR kokous suosituksen hyväksyntä ja julkaisu

Projekti	KTR: Soodakattilan tiiveydenvalvontaselvitys, Varo Oy
Tavoite	Tehdä yhteenveto käytössä olevista menetelmistä tehtailla (vuoden 2001 raportin päivitys) sekä esitellä saatavilla olevat parhaat tekniikat ja menettelyt
Tekijä	Timo Karjunen, Varo Oy
Kustannus (bud. / tot.)	12 000 eur / - eur + alv
Tilanne / aikataulu	• Kysely tiiveydenvalvonnan nykytilasta lähetettiin tehtaille 11/2016 • Esitys tuloksista Konemestaripäivillä Oulussa 1/2017 • Timo odottaa vielä tietoja laitetoimittajilta (kokemuksia viimeisimmistä projekteista) • Raportti kommentoivaksi keväällä -> esitys KTR:n syksyn kokouksessa

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	YTR: Soodakattilan NOx-päästön riippuvuus puuraaka-aineen typpipitoisuudesta – 1. osa: Puuraaka-aineen vaikutus mustalipeän typpipitoisuuteen
Tavoite	Selvittää mustalipeän typpipitoisuuden korrelaatio puun typpipitoisuuteen sekä maaperän vaikutus
Tekijä	VTT (Klaus Niemelä)
Kustannus (bud. / tot.)	- Raportin loppuunsaattaminen ja julkaisu 9000e
Tilanne / Aikataulu	Työn rakenne muutettu ja viimeistely menossa. Odotetaan kommentoitavaksi seuraavaan YTR:n kokoukseen (lokakuu). Valmis vuoden loppuun mennessä

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	YTR: Selvitys tyypillisistä savukaasuvirroista [m3/ADt] eri puulajeilla
Tavoite	Selvittää puulajin vaikutus soodakattilan savukaasumäärään sekä parantaa ja yhdenmukaistaa savukaasumäärän laskentatapoja
Tekijä	LTY: Sauli Repo / Esa Vakkilainen
Kustannus (bud. / tot.)	Kustannus 12 000€ (stipendi sis. 6kk palkan). Lisäkustannuksia tehdasvierailuista (2 vierailua viidelle tehtaalle n. 2000€).
Tilanne / Aikataulu	Diplomityöntekijä aloittanut 4.9.2017 Vaihe 1. Laaditaan excel-laskentamalli savukaasuvirtauksen laskentaan. Vaihe 2. Kerätään Soodakattilayhdistyksen kanssa Suomen tehtaiden tyypilliset savukaasuvirrat. Käydään tehtailla vierailuilla (syksy 2017 / kevät 2018) läpi laskentaa ja mitattuja tuloksia. • Käynnit tehtailla muut tiedot paitsi ominaissavukaasumäärä luottamuksellisia (kerätään datana koivu ja havusellun tuotanto) • Tehdas saa excel-laskentamallin omaan käyttöön

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	YTR: NCG-järjestelmien turvallisuusauditointi, syntyvät hajukaasumäärät ja koostumukset, tyypilliset onnettomuuteen johtavat syyt - prosessikonseptitarkastelut
Tavoite	Työssä pyritään luomaan yleisesti käytettävä tapa, jolla suoritettaisiin sulfaattisellutehtaiden NCG-turvallisuusauditointi, samalla selvittäen tehtaan sen hetkisen hajukaasujen keräilyn, käsittelyn ja polttoon johtamisen nykytila Lisäksi suositusluonnos SKY polttosuosituksen laajennuksesta keräilyyn
Tekijä	Kirsi Hovikorpi
Kustannus (bud. / tot.)	Kustannus 20 000€
Tilanne / Aikataulu	• Kirsi aloittanut väitöskirjan 1/2017, esitys ICRC 2017 • Auditointikäyntejä on tehty tähän mennessä eri laajuuksilla viidelle eri Suomen sellutehtaalle (2 pohjoisessa ja 3 etelässä) • Alustavasti 2-3 käyntiä suunnitelmissa • Esitys SKP 2017

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Projekti	ATR ja YTR: Soodakattilan päästömittausten menetelmät
Tavoite	Päivittää vuoden 2007 raportti, jossa kerättiin tehtaille annetut päästörajat sekä selvitettiin käytössä olevia päästömittauslaitteita sekä niiden käyttökokemuksia, kunnossapitoa ja huoltoa. Lisäksi uudessa raportissa käydään läpi päästömittausasioita päästötiedon tuottamisesta aina päästöjen raportointiin asti 1. Lainsäädäntö ja standardointi 2. Laskentaperiaatteet 3. Mitattavat päästökomponentit: mitä, milloin 4. Mittausepävarmuus: perusteet, miten tehdään ja sovelletaan 5. Mittalaitteet ja niiden käyttökokemukset, ongelmakohdat 6. Raportointi (VAHTI, E-PRTR)
Tekijä	Oili Tikka / Paula Juuti, Pöyry Finland Oy
Kustannus (bud. / tot.)	Kustannus 15 800 €
Tilanne / Aikataulu	Tilanneraportti YTR-kokous 30.8.2017 Esitys SKP 2017