

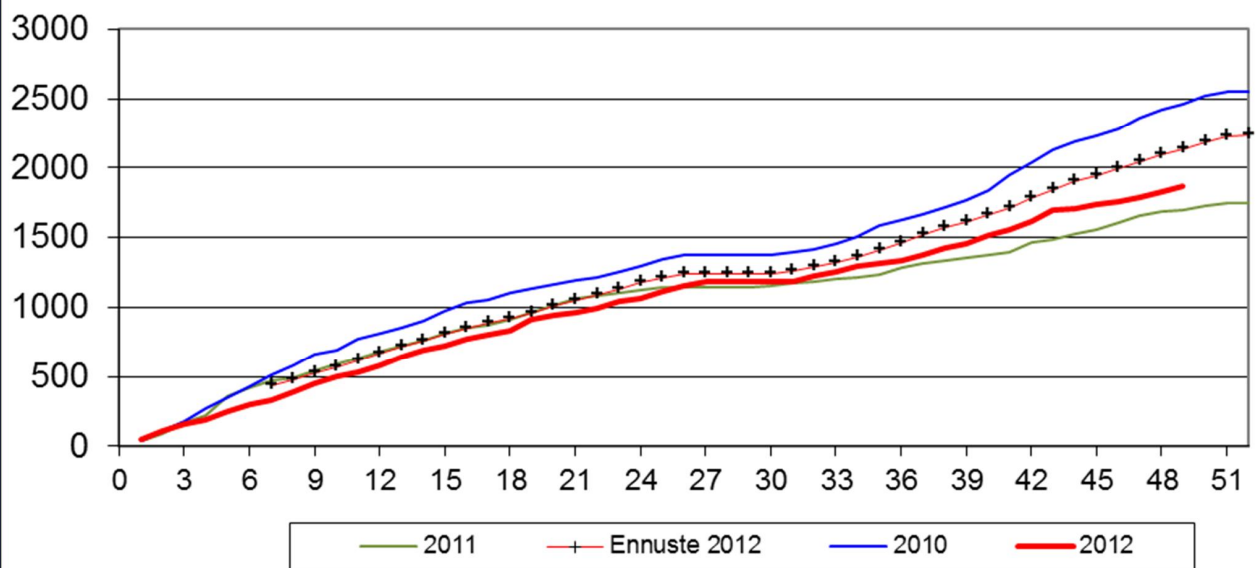
LIITE 2

Tuntiseuranta ja kassavirta

Talous

1

Kumulatiivinen tuntikertymä 2012

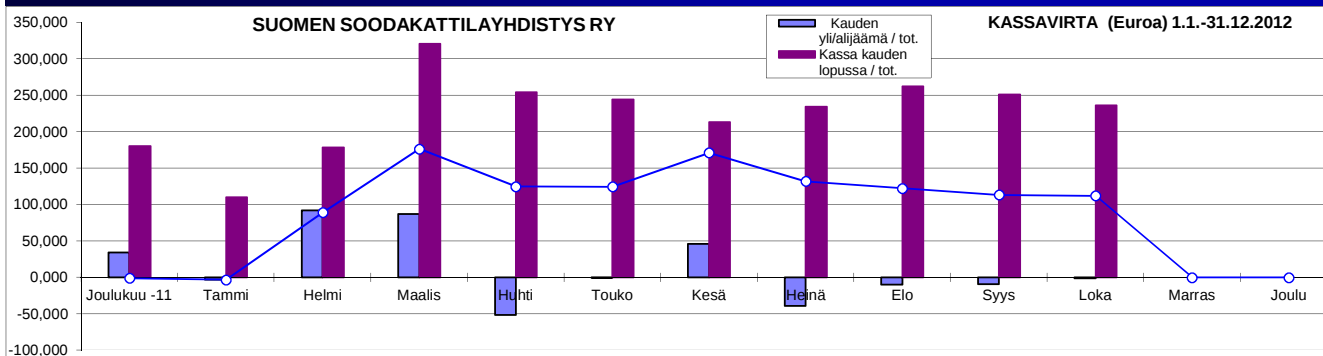


2

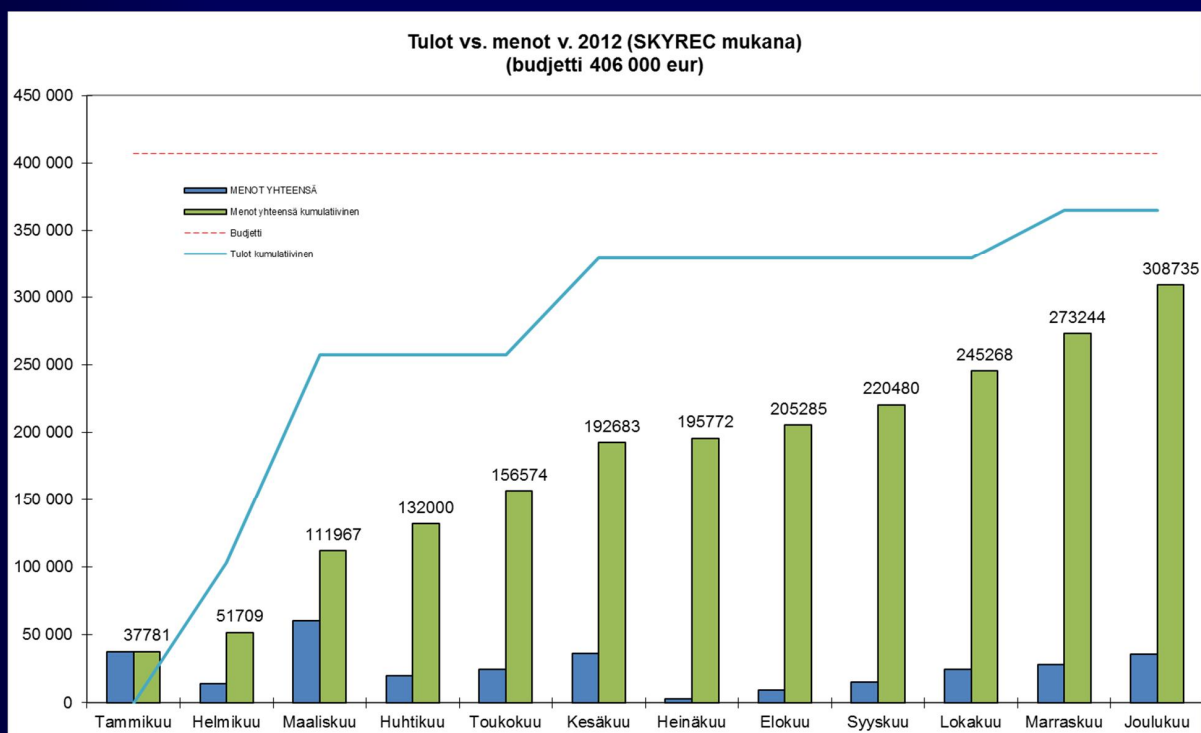
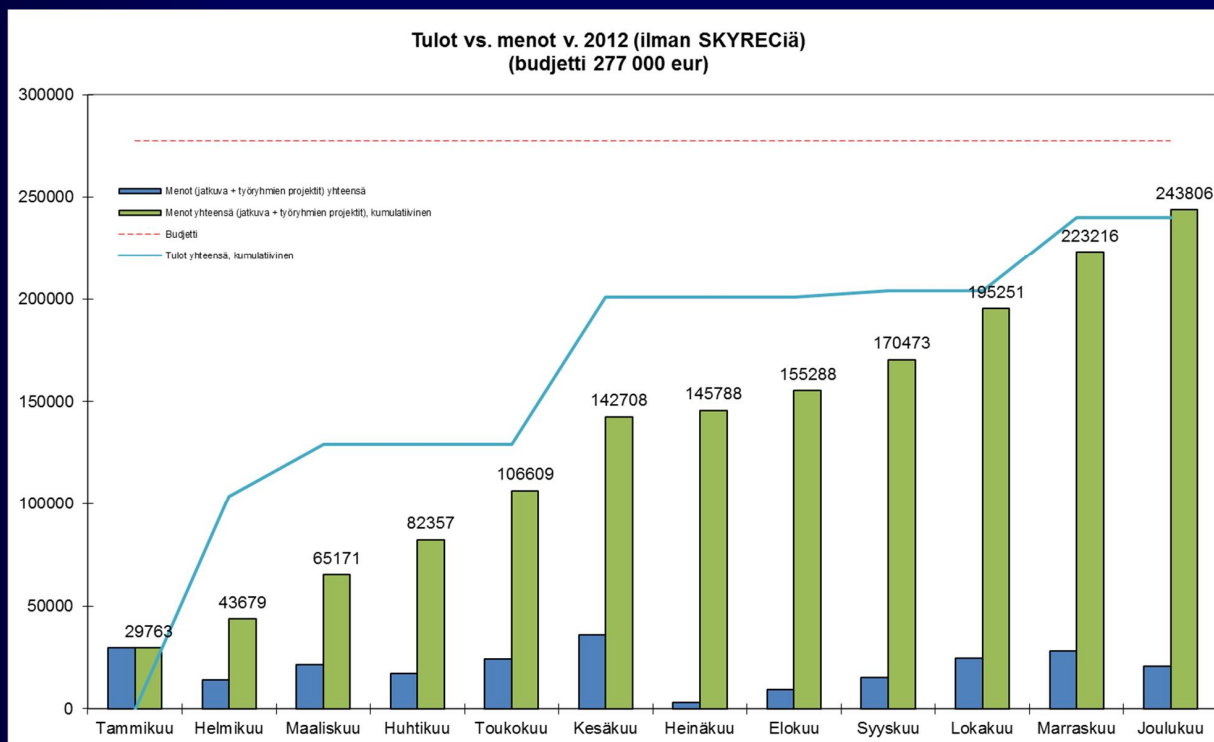
Saamiset 30.10.2012

- Ei saamisia

	Joulukuu - 11	Tammik.	Helmi	Maalis	Huhti	Touko	Kesä	Heinä	Elo	Syys	Loka	Marras	Joulu
Tulot													
<i>Tulot / tot.</i>	2,194		129,100	128,017			71,700			3,100	36,272		
Menot													
<i>Menot / tot.</i>	-32,172	2,885	36,975	40,820	51,589	0,119	25,302	39,102	9,512	12,127	37,517		
Kauden yli/alijäämä / budj.													
<i>Kauden yli/alijäämä / tot.</i>	34,366	-2,885	92,125	87,197	-51,589	-0,119	46,398	-39,102	-9,512	-9,027	-1,245		
Kumulatiivinen tulos	-0,682	-2,885	89,239	176,436	124,847	124,728	171,126	132,024	122,512	113,485	112,240		
Ed. kausien rahat ja pankkisaamiset													
Ed. kausien rahat ja pankkisaamiset		180,310	110,376	178,798	320,887	254,238	244,303	213,207	234,460	262,476	251,199	236,529	
Kassa kauden lopussa / tot.	180,310	110,376	178,798	320,887	254,238	244,303	213,207	234,460	262,476	251,199	236,529		



Jäsenmaksun 3.erä periminen



Kustannukset 2012

SKYREC

	Tammikuu	Heimikuu	Maaliskuu	Huhtikuu	Toukokuu	Kesäkuu	Heinäkuu	Elokuu	Syyskuu	Lokakuu	Marraskuu	Joulukuu	Toteuma vuonna 2012	Ennuste vuonna 2012	Budjetti vuodelle 2 012	Erotus	
Projektit																	
SKYREC	8007	0	38750	2832	312	0	0	0	0	0	0	0	14900	64 801	64 801	66 730	1 929
Ostopalvelut	927												927	927	927	1 000	
Material testing in furnace	7080												7 080	7 080	7 080	7 080	
Corrosion tests in reducing conditions –PART II A			15350										15 350	15 350	15 350	15 350	
Comparison study of active carbon grades			23400										23 400	23 400	23 400	23 400	
Economizer corrosion													14900	14 900	14 900	14 900	
Sitteeristö				2832	312								3 144	3 144	3 144	5 000	

7

Kustannukset 2012

Työryhmät

	Tammikuu	Heimikuu	Maaliskuu	Huhtikuu	Toukokuu	Kesäkuu	Heinäkuu	Elokuu	Syyskuu	Lokakuu	Marraskuu	Joulukuu	Toteuma vuonna 2012	Ennuste vuonna 2012	Budjetti vuodelle 2 012	Erotus
Kestoisuustyöryhmän tehtäväalue																
VARO-lisäokanta ylläpito					1014						6000		7 014	7 014	8 000	986
Materiaalivuostus				5000					5000				10 000	10 000	10 000	0
Savukaasujäähdytys												7800	7 800	7 800	7 800	0
Aktivihien mitoituksen varmistus ja optimointi													7 800	7 800	7 800	0
Kestoisuustyöryhmän tehtäväalue yhteensä	0	0	0	5 000	1 014	0	0	0	5 000	0	6 000	7 800	24 814	24 814	25 800	986
Liipeätyöryhmän tehtäväalue																
Syöttövesipumpun mitoitus					11900							11900	23 800	23 800	23 800	
Liipeätyöryhmän tehtäväalue yhteensä	0	0	0	0	11 900	0	0	0	0	0	0	11 900	23 800	23 800	23 800	0
Ympäristötyöryhmän tehtäväalue																
Biosludge measurements						9480							9 480	9 480	9 480	0
Lipidkiemion ammoniakkitase						15000							15 000	15 000	15 000	0
POPE										1667			1 667	1 667	9 525	7 858
Hajukaasusuostuksen päivitys (ATR/ YTR:n kanssa)	902		1654		156		234			78			3 024	3 024	5 000	1 976
Ympäristötyöryhmän tehtäväalue yhteensä	902	0	1 654	0	156	24 480	234	0	0	1 745	0	0	29 171	29 171	39 005	9 834
Automaatioityöryhmän tehtäväalue																
Turva-automaatioisuus					312		234						546	546	1 000	454
UPS-järjestelmien vika-analyysi			601		1560					715			2 876	2 876	5 000	2 124
Automaatioityöryhmän tehtäväalue yhteensä	0	0	601	0	1 872	0	234	0	0	715	0	0	3 422	3 422	6 000	2 578
Ohjelmistötyöryhmän tehtäväalue																
50-vuotisjuhla			75		736	1026		2686		234	1014		5 771	5 771	10 000	4 229
Painelatepöytä					1132			262	1967	2093	444		5 898	5 898	7 000	1 102
Opinnäytetyöapuraha						4290	468	468		2000			2 000	2 000	2 000	0
Projektitietokanta kotisivuille			2254										7 480	7 480	8 000	520
Ohjelmistötyöryhmän tehtäväalue yhteensä	0	0	2329	0	1868	5316	468	3416	1967	4327	1458	0	21 149	21 149	27 000	5 851
Työryhmien projektiehdotukset																
Suläränni (KTR)													0	0	10 000	10 000
Energialpöytä													0	0	5 000	
Muut projektiehdotukset (varaus)													0	0	29 846	29 846
Projektiehdotukset yhteensä	0	0	0	0	0	0	0	0	0	0	0	0	0	0	44 846	44 846
Työryhmien projektit yhteensä	902	0	4584	5000	16810	29796	936	3416	6967	6787	7458	19700	102355	102355	166 451	

8



Projektibudjetti 2013

- Budjetti työryhmien projekteille ollut noin 160 000 eur
- ~40 000 eur per ryhmä



SKYREC

SKYREC Budget 14.12.2012

- Projects paid: 788 171 €
- Projects to be invoiced: 14 900,00 €
- Sum (projects ordered): 803 071 €
- Funding from TEKES (350 000 €) is OK
- Project budget total: 805 000 €
- 805 000 € - 803 071 € = 1 929 € left

Projects to be invoiced

Company, Project name	will be invoiced
ÅA: Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler	14 900 €
Budget left	16 829 €
Sum	1 929 €

Things to be done: meeting 19.12.2012

- Accepting final report:
 - furnace material tests, VTT
- Results from last project:
 - Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler, ÅA
- Commenting final report

Probe Study of Corrosion in the Economizers, ÅA

- The SKYREC dew point corrosion study indicated that little to no corrosion of carbon steel will occur in flue gas heat recuperators until the material temperature was below the water dew point in the flue gases from Kraft recovery boiler.
- No acid dew point was observed, even when there was significant SO₂ present in the flue gas.
- This is most likely because any H₂SO₄ formed in the flue gas reacts with Na₂SO₄ to form NaHSO₄.

Työryhmien toiminta

Valmistuneet projektit

15

Valmistuneet projektit

- KTR: Savukaasuräjähdyksen riippuvuus savukaasun koostumuksesta, OY
- LTR: Mustalipeän viskositeetti, Labtium
- OTR: Painelaitepäivä 19.9.2012 Sokos Hotel Vantaa
- OTR: Soodakattilapäivä 25.10.2012, Tampere

16

KTR: Savukaasuräjähdyks soodakattilassa, OY

1/2

- Tutkia turvallisen savukaasukoostumuksen raja-arvoja (syttymisrajat, minimihappipitoisuus) ja niihin vaikuttavia tekijöitä (mm. lämpötila, inerttikaasut, paine).
- Selvityksessä pyrittiin löytämään turvallinen yläraja happipitoisuudelle, jonka alapuolella savukaasuräjähdyks ei voisi tapahtua
- Loppuraportti saatu -> luotettavia vastauksia kysymyksiin ei saatu, tutkimustietoa vähän saatavilla
- Hyvä tutkimus aiheeseen -> laaja lähdeluettelo

17

KTR: Savukaasuräjähdyks soodakattilassa, OY

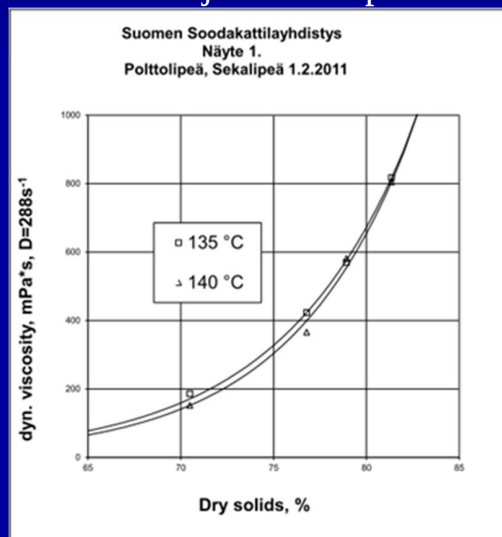
2/2

- Soodakattilassa vapautuu palavia kaasuja pyrolyysin ja koksen palamisen aikana, tärkeimmät näistä kaasuista ovat vety ja hiilimonoksidi
- Kaasu-ilmaseos palaa ainoastaan jos kaasun konsentraatio seoksessa on alemman ja ylemmän syttymisrajan välillä. Syttymisrajat määritetään kokeellisesti ja ne vaihtelevat huomattavasti eri kaasujen ja kaasuseosten välillä.
- Vaikka eri tekijöiden vaikutuksista vedyn, hiilimonoksidin ja niiden seosten syttyvyyteen löytyy kirjallisuudesta melko runsaasti tietoa, niin varsinkin korkeammissa lämpötiloissa ($> 300\text{ °C}$) saatua tutkimustietoa on saatavilla vain niukasti.

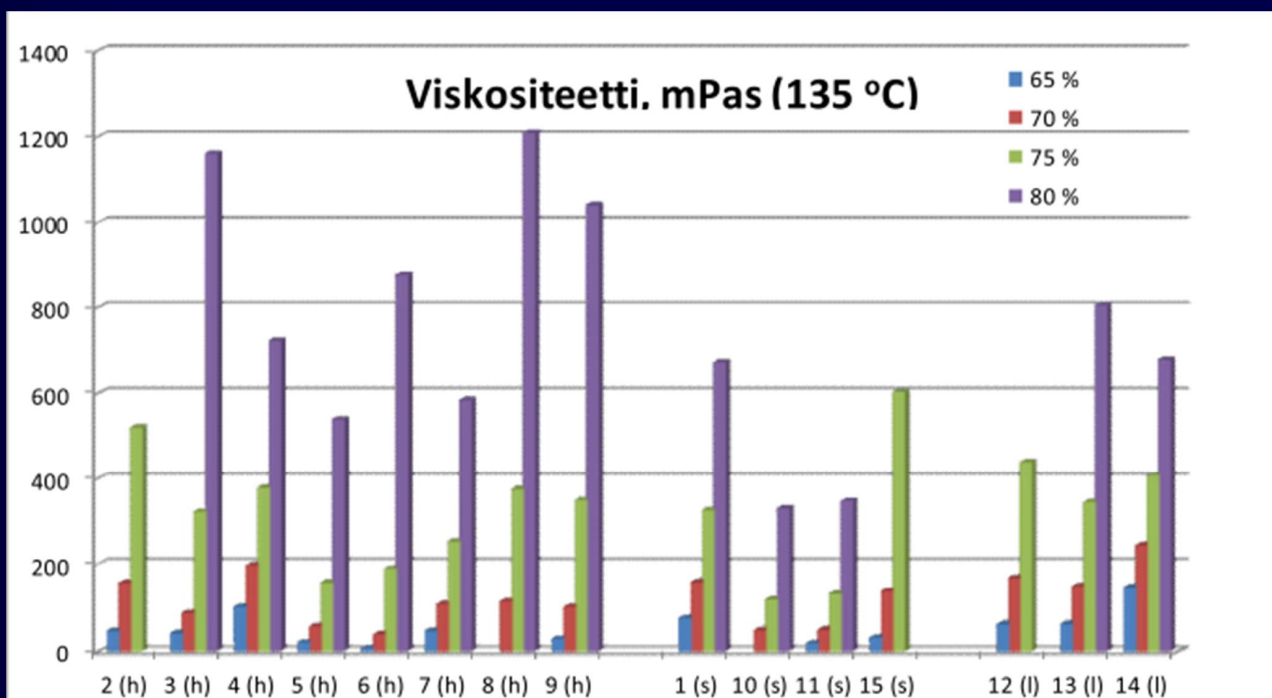
18

LTR: Mustalipeän viskositeetti, Labtium

- Työssä tutkittiin yhteensä 15 eri mustalipeää
- Jokaisesta määritettiin dynaaminen viskositeetti sekä 135 °C:ssa sekä tehtaan itsensä määrittelemässä lämpötilassa.
- Kunkin näytteen viskositeettikäyrät sekä mitatut ja lasketut pisteet on esitetty raportissa

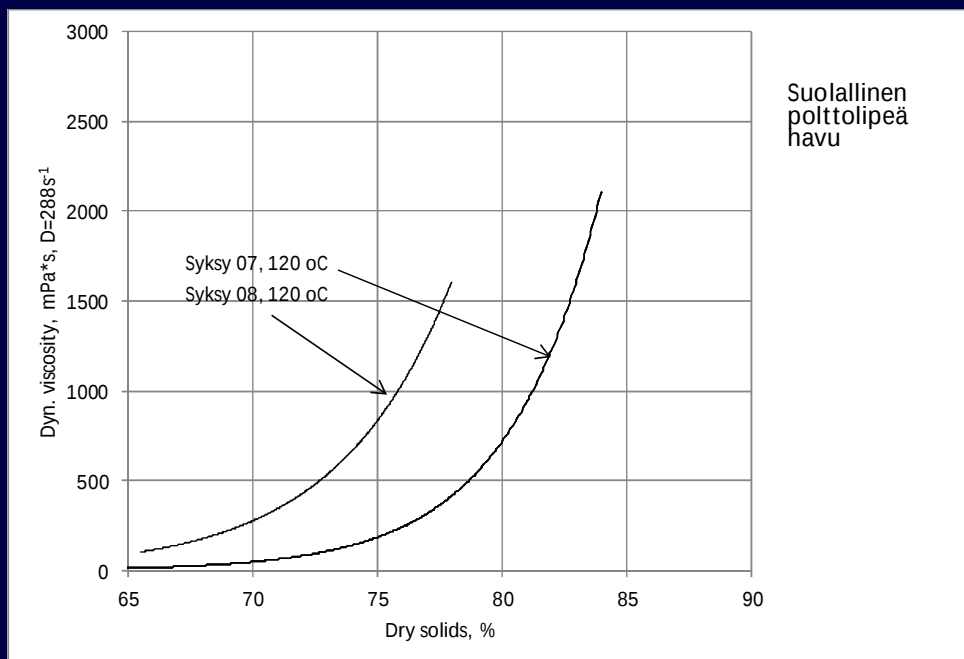


19



- Mustalipeiden viskositeetit eri kuiva-ainetasoilla (h=havulipeä, l=lehtipuulipeä ja s=sekalipeä)

20



- Havulipeän viskositeettikäyrät mitattuina vanhalla (syksy 07) ja uudella (syksy 08) viskositeettilaitteistolla. Mittauslämpötila on ollut 120 °C.

21

Painelaitepäivä 19.9.2012

Palaute

22

Palaute

- Palautettuja lomakkeita yhteensä 23 kpl
- Ilmoittautuneita 38 kpl

Kuinka arvioisit luennoitsijaa ja esityksen sisältöä?

Keskiarvo, asteikko 1-5

Jorma Partanen Painelaitesäädökset ja painelaiteturvallisuus	4.0
Kirsi Levä Painelaitteiden riskienhallinta	3.9
Tanja Välke Työturvallisuusvastuut: Omistaja/haltija/käytönvalvoja	3.4
Eskö Hyypä Olennaiset turvallisuusvaatimukset	2.6
Martin Wikström Kokemuksia vauriotietojen vaihdosta	4.2
Thomas Åström Rikkomattomat aineenkoetusmenetelmät (NDT)	4.6
Mikko Ulvinen Riskienhallintamatriisi ja polku tehokkaaseen painelaitekunnossapitoon	3.8
Silja Inkinen Materiaalit, hitsaus, eripariliitokset, lämpökäsittelyt	4.5
Martin Wikström Tiedonsiirto ja koulutus	4.2



Mielipiteesi tilaisuuden muista järjestelyistä

Keskiarvo, asteikko 1-5

Salijärjestelyt (pöytäjärjestys, kuuluvuus, näkyvyys)	4.3
Ilmoittautumis- ja vastaanottopalvelut	4.5
Tilat	4.4
Tarjoilut	4.5
Yleisvaikutelma tilaisuudesta	4.3

25



Muuta palautetta

- Hyvä kurssi, mutta aikaa oli liian vähän tai aiheita liikaa.
- Lisäarvoa olisi antanut ns. normaalin käytönvalvojan näkökulma siitä, millaisiin ongelmiin (organisatorisiin tai teknillisiin) tällä hetkellä useimmiten törmää (vrt. vilkas keskustelu vastuukysymyksistä).
- Erittäin hyvä anti ja ehjä kokonaisuus. Lyhyt tiivistelmä (Word) luentokalvoista olisi hyvä.
- Kuulijakunnasta puuttui täysin se, mihin olisi pitänyt vaikuttaa päivän viestillä -> yrityksen korkein johto.
- Jos halutaan kertoa tarkastuksista yms. Esim. Markku Virtanen, Juha M. Inspectalta kertomaan, osaavat esiintyä. M. Wikströmin osa 1 ei minulle mitään uutta asiaa lainkaan, mutta osaava ja hyvä esiintyjä.

26



Soodakattilapäivä 25.10.2012

Palaute



Palaute

- *Ilmoittautuneita*
 - 96
- *Palautettuja lomakkeita yhteensä*
 - 37 kpl
- *Vastausprosentti 38 %*

Kuinka arvioisit luennoitsijaa ja esityksen sisältöä?

Nikolai DeMartini, Ammonia Formation and Recovery in a Kraft Pulp Mill	3,8
Esa Vakkilainen, Päästötason riippuvuus tarkasteluajanjaksosta	4,1
Veli-Matti Pietarinen, Biomassan kaasutus ja kaasun käyttö meesauunissa	4,0
Erkki Välimäki, Samanaikainen korroosio-olosuhteiden ja tehtaan sulfiditeetin hallinta	4,0
Jukka Saarenpää, Prosessiputkien kuntotutkimukset röntgenkuvaustekniikalla	3,2
Emma Tolonen, Aktiivihiilisuodatus soodakattilalaitoksen lisäveden orgaanisen aineen vähentämiseksi	3,4
Esa Vakkilainen, SKYREC- mitä jäi käteen	4,2
Tero Luukkonen, Prosessiveden humuksenpoiston tehostaminen flotaatio- tai laskeutumisvaiheessa	3,8
Tiia Nousiainen, Opinnäytetyön "Crude Tall Oil Production Improvement" esittely	4,3
Markus Nieminen, Suomen, Ruotsin ja Pohjois-Amerikan soodakattilayhdistysten kuulumiset	3,9

Mielipiteesi tilaisuuden muista järjestelyistä

	Keskiarvo
Salijärjestelyt (pöytäjärjestys, kuuluvuus, näkyvyys)	4,1
Ilmoittautumis- ja vastaanottopalvelut	4,5
Tilat	4,2
Tarjoilut	4,6
Yleisvaikutelma tilaisuudesta	4,3

Toivottuja luentoaiheita

- Hajukaasujen puhdistus aktiivihiilisuodattimilla
- Laimeiden hajukaasujen poltto soodakattilassa
- Kuvaan perustuvat mittaukset
- Kattilan tehokkuus, voidaanko laskea/seurata on-line?
- Vesikemiaa lisää
- Lisää sähköntuotannon lisäykseen liittyvää juttua

Muuta palautetta

- Auditorio toimii luennoissa ehkä vähän paremmin kuin leveä huone
- -> Hki, energiamessut -> hotellikapasiteetti
- Taloyhtiöiden vesi- ja viemäriputkien röntgenkuvaus ei oikein kuulu asiaan
- Luentoaineisto värillisinä kopioina, please

Työryhmien toiminta

Käynnissä olevat projektit

33

ATR: Ohje UPS-järjestelmän periaatteeksi

- Projektia varten perustettu työryhmä jättänyt loppuraportin:
 - Sähkön syötölle tulisi mahdollisuuksien mukaan tarjota useampi toisistaan täysin riippumaton kulkutie. Yksittäisiä yhteisiä osia tulisi välttää (automaattinen syötönvaihto, yhteinen UPS kisko)
 - UPS-laitteiden lisääminen parantaa lähinnä sähkönsyötön toimintavarmuutta katkostilanteessa. Varsinkin kun huomioidaan UPS laitteiden taipumus vikaantua juurikin tarvetilanteessa
 - Oleellista on kiinnittää huomiota myös normaalitilanteen sähkönsyötön varmuuteen kriittisten laitteiden ja järjestelmien osalta
- ATR pohtii projektin jatkoa -> Ohjeen teko

34



KTR: Aktiivihiihden mitoituksen varmistus ja optimointi sekä TOC-reduktion varmistaminen, JPanalysis/OY

- Tarkoitus varmistaa suodattimen mitoitus koeajoilla eri virtaamilla
- Selvitetään aktiivihiihden suodattimen kustannukset ja toimittajat
- Lisäksi vertaillaan kahden TOC-laitteiston antamia tuloksia.
- Työ viivästynyt TOC-laitteen hajoamisen takia -> työt päästy aloittamaan -> valmistuu ensi vuoden alussa
- Aktiivihiihden huuhtelut tehty -> TOC reduktio ~70%, putoaa kun virtaama kasvaa



KTR: Vauriot

- 5/2012 Imatra, keittoputkisto
- 6/2012 Imatra, keittoputkisto
- 7/2012 Imatra, sularänni

KTR: Soodakattilanmateriaalit ja tarkastukset (Suojaussuosituksen päivitys)

- VTT päivittänyt osan 2 (Soodakattilan pinnoitteet)
- Pinnoitettavia kohteita ovat yleensä
 - ”mustan” ja compound-putken raja, jossa pinnoitteella estetään galvaanista korroosiota
 - tulistinputkien mutkat, joissa pyritään estämään hapettumisen ja korroosion kautta tapahtuvaa ohenemista
 - paikalliset compound-putkien säröytymien korjaus
- Tartunta tärkeää
- Korjaaminen hankalaa/mahdotonta

37

POPE, Itä-Suomen yliopisto

- Projektissa tutkitaan soodakattilan, meesauunin, hakevoimalaitoksen, pienpolton (tulisija ja arinakattila) päästöjen haitallisuutta uudella tutkimusmenetelmällä
- Hiukkasmittauksia tehty Kymillä soodakattilasta (pesurin jälkeen) vko 34 -> vaikeuksia saada tarpeeksi hiukkasia impaktoriin
- SK uusinta mittaukset vko 48 sekä pesurin että sähkösuodattimen jälkeen
- Meesauunimittaus tulossa
- Johtoryhmän kokous oli 20.11.2012
- Seuraava kokous 13.6.2013 Kuopio

38

BAT-dokumentin kommentointi / NO_x

- Marraskuun lopussa oli selluluvun läpikäynti Sevillassa
 - Etelä-Eurooppa tehtaot -> rikki
 - Mg/Nm³ ja kg/ADt herättää kysymyksiä
 - CO päästöraja
 - Hajukaasukattilan low-NO_x poltin vaatimus
 - Hardwood/Softwood määrittely
 - Häiriötilanteen päästöt?
- Tammi/helmikuussa 2013 pidetään teknisen työryhmän (TWG, technical working group) kokous

39

28. In order to reduce NO_x emissions from recovery boilers, BAT is to use an optimised firing system including all of the following features:

	Technique
a	Computerised combustion control
b	Proper mixing of air and fuels
c	Staged air feed systems, e.g. by using different air registers and air inlet ports.

Applicability

Technique c is applicable to new recovery boilers and in case of major refurbishment of recovery boilers as this technique requires considerable changes to the air feed systems and the furnace.

Table 8.8 BAT-associated emission levels for NO_x and CO emissions from recovery boilers

Parameter		Daily average mg/Nm ³ at 6 % O ₂	Yearly average mg/Nm ³ at 6 % O ₂	Yearly average kg pollutant/ADt
NO _x	Softwood	140 – 200 ⁽¹⁾	120 – 180 ⁽¹⁾	DS < 75 % ⁽²⁾⁽³⁾ : 0.8 – 1.0
				DS 75 - 83 % ⁽³⁾ : 0.8 – 1.2
	Hardwood	160 – 240 ⁽¹⁾	120 – 200 ⁽¹⁾	DS < 75 % ⁽²⁾⁽³⁾⁽⁵⁾ : 1.0 – 1.2
				DS 75 - 83 % ⁽⁴⁾⁽³⁾⁽⁵⁾ : 1.0 – 1.4
Carbon monoxide		< 50 – 100	< 50 – 70	-

⁽¹⁾ The lower end of the range refers to dry solids content in black liquor of < 75 %, lower nitrogen content in the black liquor, low excess air for combustion and a normal (or below design capacity) load on the recovery boiler. The upper end of the range refers to dry solids content in black liquor of ≥ 75 %, higher nitrogen content in the black liquor and combustion of strong or NCG, condensate-containing methanol, dissolving tank vent gases (DTVG) or bio-sludge in the recovery boiler.

⁽²⁾ The higher the dry solid content, the higher the NO_x emission load.⁽³⁾ In each of the two following cases the BAT-AEL mentioned may be increased by 0.1 kg NO_x/ADt:

- if nitrogen-containing flows like dissolving tank vent gas, methanol separated from the condensate, or biosludge are burnt in the recovery boiler and/or
- if nitrogen-containing CNGs are burnt together with the black liquor in the recovery boilers.

NB: DS=dry solid content of black liquor.

40

32. In order to reduce NO_x emissions from the lime kiln, BAT is to apply a combination of the following techniques:

	Technique	Description
a	Optimised combustion and combustion control	See Section 8.7.1.3
b	Good mixing of fuel and air	
c	Low NO _x burner	
d	Fuel selection/Low-N fuel	

BAT associated emission levels

see Table 8.12

Table 8.12: BAT-associated emission levels for NO_x and CO emissions from the lime kiln

Parameter		Daily average mg/Nm ³ at 6 % O ₂	Yearly average mg/Nm ³ at 6 % O ₂	Yearly average kg NO ₂ /ADt
NO _x	Oil	100 – 250	100 – 200	0.1 – 0.2
	Gas / biofuel	200 – 400	200 – 350	0.1 – 0.3
Carbon monoxide		< 50	< 50	-

(¹) If nitrogen-containing CNGs are burnt in the lime kiln instead of in the NCG burner, the BAT-AEL mentioned may be increased by 0.1 kg NO_x/ADt for the specific load and by 100 mg/Nm³ for the concentration levels.

[This BAT conclusion is based on information given in Section 3.3.21.]

Hajukaasusuosituksen päivitys

- Päivitystyö melkein valmis, teksti läpikäyty kaksi kertaa
 - Metanolin/tärpätin poltto-kappale vielä tarkistettava
- Edellinen kokous 10.12.2012
- Vielä yksi kokous 23.1.2013 Imatralla, Konemestaripäivien yhteydessä
- Suurimmat muutokset:
 - Väkevien polton voi aloittaa aikaisemmin tiettyjen ehtojen täytyttyä
 - Väkevien poltossa tukiliekkin voi sammuttaa tiettyjen ehtojen täytyttyä
- Suosituksen laajentaminen keräilyyn?

YTR/ATR: Hajukaasujen polttosuosituksen päivitys

- Päivitystyöryhmä kokoontui edellisen kerran 16.3.2012 Kuusankoskella
- Teksti käyty läpi ja kommentoitu, vielä yksi kokous jossa katsotaan kokonaisuus
- Suurimmat muutokset:
 - Väkevien polton voi aloittaa aikaisemmin tiettyjen ehtojen täytyttyä
 - Väkevien poltossa tukiliekkin voi sammuttaa tiettyjen ehtojen täytyttyä
- Suosituksen laajentaminen keräilyyn?

43

LTR: Syöttövesipumppujen säätö, LUT

- Työssä tehdään esiselvitys kolmen SKY:n valitseman soodakattilan syöttövesipumppauksen mahdollisuuksista säästää sähköä toteuttamalla pumppauksen säätö uudella tavalla
 - Taustalla on ABB:n rahoittama väitöskirja jossa on tutkittu taajuusmuuttajapumppujen energiataloudellista ajotapaa
 - Samalla mietitään miten suurella syöttövesisäiliöllä kukin soodakattila pärjäisi.
 - Lisäksi mietitään mikä olisi energiataloudellisen syöttövesipumppu konfiguraatio
- Tutkittavat kattilat: Veracel (data puuttuu), Fray Bentos (data puuttuu), Joutseno (data puuttuu)

44

Konemestaripäivät 23-24.1.2013

- Konemestaripäivät järjestetään 23.–24.1.2013 Imatran Valtionhotellissa ja tehdasvierailu Metsä Fibren Joutsenon tehtaalla.
- Ajankohtaa jouduttiin aikaistamaan viikolla tehdasvierailun vuoksi
- Ohjelma:
 - Henkilöturvallisuuden parantaminen soodakattilalaitoksessa RFID avulla, <http://www.visi.fi/>
 - Soodakattila- ja turbiinivauriot, Thomas Åström (Pohjola)

45

SKY 50v ja ICRC 2014 9.6-13.6.2014

- ICRC-seminaari 9.-13.6.2014 Tampere-talossa
- 50v-toiminkunta on perustettu miettimään juhlapäivän konferenssin (11.6) ohjelmaa/ luennoitsijoita
 - Timo-Pekka Veijonen, Keijo Salmenoja, Mikko Hupa, Klaus Niemelä, Esa Vakkilainen
- Alustavat nettisivut (ei vielä julkaistu):
http://www.soodakattilayhdistys.fi/secure/ICRC/ICRC_index.html

46



Vuosikokous 2013

- Helsingissä 18.4.2013
- Saman konseptin mukaan viime kerralla (itse kokous iltapäivällä ja iltaohjelma sen jälkeen)
- Sihteeri kartoittaa mahdollisia kokouspaikkoja (musiikkiteattereita).



Projektiehdotukset

Projekti ehdotukset

- Projektitietokanta yhdistyksen sivuilla:
 - LTR: Mustalipeän ei-Newtonilaisuus ja pisaroituminen
 - LTR: Suolallisen mustalipeän kuiva-aineen määrittäminen ja tuloksen ilmaisu
 - LTR: Econimizer corrosion, part 2
 - LTR: Feeding and Combustion of Black Liquor Pellets
 - LTR: Smelt Dissolution Kinetics
 - YTR: Kustannustehokas tapa siirtää ammoniakkia talteenottokierrosta jätevesilaitokselle
 - YTR: Sähkösuodintuhkan hyötykäyttö
 - YTR: Hiukkaskokojakaumat ja pölyemissiot
 - KTR: Sularännit, käyttöongelmat ja soodasulan juoksevuus
 - OTR: Energiapäivä

LIITE 3

ATR: Soodakattilan UPS järjestelmä-ohjeen sisältö

Päiväys 18.10.2012

Sivu 1 (2)

SUOSITUS SOODAKATTILALAITOSTEN VARMENNETUN JÄNNITEJAKELUN PERIAATTEEKSI

Sisältö

- 1 Johdanto
- 2 Sähkökatkoksen vaikutukset soodakattilan toimintaan
- 3 Varmennetuista verkoista syötettävät kuormat
- 4 Suositeltavat UPS-verkon rakenteet
- 5 UPS-verkon suunnittelussa huomioon otettavia näkökohtia
- 6 UPS laitevalinnassa huomioitavia seikkoja
- 7 Suosituksia testauskäytännöstä ja kunnossapidosta

Liitteet

Jakelu

1 JOHDANTO

2 SÄHKÖKATKOKSEN VAIKUTUKSET SOODAKATTILAN TOIMINTAAN

- jos järjestelmä tai operointinäytöt eivät toimi operaattorit eivät tiedä mitä prosessissa tapahtuu eivätkä voi ohjata prosessia
- vaarat
- vahingot
- sähkölaitteiden tarkastukset katkoksen jälkeen, lyhyesti
- pidetään tästä ja seuraavasta kohdasta erillinen kokous (työryhmä)

3 VARMENNETUISTA VERKOISTA SYÖTETTÄVÄT KUORMAT

- alustava lista on jo Pöyryn ohjeessa - täsmennetään
- listataan erikseen UPS- ja dieselvarmennetut kuormat ja perustellaan tarpeet
- kenttävyölien sähkönsyöttö
- pidetään tästä erillinen kokous. Käydään läpi esimerkkikaavioiden kanssa yhden Metson ja yhden Andritzin kattilan suositeltavat UPS ja diesel kuormat. Mietitään tässä istunnossa myös sisältöä kohtaan 2

4 SUOSITELTAVAT UPS-VERKON RAKENTEET

- tekstiä on jo Pöyryn ohjeessa- täydennetään
- kerrotaan verkon rakenne järjestelmällisesti
- piirretään kaaviot kokonaan yhteen kuvaan
- riittääköhän yksi vaihtoehtoisia toteutustapoja?
- viitataan tehtyihin vikapuuanalyysihin
- kaavioissa ja tekstissä yhdenmukaiset nimikkeet esim. eri syötöistä

5 UPS-VERKON SUUNNITTELUSSA HUOMIOON OTETTAVIA NÄKÖKOHTIA

- mitoitus, selektiivisyys jne., näitä olikin jo Pöyryn ohjeessa - täydennetään
- perustelut erotusmuuntajien käytölle ja muuntajien mitoitus
- 230 V vaihtoaunomaatikka – kontaktorin mitoitus
- akuston mitoitus ja muut vaatimukset
- pikatyhjennysventtiilien porrastus
- standardit, EN 50156
- UPS:n sijoituspaikka, muut osastot?

6 UPS LAITEVALINNASSA HUOMIOITAVIA SEIKKOJA

- luotettava valmistaja
- huolto / varaosat
- referenssit
- akuston rakenne
- diagnostiikka / hälytysten käsittely

7 SUOSITUKSIA TESTAUSKÄYTÄNNÖSTÄ JA KUNNOSSAPIDOSTA

- kaikkia vaihtoehtoisia syöttömahdollisuuksia testattava, että eivät jumiudu

- akustojen kunnon tarkkailu – automaattiset testaukset ja tyhjennykset/lataukset
- laajennusvara / muutosten hallinta
- testausvaiheessa sähköt pois

LIITE 4
YTR: POPE, Itä-Suomen Yliopisto
– pöytäkirja 20.11.2012



Polttoeräisten päästöjen ja nanohiukkasten haitallisuuden määrittäminen uudella tutkimusmenetelmällä (POPE)

Rahoituspäätöksen numero 40469/10

Diaarinumero 2175/31/2010

Johtoryhmän 4. kokous

Aika: Tiistaina 20.11.2012 klo 14.00 – 15.00
Paikka: Itä-Suomen yliopisto, Kuopion kampus, Melania 220 kokoushuone

Läsnäolijat: Maija-Riitta Hirvonen, UEF
Jorma Jokiniemi, UEF
Kari Lehtinen, Ilmatieteen laitos
Pekka Matilainen, Ecocat Oy
Kati Takala, Energiategollisuus
Timo-Pekka Veijonen, Stora Enso / Soodakattilayhdistys
Stefanie Kasurinen, UEF
Kari Kuuspalo, UEF
Ari Leskinen, Ilmatieteen laitos
Mikko Happonen, UEF
Karin Koivisto, UEF(sihtööri)

1. Kokouksen avaus

- Maija-Riitta Hirvonen avasi kokouksen klo 14.00.

2. Puheenjohtajan ja sihteerin valinta

- Puheenjohtajaksi ehdotettiin Maija-Riitta Hirvosta ja sihteeriksi Karin Koivistoa. Puheenjohtajan ja sihteerin valinta hyväksyttiin.
- Kokoukseen osallistujat esittäytyivät.

3. Esityslistan hyväksyminen

- Esityslista hyväksyttiin työjärjestykseksi.

4. Edellisen kokouksen pöytäkirjan hyväksyminen

- Edellisen kokouksen pöytäkirjan hyväksyminen: ei muutoksia, pöytäkirja hyväksyttiin.

5. Projektin tilannekatsaus:



- Jorma Jokiniemi esitteli projektin taustat ja tavoitteet ('Chain of events from heater emissions to health impacts'). Polttoperäisten päästöjen ja nanohiukkasten haitallisuuden määrittämisessä käytetään tutkimusympäristöä, joka mahdollistaa sekä tuoreiden että ikääntyneiden päästöjen haitallisuuden selvittämisen solukokein todellista altistumista vastaavissa olosuhteissa. Käytiin läpi eri päästötilanteet, joita projektissa on tarkoitus tutkia. Projektissa on edetty suunnitelman mukaisesti.
- Maija-Riitta Hirvosen ryhmä tutkii mekanismeja eri terveyshaittojen taustalla. Tunnetaan neljä päämekanismia, jotka osallistuvat terveyshaittojen muodostumiseen: DNA-vauriot, solukuolema, oksidatiivinen stressi ja tulehdus. Projektissa selvitetään hiukkasten osuutta niihin ja selvitetään mahdollista syy-seuraussuhdetta.

a) Soodakattila

- Kari Kuuspalo kertoi, että viikolla 48 kerätään DGI-impaktorilla soodakattilan piipun päästöstä hiukkasmassaa, josta tehdään kemialliset ja toksikologiset analyysit. Mitattavia parametreja ovat mm. hiukkasmassan pitoisuus ja lentotuhka (K, Cd, Ca).
- Soodakattilan osalta hiukkasten keräyksiä tehtiin syyskuun 2012 alusta vanhalla menetelmällä, mutta saatu hiukkasmassa oli riittämätön tarvittaviin mittauksiin (24 mg kerätty, kun tarve olisi ollut 40 mg). Riittävän massan keräämiseksi sekä toksikologiaan että kemiallisiin analyysihin näytteenottoja jatketaan viikolla 48, ja suunnitellut analyysit suoritetaan mahdollisimman pian.

b) Hakelaitos

- Kari Kuuspalo kertoi että hakelaitoksen mittaukset tehdään vasta talven aikana, jotta kuormat vastaavat todellista tilannetta lämmityskaudella ja kattilan toimiessa normaaliteholla.
- On toivottu, että laitoksessa käytettäisiin tasalaatuisia pellettejä näytteiden keruun aikana, jotta saataisiin kerätyksi mahdollisimman tasalaatuinen näyte.

c) ILMARI:n tilanne

- Stefanie Kasurinen esitteli hopeananohiukkasilla tehtyjen solualtistuskokeiden tuloksia, jotka hän on esittänyt AAAR konferenssissa Minneapolisissa tänä syksynä ('Evaluation of the Toxicological Potential of Silver Nanoparticles').
- Kokeissa käytettiin "air-liquid interface" menetelmää, jonka tarkoitus on jäljitellä *in vivo* olosuhteita mahdollisimman tarkasti.
- *Air-liquid interface*: solut kasvatetaan inserteillä, joissa ne ovat suoraan kosketuksissa tutkittavan näytteen kanssa, mukaan lukien kaasut.
- Muistuttaa todellisia altistusolosuhteita, mutta on teknisesti haastava.
- Alkuperäisen Vitrocell-yksikköön tehtyjen muutosten jälkeen onnistuttiin saamaan parempi hiukkasdepositio.



- Hopeahiukkaset lisäsivät etenkin IL-8 ja IL-6 tuotantoa, muiden mitattujen sytokiinien kohdalla vastetta ei ollut tai se oli selvästi alhaisempi.
- Tulevaisuudessa tulisi nanopartikkelidepositioiden tehokkuutta ja tasalaatuisuutta kehittää, sekä tuottaa malleja joissa käytetään useampaa kuin yhtä solutyyppeä, jotta voidaan jäljitteellä paremmin keuhkoissa vallitsevia olosuhteita.
- Pasi Jalava on tällä hetkellä Saksassa, Hannoverissa, Fraunhofer- Instituutissa, missä hän työskentelee edellä mainitun kaltaisten solumallien kanssa. Myöhemmin tätä tietoa voidaan soveltaa myös Hirvosen ryhmän tutkimuksissa.
- Maija-Riitta Hirvosen mielestä depositiota täytyy vielä parantaa ja kosteutta pitää olla enemmän solualtistuksen aikana.
- Maija-Riitta Hirvonen kertoi, että aerosolien ja päästöjen altistusyksikkö projekti on aloitettu. Tässä EU:n rakennerahaston rahoittamassa projektissa rakennetaan koe-eläinten altistusyksikkö, joka mahdollistaa solu- ja eläinaltistusten tekemisen samanaikaisesti.

6. Talousasiat

- Karin Koivisto esitteli projektin tämän hetkisen rahatilanteen UEF:n osalta.
- Ari Leskinen esitteli projektin rahatilanteen FMI:n osalta.

7. Julkaisut

- Kansainvälisesti referoituja julkaisuja ei ole vielä julkaistu, mutta tuloksista on raportoitu mm. EAC 2012 kokouksessa Granadassa Espanhassa ja AAAR 2012 kokouksessa Minneapolisissa USAssa. Seuraavaksi tuloksia esitellään SOT 2013 kokouksessa San Antoniossa Texasissa USAssa. Jatkossa tuloksista raportoidaan kansainvälisissä kokouksissa sekä referoiduissa julkaisuissa.
- Seuraava EAC Konferenssi (European Aerosol Conference) järjestetään Prahassa, 1.-6.9.2013.
- Stefanie Kasurinen tekee väitöskirjan projektin puitteissa (Maija-Riitta Hirvosen ryhmän jäsen).
- Jorma Jokiniemi mainitsi, että myös hänen ryhmänsä käyttää projektiin liittyviä tieteellisiä julkaisuja väitöskirjojen osatoina.
- Soodakattilasta ja hakelaitokselta otetut näytteet ja niiden analyysit julkaistaan.

8. Muut asiat

- Kaikki johtoryhmän jäsenet eivät ole vielä nähneet ILMARI tutkimuslaboratoriota. Siksi päätettiin tehdä vierailukierros heti tämän kokouksen jälkeen.

9. Seuraava kokous

- Torstaina 13.6.2013, klo. 13.00 - 15.00, Itä-Suomen yliopisto, Kuopion kampus, Melania 220 kokoushuone. Ari Leskinen lähettää kutsut.
- Puheenjohtaja päätti kokouksen klo. 15.00



ITÄ-SUOMEN
YLIOPISTO

22.11.2012

- LIITTEET:**
1. Kokouksen agenda 20.11.2012
 2. Johtoryhmän osallistujalista 20.11.2012

Polttooperäisten päästöjen ja nanohiukkasten haitallisuuden määrittäminen uudella tutkimusmenetelmällä, POPE

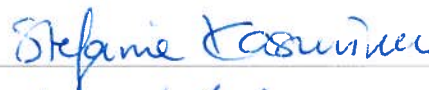
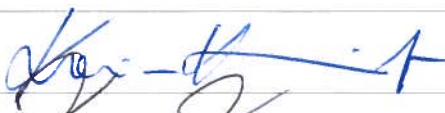
Johtoryhmän 4. Kokous

Melania 220, Kuopion Kampus 20.11.2012

klo. 14.00–16.00.

Esityslista

1. Kokouksen avaaminen
2. Puheenjohtajan ja sihteerin valinta
3. Esityslistan hyväksyminen
4. Edellisen kokouksen pöytäkirjan hyväksyminen
5. Projektin tilannekatsaus
 - a) Soodakattila
 - b) Hakelaitos
 - c) ILMARI:n tilanne
6. Talousasiat
7. Julkaisut
8. Muut asiat
9. Seuraavasta kokouksesta sopiminen

POPE osallistujat			
20.11.2012, klo 14.00, Melania 220			
	kyllä	ei	allekirjoitus
Tarmo Hattunen		x	
Maija-Riitta Hirvonen	x		
Jorma Jokiniemi	x		
Jens Kohlmann			
Juha Kouki		x	
Kari Lehtinen	x		
Pekka Matilainen	x		
Markus Nieminen			
Annamari Soikkeli		x	
Kati Takala	x		
Juha Timonen		x	
Timo-Pekka Veijonen	x		
Stefanie Kasurinen	x		
Ari Leskinen	x		
Pasi Jalava		x	
Olli Sippula		x	
Jarkko Tissari	x	x	
Karin Koivisto	x		
Kari Kuuspallo	x		
Mikko Happonen	x		

LIITE 5

**LTR: Mustalipeän ei-Newtonilaisuus ja pisaroituminen
Labtium/Aalto yliopisto – tarjous 4.12.2012**

Asia: Projektiehdotus Suomen Soodakattilayhdistykselle

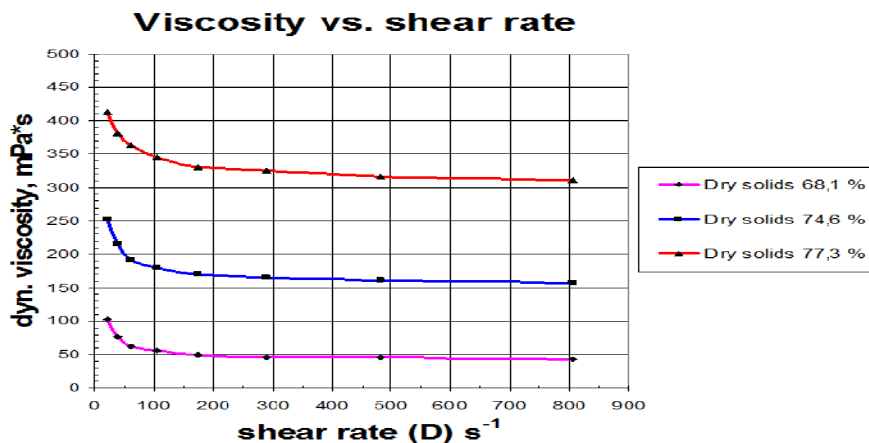
Ehdottajat:

- Jorma Torniainen/Labtium
- Ari Kankkunen/Aalto Yliopisto
- Mika Järvinen/Aalto Yliopisto

Mustalipeän ei-Newtonilaisuus ja pisaroituminen

1. Taustaa

Mustalipeän viskositeetti on tärkeä soodakattiloiden ja haihdutinyksiköiden toimintaan vaikuttava suure. Viskositeettiin vaikuttavat lipeän koostumuksen lisäksi mm. lämpötila ja kuiva-aine. Pienellä leikkausnopeudella viskositeetti on erittäin suuri, mutta kun leikkausnopeus kasvaa, niin viskositeetti laskee vakiotasolle (kts kuva 1.)



Kuva 1. Viskositeetti leikkausnopeuden funktiona.

Tätä viskositeetin vakiotasoa (leikkausnopeus 288 s⁻¹) käytetään yleisesti, kun viskositeetti määritetään eikä pienen leikkausnopeuden suurempaa viskositeettiarvoa yleensä huomioida. Ainakin pisaroitumisessa esiintyy pieniä leikkausnopeuksia ja ilmeisesti myös haihduttimissa. On viitteitä siitä, että lehtipuulipeän ei-Newtonilaisuus tulee esiin alhaisemmissa pitoisuuksissa ja lämpötiloissa/viskositeeteissa kuin havupuulla. Alhaisilla kuiva-aineilla ja alhaisissa lämpötiloissa tehdyt kokeet viittaavat siihen, että ei-Newtonilaisuutta esiintyy kuiva-aineen kohotessa yli 50-70%. Asiaa ei ole merkittävästi tutkittu, koska sopivia paineistettuja helppokäyttöisiä mittalaitteita ei ole ollut yleisesti saatavilla. Tällainen laite ja pitkä käyttökokemus ovat tarjolla Labtiumissa.

2. Tutkimuksen toteutus

Tutkimus toteutetaan neljällä erilaisella lipeällä; lehtipuu-, havupuu-, seka- ja eukalyptuslipeällä. Kussakin tapauksessa viskositeettimittaus tehdään viidessä eri lämpötilassa:

1. Tehtaan ruiskutuslämpötilassa
2. Lämpötiloissa 120 °C, 135 °C, 140 °C ja 150 °C. (135°C on vertailulämpötila, josta on jo olemassa dataa Soodakattilayhdistyksen edellisestä viskositeettityöstä)

Tuloksena saadaan kattava tietokanta erilaisten lipeden ei-Newtonilaisesta käyttäytymisestä.

On todennäköistä, että lipeden ei-Newtonilaisuutta selittää jokin mustalipeän erityinen ominaisuus. Tämän takia kustakin lipeestä määritetään:

1. Kuiva-aine
2. Jäännösalkali
3. epäorgaanisen/orgaanisen aineen suhde
4. polysakkaridit

Kokeelliset mittaukset tehdään Labtiumissa. Labtiumilla on pitkä kokemus mustalipeän viskositeetin ja muiden ominaisuuksien mittaamisesta.

Aalto yliopiston Energiatekniikan laitoksen tutkijat Ari Kankkunen ja Mika Järvinen vastaavat tulosten raportoinnista ja liittävät tulokset soodakattilan toimintaan, erityisesti mustalipeän ruiskutukseen. Ei-Newtonilaisuus vaikuttaa useilla tavoilla pisarakokoon. Ruiskun painehäviö ja höyrykuplien kasvunopeus ruiskussa riippuvat mustalipeän todellisesta viskositeetista. Muodostuva pisarakoko tulipesässä riippuu kuplien kasvunopeudesta pisan sisällä ja yksi tähän vaikuttava muuttuja on viskositeetti. Pintajännitys on pisanmuodostuksen (kuroutuminen palloksi) ajava voima ja viskositeetti vastustaa tätä voimaa. Myös ei-Newtonilaisuuden vaikutusta putkivirtauksiin, pumppuihin ja haihduttamoihin arvioidaan lyhyesti. Lisäksi yhdellä tehtaalla on tarkoitus tehdä painehäviöön perustuva viskositeettimittaus (on-line mittaus tehtaalla) ja verrata sen tuloksia laboratoriossa saatuun viskositeettitulokseen. Kankkusella ja Järvisellä on pitkä kokemus mustalipeän ruiskuttamiseen liittyvästä kokeellisesta ja laskennallisesta tutkimuksesta. Tulokset julkaistaan tieteellisenä julkaisuna.

3. Kustannukset ja aikataulu

Labtium:

Analyysikustannukset	14000 € (+ALV)
Näytteenotto (4 tehdasta)	<u>6 000 €</u> (+ALV)
Labtium yhteensä	20 000 € (+ALV)

Aalto yliopisto:

Uuden viskositeettitiedon liittäminen pisaroitumiseen ja soodakattilan toimintaan	15 000 € (+ALV)
Viskositeettimittaus tehtaalla (on-line)	<u>3 000 €</u> (+ALV)
Aalto yhteensä	18 000 € (+ALV)

Kokonaiskustannus koko työn osalta tulee olemaan **38 000 € (+ALV)**.

Aikataulu: Työ voidaan aloittaa keväällä 2013.

LIITE 6
LTR, Smelt Dissolution Kinetics
ÅA - tarjous 26.11.2012

Proposal – Smelt Dissolution Kinetics

26 Nov 2012

Nikolai DeMartini, ÅAU

The kinetics of smelt dissolution is relevant to the design and safety of smelt dissolving tanks and their operation. Smelt dissolution will depend predominantly on smelt particle size, salt solubility, agitation and cooling of the hot smelt particle down to below the boiling point of the liquor. Salt solubility in the case of smelt dissolution is interesting in that there are two potentially important salt solubility limits. One is pirssonite which is a $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$ double salt and the second is the solubility of sodium salts such as sodium carbonate or burkeite which have a much higher solubility than pirssonite [1,2], Figure 1. Once calcium in green liquor is consumed in the formation of pirssonite, the next salt will be sodium carbonate or burkeite depending on the $\text{CO}_3:\text{SO}_4$ mole ratio of the smelt [3]. The implication is that the driving force for salt dissolution will still be high even as the pirssonite solubility limit is approached, because the salt should continue to dissolve once all the calcium in the smelt/weak wash is consumed.

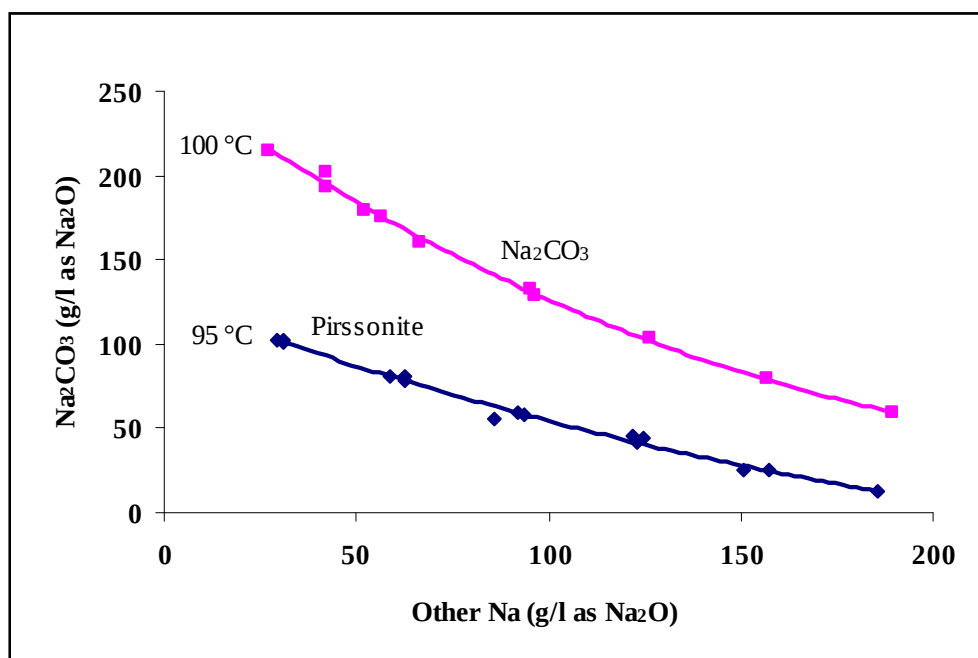


Figure 1. Literature values for the solubility limits of pirssonite at 95 °C [1] and sodium carbonate at 100 °C [2]. Note: Sodium carbonate has inverse solubility, so at 95 °C, sodium carbonate will be slightly more soluble than at 100 °C.

This work would focus on the variables: temperature, salt composition, crystal size and agitation speed. The temperature and smelt composition will affect the solubility limits. Mill smelt will be crushed in a glovebox and sieved in a glove box and heated to 100 °C and then added to the mill weak wash which will be preheated to the desired dissolution temperature. Samples will be taken at regular time intervals to measure the dissolution. Different temperatures will result in different initial solubility limit driving forces.

This work will provide fundamental data to improve our understanding of dissolution in smelt dissolving tanks. This has implications for operation and design and safety. This data combined with ongoing research at the University of Toronto and for the AF&PA can also help understand what variables are crucial in understanding smelt dissolving tank explosions. The heat transfer away from molten smelt particles needs to be studied by modeling in a follow up project, but is sufficiently complicated because of the 3 phase flow that it would need to be accounted for.

The cost for this project is **18 800 €** + VAT.

References

1. Frederick, W.J. Jr.; Krishnan, R.; Ayers, R.J. Pirssonite deposits in green liquor processing. TAPPI J. 73(2): 135-140 (1990).
2. Green, S.J.; Frattali, F.J. The system sodium carbonate-sodium sulfate-sodium hydroxide-water at 100°. J. Am. Chem. Soc. 68: 1789-94 (1946).
3. Shi, B.; Frederick, W. J. Jr.; Rousseau, R. W., Nucleation growth and composition of crystals obtained from solutions of Na₂CO₃ and Na₂SO₄. Ind. Eng. Chem. Res., 42(25): p. 6343-6347 (2003).

LIITE 7
LTR, Feeding and Combustion of Black Liquor Pellets, ÅA
– tarjous 26.11.2012

Proposal – Feeding and Combustion of Black Liquor Pellets

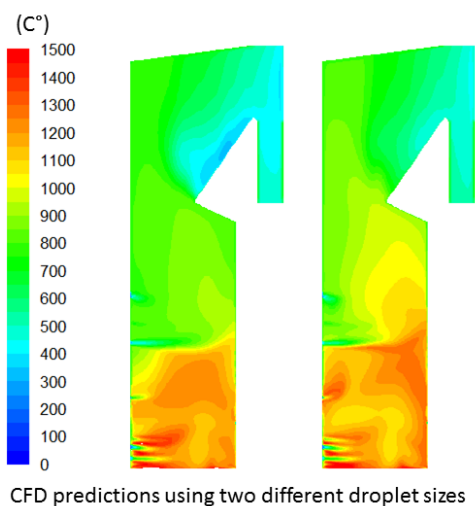
Anders Brink, Markus Engblom, Nikolai DeMartini, Mikko Hupa

Laboratory of Inorganic Chemistry at Åbo Akademi University

This project is designed to make a preliminary study of the feeding and combustion of black liquor pellets in a Kraft recovery boiler. The uniform distribution of fed particle size has interesting implications for the practical operation of a Kraft recovery boiler and could lead to better control of operational challenges such as carryover and emissions. The proposal is composed of two parts – CFD modeling of a Kraft recovery boiler firing pellets and laboratory work to support the CFD modeling. The CFD modeling will use an existing model, of a modern Kraft recovery boiler, modified for pellet feeding rather than black liquor spraying. The CFD model will give some preliminary information on how recovery boiler operation (for ex. air staging) will change with pellet firing. The two main parameters to be considered are pellet size and feeding location. Two pellet sizes and two feeding locations will be modeled.

The laboratory work will be a small part of the project to support the CFD modeling. The laboratory work will be done to determine the softening temperature of the pellets, the swelling and pyrolysis behavior and combustion times. Emissions will also be obtained. Pellets from both black liquor and black liquor mixed with 10% sawdust will be made in the lab and tested. The pellets with 10% sawdust will be tested for comparison to the behavior of pellets from black liquor only, but will not be considered in the CFD modeling in this project. The pellets will be pressed at ÅAU using dried black liquor and air dried sawdust. The pelletizing work will provide some initial feel for the pelletizing of dry black liquor. The laboratory work will be carried out in a single particle reactor which has been used to characterize both black liquor and pellet behavior during combustion at ÅAU.

The cost for this project will be **20 700 € + VAT**.



LIITE 8

**SKYREC/KTR: Characterisation of probe test samples exposed to BLRB
lower furnace environments, VTT – draft report 26.11.2012**



Characterisation of probe test samples exposed to BLRB lower furnace environments

Author: Pekka Pohjanne

Confidentiality: Confidential

Report's title Characterisation of probe test samples exposed to BLRB lower furnace environments		
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Abstract Current trend to increase electricity generation of recovery boilers possess new demands for the tube materials, when the material temperatures are increased due to higher steam values. Operational experiences from current boilers have shown that the AISI 304 L compound tubes suffer from accelerated corrosion in furnace wall, when the material temperatures are increased from normal values due to the internal surfaces scales. This indicates that the AISI 304L might be unsuitable cladding material for the future high pressure boilers. The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours. The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. According to the wall thickness measurements the test materials can be put in following order based on increased resistance: C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67.		
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Contents

1	Introduction.....	3
2	Goal.....	3
3	Experimental.....	3
3.1	Test materials, specimens and evaluation procedures	3
3.2	Test conditions.....	6
4	Results	7
4.1	Probe test No.1	7
4.1.1	Corrosion rates	8
4.1.2	Metallography	18
4.2	Probe test No.2	20
4.2.1	Corrosion rates	21
4.2.2	Metallography	30
4.3	Probe test No. 3	32
4.3.1	Corrosion rates	33
4.3.2	Metallography	43
4.4	Probe test No. 4	45
4.4.1	Corrosion rates	46
4.4.2	Metallography	56
4.5	Probe test No. 5	58
4.5.1	Corrosion rates	59
4.5.2	Metallography	66
5	Conclusions.....	68
6	Summary	70

1 Introduction

Increasing boiler pressure induces a corresponding increase in tube temperature in steam generator. Operational experiences from current boilers indicate that AISI 304L (3R12), which has been the most commonly used cladding material, suffers from accelerated corrosion at higher than normal operation temperatures, which are sometimes encountered when internal surfaces in furnace wall tubes are covered with thick scale. These temperatures would be normal at high pressure boilers, and thus AISI 304L appears non-suitable cladding material for high pressure boilers. Currently few alternative materials are used, such as Sanicro38 (mod. UNS N08825) and HR11N, but their corrosion resistance at high temperatures has not been thoroughly studied and operational experiences are still limited. Also other highly alloyed materials are available, but data on their corrosion resistance are lacking.

2 Goal

The goal of this study was to test different potential cladding materials in actual recovery boiler lower furnace conditions, but at higher than current temperatures, in order to determine what materials could be suitable for future high pressure recovery boilers. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT.

3 Experimental

3.1 Test materials, specimens and evaluation procedures

The test materials were carbon steel (P265GH), three austenitic stainless steels 3R12 (AISI 304L), 3RE28 (AISI 310) and 3XRE28, three austenitic high nickel alloys Sanicro 28 (UNS N08028), Sanicro 38 (mod. UNS N08825) and HR11N and two austenitic nickel base alloys Sanicro 67 (UNS N06690) and Super 625. Chemical compositions of the test materials are shown in Table 1.

After exposure the material performance was assessed with wall thickness measurements and metallographic analysis. Before measurements, after cutting from the probe, the samples were thoroughly washed under water with nylon brush and rinsed with ethanol to remove deposits. The wall thickness profiles of the test samples were measured before and after testing with coordinate measurement machine as a function of circumference from three axial locations ($Z = 15, 25$ and 32 mm) so that from each location 100 points were measured, Figure 1.

In tests No.1 - 3 the 3R12, 3RE28, 3XRE28, Sanicro 28, Sanicro 38 and Sanicro 67 specimens were cut from composite tubes and tested in as received condition, whereas the HR11N and Super 625 specimens were machined from larger solid pieces and tested in as machined condition. In tests No.4 and 5 the outer and inner surfaces of all specimens were machined and hand grinded/polished prior assembly to the probe (Figure 2) to improve the accuracy of wall thickness measurements. The average corrosion rates were calculated on the basis of

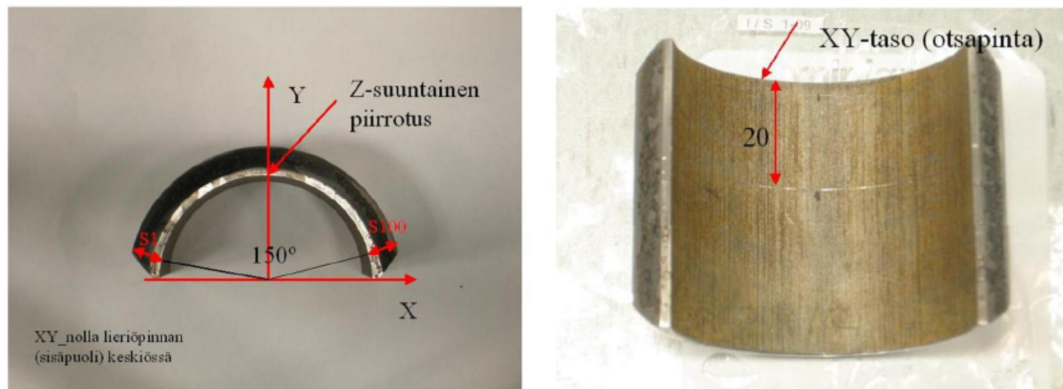
average wall thickness loss at the specimen apex (ca. 35...50 points/30...45° angle at apex). The maximum corrosion rates were calculated from the wall thinning curved derived from the wall thickness measurements.

For metallographic analysis one cross-section per sample (Z = 15 mm) was prepared and analysed with scanning electron microscope (SEM). The composition of oxide layers and deposits was determined with energy dispersive spectroscopy (EDS).

Table 1. Nominal composition of the test materials if not otherwise mentioned.

Material	%C	%Mn	%Si	%Cr	%Ni	%Mo	%Fe	%Cu	Other
Carbon steel									
P265GH	≤0.2	0.80 - 1.40	≤0.40	≤0.30	≤0.30	≤0.08	bal.	≤0.30	
Austenitic stainless steels									
3R12 [304L]	≤0.02	1.3	0.4	18.5	10.5	...	bal.	...	
3RE28 ^{A)} [310]	0.023	1.77	0.39	25.6	21.0	0.06	bal.	0.06	
3xRE28 ^{A)}	0.012	1.63	0.35	25.2	21.3	0.25	bal.	0.14	
High nickel alloys									
Sanicro 28 [UNS N08028]	≤0.02	≤2.0	≤0.6	27	31	3.5	bal.	1.0	
Sanicro 38 [mod. 825]	≤0.03	0.8	≤0.5	20	38.5	2.6	bal.	1.7	Ti: 0.8
HR11N	0.03	2.0	0.6	27.0	38	0.5 - 1.5	bal.		N: 0.1
Nickel base alloys									
Sanicro 67 [Alloy 690]	0.02	≤0.5	≤0.5	30	60	...	bal.	...	Co: <0,05
Super 625	0.1	≤0.5	≤0.5	20 - 23	bal.	...	≤5.0	...	W: 3.15-4.15 Al: 0.4 Co ≤ 1.0

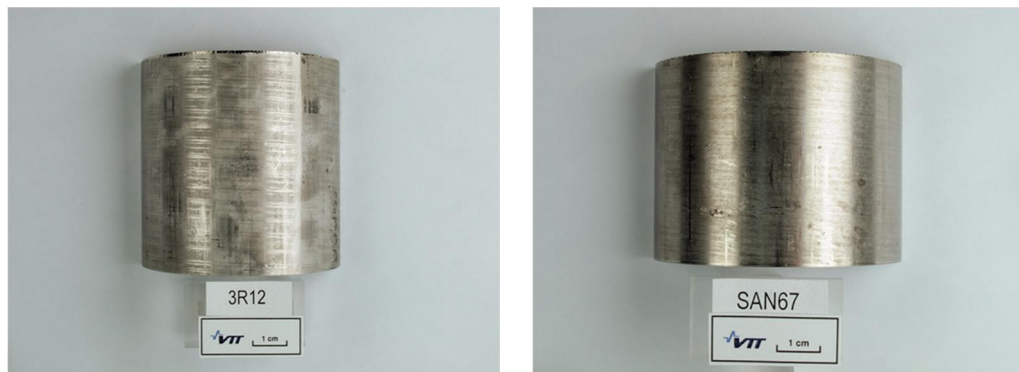
A) Tube samples analysed by VTT



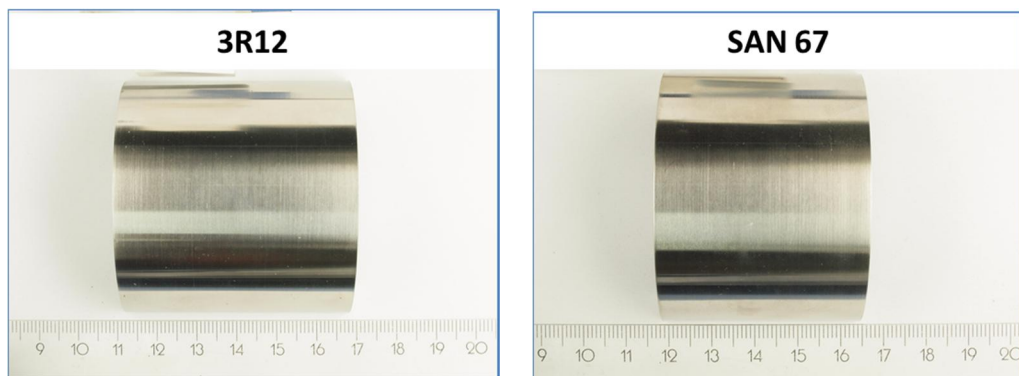
a)

b)

Figure 1. The wall thickness profiles were measured before and after testing with coordinate measurement machine a) as a function of circumference b) from three axial locations ($Z = 15, 25$ and 32 mm).



a)



b)

Figure 2. Examples of sample surfaces prior exposure: a) in as received condition for the probe No. 2 and b) after machining and hand grinding for the probe No. 7.

3.2 Test conditions

The probe tests were conducted in Metsä Fibre Joutseno mill by Boildec Oy. The test matrix and test conditions are summarised in Table 2 and Table 3, more detailed information from the test set-up and parameters can be obtained from the probe test reports /1...5/. Maximum cladding temperatures in a high pressure boiler are about 400°C, when internal surfaces are clean. With scaling, cladding temperatures may become higher and, consequently, the test temperature was selected to be 440°C. The exposure durations varied from 1006 to 2700 hours so that target duration of 1000 h was applied in the first three tests and it was extended to above 2000 h in the last two tests to ensure the validity of the results.

Table 2. Test matrix.

Test No.	Materials	Total test duration
1	3R12, 3RE28, Sanicro 28, Sanicro38	1006
2	3R12, 3XRE28, HR11N, Sanicro 67	1023
3	3R12, HR11N, Sanicro 38, Super 625	1250
4	3R12, carbon steel, Sanicro 67, Super 625	2700
5	3R12, Sanicro 28, HR11N, Sanicro 38	2630

Table 3. Summary of the test conditions during exposure tests.

Test No.	Test duration [h]		Effective temperature [°C]
	Total	Effective ^{A)}	
1	1006	906 (pressure over 9 bar)	~440
2	1023	744 (pressure over 8 bar)	~440
3	1250	750 (pressure over 7 bar)	~430
4	2700	2154 (pressure over 9 bar)	~440
5	2630	2157 (pressure over 9 bar)	ca. 440°C

^{A)} Used in corrosion rate calculations

4 Results

4.1 Probe test No.1

Total test duration of the test No. 1 was 1006 hours from which 906 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3RE28, Sanicro 28 and Sanicro 38, Figure 3. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.



a)



b)

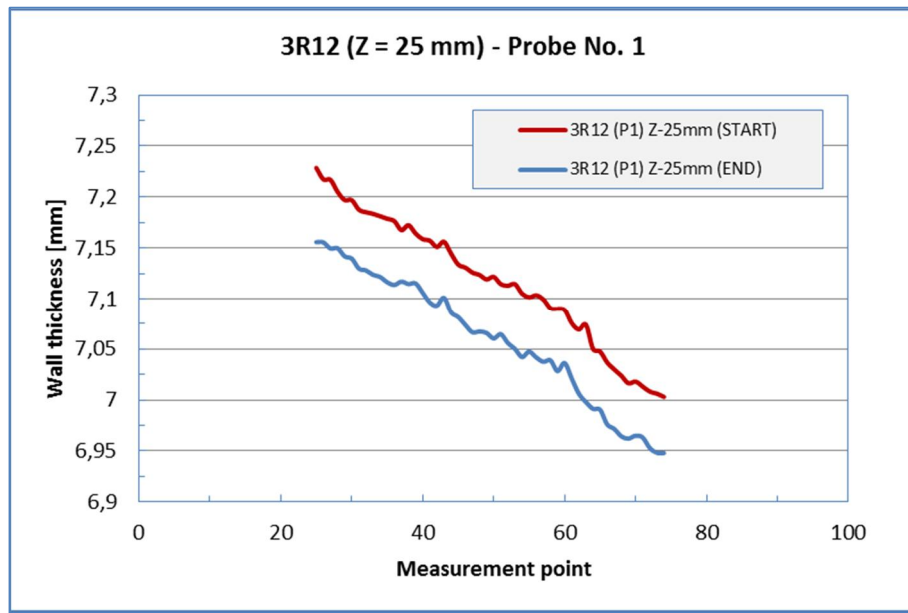
Figure 3. Macrographs taken from the probe No. 1 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

4.1.1 Corrosion rates

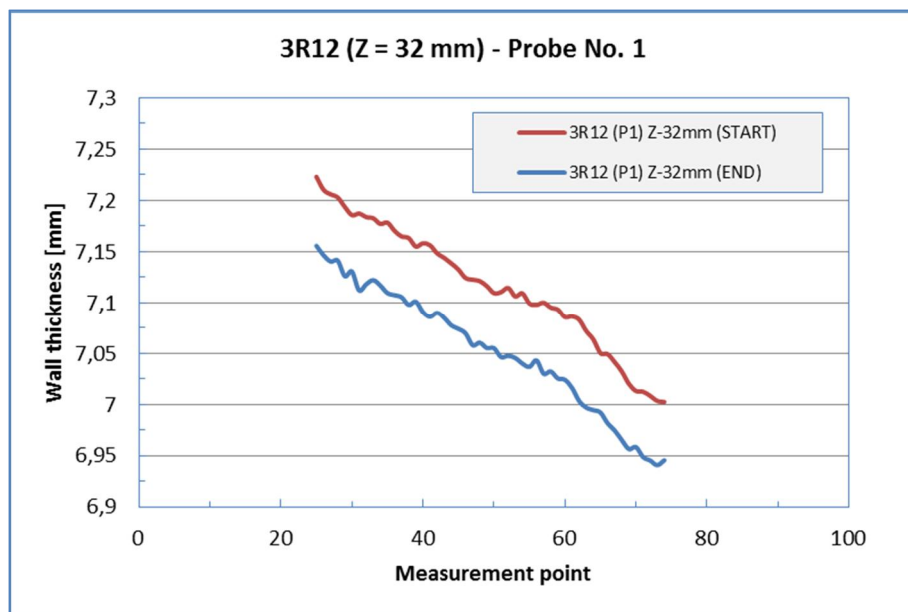
The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 4...11. The results showed that marked wall thinning had taken place on the 3R12 specimen. For the other materials the data was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that tube wall thicknesses varied a lot as a function of circumference.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate, order of 0.7 mm/a, was measured for the 3R12 material. Corrosion rate was next highest in the Sanicro 38, for which a maximum corrosion rate of ca. 0.2 mm/a was determined. The maximum corrosion rates of Sanicro 28 and 3RE28 materials were in the order of 0.1 mm/a and they were best performing materials in this test.

The reason to the negative values in average corrosion rates is that the washing and brushing with nylon brush was not effective enough to remove all deposits from the surfaces prior wall thickness measurements, indicating that average corrosion rates may give too optimistic result. Respectively the maximum corrosion rates may give too conservative results, if there are some problems in specimen alignment during WT measurements; this is a specific concern of samples with scratches or dents.

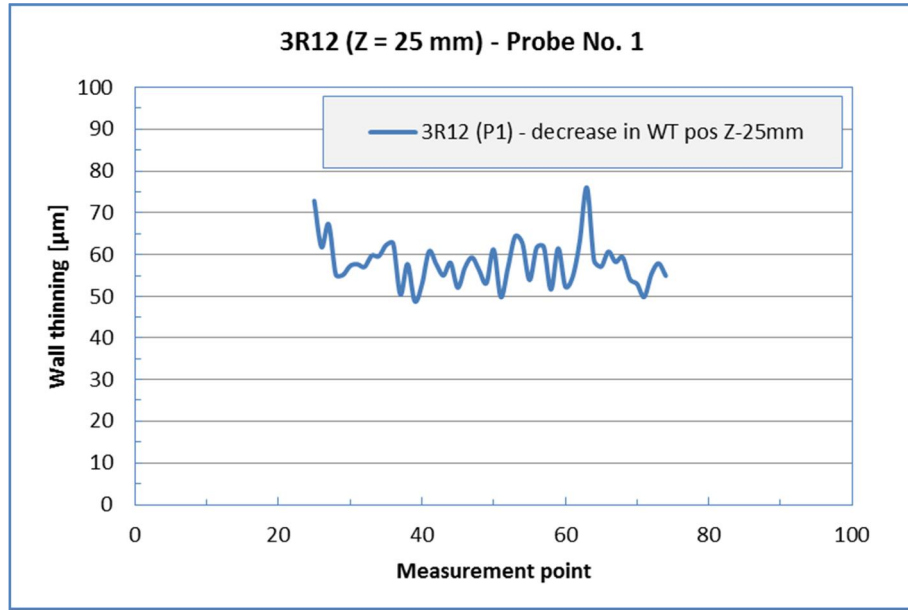


a)

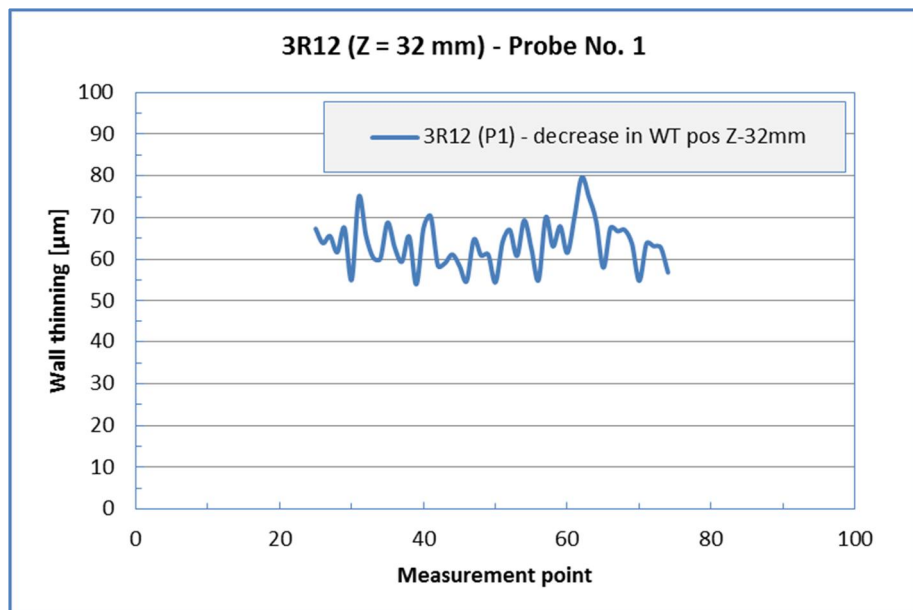


b)

Figure 4. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

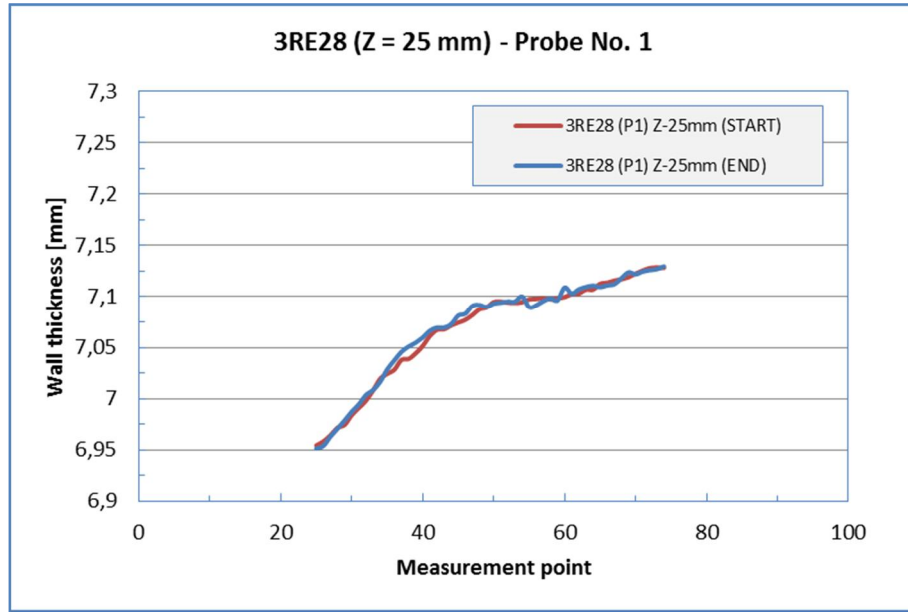


a)

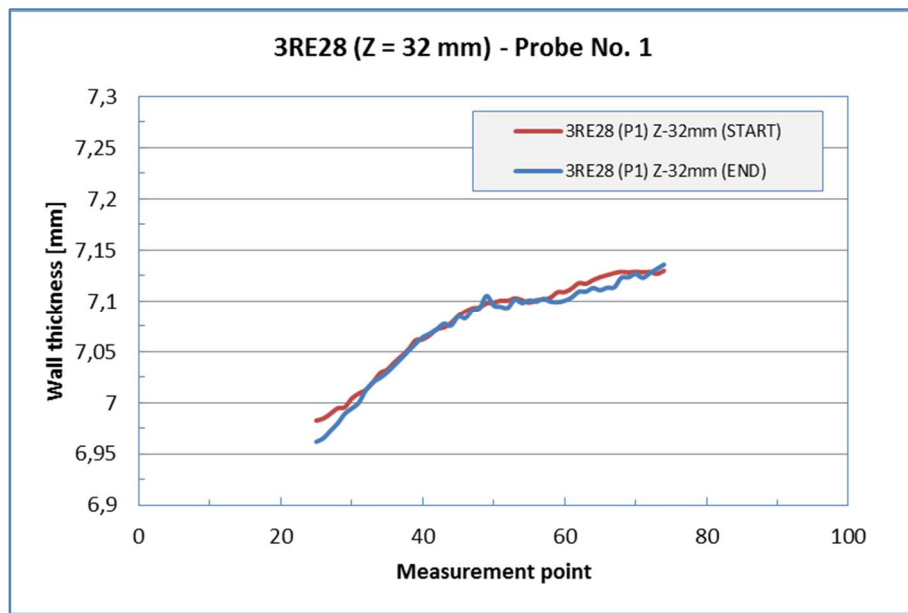


b)

Figure 5. Circumferential wall thinning curves from 3R12 specimen (Probe No. 1):
a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 6. Circumferential wall thickness profiles from 3RE28 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

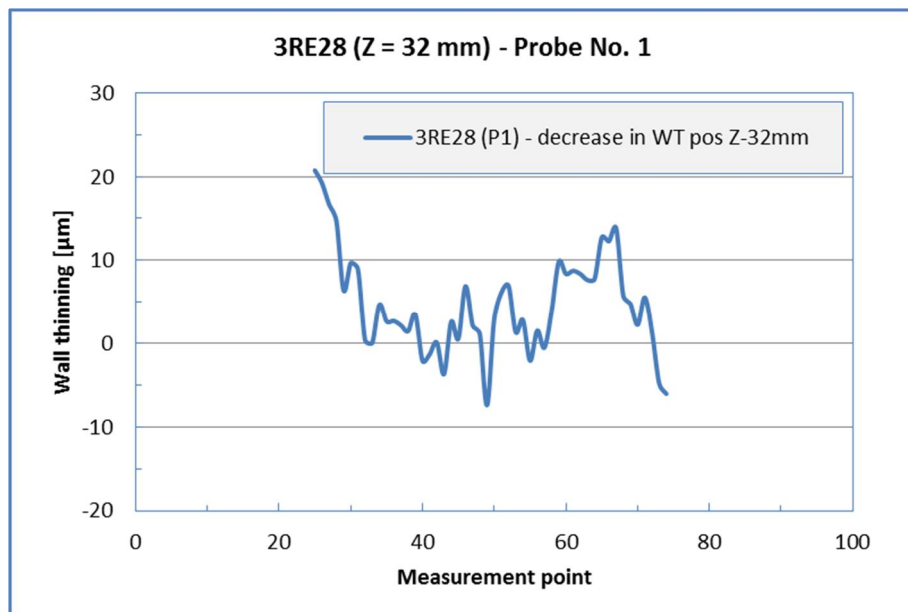
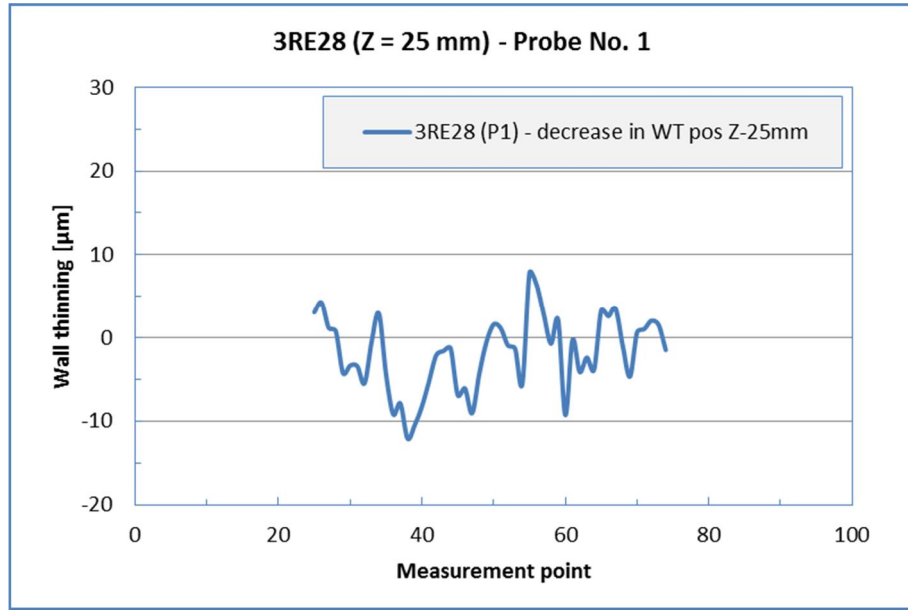
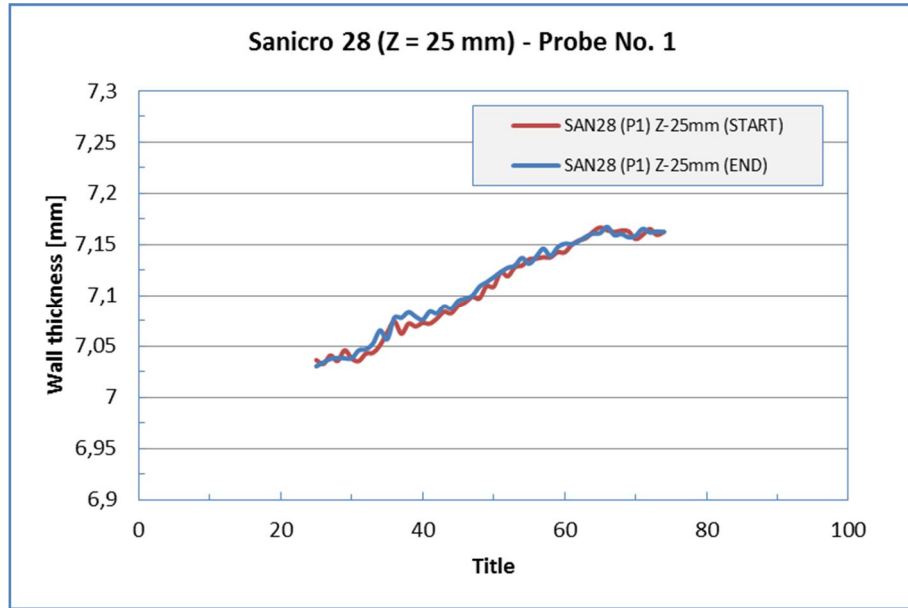
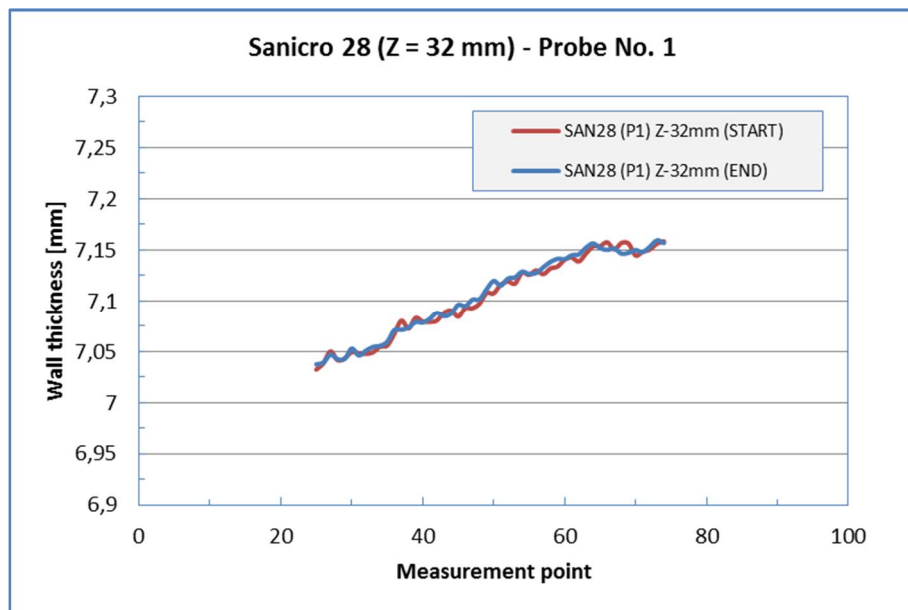


Figure 7. Circumferential wall thinning curves from 3RE28 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 8. Circumferential wall thickness profiles from Sanicro 28 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

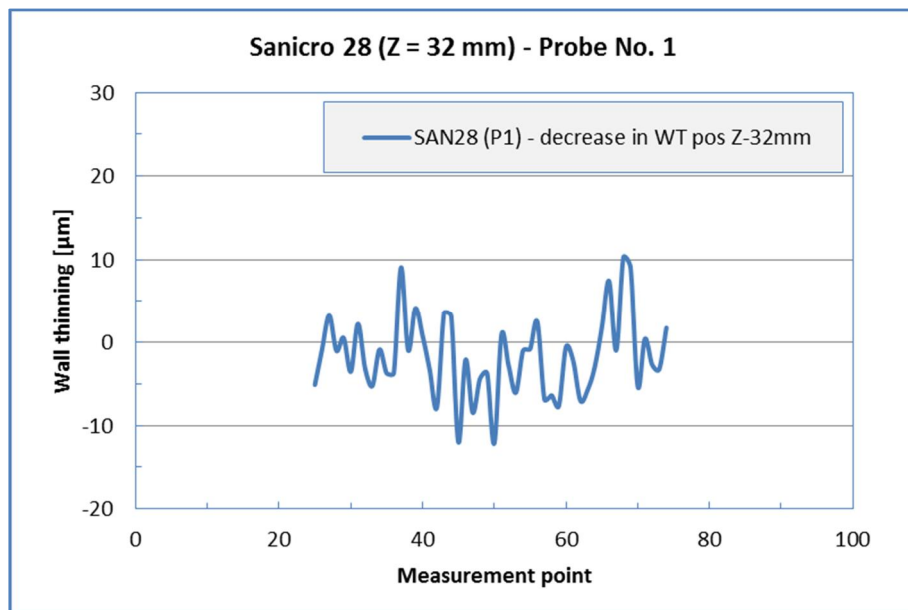
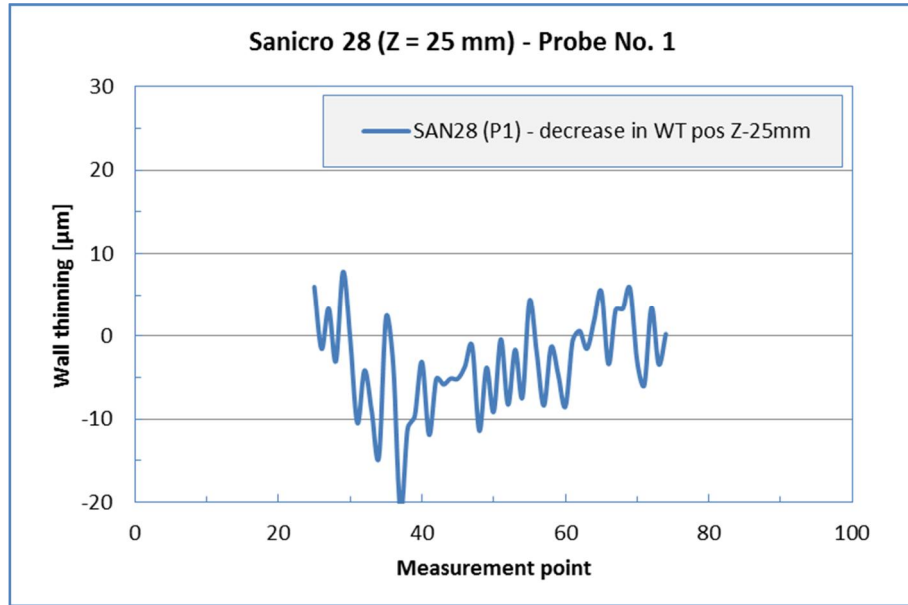
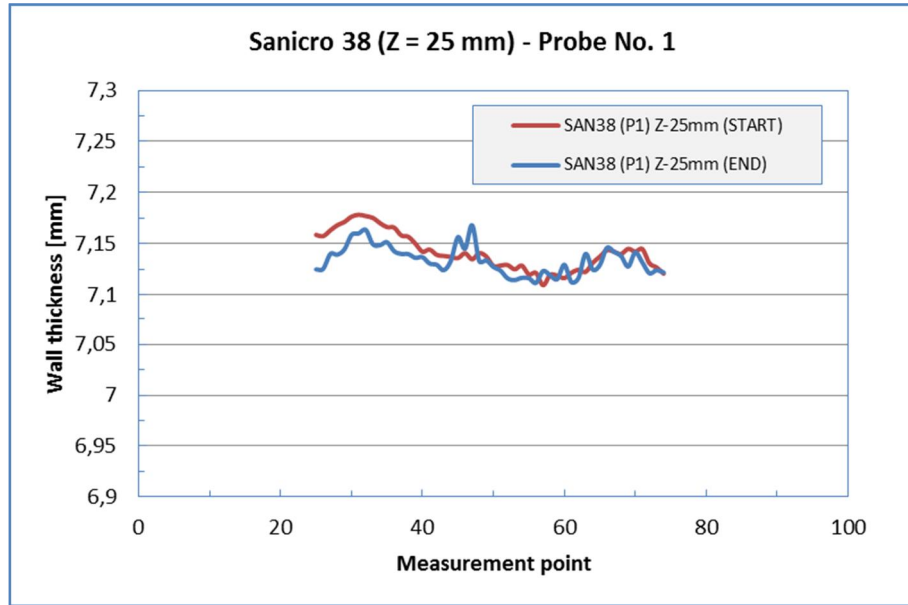
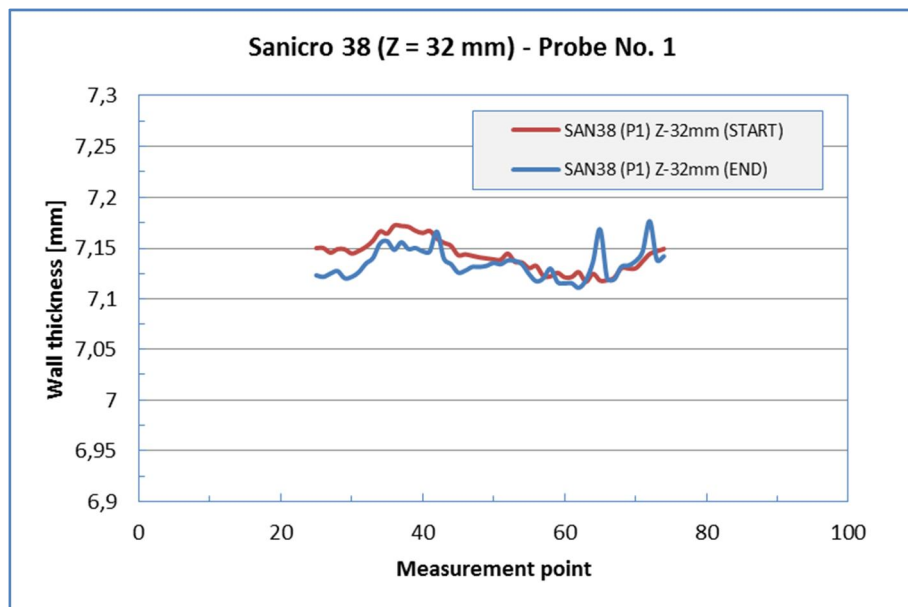


Figure 9. Circumferential wall thinning curves from Sanicro 28 specimen (Probe No. 1): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)



b)

Figure 10. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

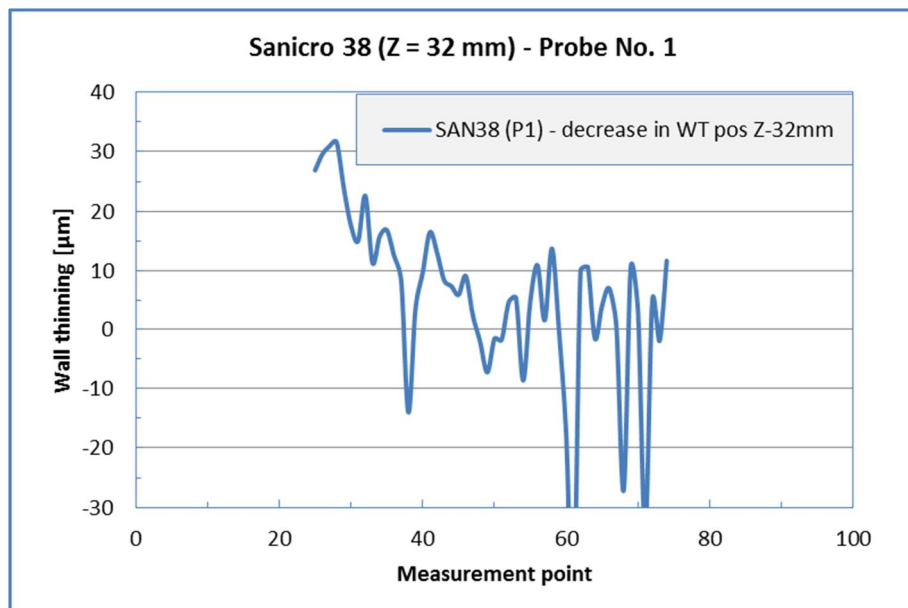
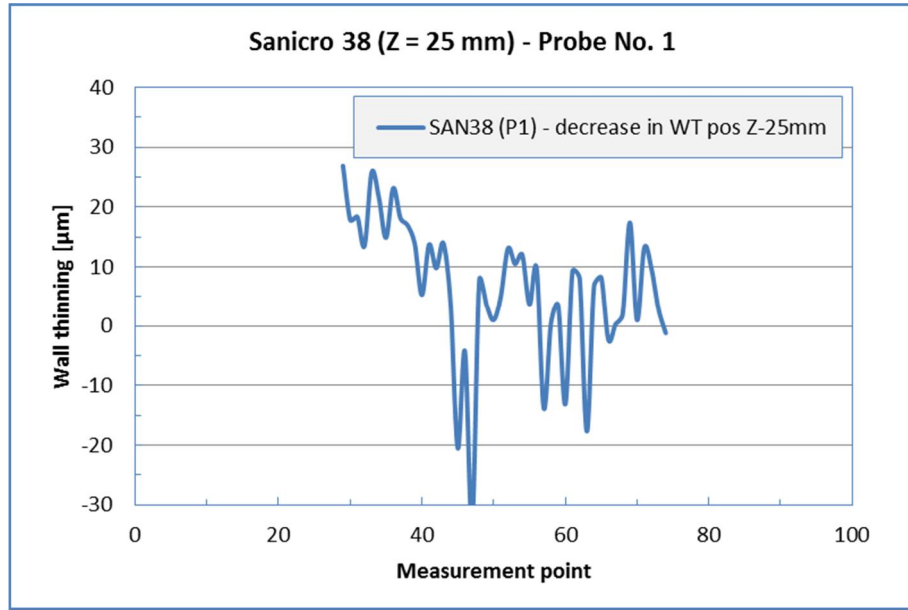
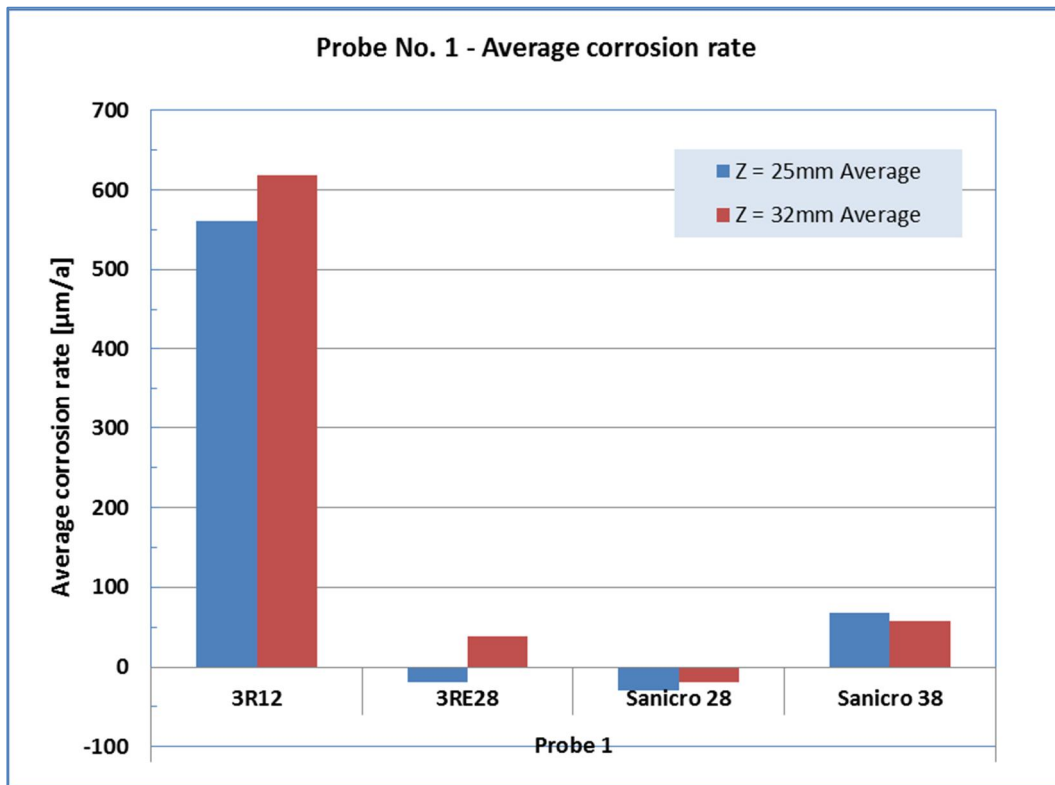
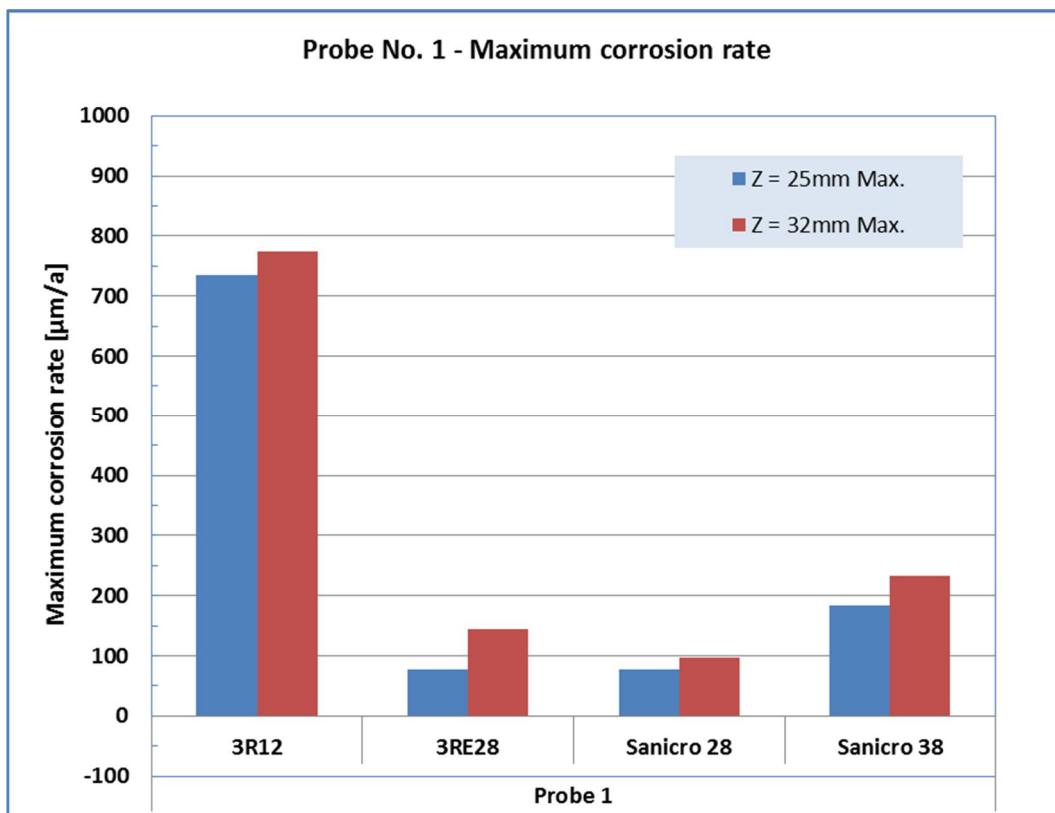


Figure 11. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 1): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)

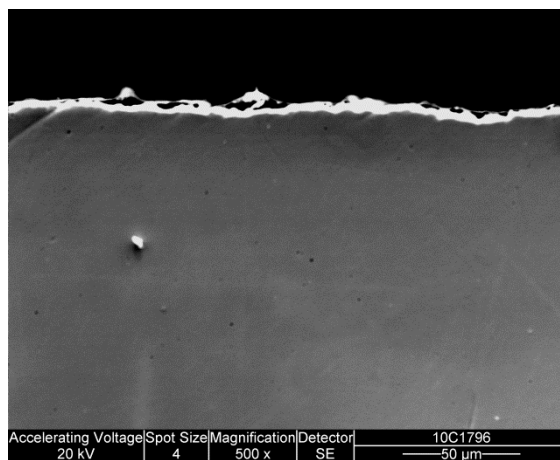


b)

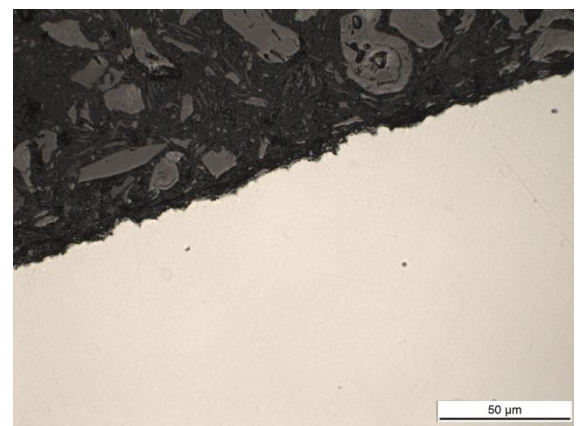
Figure 12. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 906 h exposure in lower furnace at 440 °C (Probe test No. 1).

4.1.2 Metallography

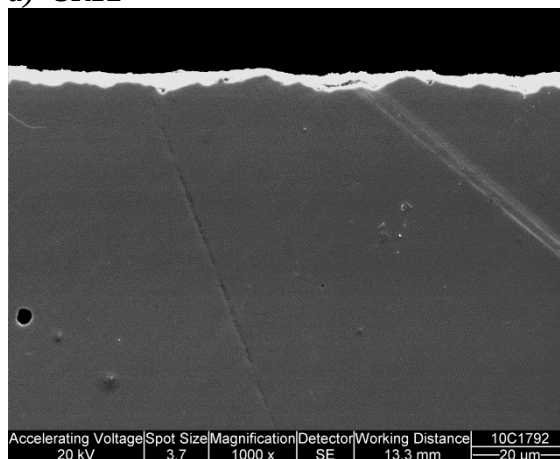
After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed, Figure 13. According to the EDS (Figure 14) analysis the thin layers (thickness ca. 5 µm) on 3RE28 and Sanicro 28 were depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. Whereas the composition of thin layer on 3R12 was similar to the base material and no sulphur was detected.



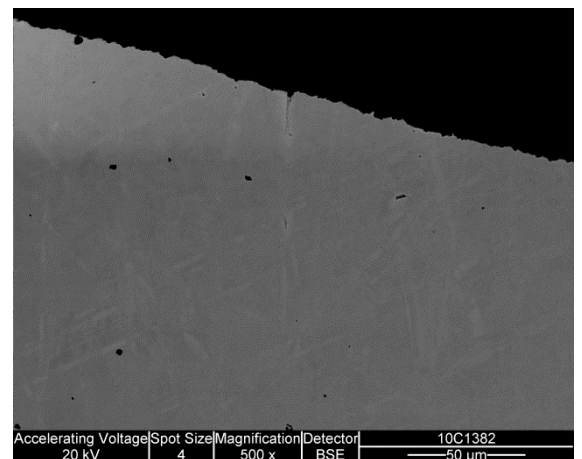
a) 3R12



b) 3RE28



c) Sanicro 28



d) Sanicro 38

Figure 13. Cross sections from a) 3R12, b) 3RE28, c) Sanicro 28 and d) Sanicro 38 after 906 h exposure in lower furnace at 440 °C (Probe test No. 1)

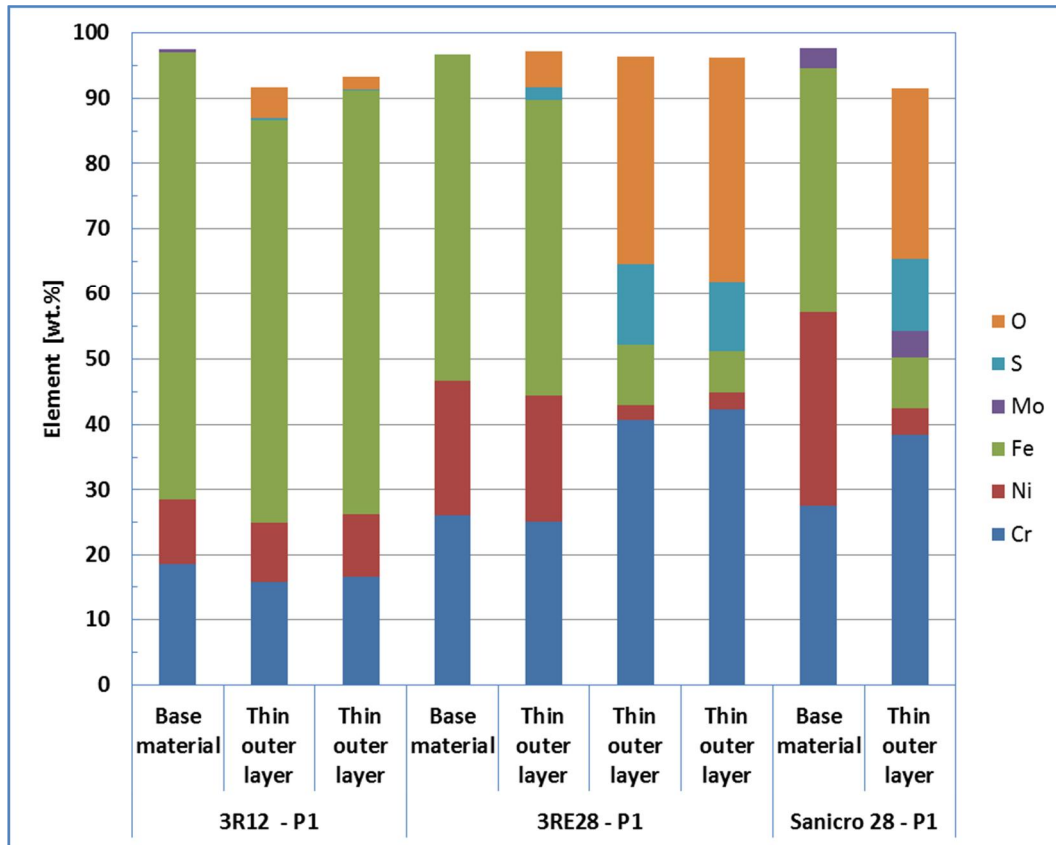


Figure 14. Results from the EDS analysis performed for the 3R12, 3RE28 and Sanicro 28 specimens after 906 h exposure in lower furnace at 440 °C (Probe test No. 1). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.2 Probe test No.2

Total test duration of the test No. 2 was 1023 hours from which 744 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, 3XRE28, HR11N and Sanicro 67, Figure 15. According to visual inspection the inner surfaces of the specimens were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed. The outer surfaces of the specimens appeared to be in good condition but the thin dark and white deposits on the surfaces hindered accurate examinations.



a)

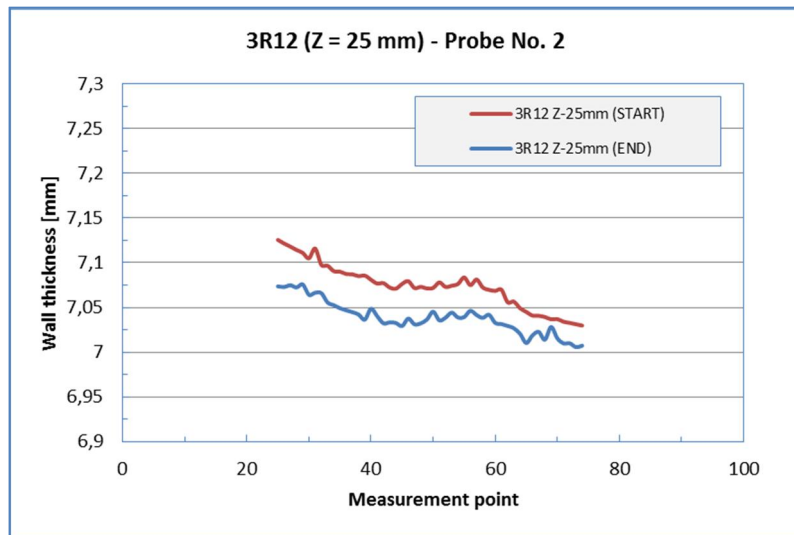


b)

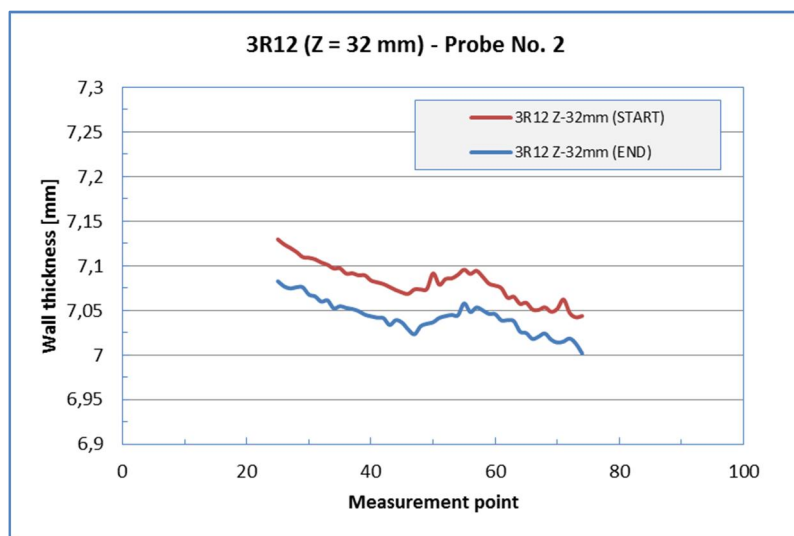
Figure 15. Macrographs taken from the probe No. 2 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

4.2.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 16...23. The results showed that marked wall thinning had taken place on the 3R12 specimen and lesser degree also on the HR11N specimen. The data of the 3XRE28 and Sanicro 67 materials was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. Measurements showed also that the wall thickness variations were smaller in the machined HR11N specimen than in the other specimens tested in as received condition. The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 12. In this test highest corrosion rate in the order of 0.6 mm/a was measured for the 3R12 material. The corrosion resistance of the 3XRE28, HR11N and Sanicro 67 was practically at the same level.

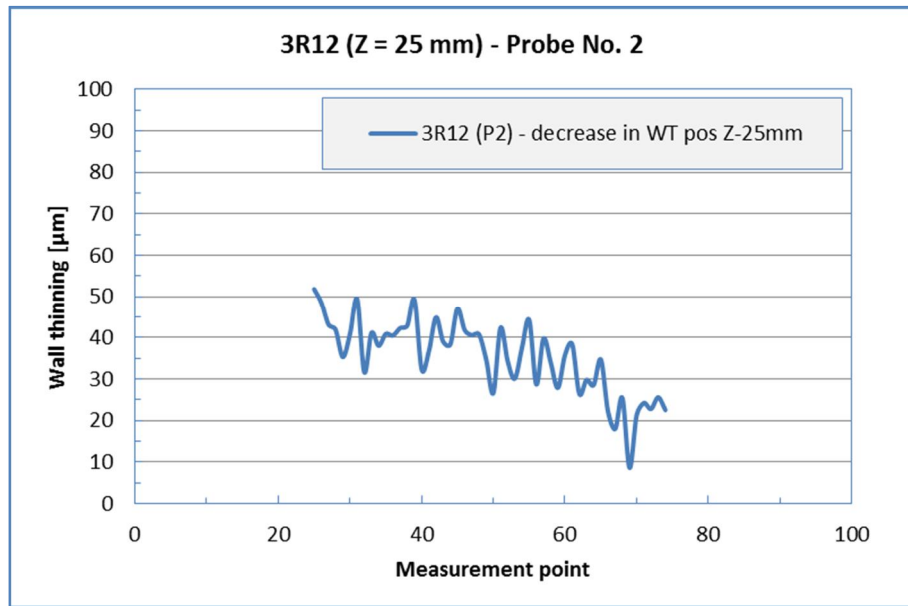


a)

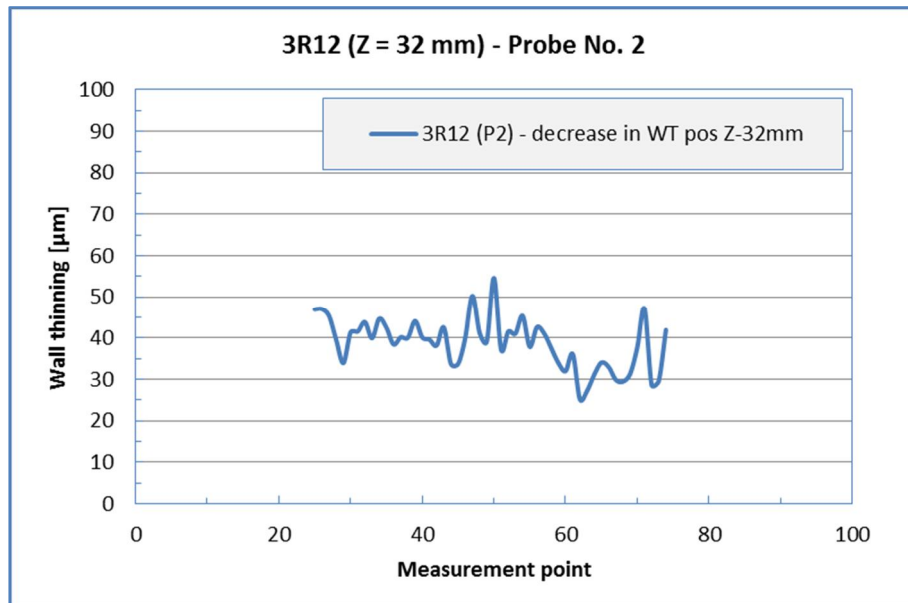


b)

Figure 16. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

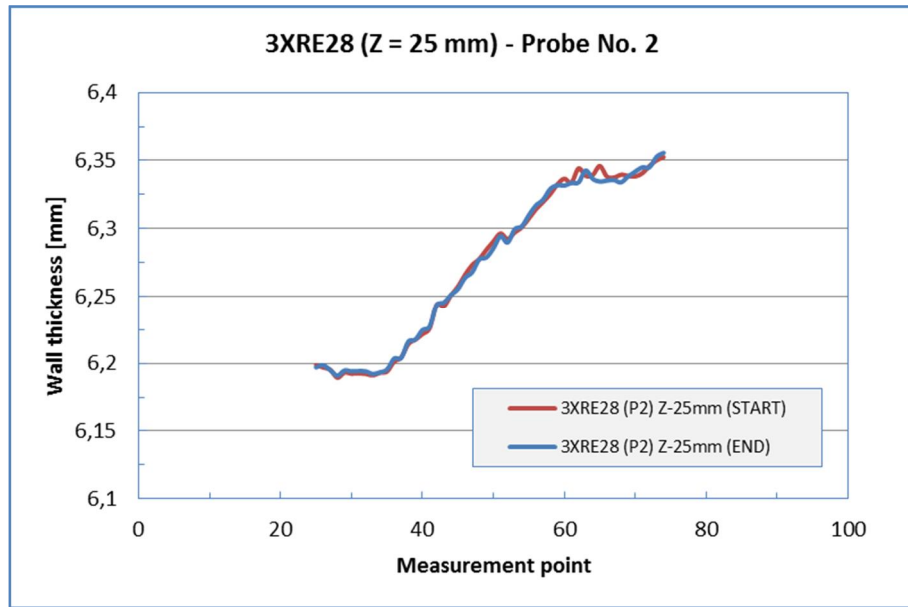


a)

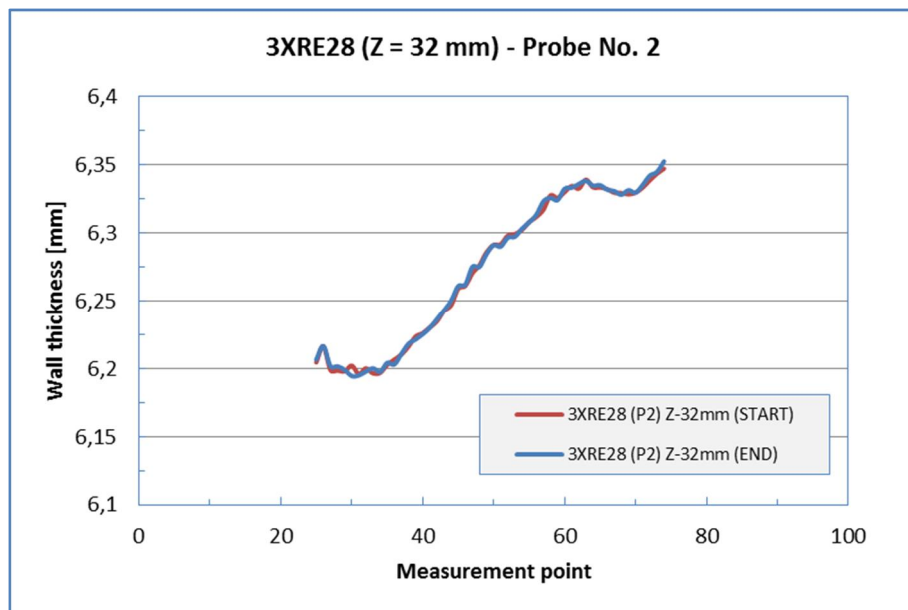


b)

Figure 17. Circumferential wall thinning curves from 3R12 specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

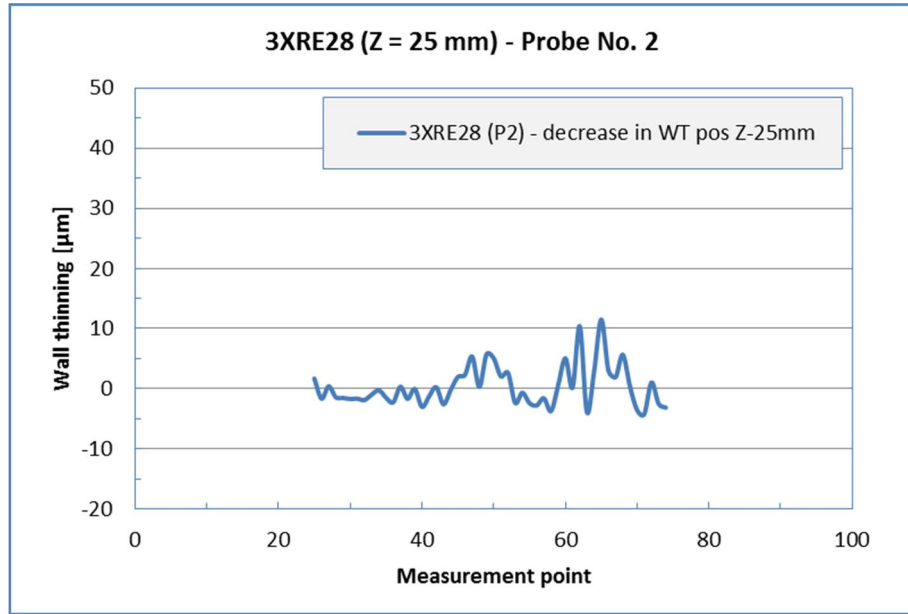


a)

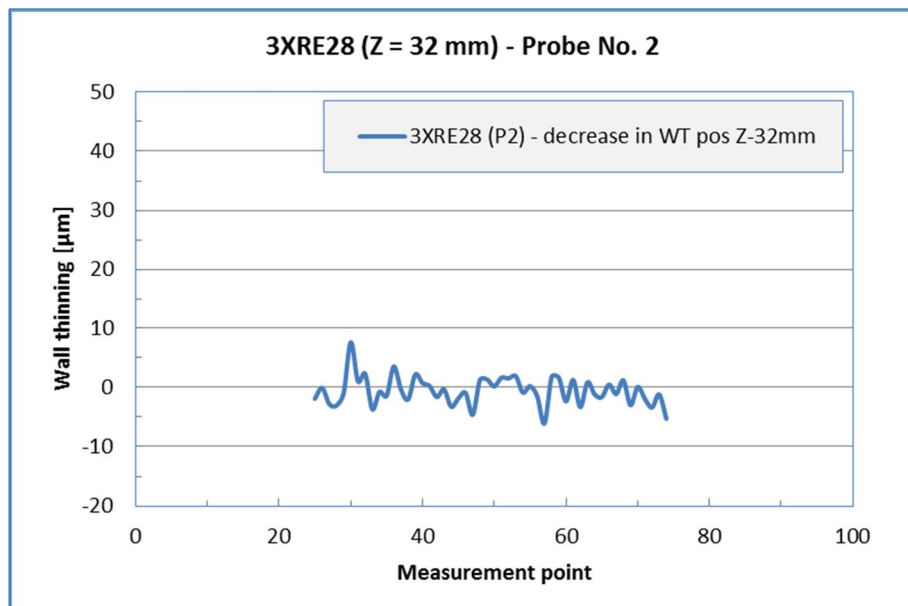


b)

Figure 18. Circumferential wall thickness profiles from 3XRE28 specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

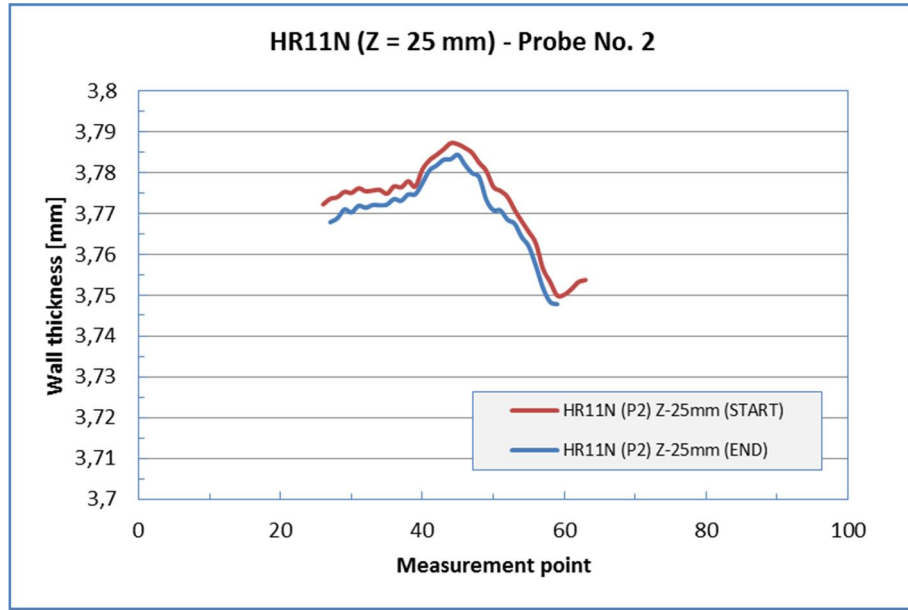


a)

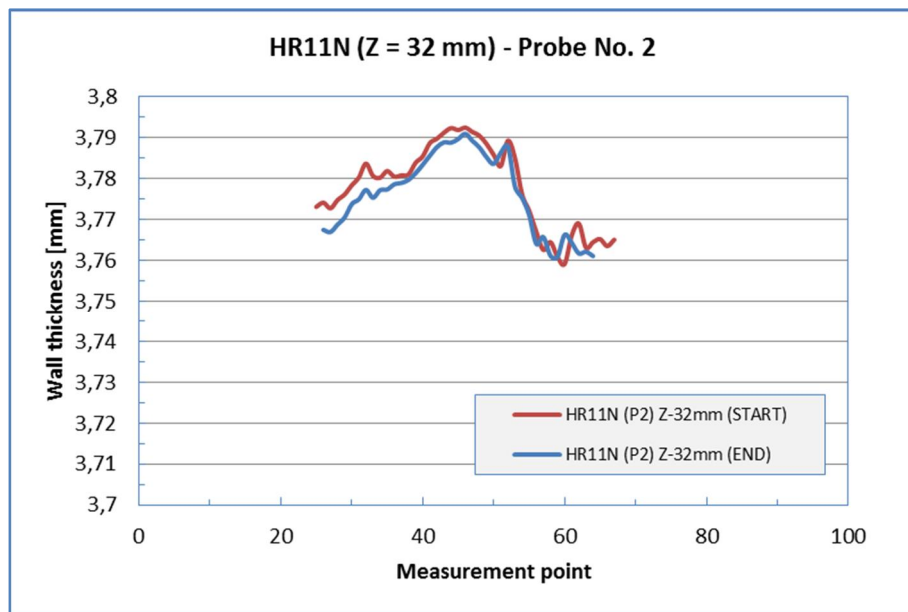


b)

Figure 19. Circumferential wall thinning curves from 3XRE28 specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

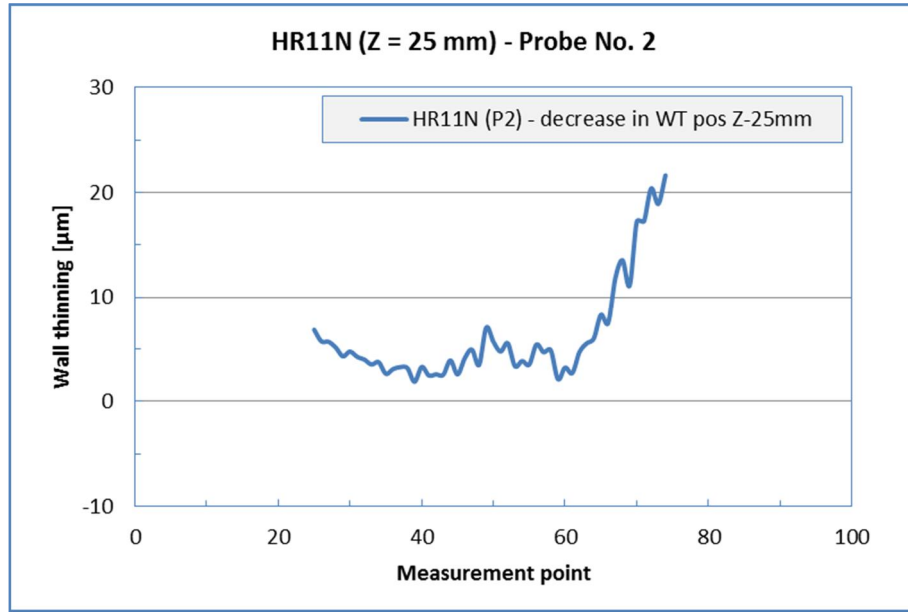


a)

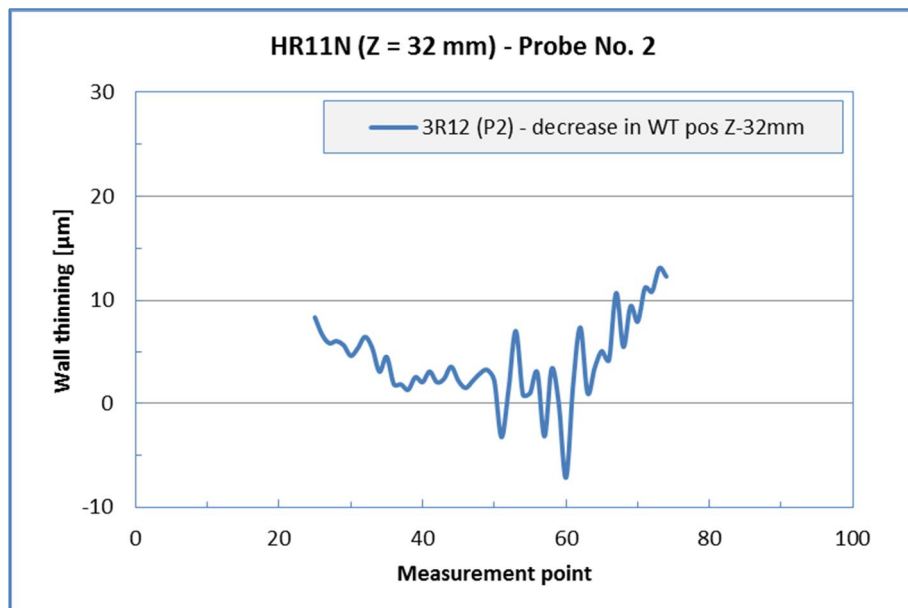


b)

Figure 20. Circumferential wall thickness profiles from HR11N specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 21. Circumferential wall thinning curves from HR11N specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

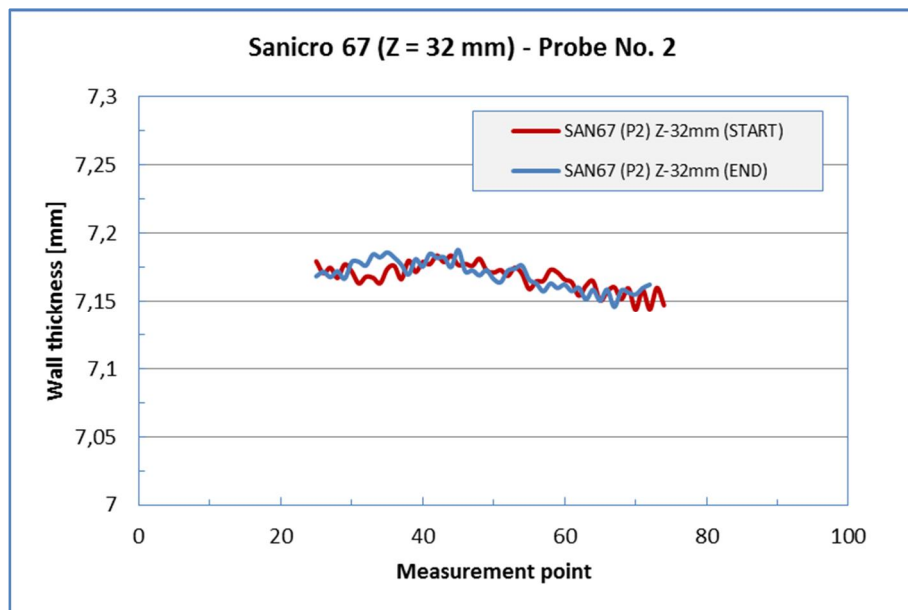
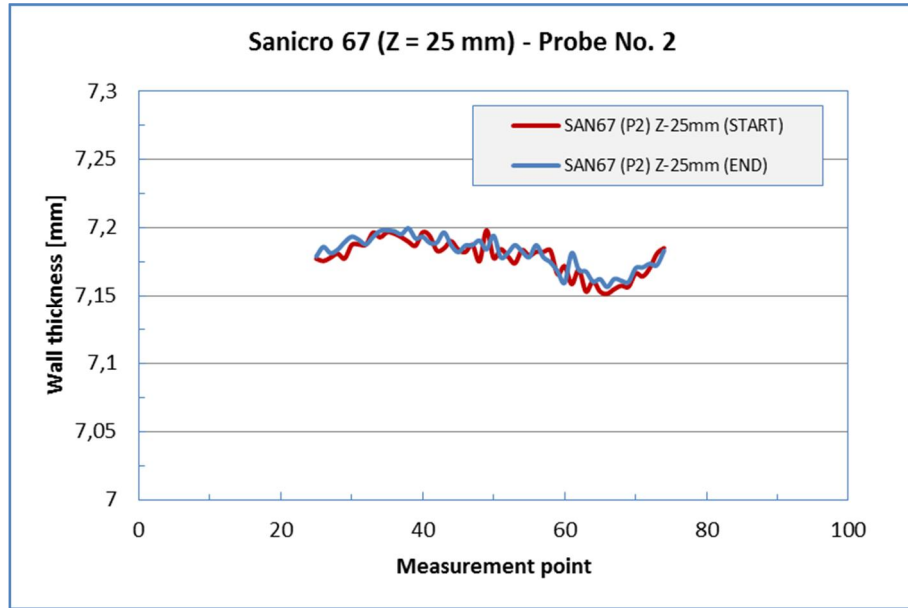
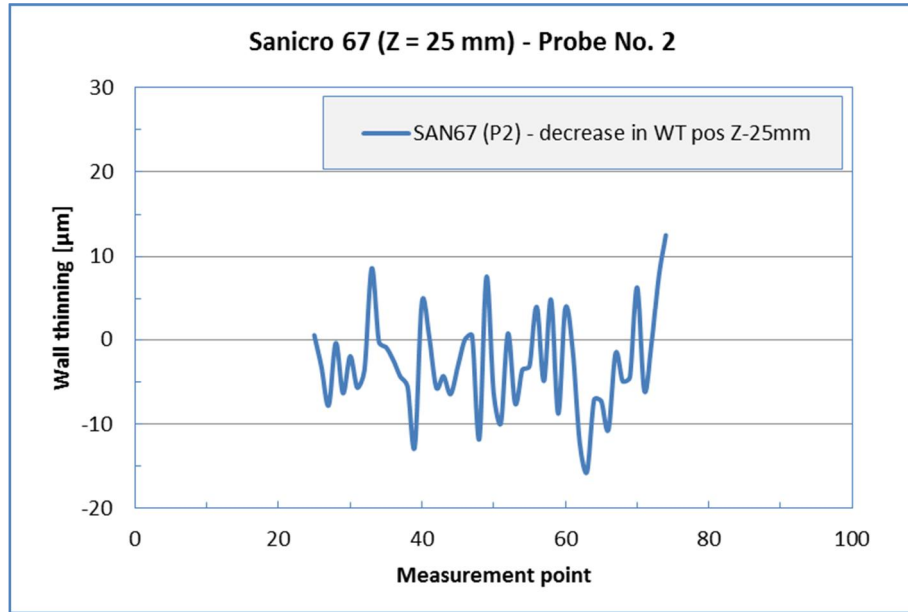
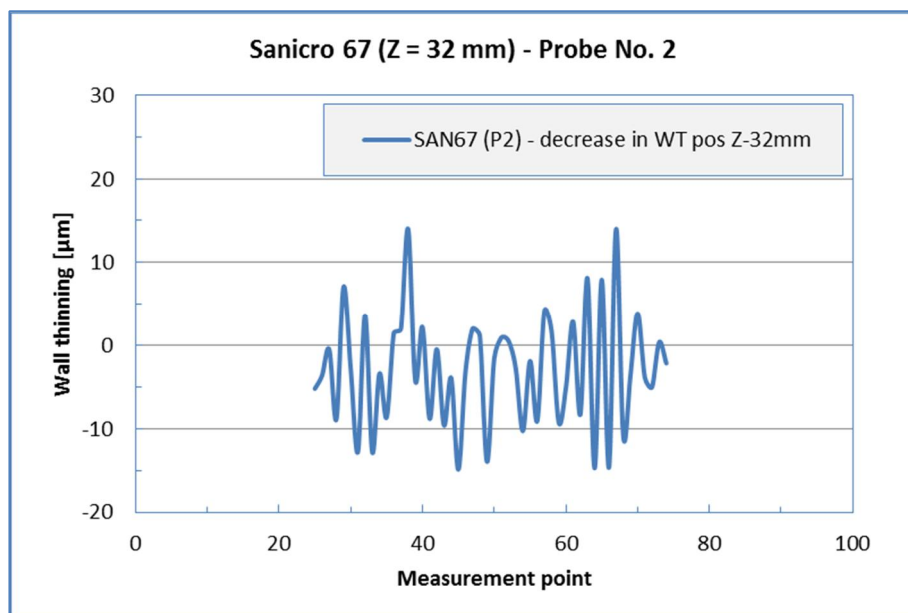


Figure 22. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 2): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

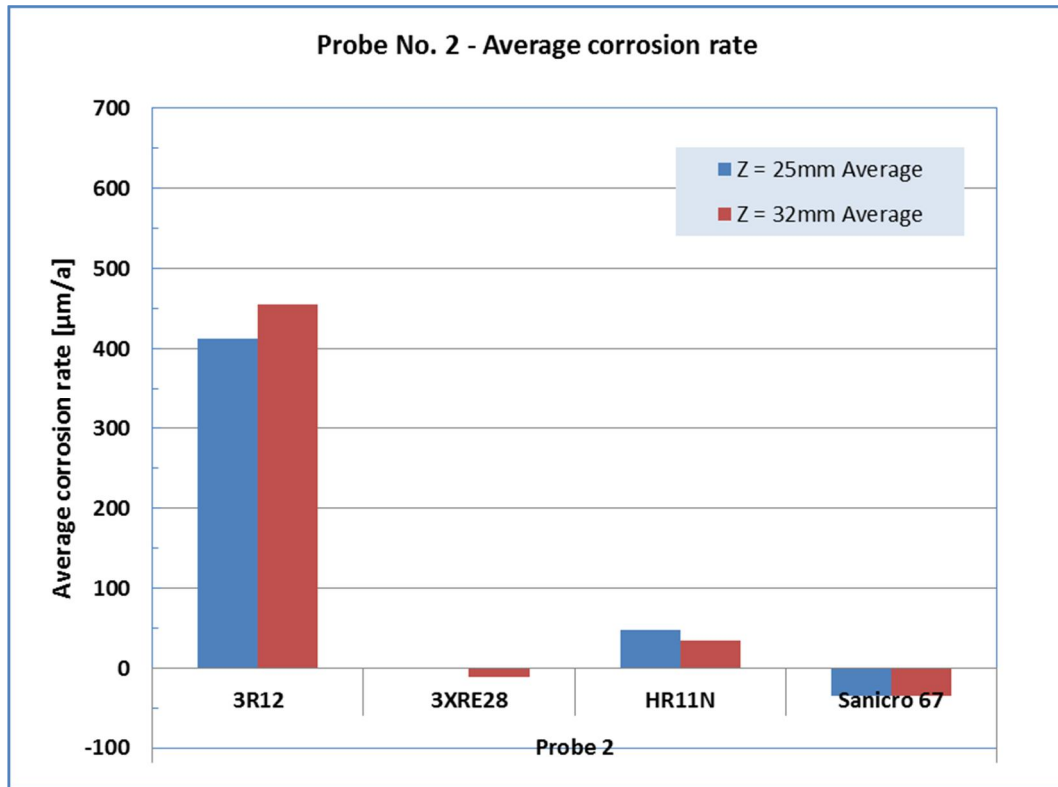


a)

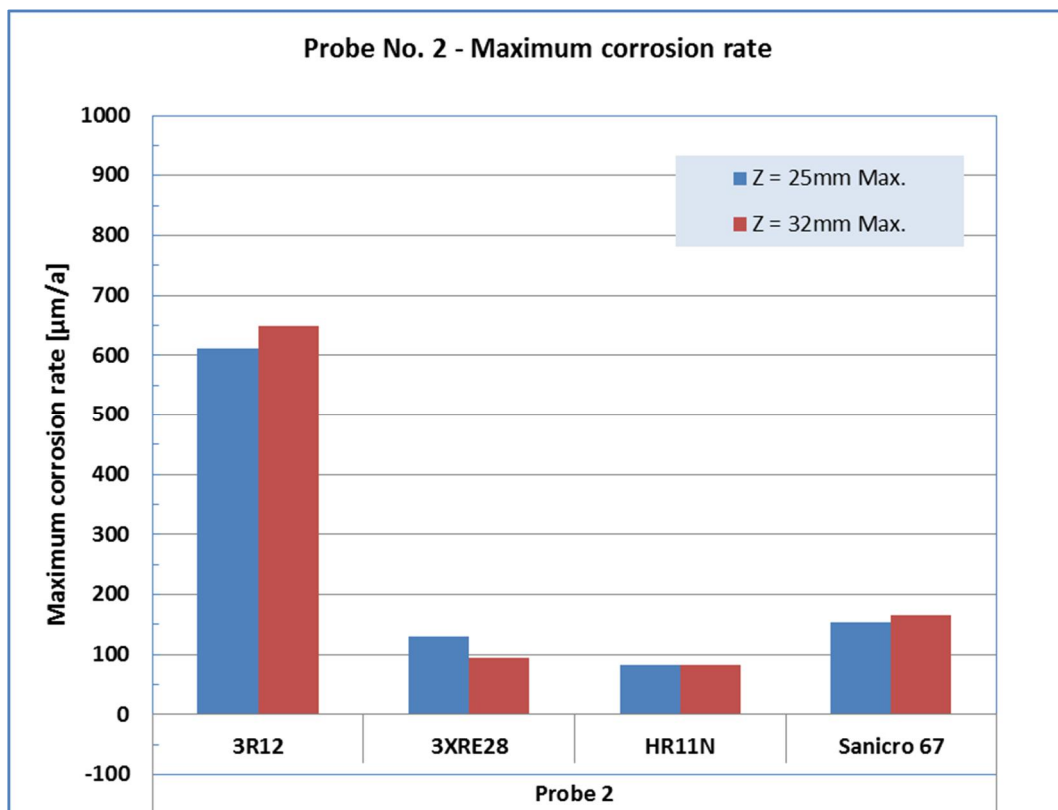


b)

Figure 23. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 2): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)



b)

Figure 24. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 744 h exposure in lower furnace at 440 °C (Probe test No. 2).

4.2.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 25. According to the EDS analysis (Figure 26) the thin, a few μm thick layer, observed on 3XRE28 was depleted in iron and nickel and enriched in chromium and contained also high amounts of sulphur. The similar thin layer on Sanicro 67 contained high amounts of sulphur and was depleted in nickel and iron whereas chromium content was at the same level than in the base material.

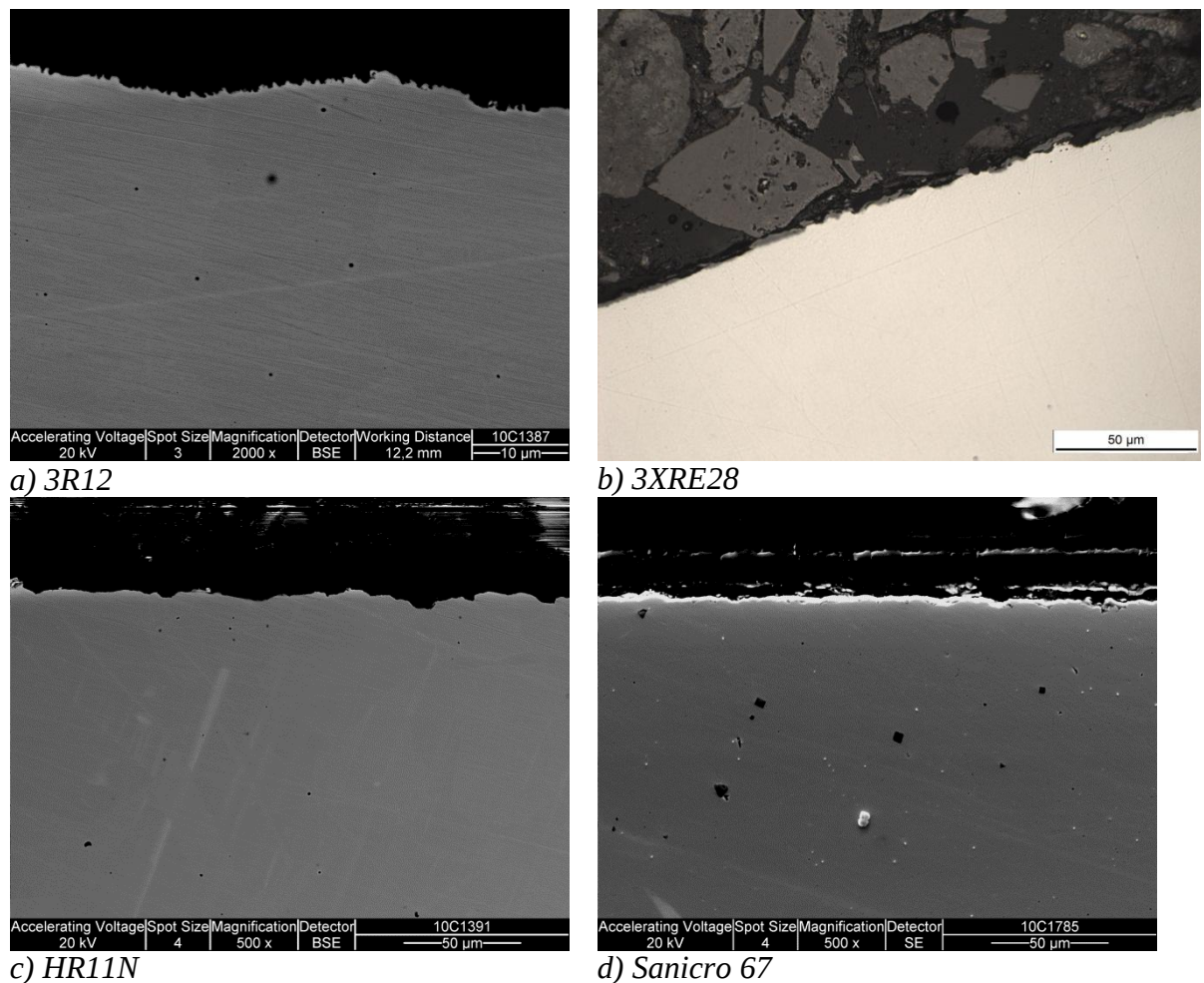


Figure 25. Cross sections from a) 3R12, b) 3XRE28, c) HR11N and d) Sanicro 67 after 744 h exposure in lower furnace at 440 °C (Probe test No. 2)

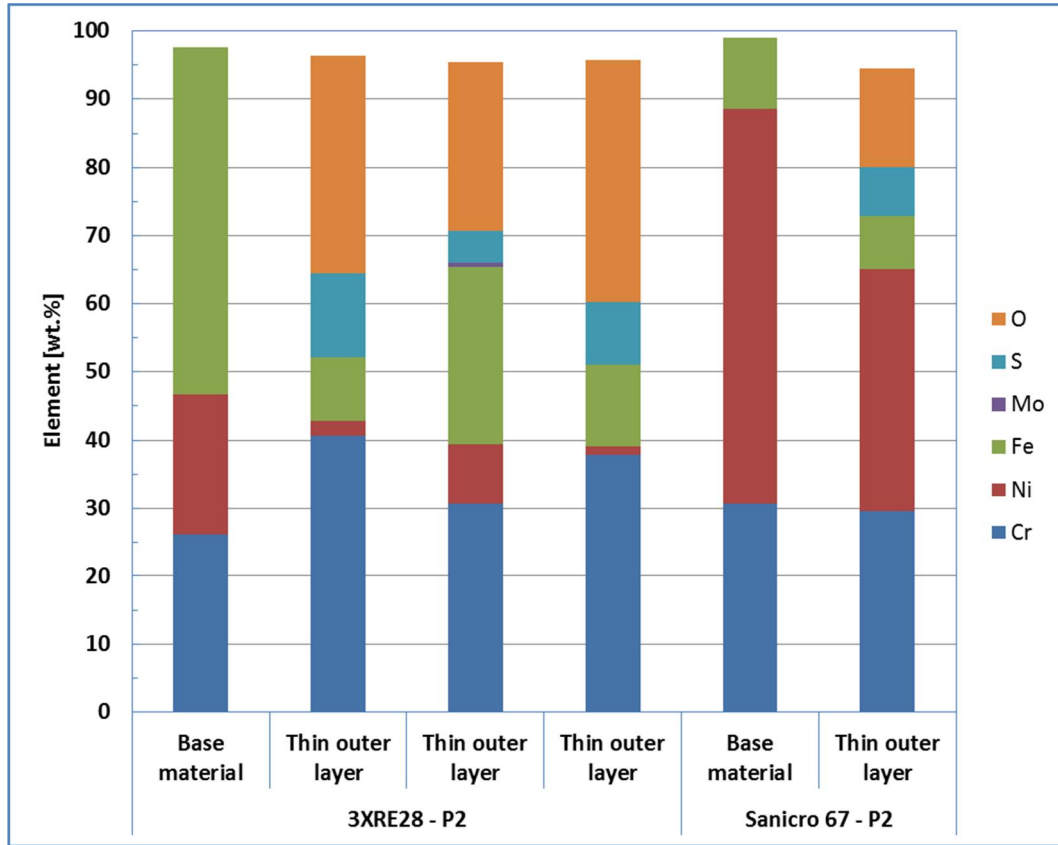


Figure 26. Results from the EDS analysis performed for the 3XRE28 and Sanicro 67 specimens after 744 h exposure in lower furnace at 440 °C (Probe test No. 2). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.3 Probe test No. 3

Total test duration of the test No. 3 was 1250 hours from which 750 hours at the target temperature of 430 °C. The test materials in this exposure were 3R12, HR11N, Sanicro 38 and Super 625, Figure 27.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. Some deposits were observed on the inner surfaces but based on their appearance they originate from the probe cutting conducted after the probe has been removed from the boiler. The outer surfaces of the specimens were covered with dark and brown deposits but appeared to be in good condition.



a)



b)

Figure 27. Macrographs taken from the probe No. 3 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid.

4.3.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 28...35. The results showed that marked wall thinning had taken place only on the 3R12 specimen. Some wall thinning was observed also on the Super 625 specimen. The data of the HR11N and Sanicro 38 was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. In addition the data in this test was more scattered than in the previous test indicating that all deposits were not removed from the surfaces in washing performed for the specimens' prior measurements.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 36. In this test the corrosion rate of 3R12 was in the order 0.4 mm/a, i.e. about 0.2 mm/a lower than in the first two tests, most probably due the lower probe temperature. The corrosion rate of the Super 625 was unexpectedly high ca. 0.3...0.4mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.1 mm/a, and they were best performing materials in this test.

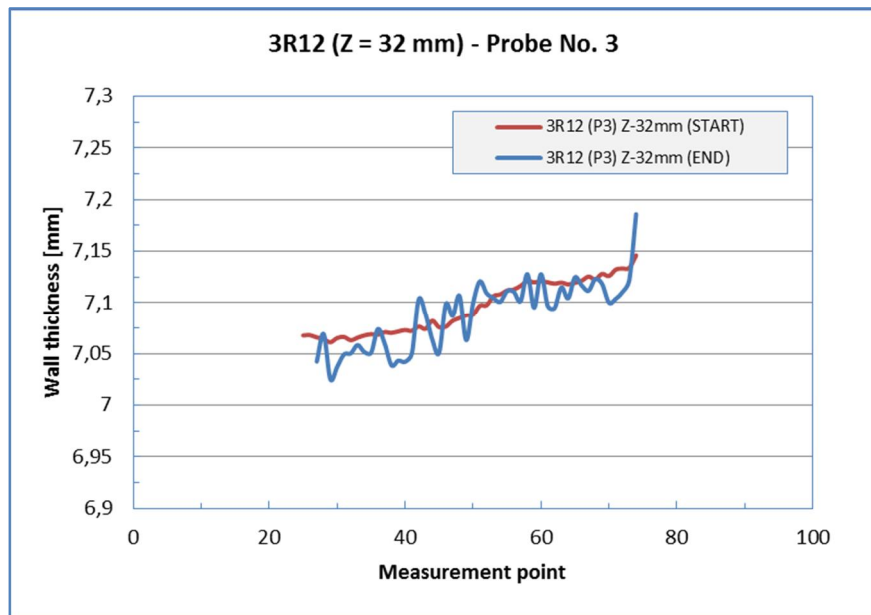
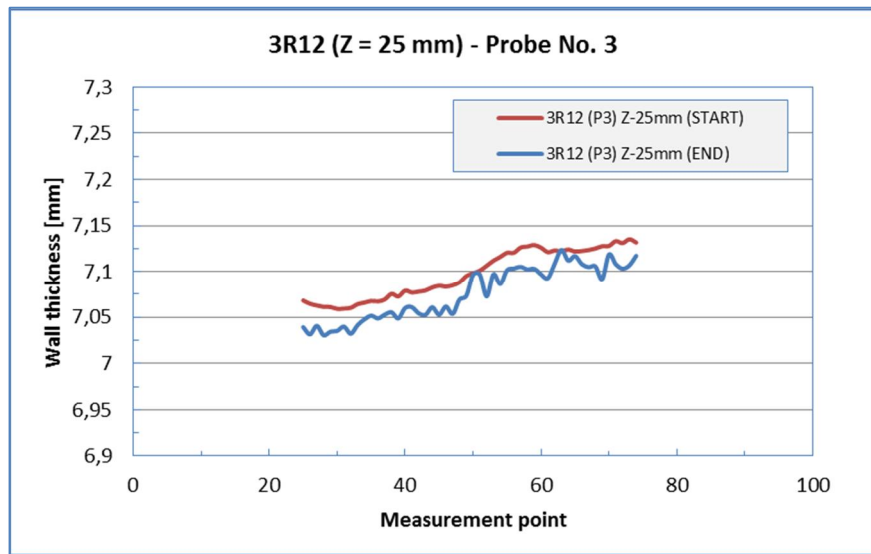
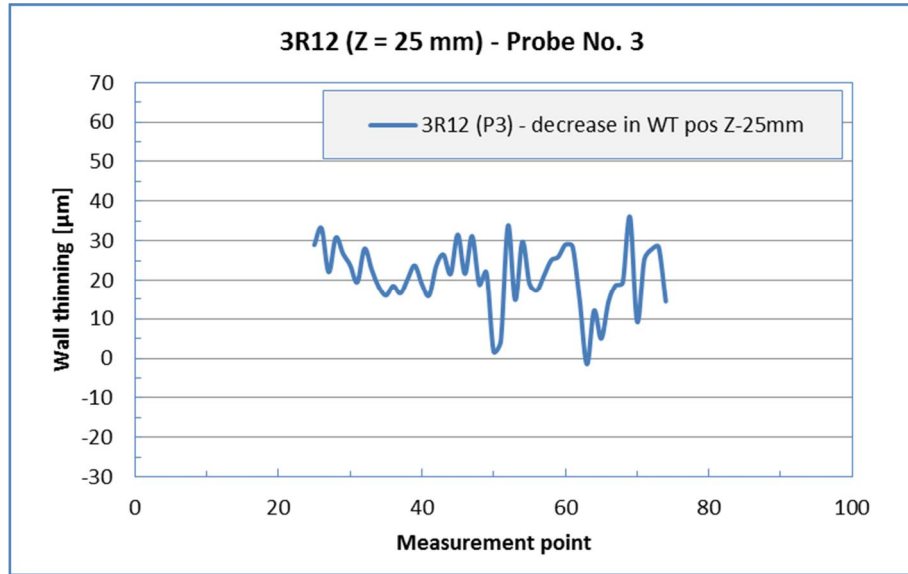
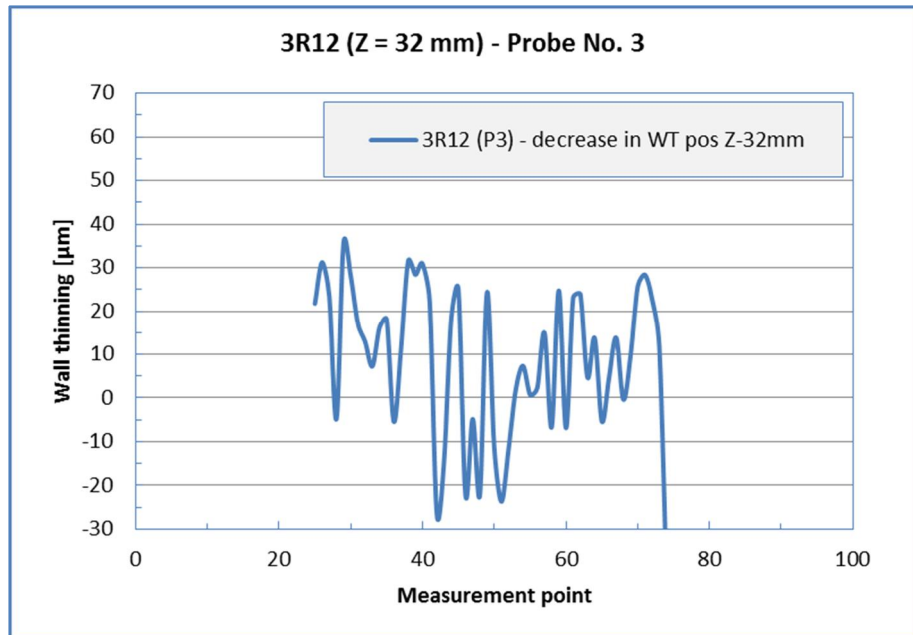


Figure 28. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

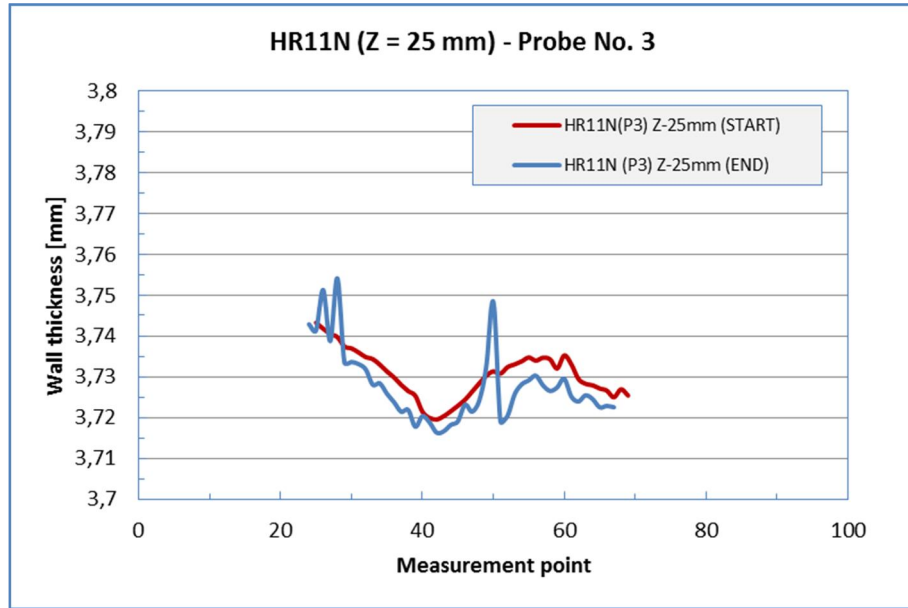


a)

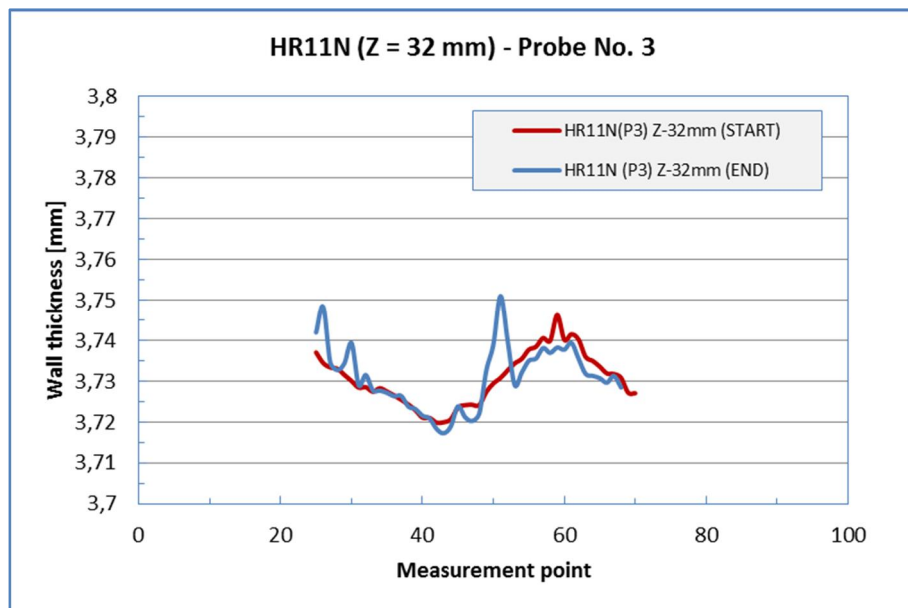


b)

Figure 29. Circumferential wall thinning curves from 3R12 specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

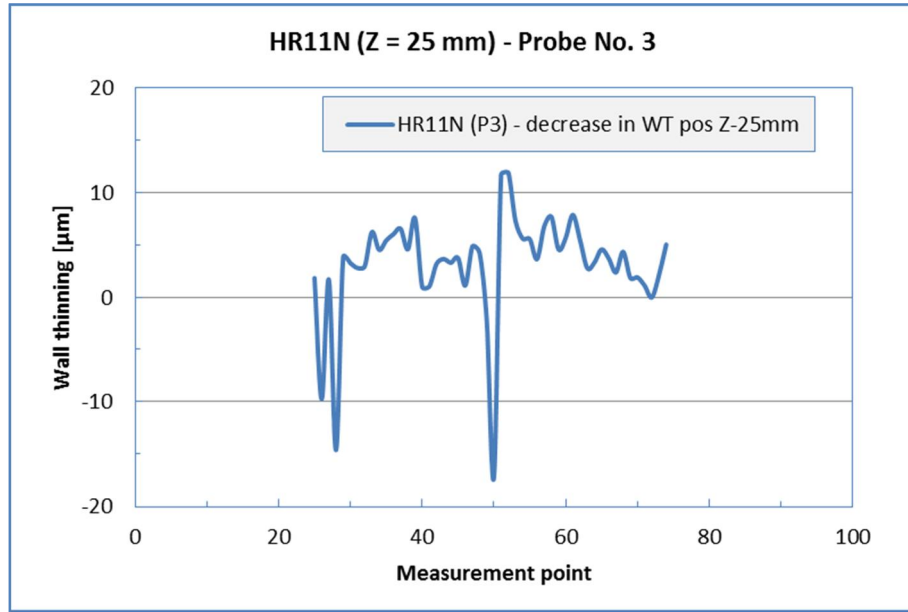


a)

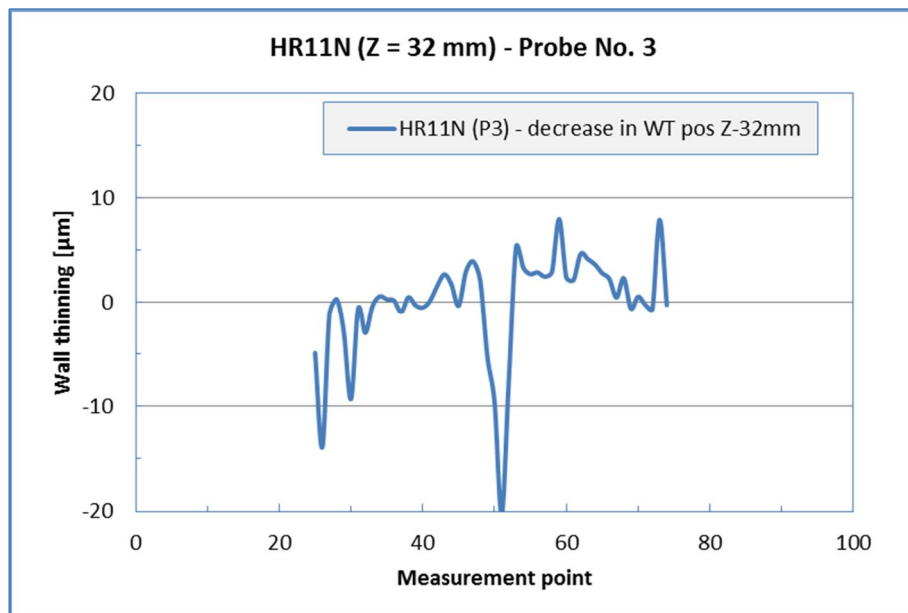


b)

Figure 30. Circumferential wall thickness profiles from HR11N specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 31. Circumferential wall thinning curves from HR11N specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

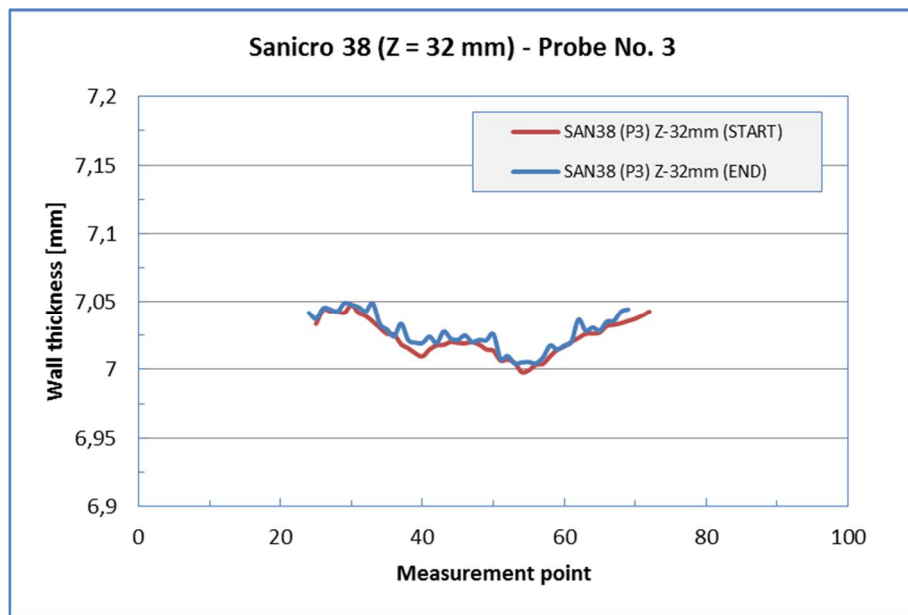
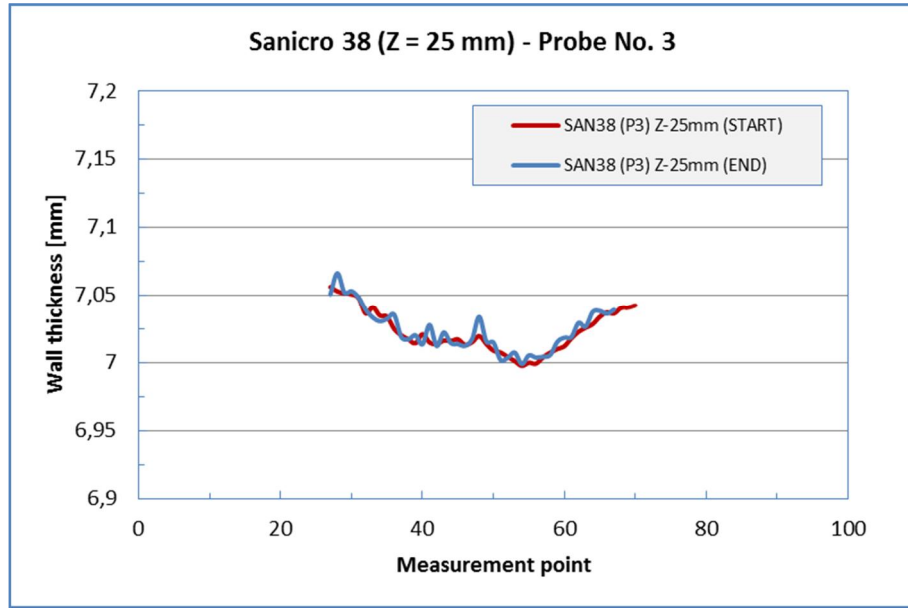
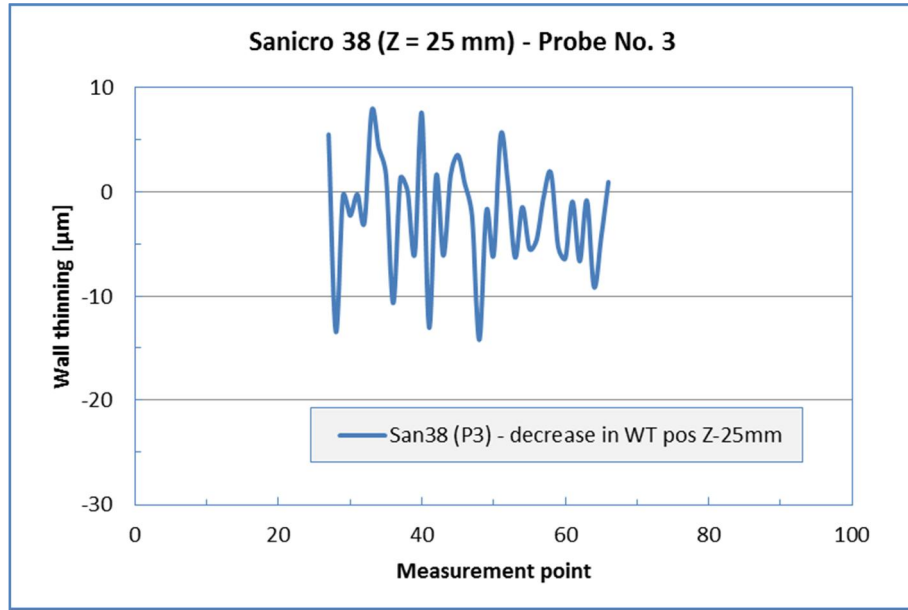
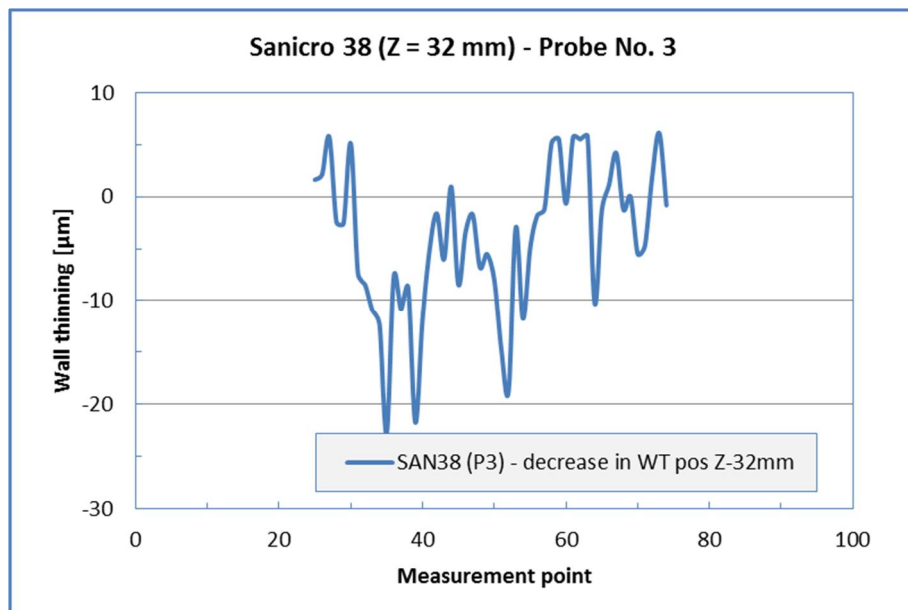


Figure 32. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

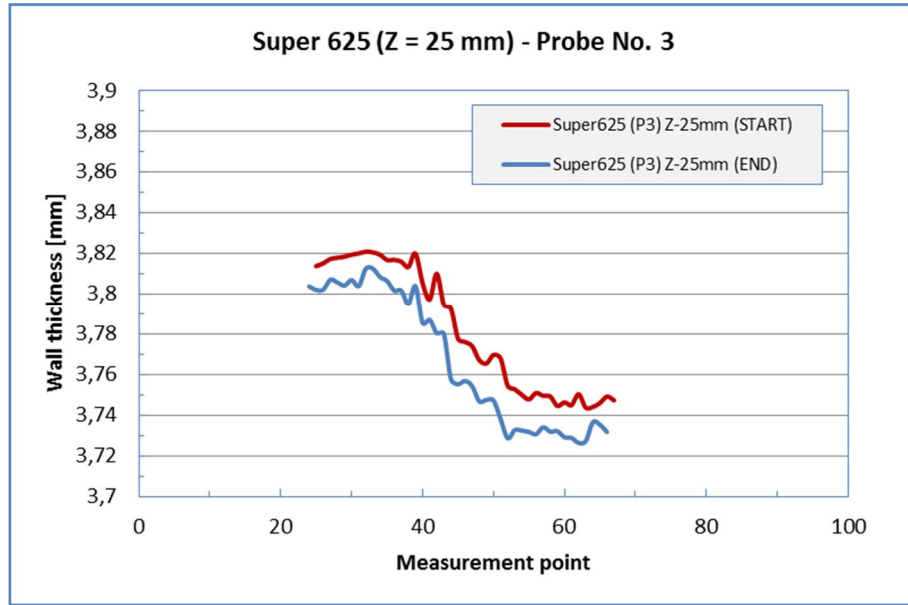


a)

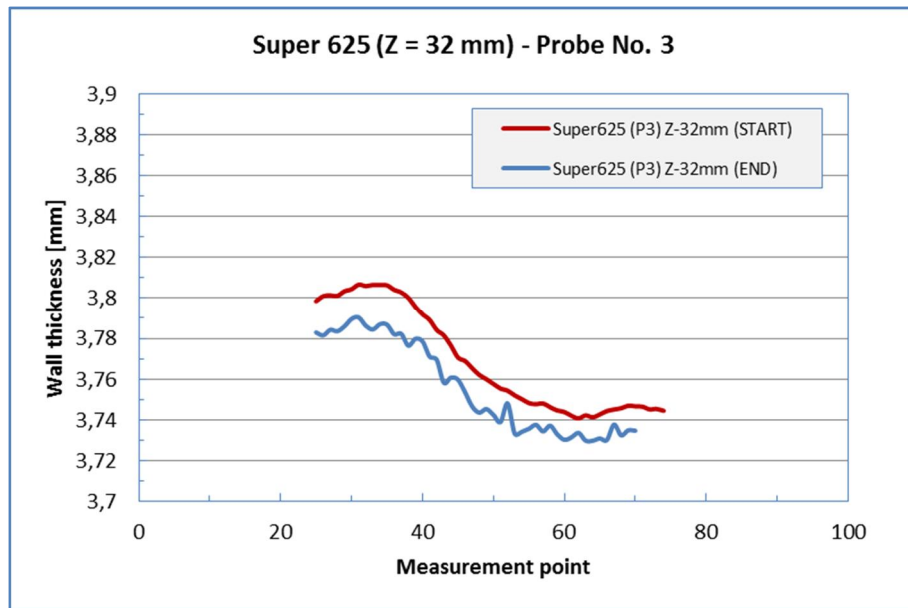


b)

Figure 33. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 3): a) axial location $Z = 25 \text{ mm}$ and b) axial location $Z = 32 \text{ mm}$.



a)



b)

Figure 34. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 3): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

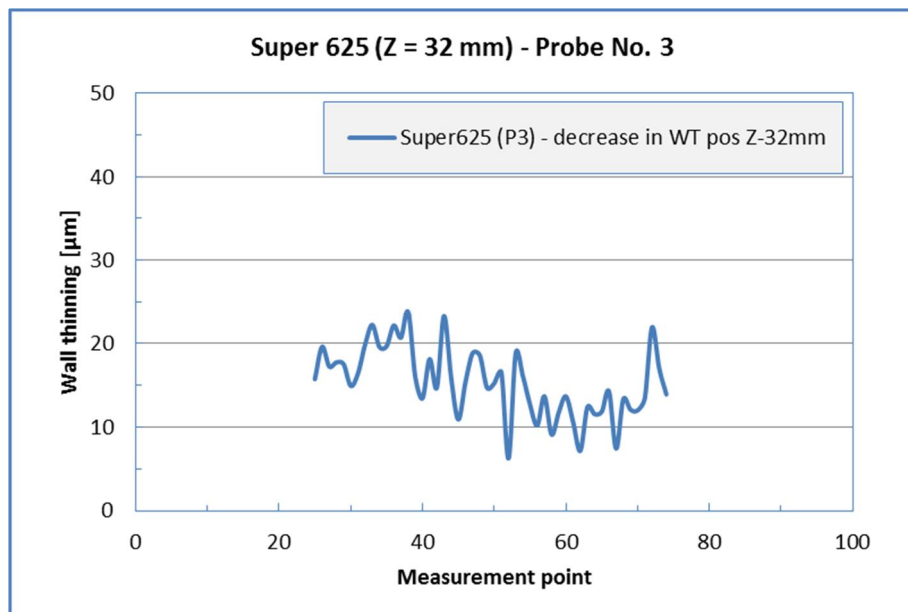
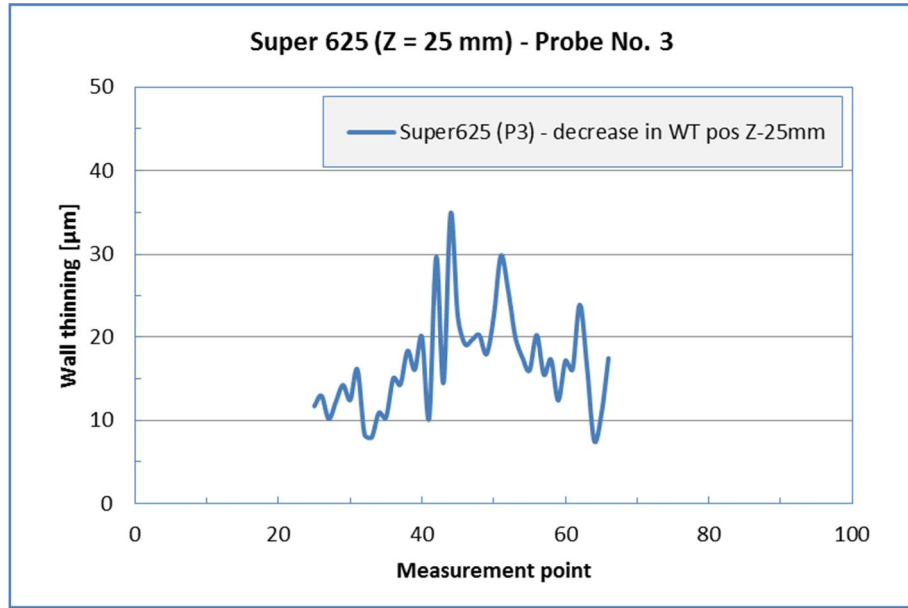
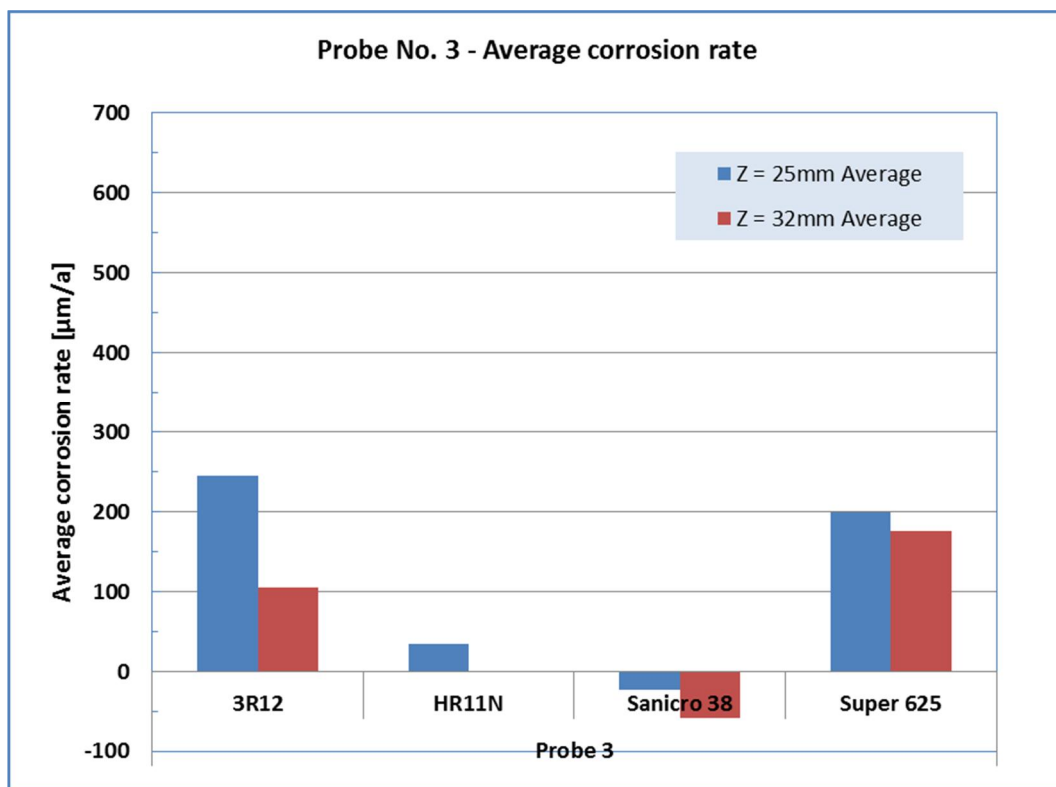
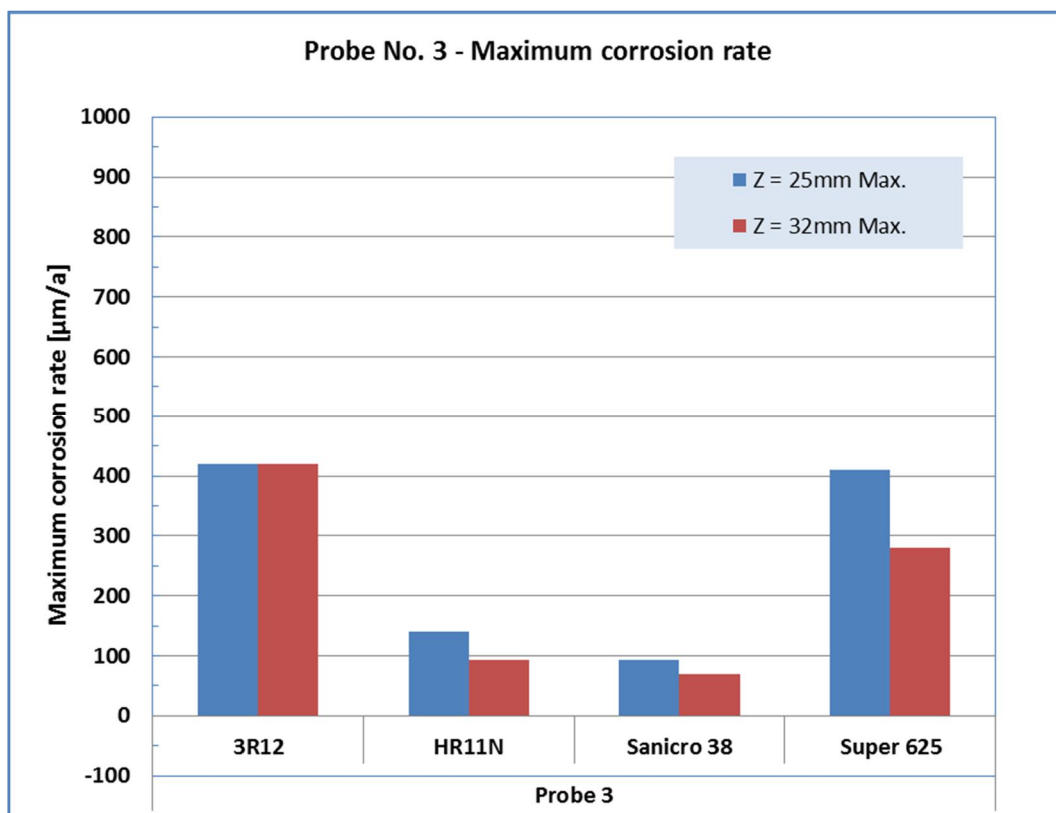


Figure 35. Circumferential wall thinning curves from Super 625 specimen (Probe No. 3): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 36. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)

4.3.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning. The layers formed on 3R12, HR11N and Sanicro 38 were thin ca.5 μm in thickness. Whereas on the Super 625 ca. 10...20 μm thick peeling like scale was observed.

According to the EDS analysis (Figure 38) the layers on 3R12, HR11N and Sanicro 38 were depleted in iron and nickel and enriched in chromium and contained also sulphur. The layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur. Reference analysis made from unexposed reference samples showed that the depleted/enriched layers are formed during exposure and do not originate from the specimen manufacturing process.

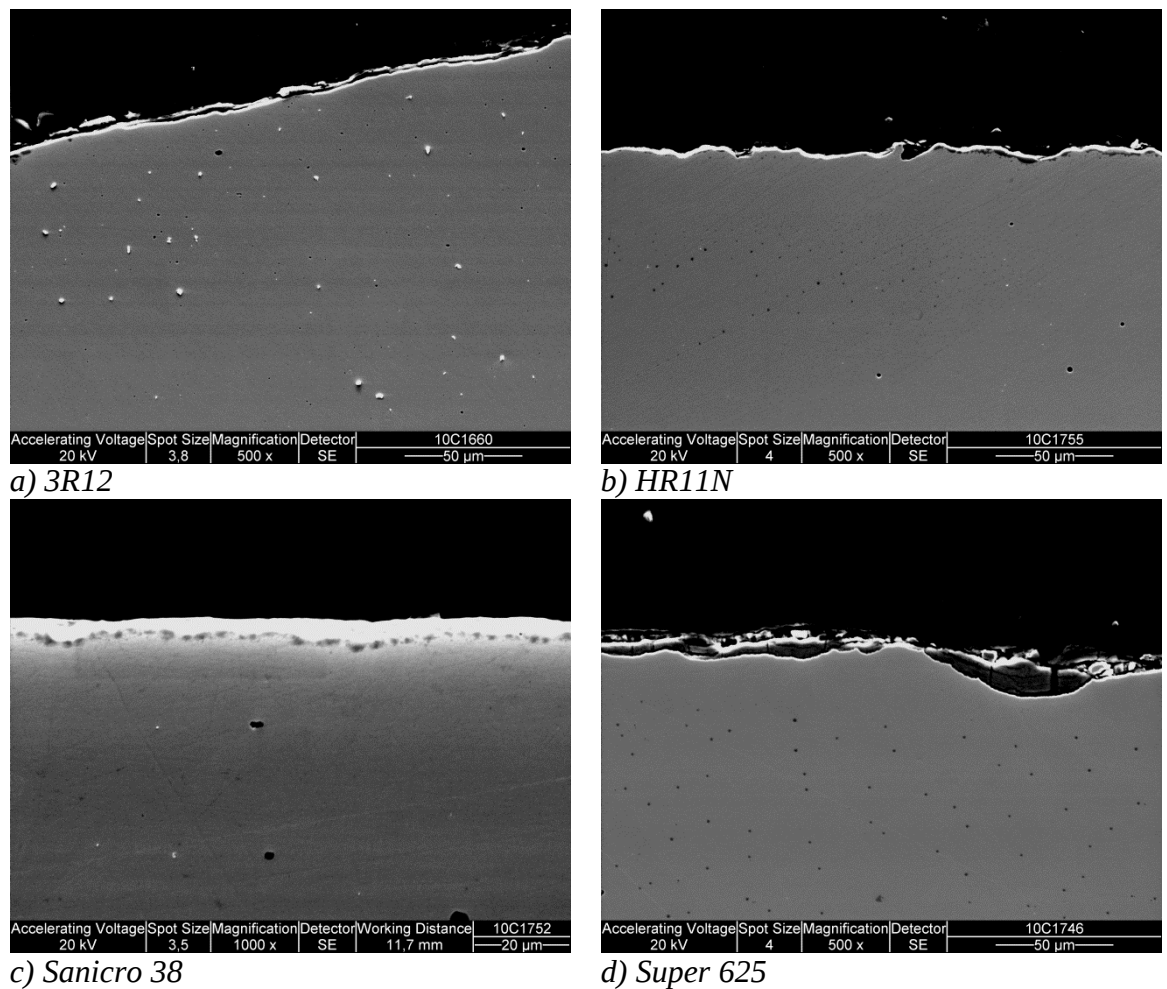


Figure 37. Cross sections from a) 3R12, b) HR11N, c) Sanicro 38 and d) Super 625 after 750 h exposure in lower furnace at 430 °C (Probe test No. 3)

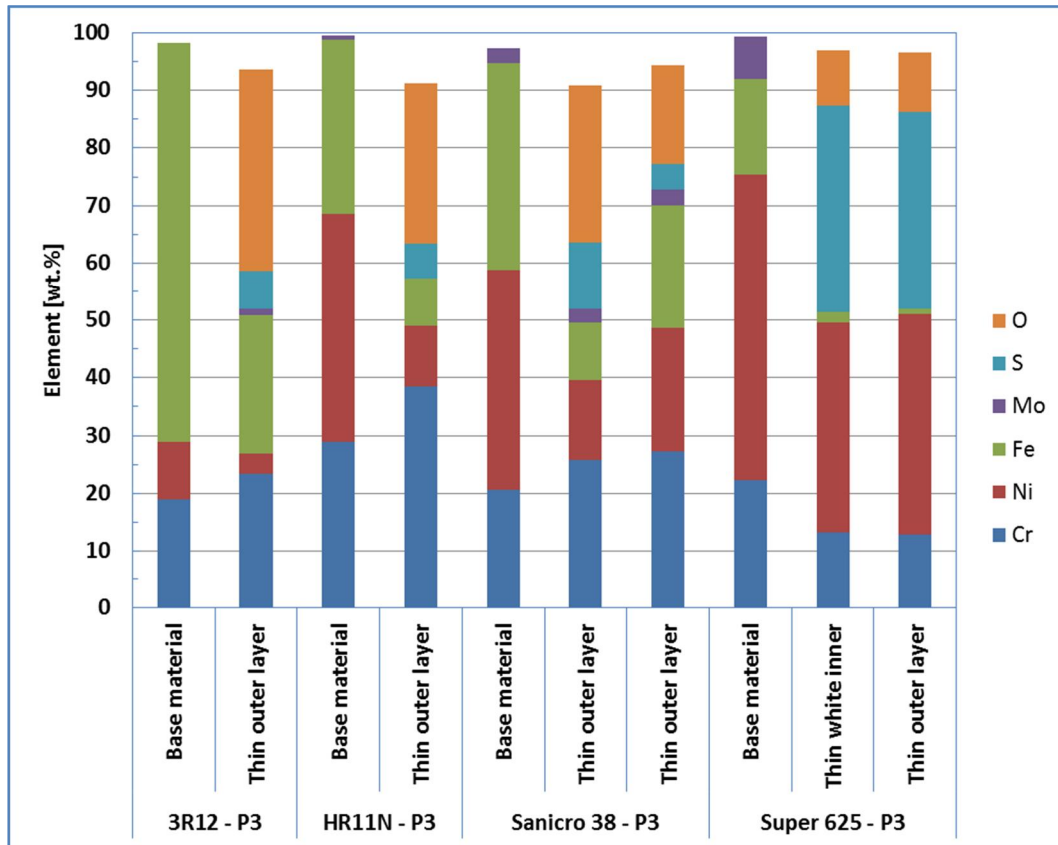


Figure 38. Results from the EDS analysis performed for the 3R12, HR11N, Sanicro 38 and Super 625 specimens after 750 h exposure in lower furnace at 430 °C (Probe test No. 3). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

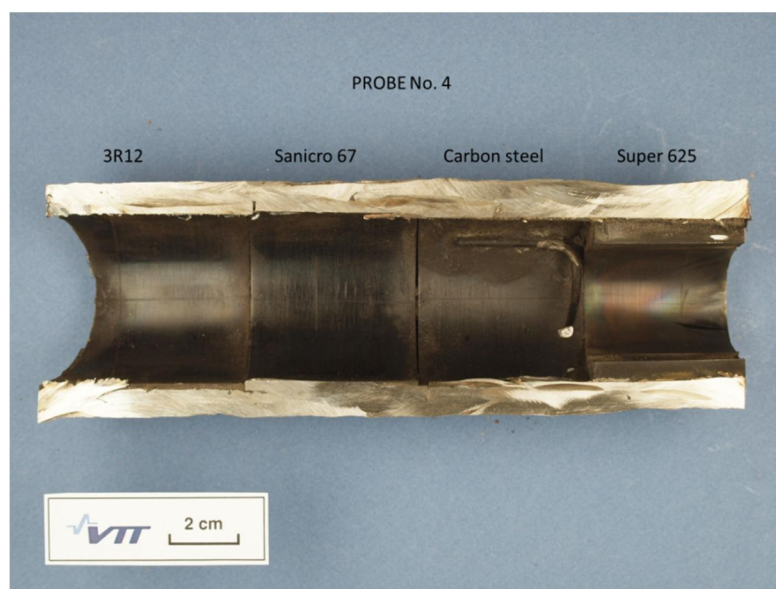
4.4 Probe test No. 4

Total test duration of the test No. 4 was 2700 hours from which 2154 hours at the target temperature of 440 °C. The test materials in this exposure 3R12, carbon steel, Sanicro 67 and Super 625, Figure 39.

According to visual inspection the inner surfaces of the specimens were in good condition after testing. The outer surfaces of the 3R12, Sanicro 67 and Super 625 specimens were covered with thin dark deposits but appeared to be in good condition. The carbon steel specimen was heavily corroded.



a)



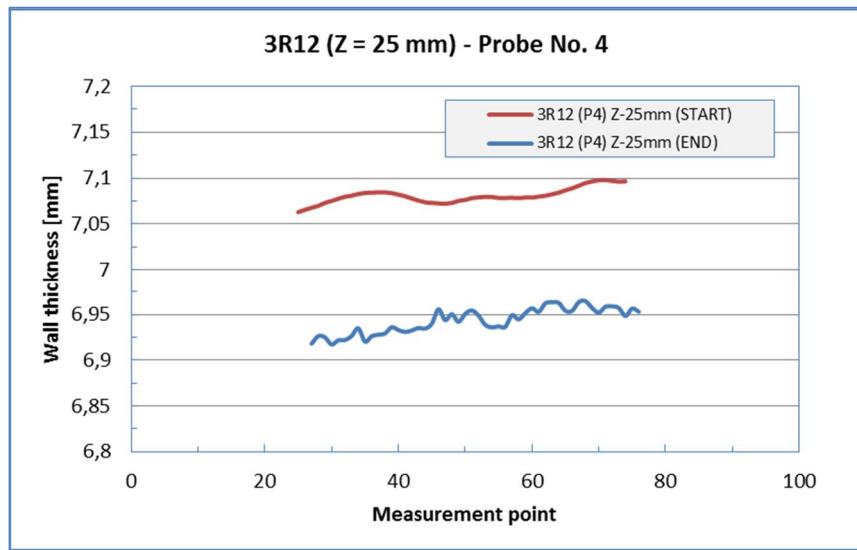
b)

Figure 39. Macrographs taken from the probe No. 4 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the side surface of carbon steel specimen is clearly visible on inner surface.

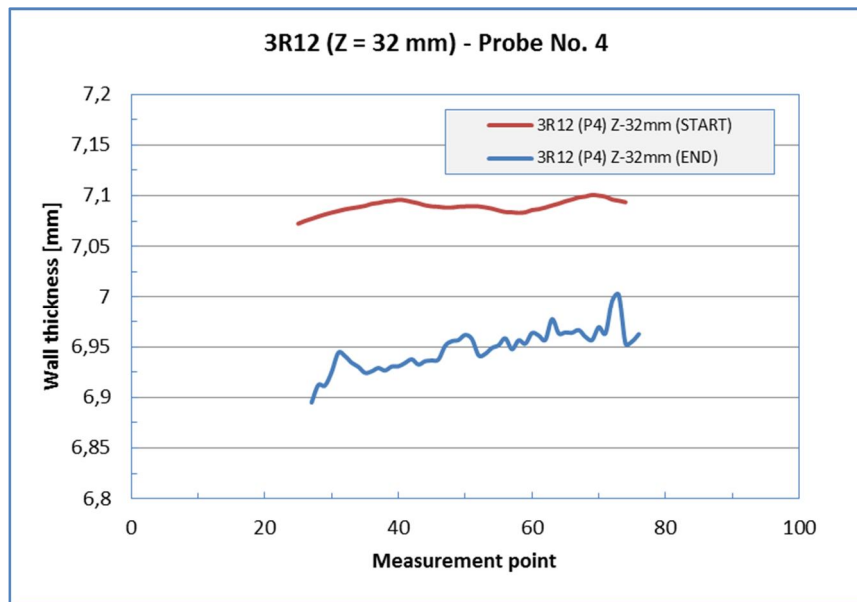
4.4.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them are presented in Figures 40...47. The results showed that intense wall thinning had taken place on carbon steel specimen. Marked wall thinning was also observed on the 3R12 specimen and lesser degree also on the Super 625 specimen. The data of the Sanicro 67 specimen was more scattered showing that wall thinning and deposit formation (increase in wall thickness) had taken place locally. The results showed also that surface polishing prior testing together with longer exposure time reduced data scatter and thus improved accuracy.

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. Highest corrosion rates, ca. 4 mm/a, were measured for the carbon steel as expected. The 3R12 had the second highest corrosion rates, order of 0.6 mm/a. Maximum corrosion rate of the Super 625 was in the order 0.1 mm/a in this test, i.e. significantly lower than in the test No.3, where a maximum corrosion rate of 0.2...0.3 mm/a was observed. The best material in this test was Sanicro 67, its maximum corrosion rate was only about 0.02 mm/a.

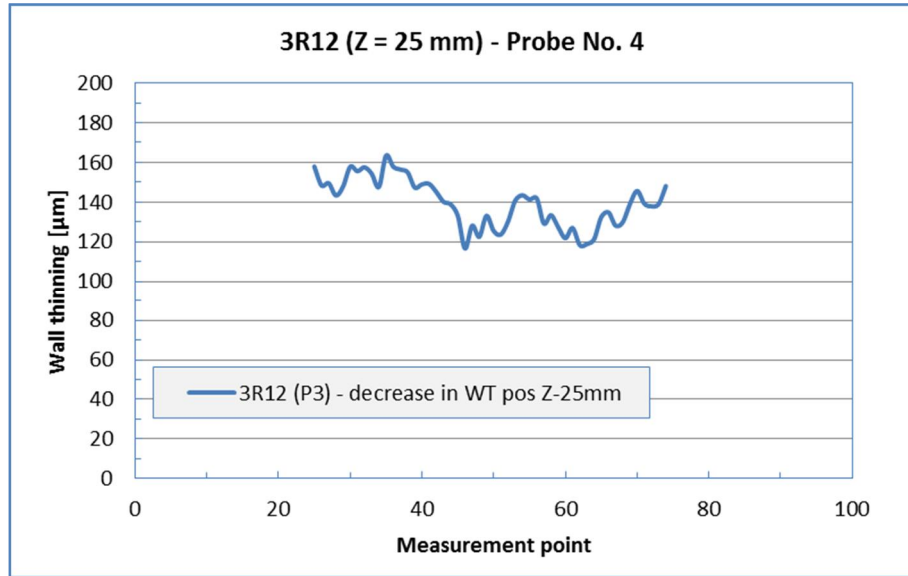


a)

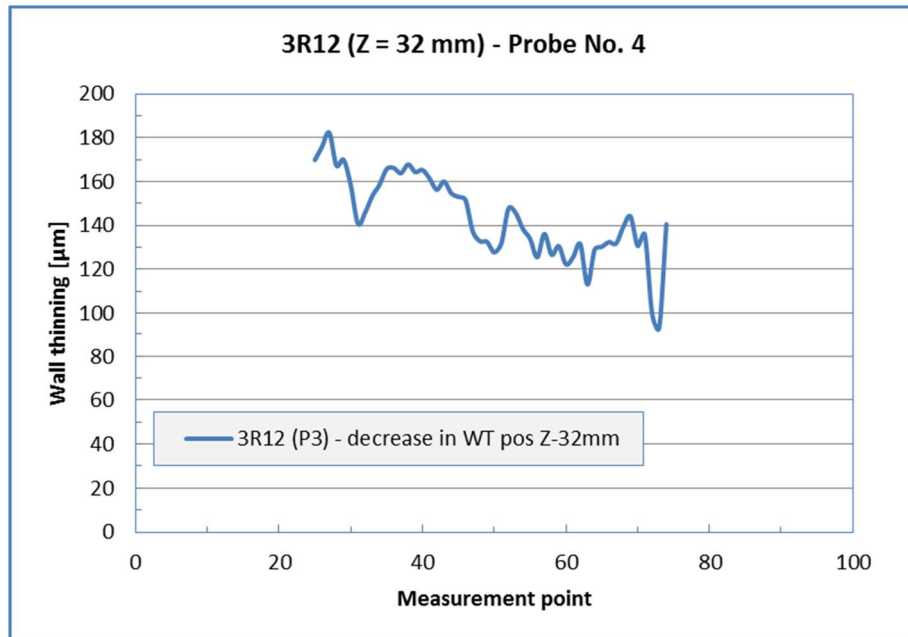


b)

Figure 40. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

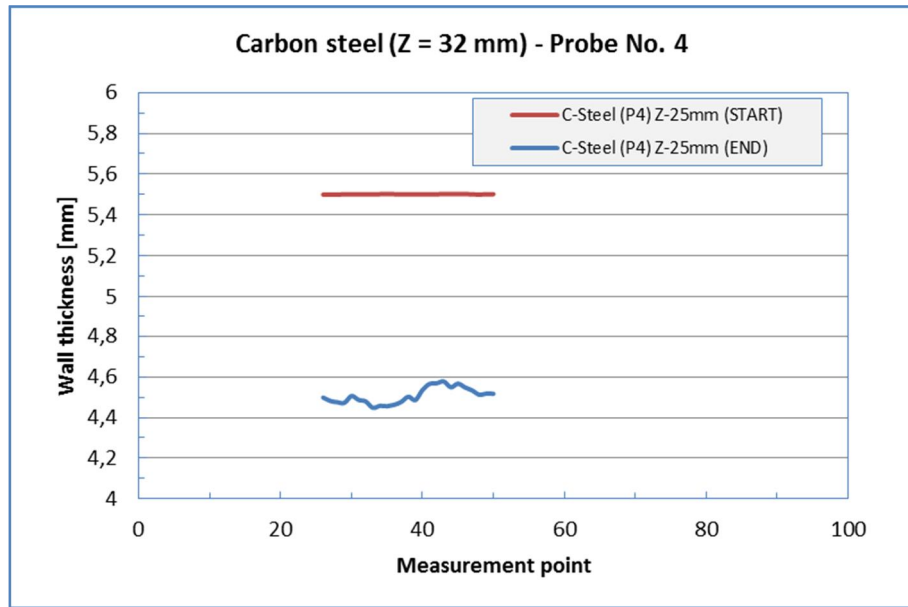


a)

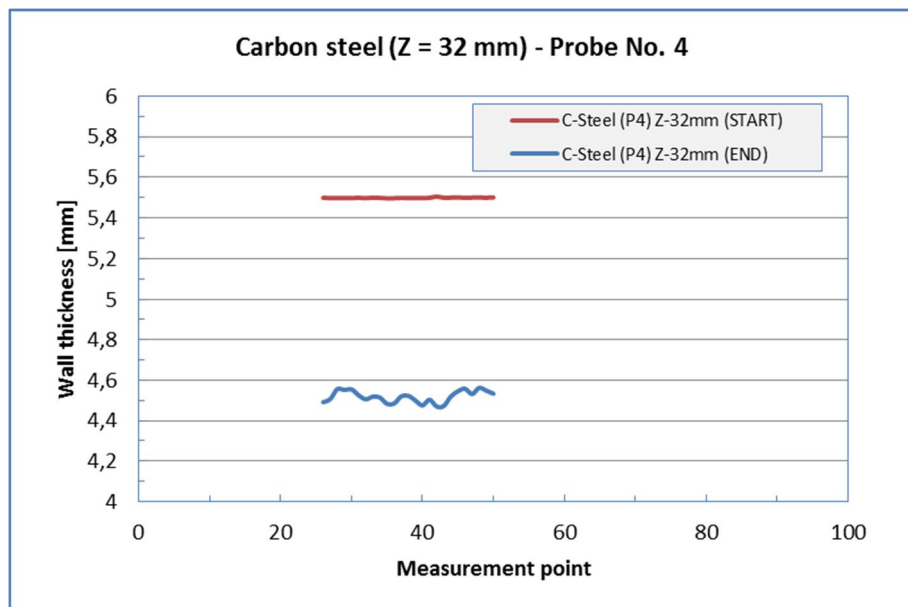


b)

Figure 41. Circumferential wall thinning curves from 3R12 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

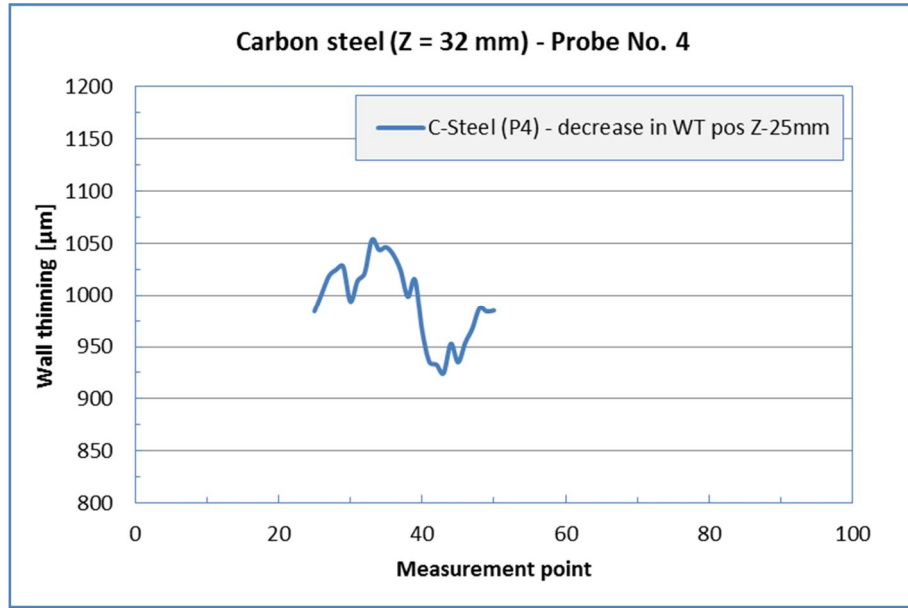


a)

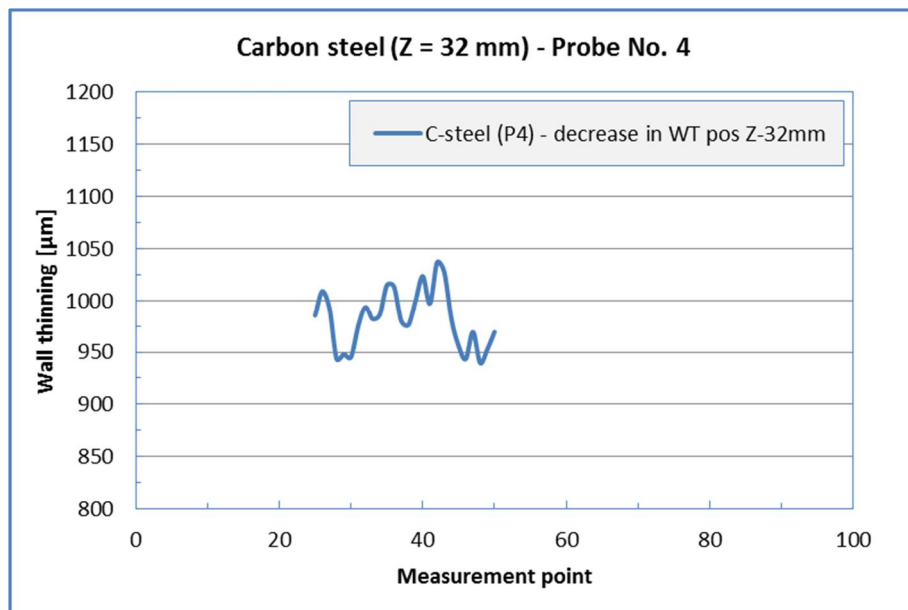


b)

Figure 42. Circumferential wall thickness profiles from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.

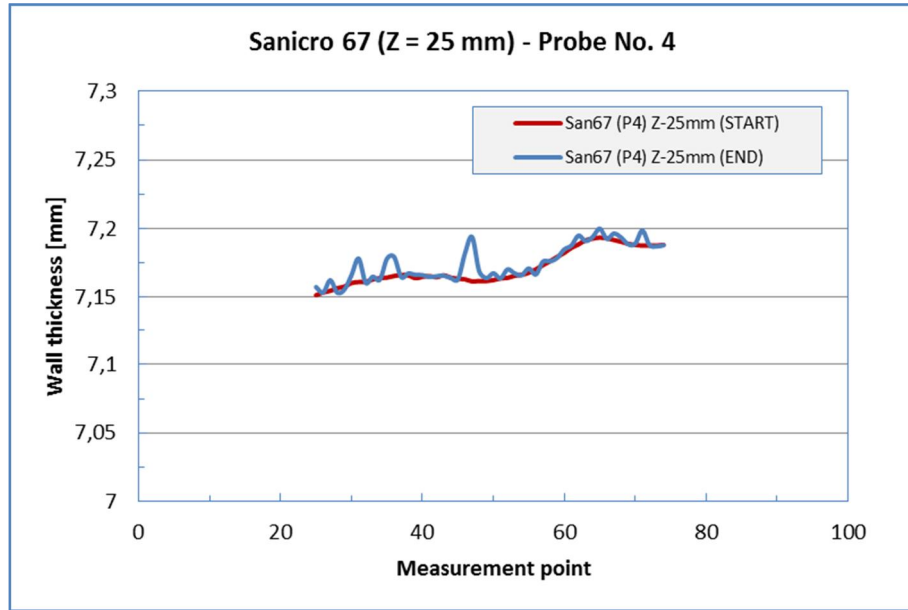


a)

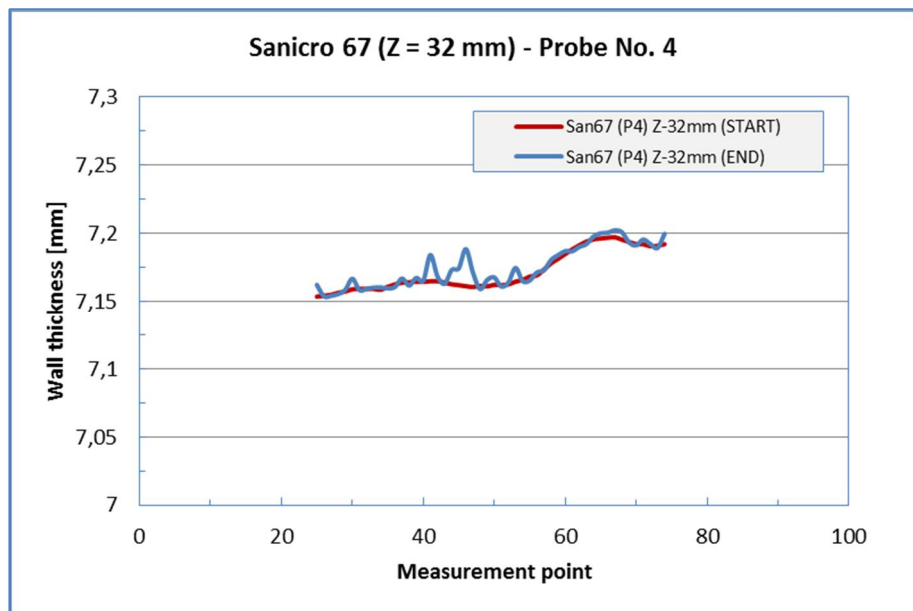


b)

Figure 43. Circumferential wall thinning curves from carbon steel specimen (Probe No. 4): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)



b)

Figure 44. Circumferential wall thickness profiles from Sanicro 67 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

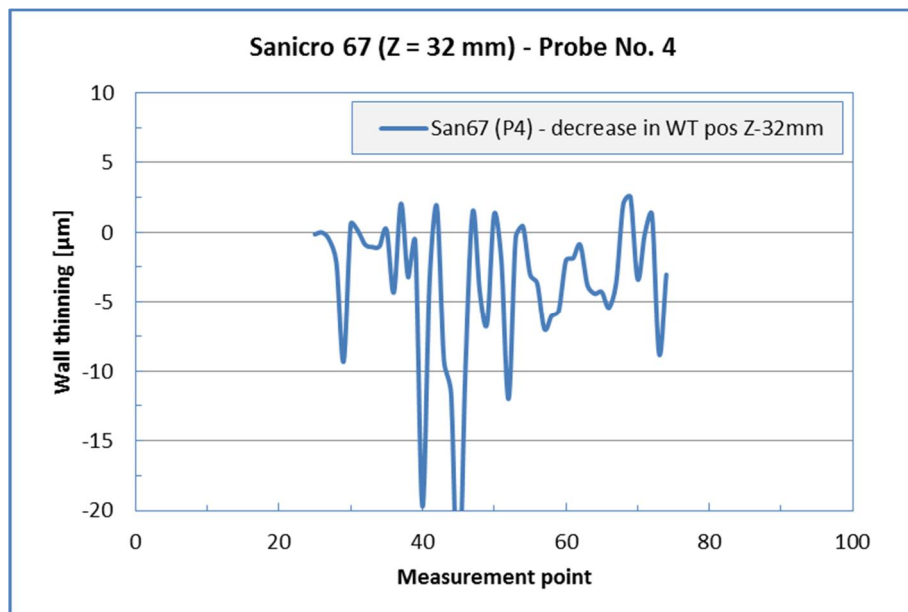
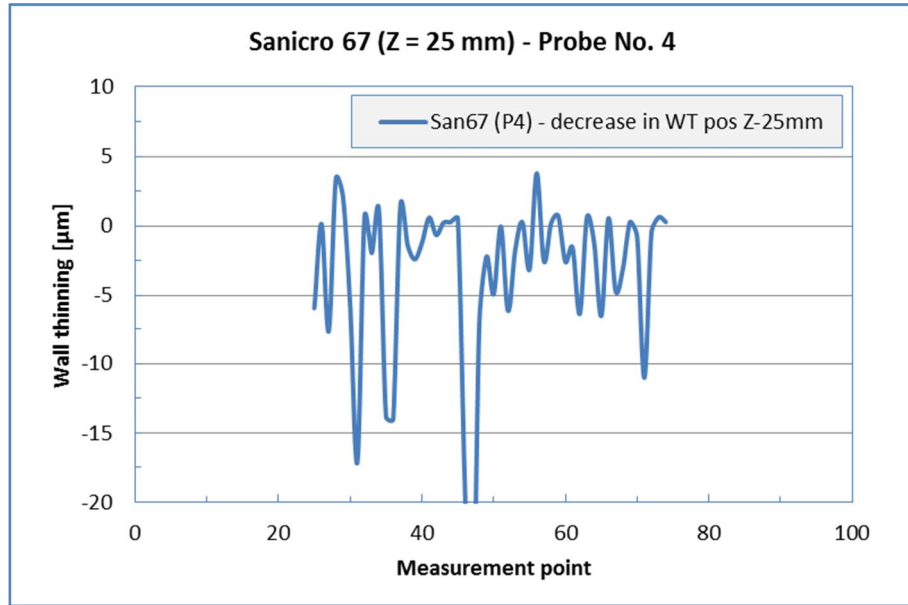
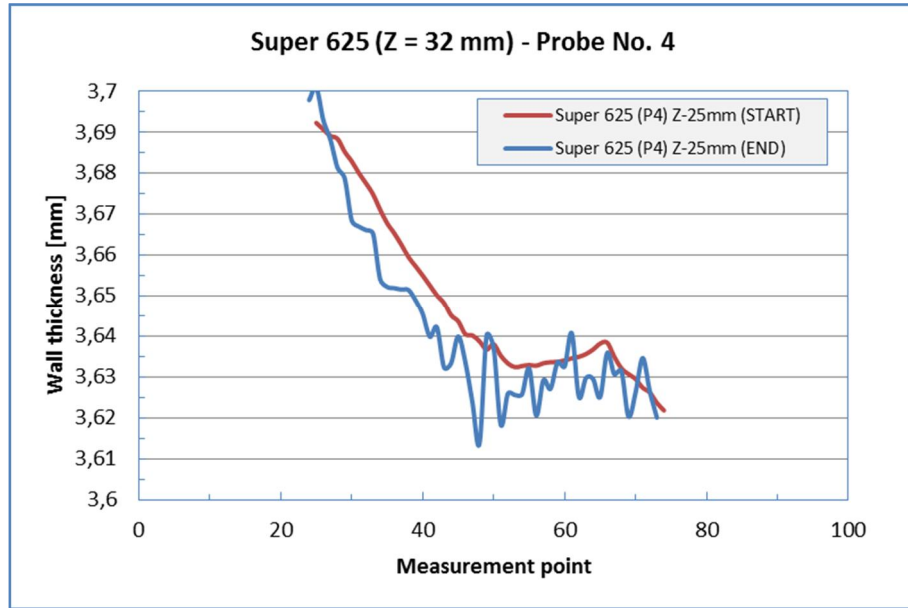
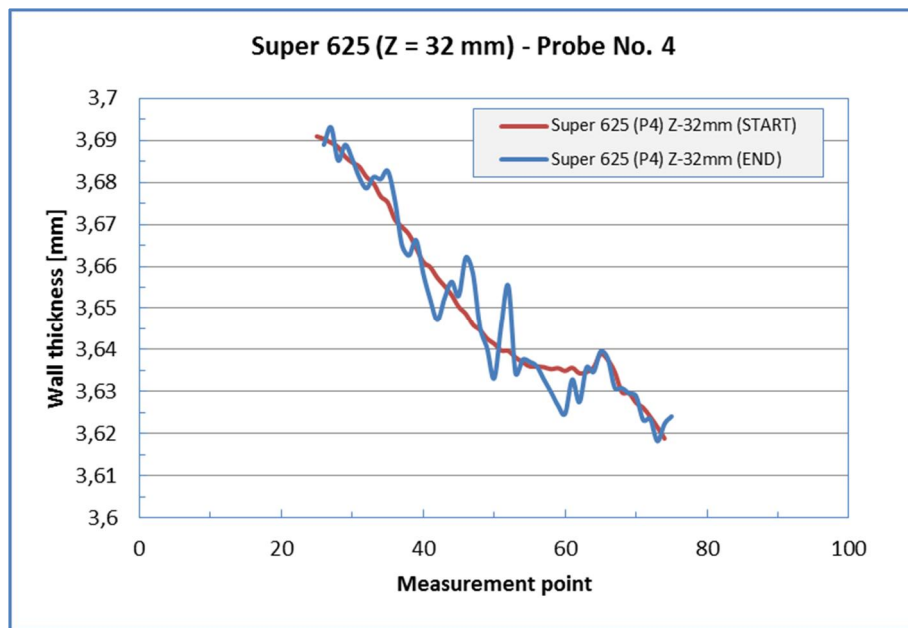


Figure 45. Circumferential wall thinning curves from Sanicro 67 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

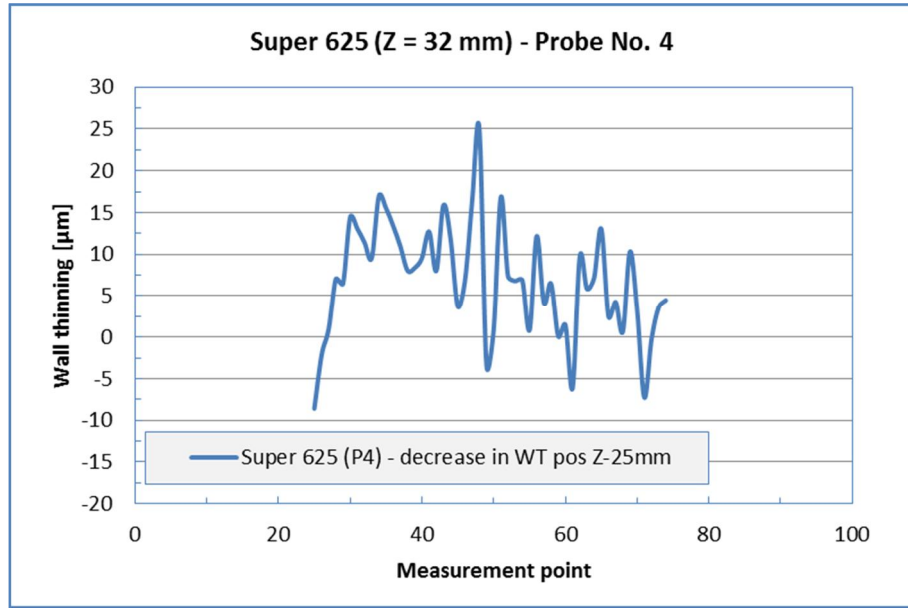


a)

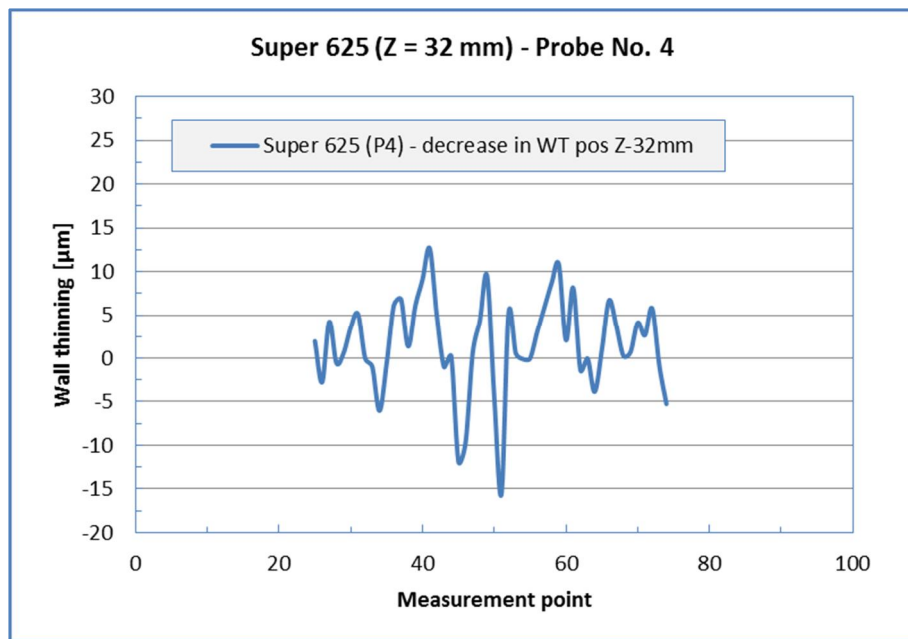


b)

Figure 46. Circumferential wall thickness profiles from Super 625 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

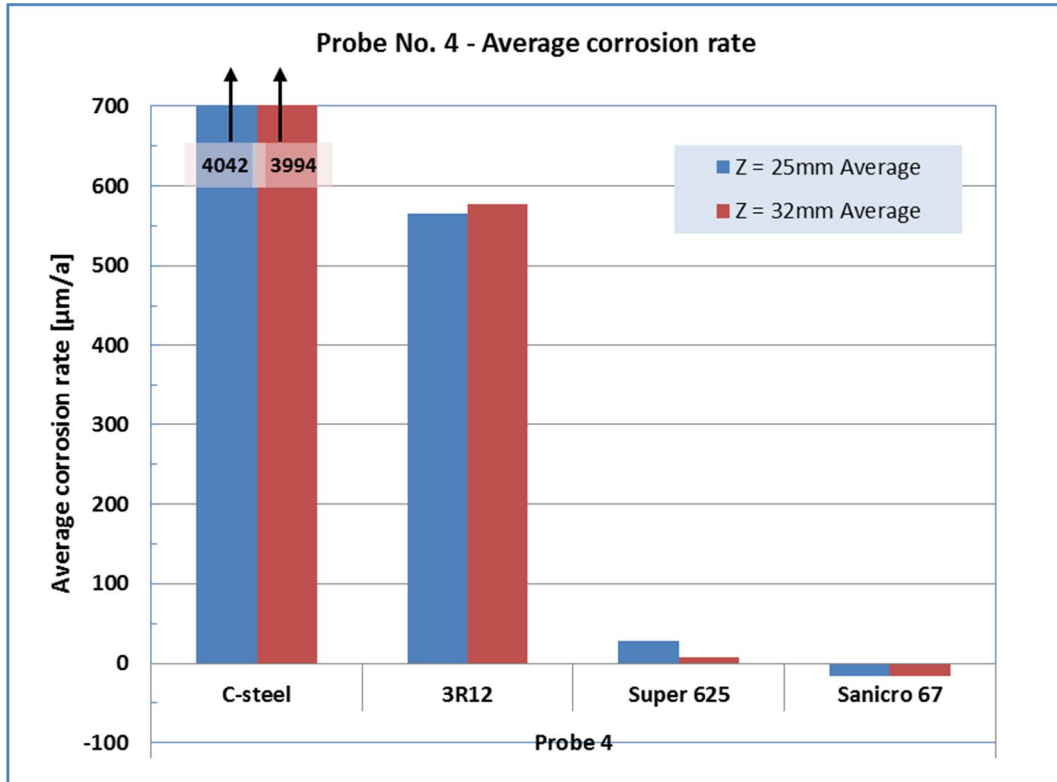


a)

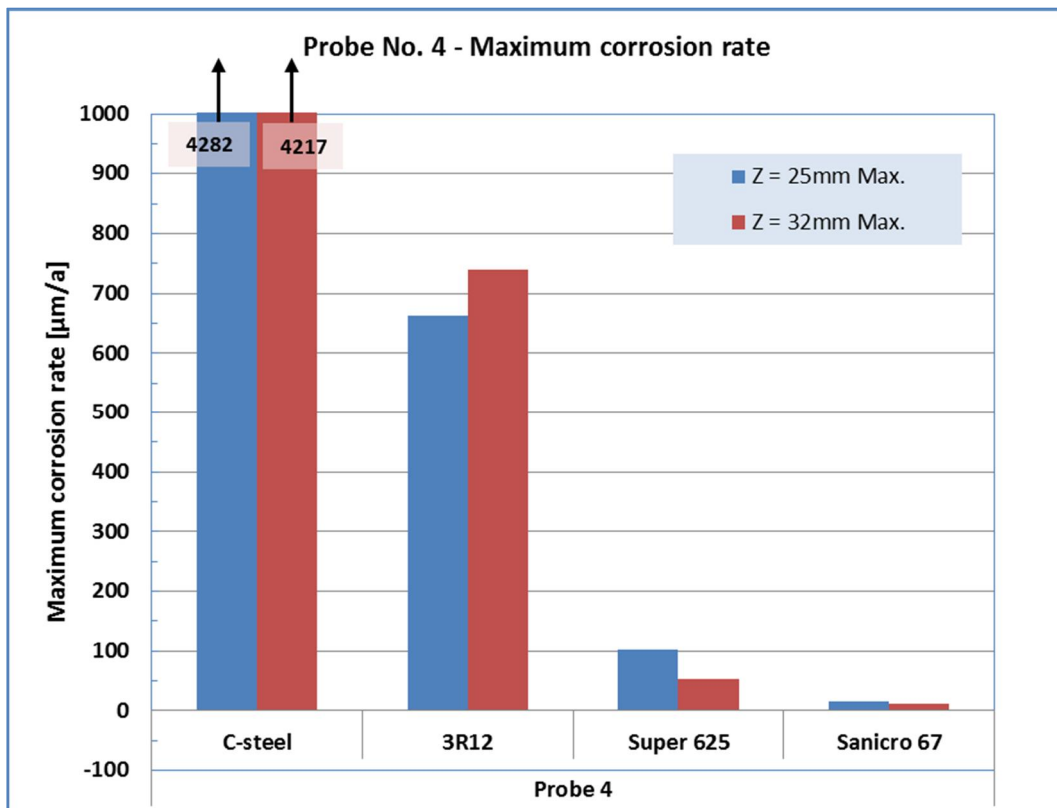


b)

Figure 47. Circumferential wall thinning curves from Super 625 specimen (Probe No. 4): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 48. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4).

4.4.2 Metallography

After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning, Figure 49. The carbon steel showed scale thickness of about 25 μm after 2700 h exposure. The layers formed on 3R12 and Sanicro 67 were thin ca.5 μm in thickness. Whereas on the Super 625 ca. 10...20 μm thick peeling like scale was observed.

According to the EDS analysis (Figure 50) the layer on 3R12 was depleted in iron and nickel and enriched in chromium and contained also sulphur. The layer on Sanicro 67 contained sulphur and was depleted in iron and nickel, but the chromium content was at the same level than in the base material. The outermost layers on the Super 625 were depleted in iron, nickel, molybdenum and chromium and contained high amounts of sulphur.

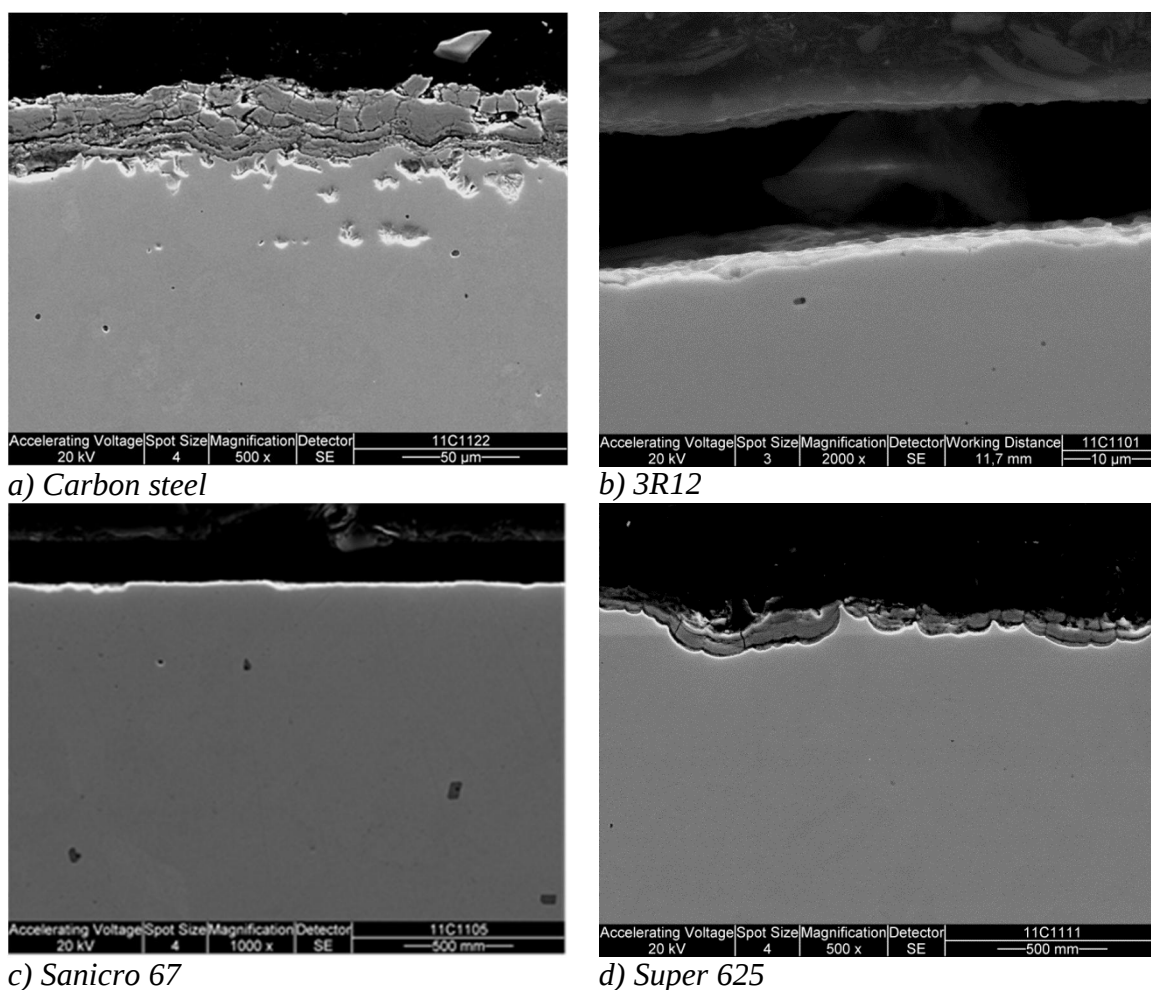


Figure 49. Cross sections from a) carbon steel b) 3R12, c) Sanicro 67 and d) Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4).

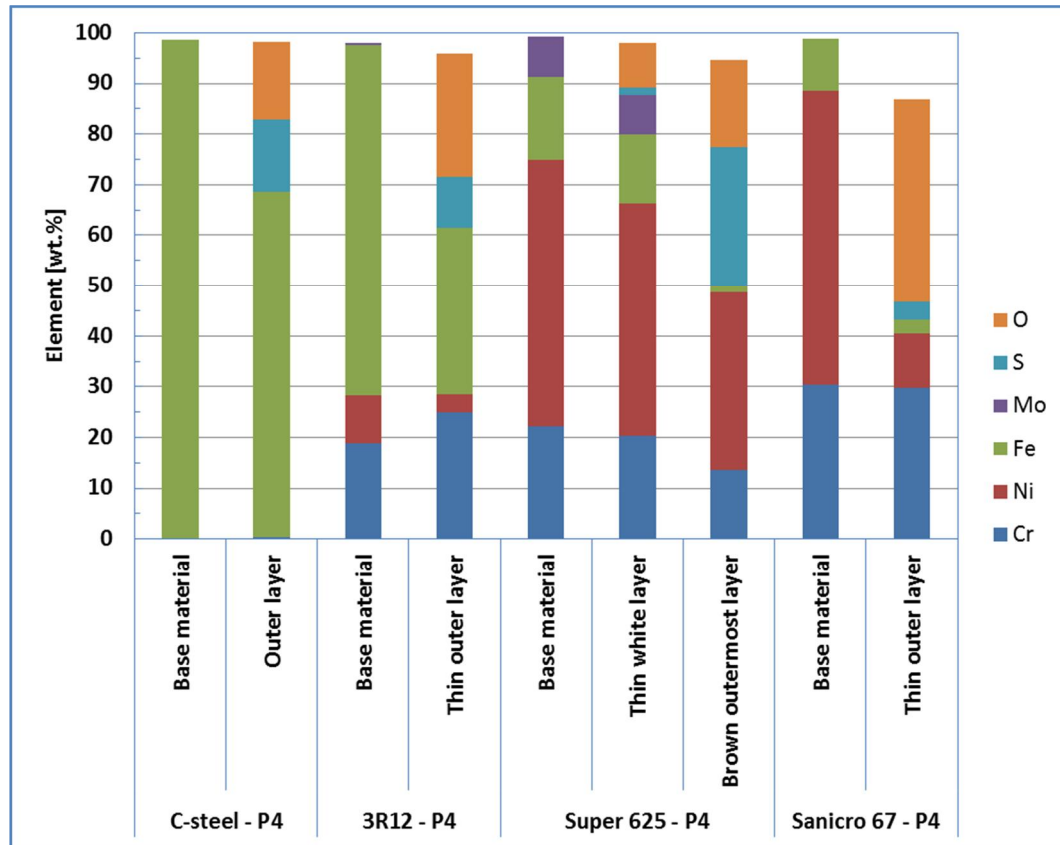


Figure 50. Results from the EDS analysis performed for the carbon steel, 3R12, Sanicro 67 and Super 625 after 2154 h exposure in lower furnace at 440 °C (Probe test No. 4). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

4.5 Probe test No. 5

Total test duration of the test No. 5 was 2630 hours from which 2157 hours at the target temperature of 440 °C. The test materials in this exposure were 3R12, Sanicro 28, HR11N and Sanicro 38, Figure 51. According to visual inspection all samples were in good condition after testing i.e. neither marked general or localised corrosion nor deposits or oxide scales were observed either on outer or inner surfaces.



a)



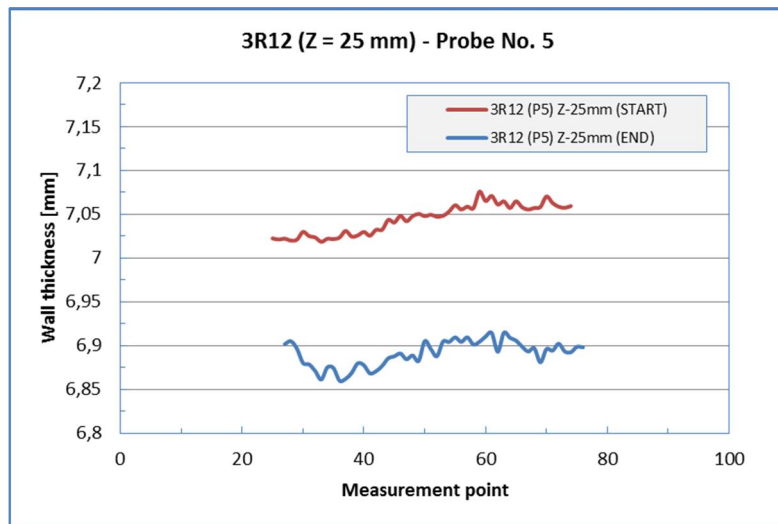
b)

Figure 51. Macrographs taken from the probe No. 5 head after exposure: a) outer surface exposed to the furnace side and b) inner surface exposed to the cooling liquid. A thermocouple soldered on the middle of Sanicro28 specimen, that hindered WT measurements after exposure, is clearly visible on inner surface.

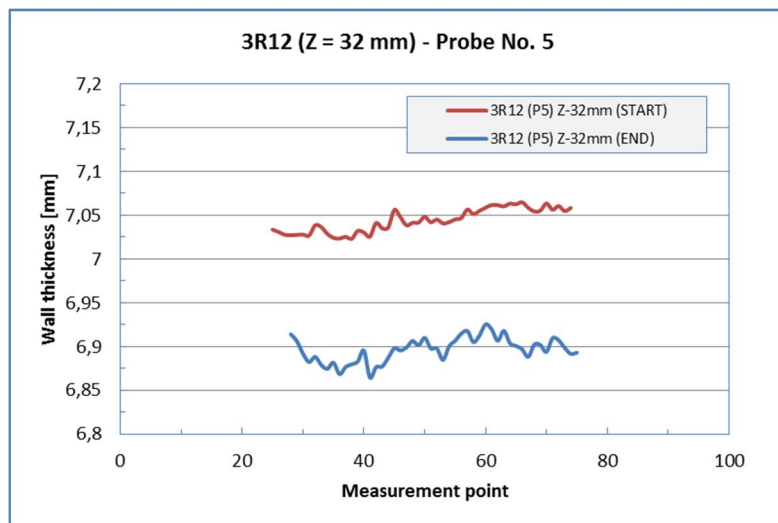
4.5.1 Corrosion rates

The results of the wall thickness profile measurements and the wall thinning curves derived from them for 3R12, HR11N and Sanicro 38 are presented in Figures 52...57. The results showed that marked wall thinning had taken on the 3R12 specimen. Some wall thinning was observed also on the Sanicro 38 specimen and locally also on the HR11N specimen. The WT profile measurements for the Sanicro 28 sample after the test failed due to the thermocouple that was soldered on the inner surface of the specimen (Figure 51b).

The average and maximum corrosion rates calculated on the basis of the wall thickness measurements are presented in Figure 48. In this test the corrosion rate of the 3R12 was in the order 0.8 mm/a. The maximum corrosion rates of HR11N and Sanicro 38 were in the order of 0.15 mm/a, i.e. at the same range than in the previous tests.

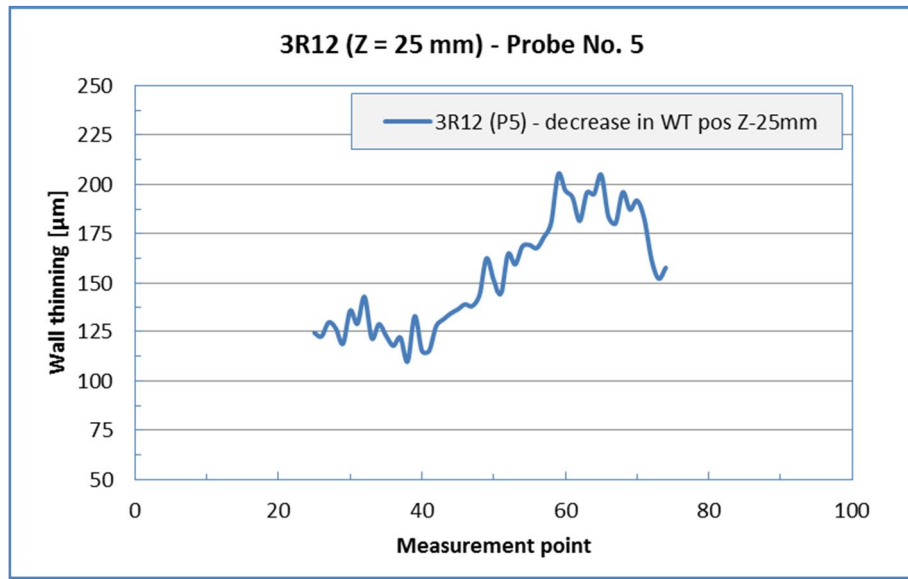


a)

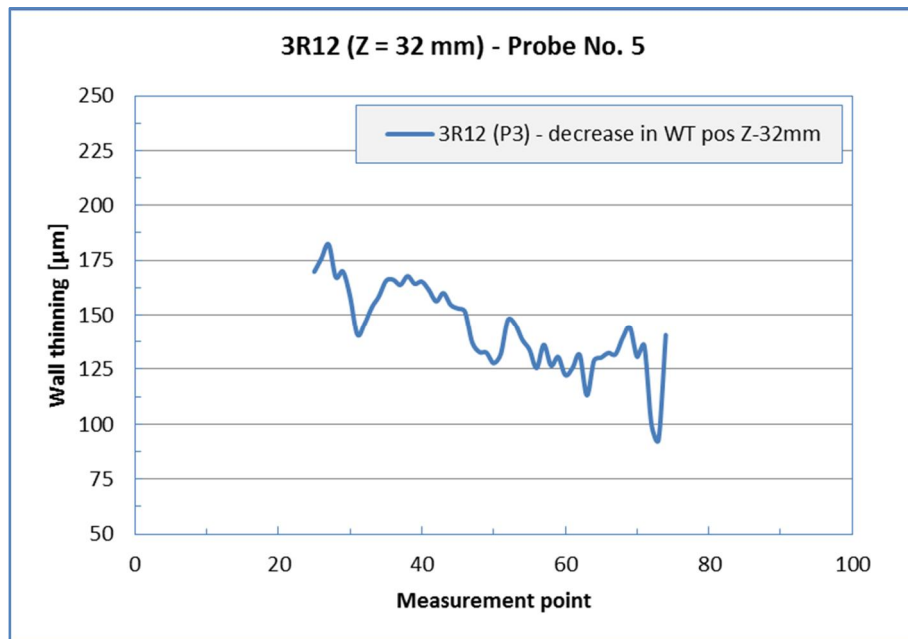


b)

Figure 52. Circumferential wall thickness profiles from 3R12 specimen (Probe No. 5): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

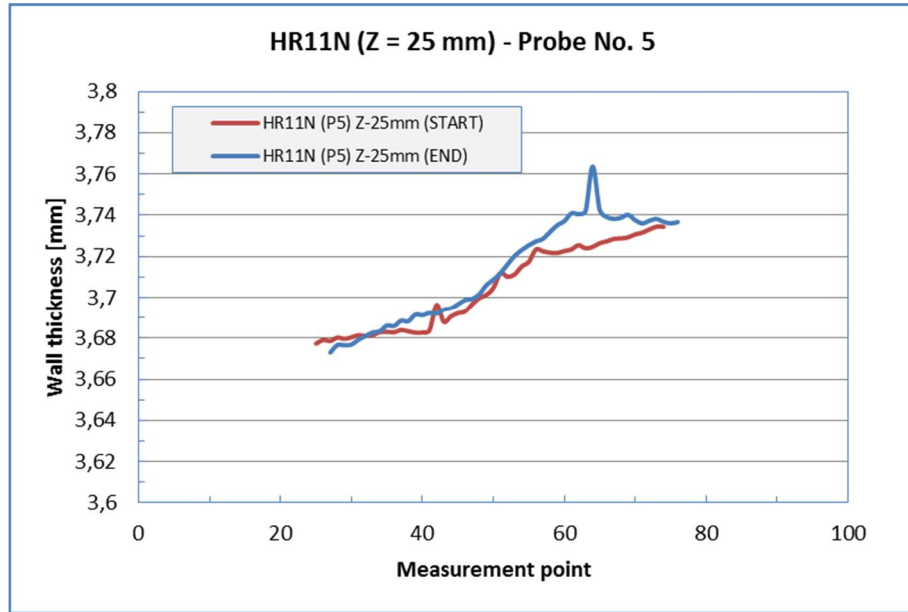


a)

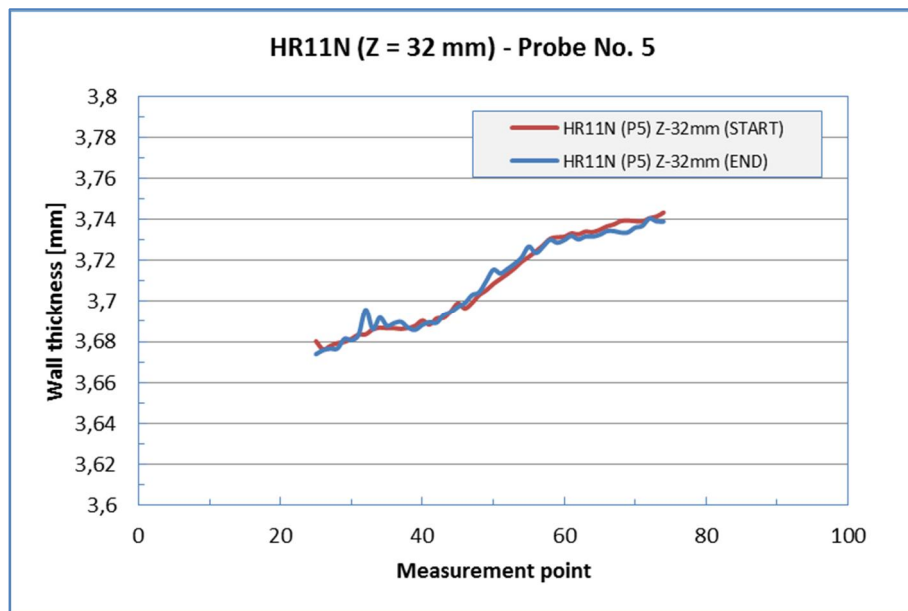


b)

Figure 53. Circumferential wall thinning curves from 3R12 specimen (Probe No. 5): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

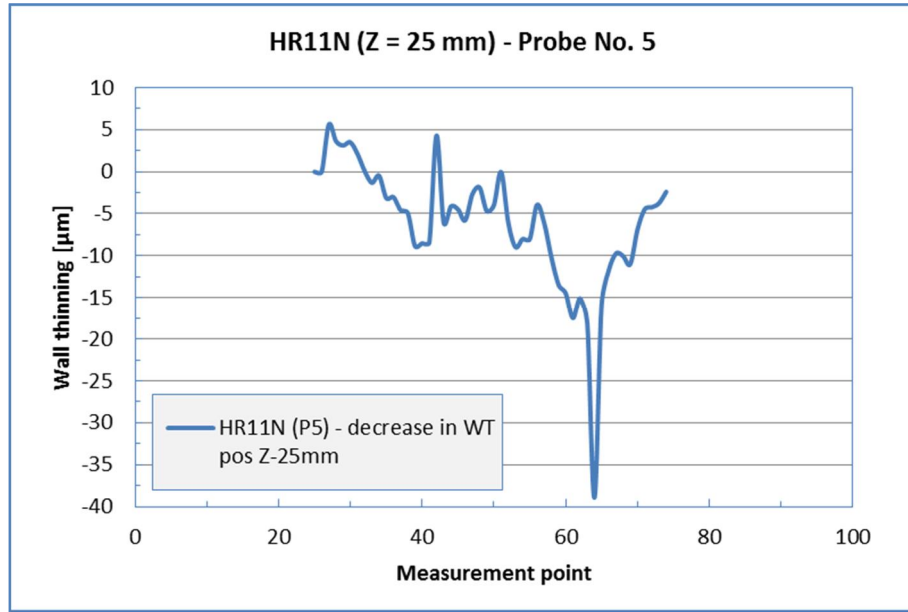


a)

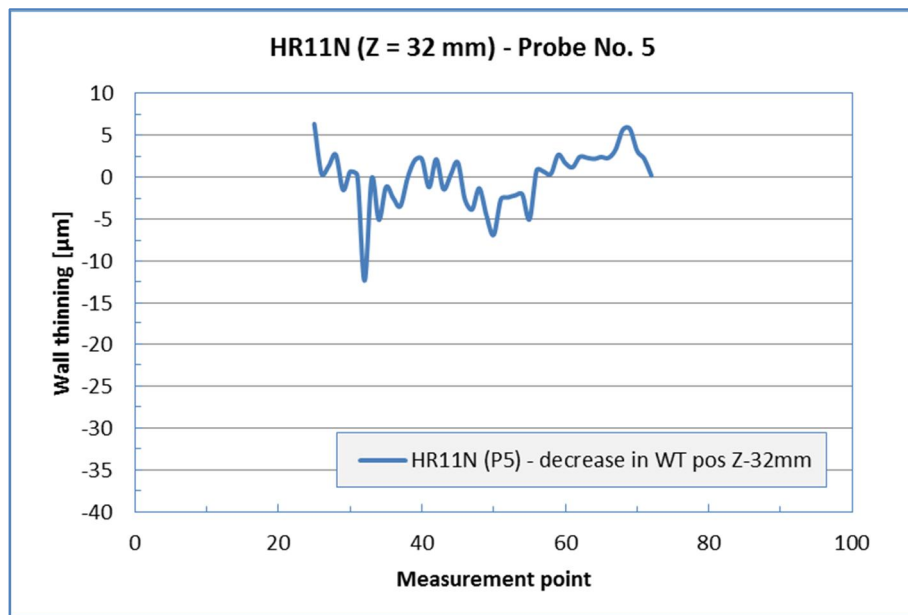


b)

Figure 54. Circumferential wall thickness profiles from HR11N specimen (Probe No. 5): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.

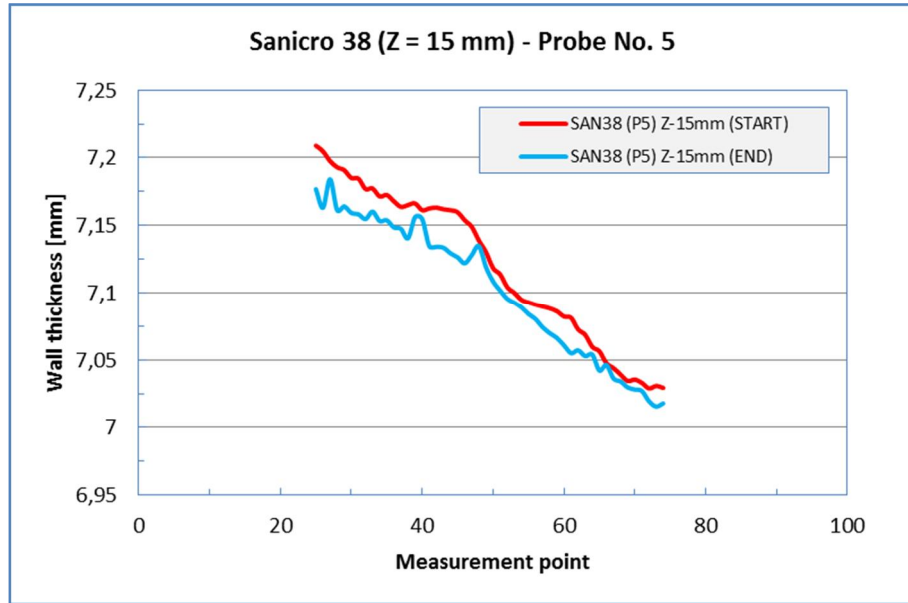


a)

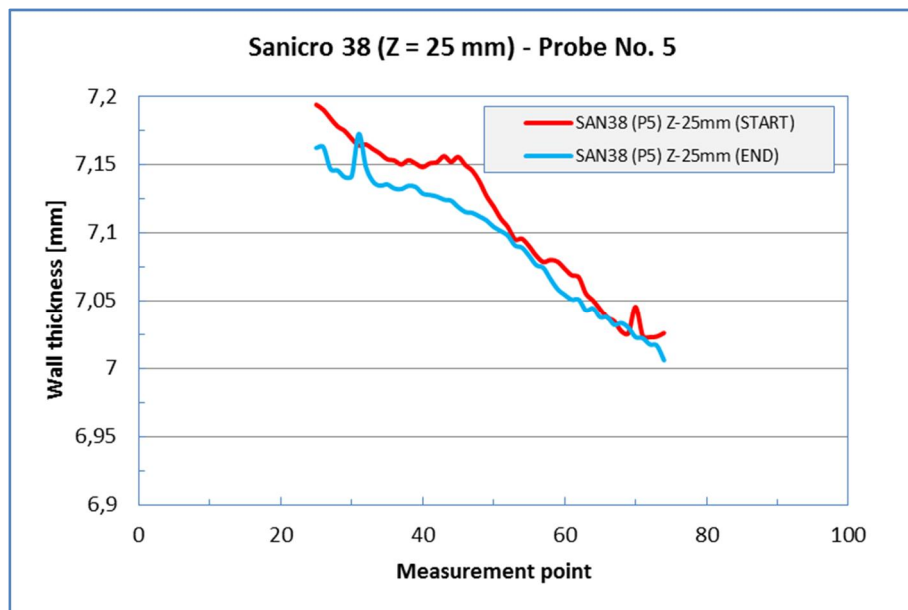


b)

Figure 55. Circumferential wall thinning curves from HR11N specimen (Probe No. 5): a) axial location $Z = 25$ mm and b) axial location $Z = 32$ mm.



a)



b)

Figure 56. Circumferential wall thickness profiles from Sanicro 38 specimen (Probe No. 5): a) axial location $Z = 15$ mm and b) axial location $Z = 25$ mm.

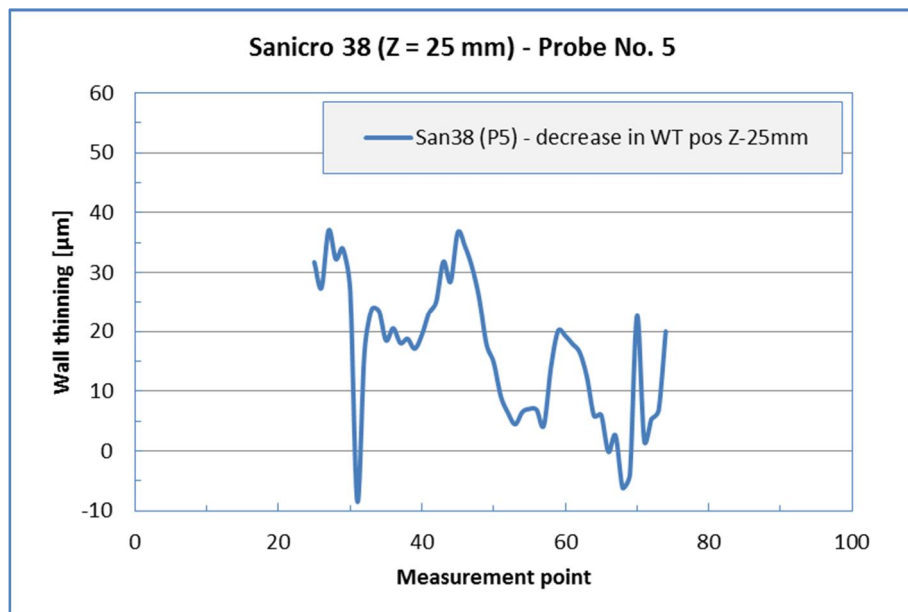
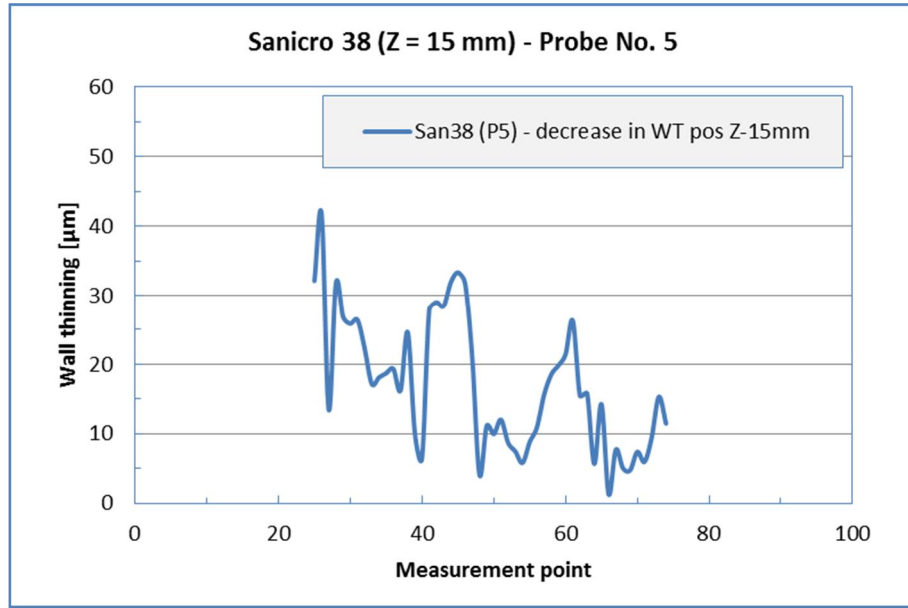
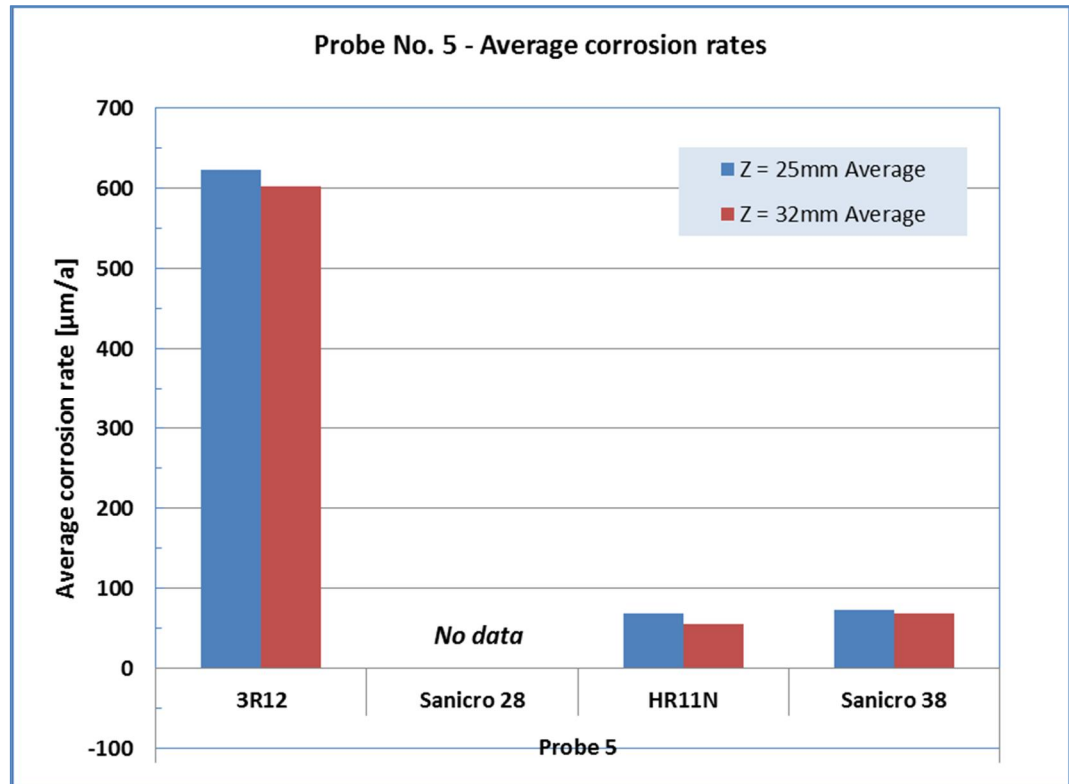
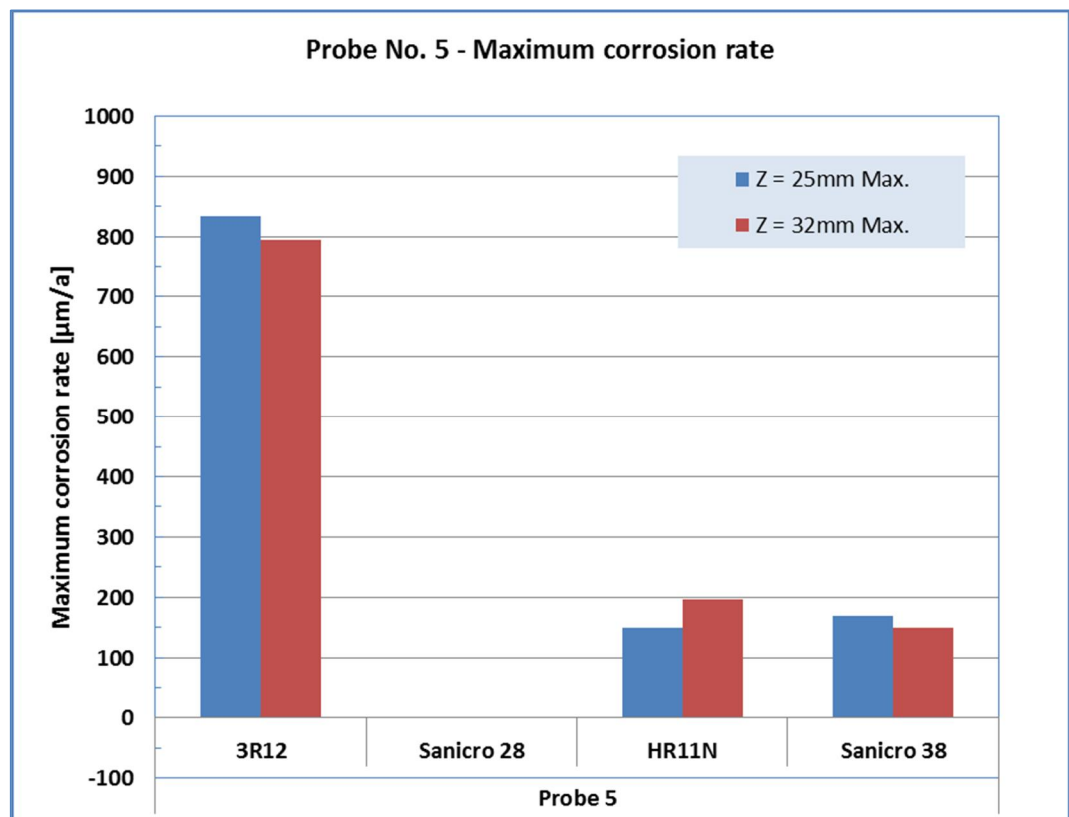


Figure 57. Circumferential wall thinning curves from Sanicro 38 specimen (Probe No. 5): a) axial location Z = 25 mm and b) axial location Z = 32 mm.



a)

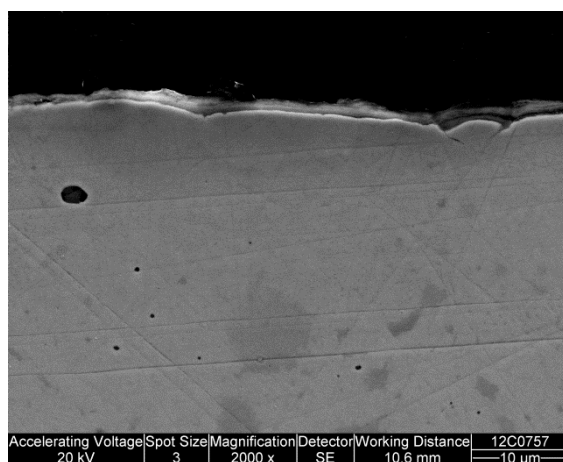


b)

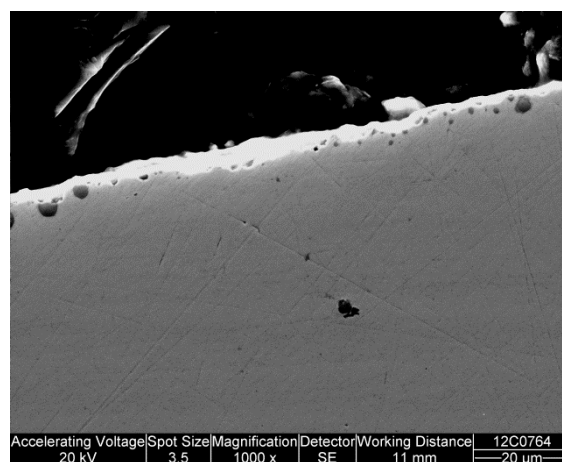
Figure 58. a) Average and b) maximum corrosion rates of the test materials calculated on the basis of the wall thickness measurements after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5).

4.5.2 Metallography

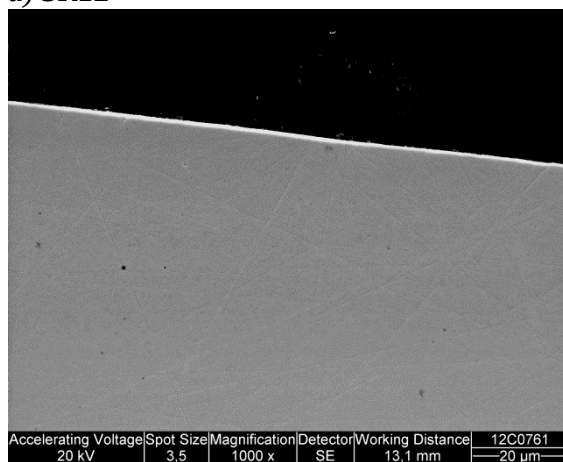
After the tests the samples were examined with optical microscope and/or SEM to determine the type of the corrosion attack. All samples had suffered from general thinning and no marked deposits or oxide/sulphide scales were observed on the surfaces, Figure 49. The layers found on 3R12, Sanicro 28, HR11N and Sanicro 38 were very thin ca. 2 μm in thickness. EDS analysis showed that iron and nickel depletion and chromium enrichment had taken place in some locations in all materials and that in these locations sulphur was also detected (Figure 50).



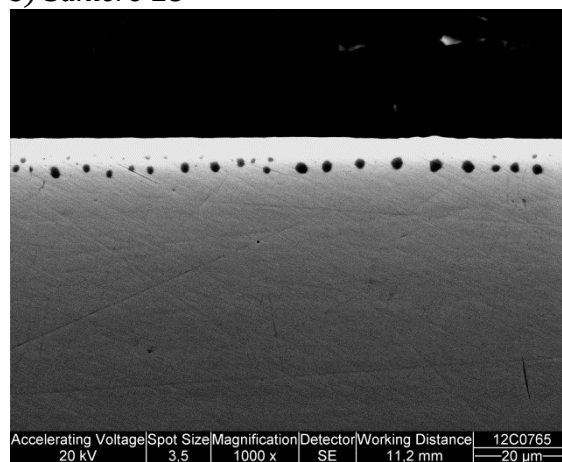
a) 3R12



b) Sanicro 28



c) HR11N



d) Sanicro 38

Figure 59. Cross sections from a) 3R12, b) Sanicro 28, c) HR11N and d) Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5).

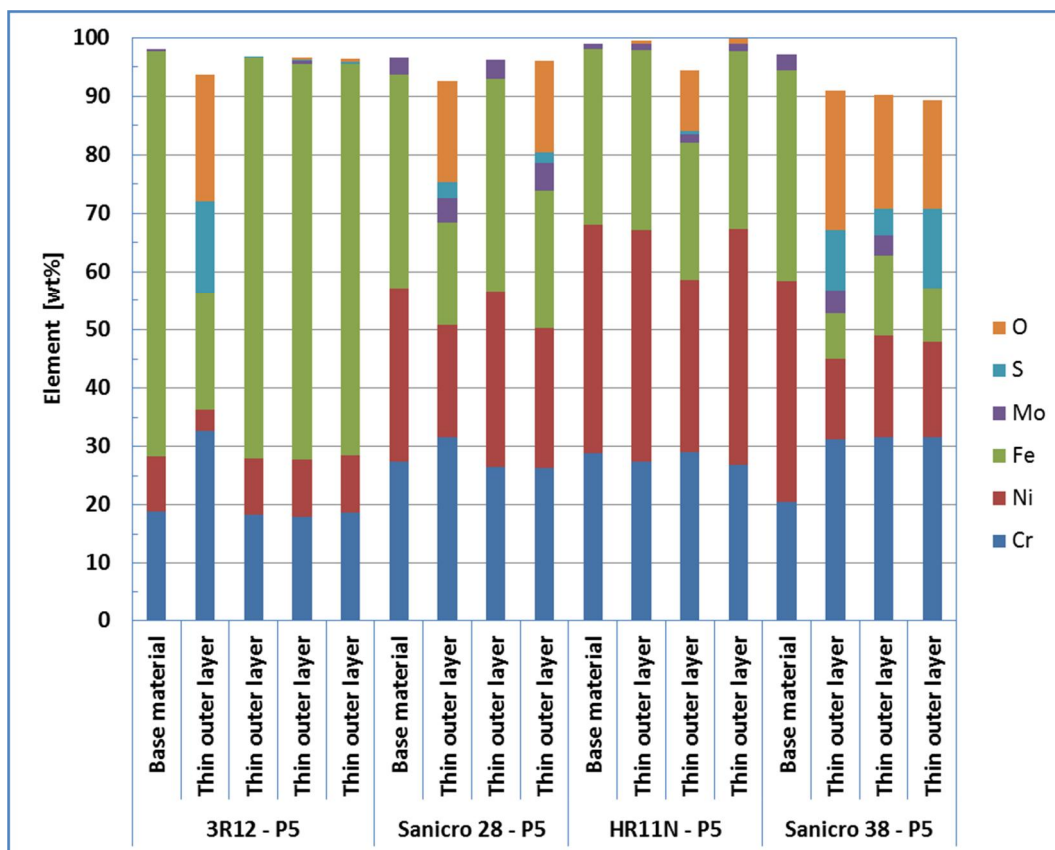


Figure 60. Results from the EDS analysis performed for the 3R12, Sanicro 28, HR11N and Sanicro 38 after 2157 h exposure in lower furnace at 440 °C (Probe test No. 5). Note: Quantitative results from cross sections, carbon excluded. Data from layers are from point analysis, whereas area analysis was used for base materials.

5 Conclusions

The coordinate measurement machine proved its applicability to determine wall thickness profiles from difficult shapes. In current samples the biggest problem was the specimen alignment i.e. it was impossible to measure the thickness profiles exactly from the same location before and after the test. This caused some error to the measurement results; especially to the maximum corrosion rates calculated from the tests No. 1-3, where the materials were tested in as received condition i.e. when the samples had surface scratches and dents. Another factor that affected to the accuracy was the surface deposits that were not completely removed during washing. Their adverse effect was clearly seen as negative average corrosion rate values in most resistant alloys.

Tests showed that polishing together with longer exposure time improves the accuracy, both of which are recommended to be used in future tests and especially when evaluating highly alloyed materials.

In current tests highest corrosion rate, ca. 4 mm/a, was measured for the carbon steel as expected. The traditional composite tube material 3R12 had the second highest corrosion rate, order of 0.6...0.8 mm/a at the temperature of 440 °C and ca. 0.4 mm/a at 430 °C (Figure 61). Based on the results of 3R12 the reproducibility of the probe tests was so good that different probe tests can be used to compare different materials to each other.

In current tests no marked differences were observed between Sanicro 38 and HR11N. Their maximum corrosion rates were in the order of 0.15...0.2 mm/a in the long term (>2000 h) test, i.e. about four times lower than that of the 3R12 (Figure 61).

In short term (<1000 h) tests the corrosion resistance of the 3RE28, 3XRE28 and Sanicro 28 were as good as or even slightly better than that of the Sanicro 38 or HR11N (Figure 62). Because the 3RE28 and 3XRE28 were not included in the long term tests and no results were obtained for the Sanicro 28 from the long term test No. 5, due to the misplaced thermocouple, it is recommended to verify their promising performance with long term tests in the future.

The results for the Super 625 were inconsistent. In short term 750 h test at 430 °C it's corrosion resistance was only slightly better than that of the 3R12, but in the long term 2154 h test at 440 °C it's resistance was even better than that of the Sanicro 38 and HR11N (Figure 62). Similar kind of behaviour was observed in Sanicro 67. In short term 744 h test at 440 °C it's corrosion resistance was only slightly better than that of the Sanicro 38 and HR11N, but in the long term 2154 h test at 440 °C it's corrosion rate was only 1/10 of that of the Sanicro 38 and HR11N and 1/5 of the Super 625.

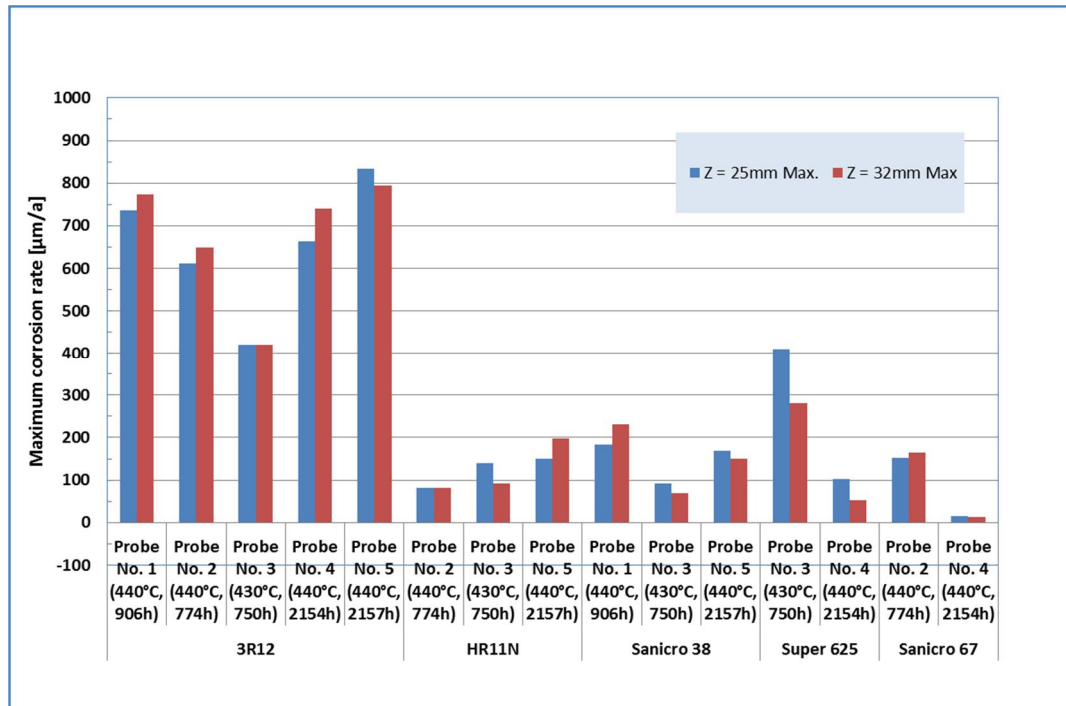


Figure 61. Calculated maximum corrosion rates for the 3R12, HR11N, Sanicro 38, Super 625 and Sanicro 67 materials from the probe test No. 1 - 5.

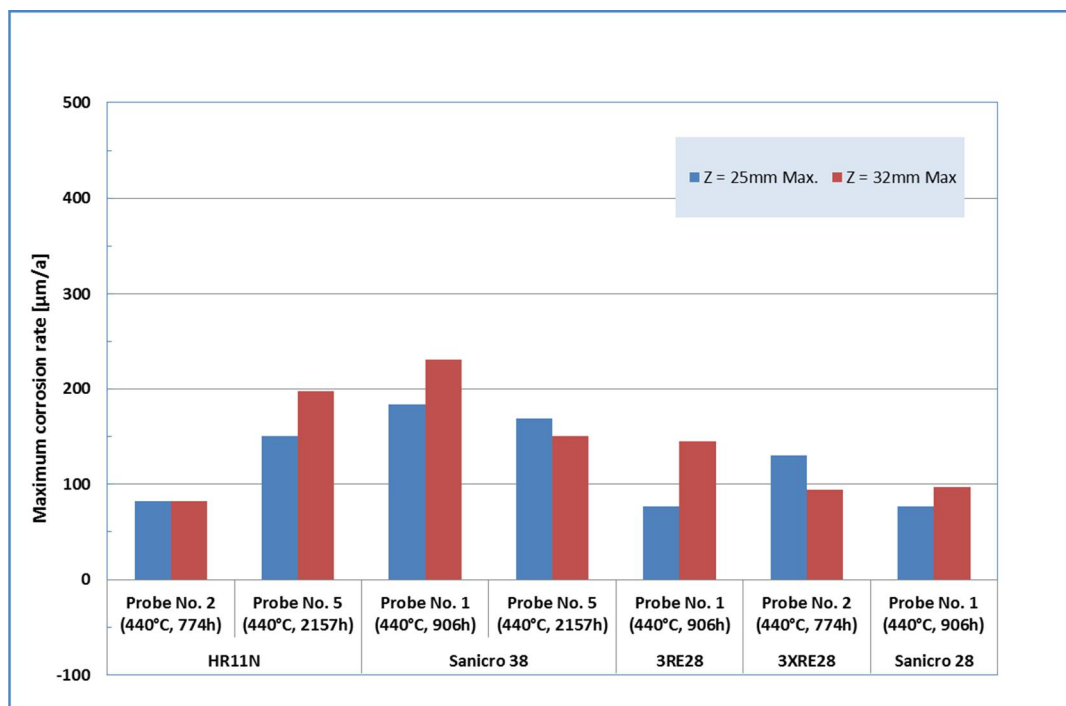


Figure 62. Calculated maximum corrosion rates for the 3RE28, 3XRE28, HR11N and Sanicro 38 from the probe test No. 1-3 and 5.

6 Summary

The aim of this study was to evaluate different potential cladding materials for compound tubes in actual recovery boiler lower furnace conditions. The work was divided so that specimen manufacturing and probe tests were conducted by Boildec Oy, whereas the sample characterisation was performed by VTT. The test materials were carbon steel; austenitic stainless steels 3R12, 3RE28 and 3XRE28; high nickel alloys Sanicro 28, HR11N and Sanicro 38 and two nickel base alloys Super 625 and Sanicro 67. The test temperature was 440°C and test duration varied from 1000 to 2700 hours.

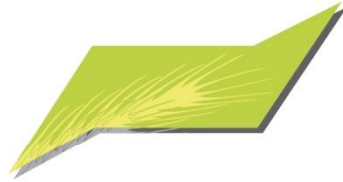
The results show that materials with superior corrosion resistance to AISI 304L exist and hence corrosion in lower furnace can be managed by proper material selection. Corrosion resistance in lower furnace conditions is improved by alloying, especially by chromium. According to the wall thickness measurements the test materials can be put in following order based on increased resistance:

C-steel << 3R12 < HR11N ~ Sanicro 38 (~ Sanicro 28 ~ 3RE28/3XRE28) < Super 625 < Sanicro 67

The carbon steel corroded at extremely high rate (>4 mm/a) at the temperature of 440 °C. Also the 3R12 (AISI 304L) corrodes in such high rate (>0.6 mm/a) at 440 °C that it can't be safely used in the lower furnace in the future high pressure recovery boilers, where material temperatures are expected to rise to level of 400...440 °C. The performance of the Sanicro 38 and HR11N was satisfactory in long term test at 440 °C ($CR_{max} \sim 0.1...0.2$ mm/a), but it is recommended to verify their performance also at lower temperature (400 °C). The new material group which looks promising is the high chromium alloys 3RE28/3XRE28 and Sanicro 28, but their long term performance should be verified in the future. If the corrosion resistance is the determining factor, the Sanicro 67 seems to be a good material for future boilers, since its corrosion rate was lowest from the studied alloys. Based on the long term test the Super 625 in the second best choice for the future high pressure boiler, but because of its relatively high corrosion rate in short term test more and longer tests are needed to verify its performance.

LIITE 9

**SKYREC/LTR: Probe Study of Corrosion in the Economizers of a Kraft
Recovery Boiler – presentation 17.12.2012**



PROCESS CHEMISTRY CENTRE



Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler

Tor Laurén

Emil Vainio

Nikolai DeMartini

Mikko Hupa

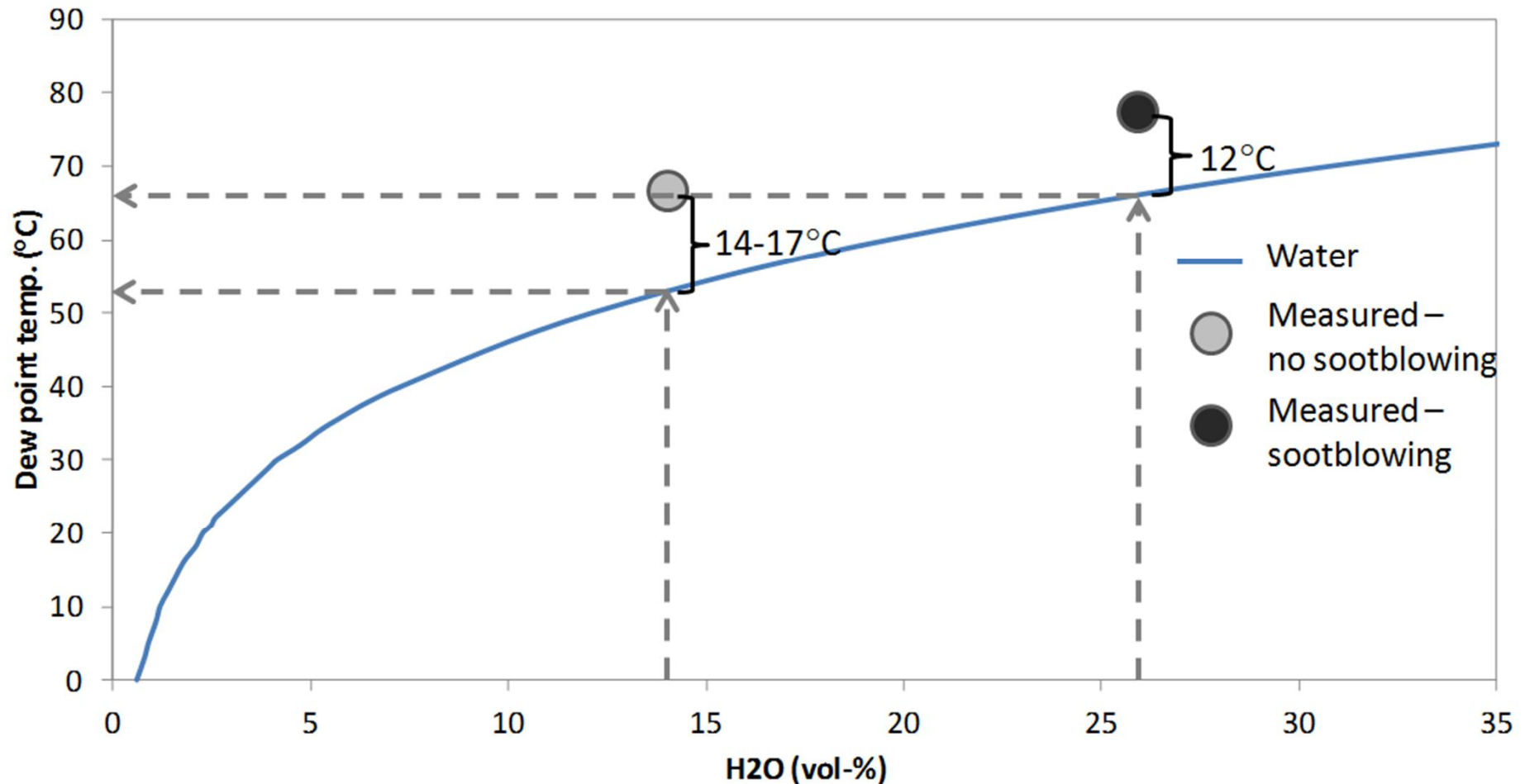
Objectives

To better understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler

Continuation of the dew point project made in two recovery boilers.

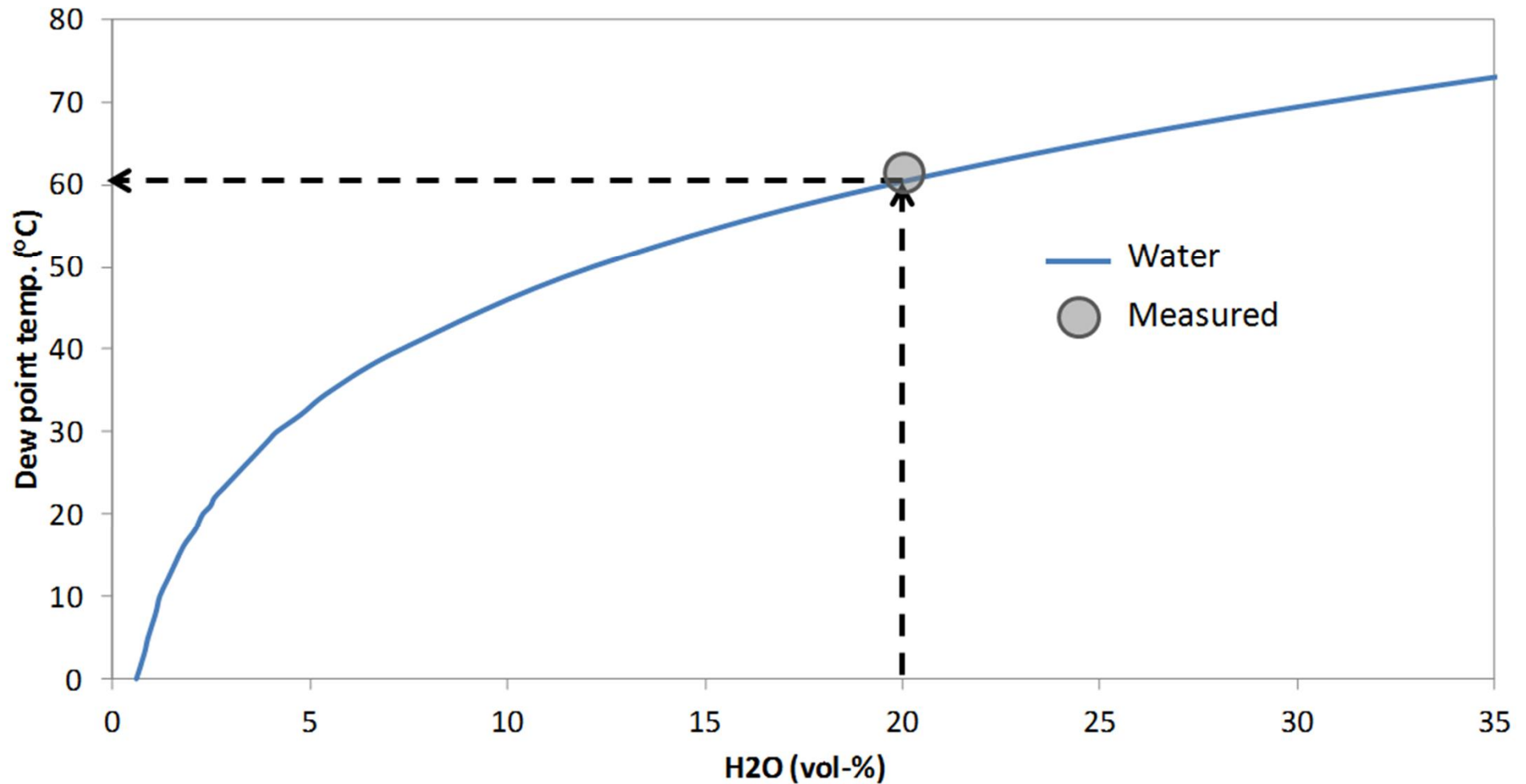


Water dew point and measured dew point- Heinola



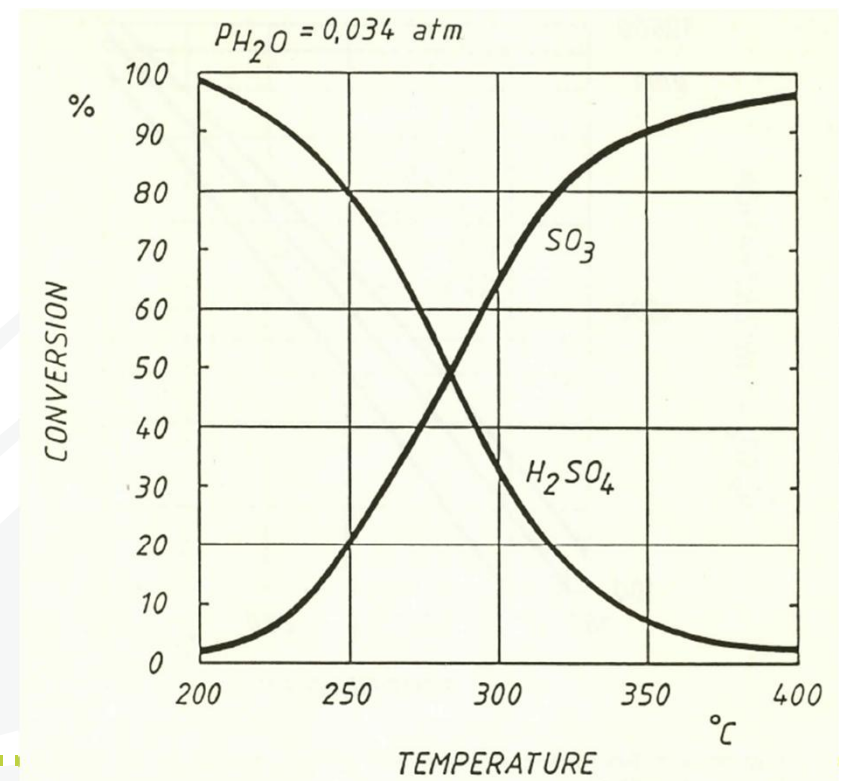
Elevated dew point due to hygroscopic salts: Na_2SO_4 (84% RH) ja NaHSO_4 (52% RH)

Water dew point and measured dew point - Rauma



$\text{SO}_3(\text{g})$ and $\text{H}_2\text{SO}_4(\text{g})$ formation

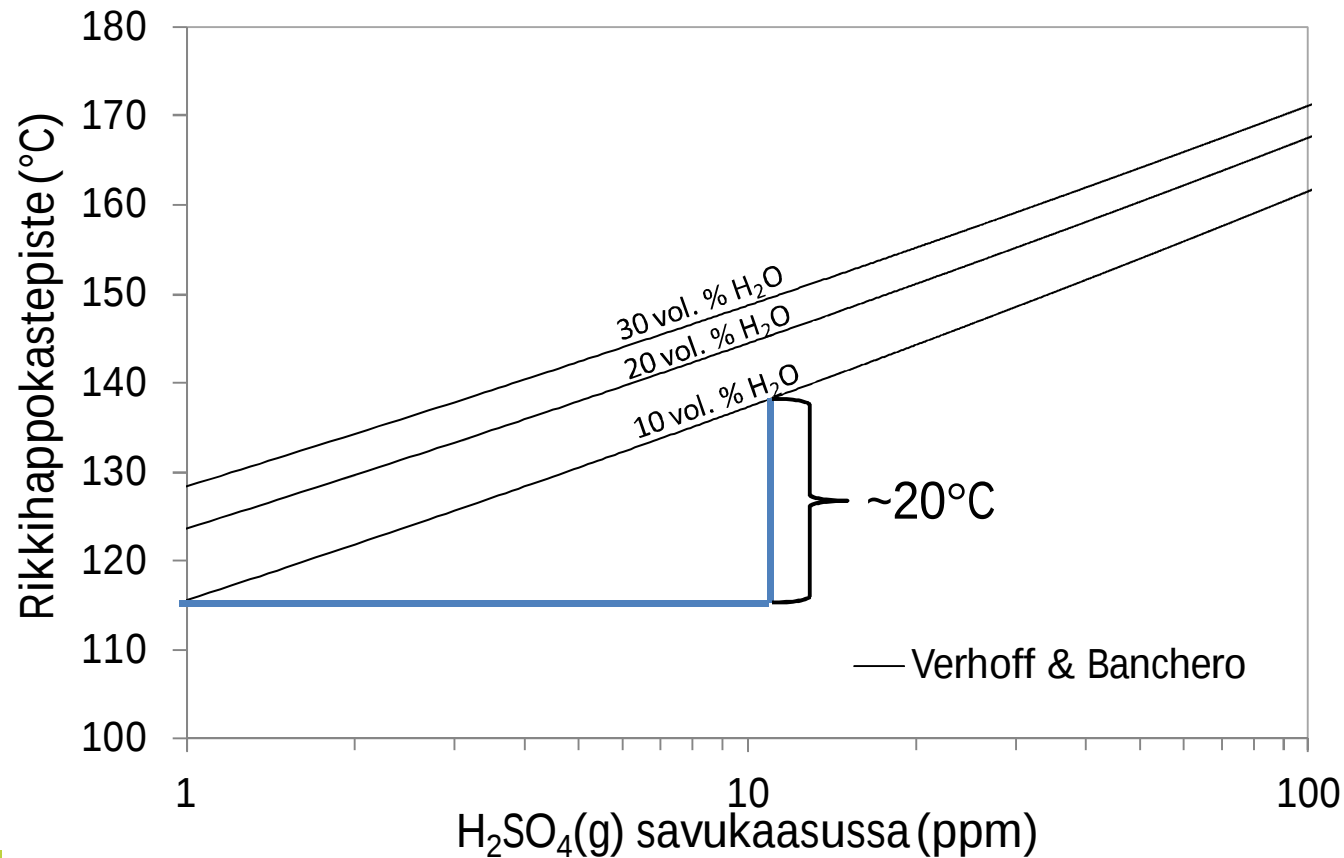
- Sulfur in fuel is oxidized to SO_2
- A fraction of the SO_2 is further oxidized to SO_3
- $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{g})$
- At 200°C mostly $\text{H}_2\text{SO}_4(\text{g})$
- Condensation of sulfuric acid may lead to severe low temp corrosion



R. Backman et al.

Sulfuric acid dew point

- When the $\text{H}_2\text{SO}_4(\text{g})$ concentration is known the dew point temperature can be estimated

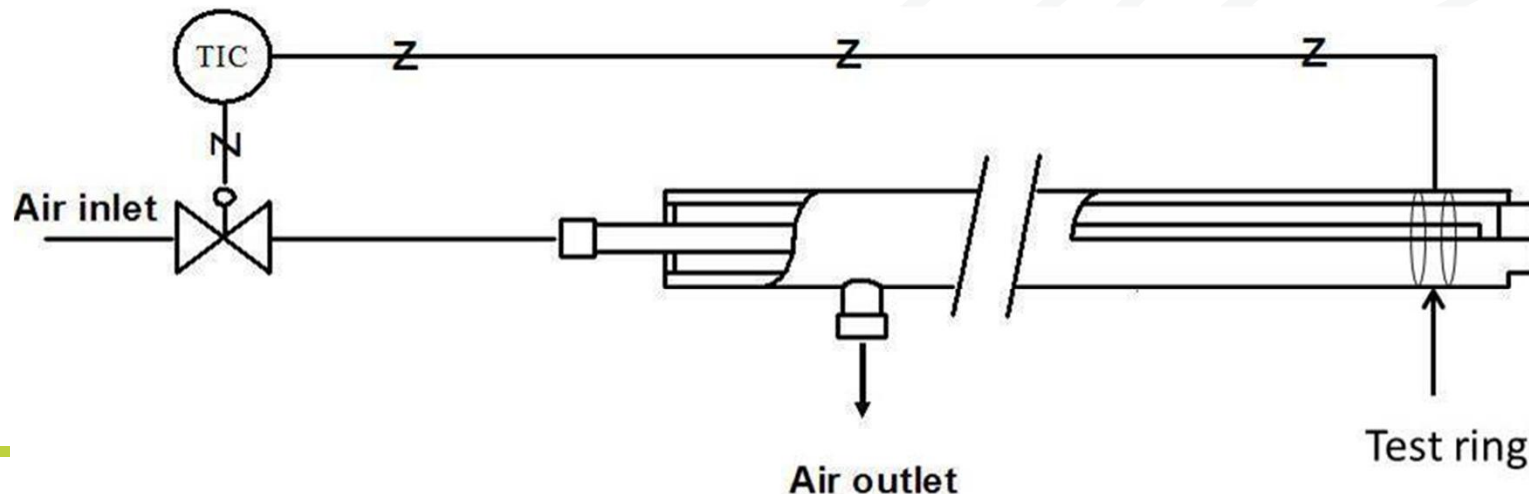


Methods

1. Corrosion measurements with a corrosion probe during:
 - Normal operation
 - Water wash
 - Oil firing
 2. $\text{H}_2\text{SO}_4(\text{g})$ and SO_2 measurements during oil combustion
 3. Dew point measurements (Land)
-

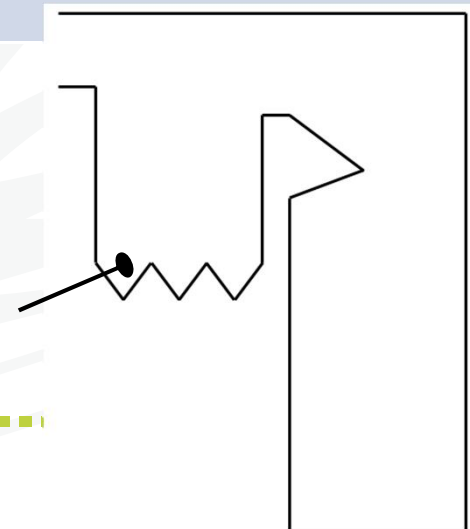
1. Corrosion test

- Corrosion probe
- Exchangable carbon steel ring in probe tip
- Ring is weighed before and after exposure
- Thermocouple located in the ring, temperature adjusted with pressurized air (PID-controller)
- 90°C was used was ring temperature



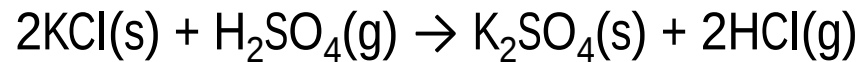
Corrosion probe tests

Date In	Date Out	Probe Temperature	Comments
31.8.2012	31.8.2012	80 °C	2h probe test
31.8.2012	31.8.2012	75 °C	2h probe test
31.8.2012	4.10.2012	90 °C	811h probe test, probe pulled before water wash
31.8.2012	17.10.2012	90 °C	1124h probe test, probe pulled after water wash, but before acid wash (oil firing)
19.10.2012	19.10.2012	90 °C	2h probe test during acid wash (oil firing)

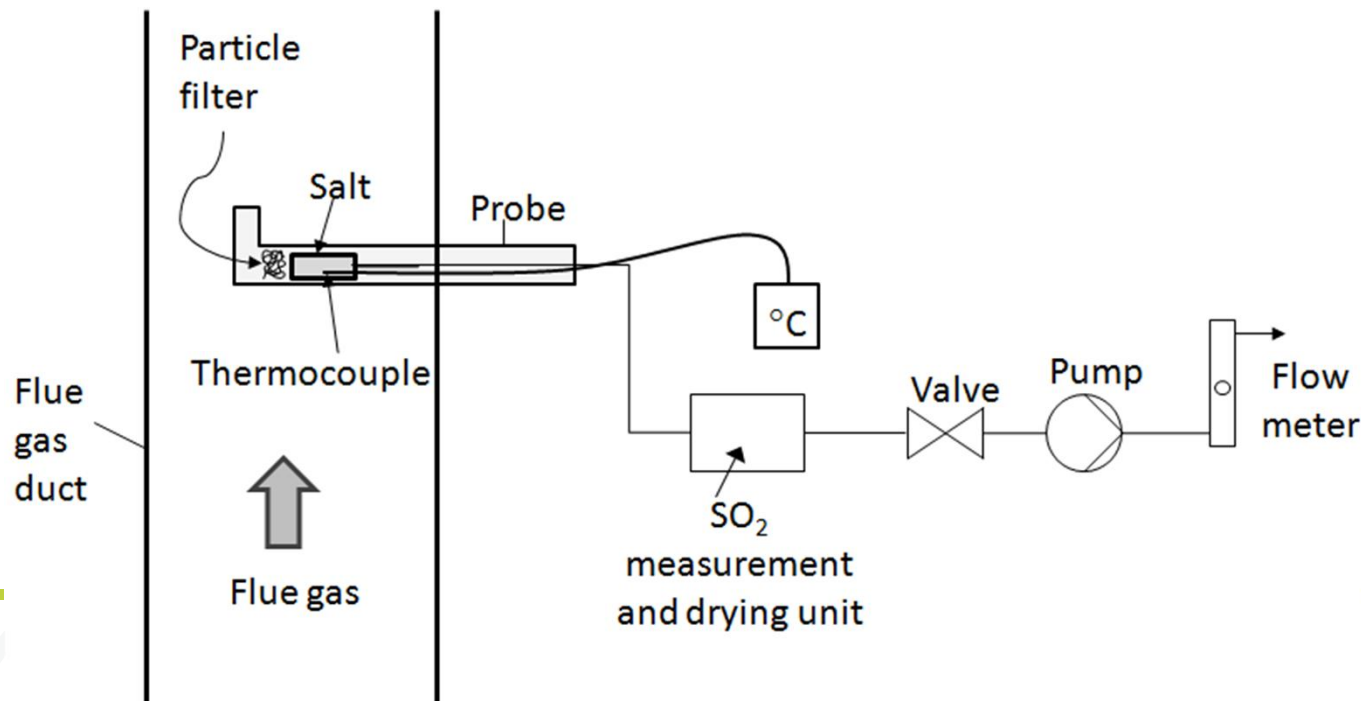


2. H₂SO₄(g) measurements

- Flue gas led through a salt (KCl) and H₂SO₄ is absorbed in the salt



- Salt dissolved in deionized distilled water and analyzed for sulfate ions with ion chromatography

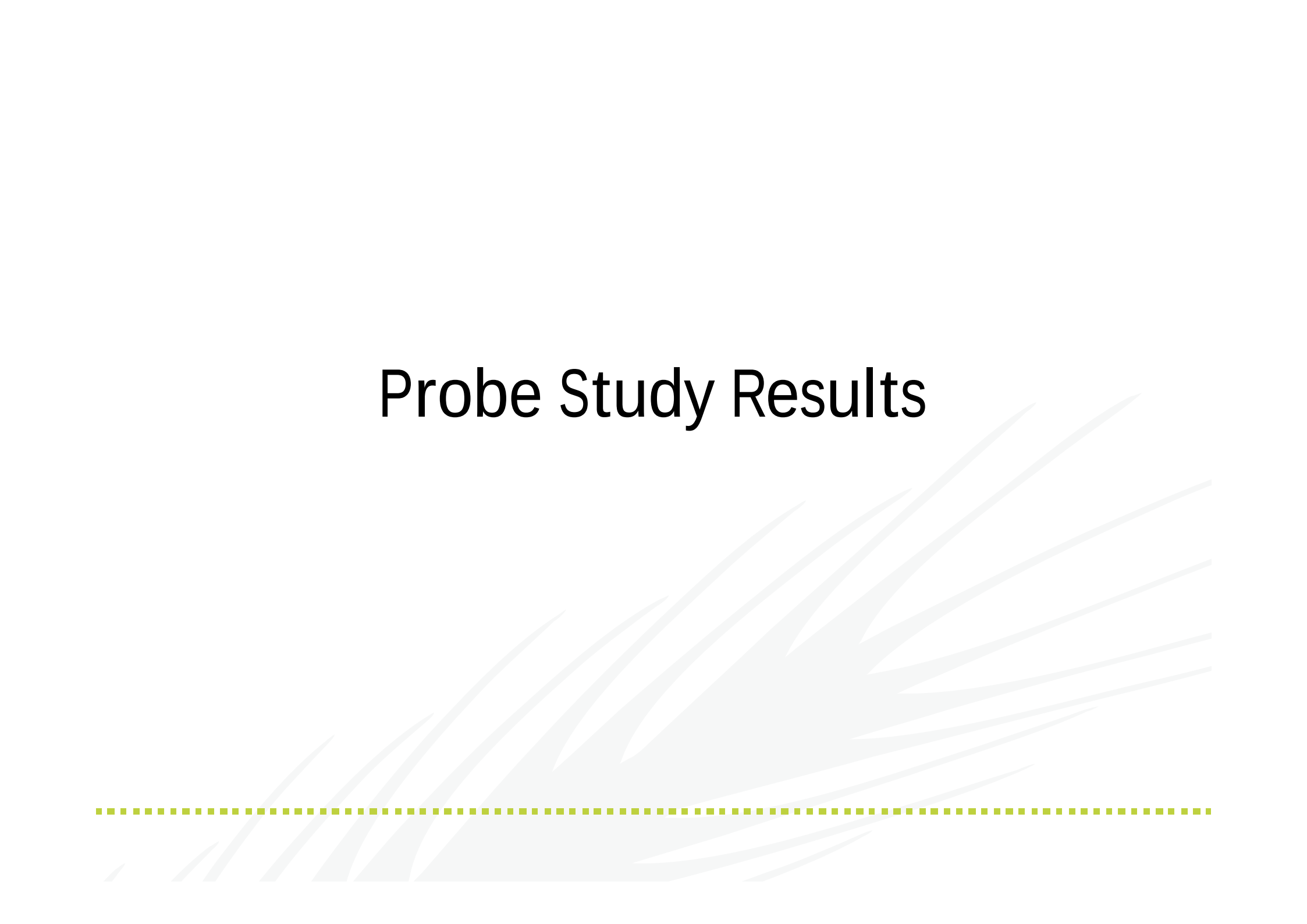


3. Dew point measurement

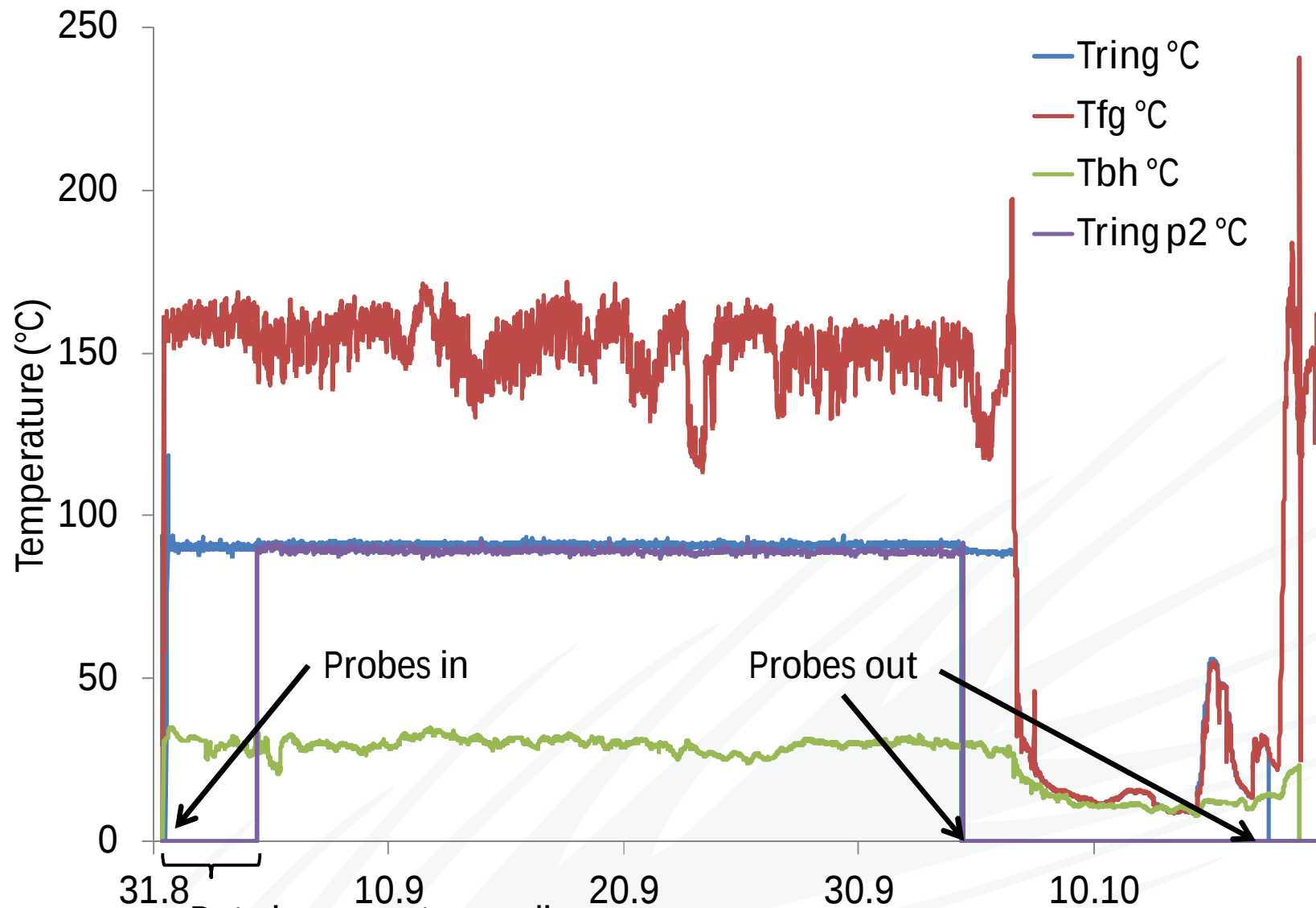
- Dew point probe (Land)
- Two electrodes in the probe tip
- Probe tip cooled with pressurized air
- When dew point reached, water or acid, a current is detected



Probe Study Results



Probe and Flue Gas Temperatures



Tbh: Boiler House T

Probe After 811h of Normal Operation



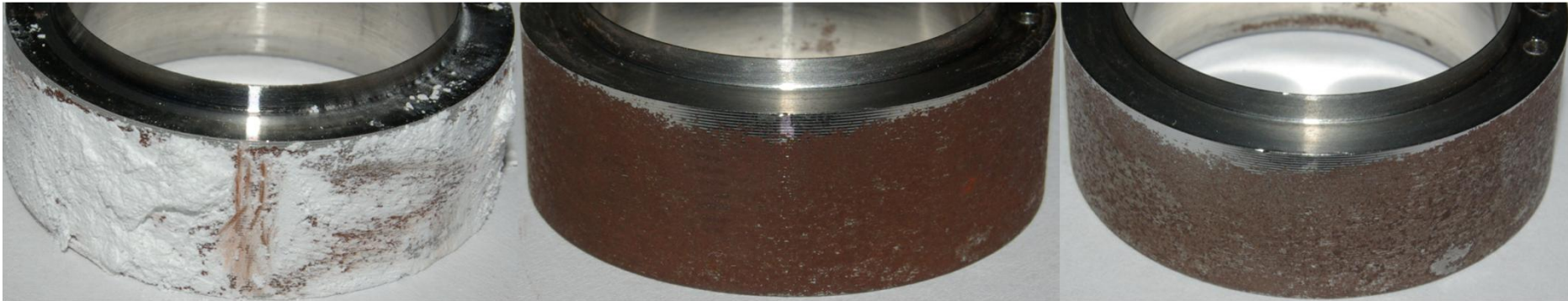
Ring after 811h normal operation

up

uncleaned ring

water+aceton+paper

30s acid wash



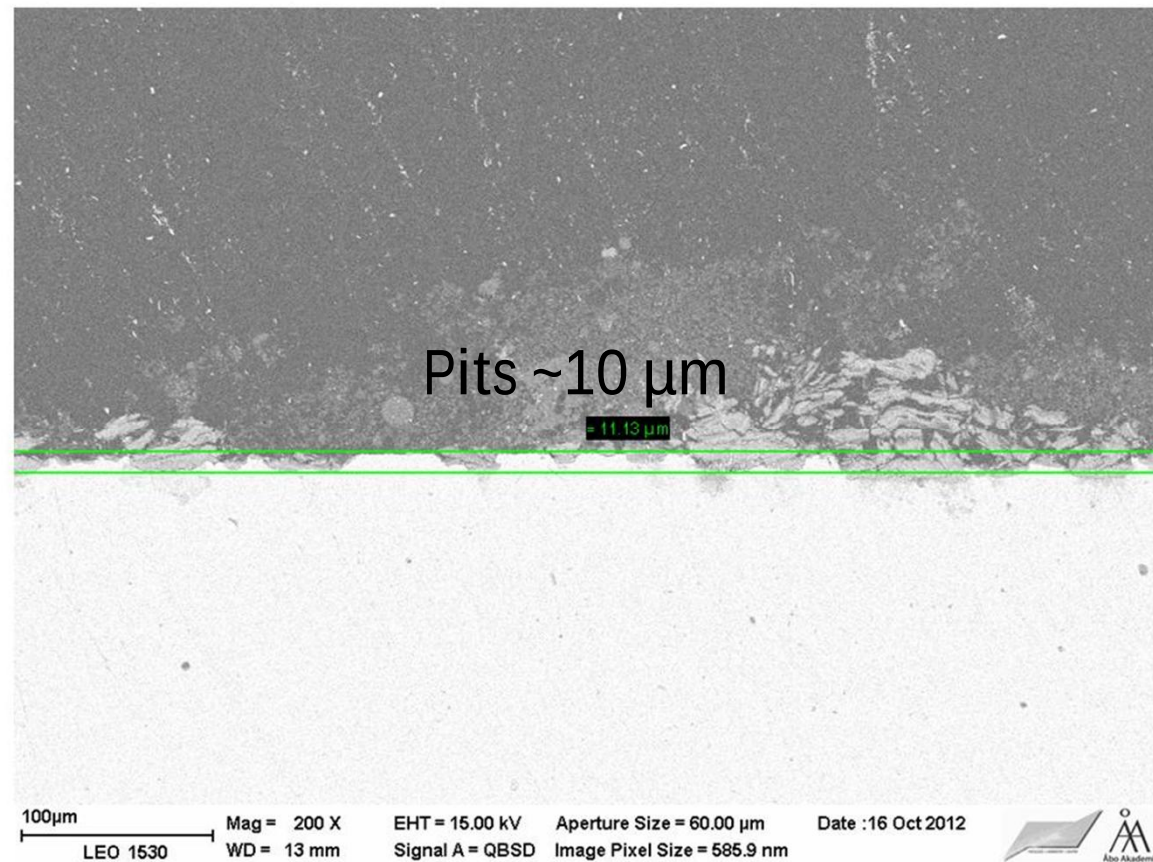
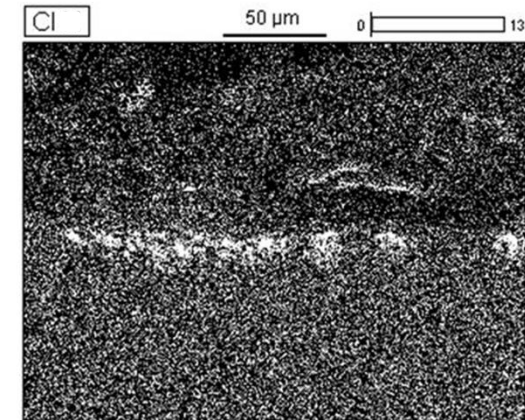
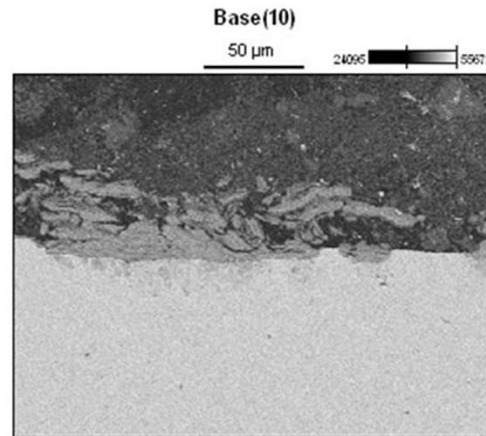
down

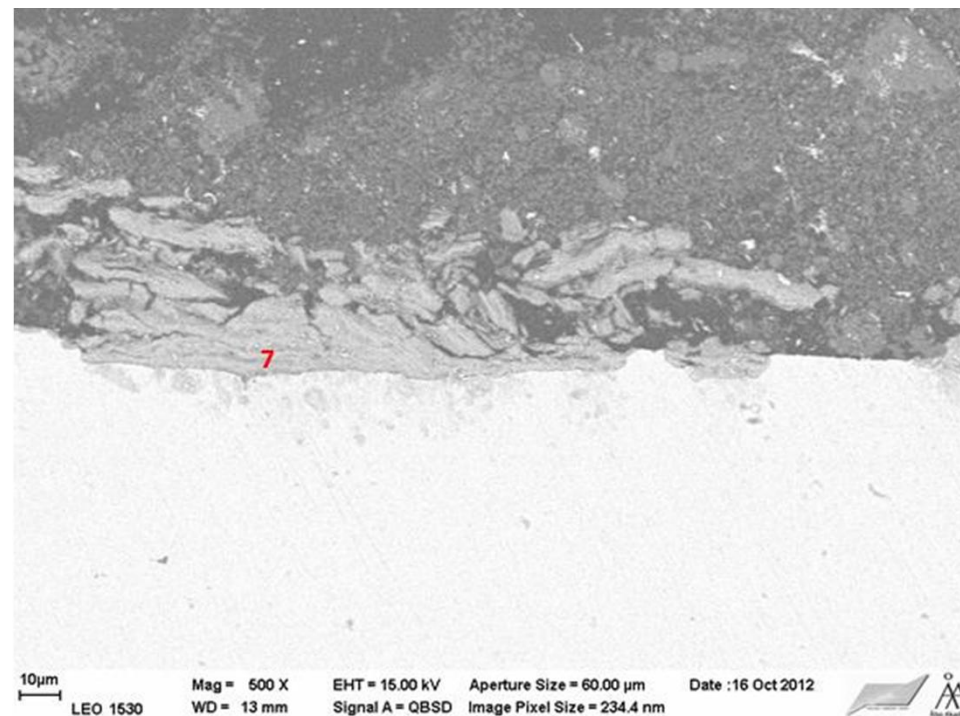
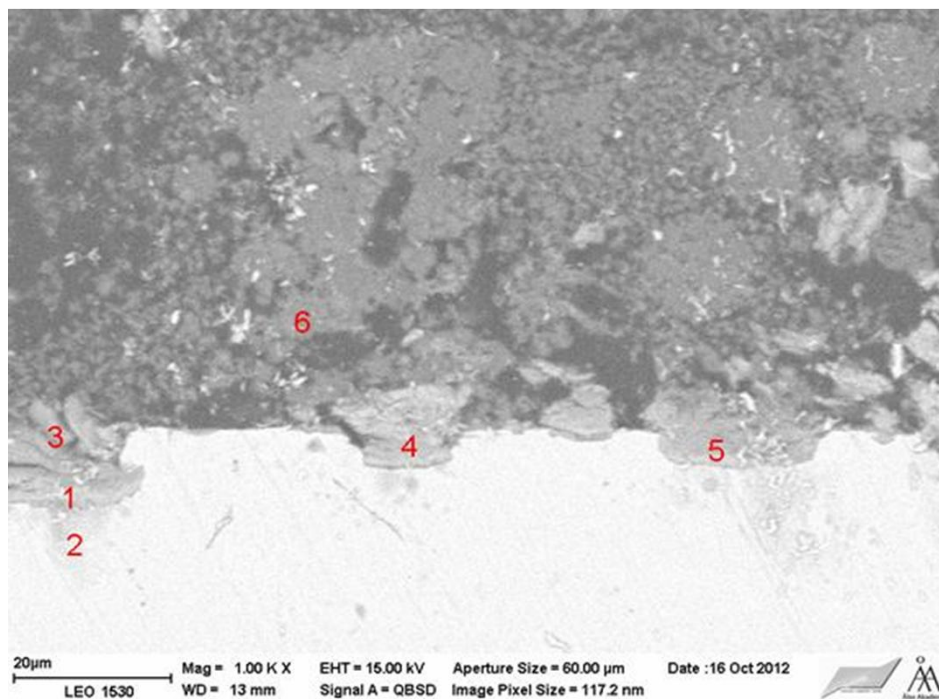


Note: Side pointing downwards (gravimetrically) -> No iron oxide



811h exposure
"normal" plant
operation





atom-%

Spot	Na	Al	Si	S	Cl	K	Mn	Fe
1	1.3	0.3	0.2	0.1	0.5	0.1	0.4	38.2
2	0.0	0.3	0.2	0.0	0.6	0.0		39.3
3	3.1		0.3	1.4	0.4	1.5		34.9
4	3.7	0.3	0.2	0.6	0.7	0.3		36.4
5	1.7	0.5	0.2	0.2	1.2	0.4	0.4	37.2
6	20.5			13.5	2.3	7.3		1.1
7	0.4	0.5	0.3	0.1	2.5	0.1	0.3	37.5

Cl not balanced by Na or K

Probe after water wash - 1124h total
(811h "normal" operation + water wash)



Ring after 1124h

up uncleaned ring



water+aceton+paper



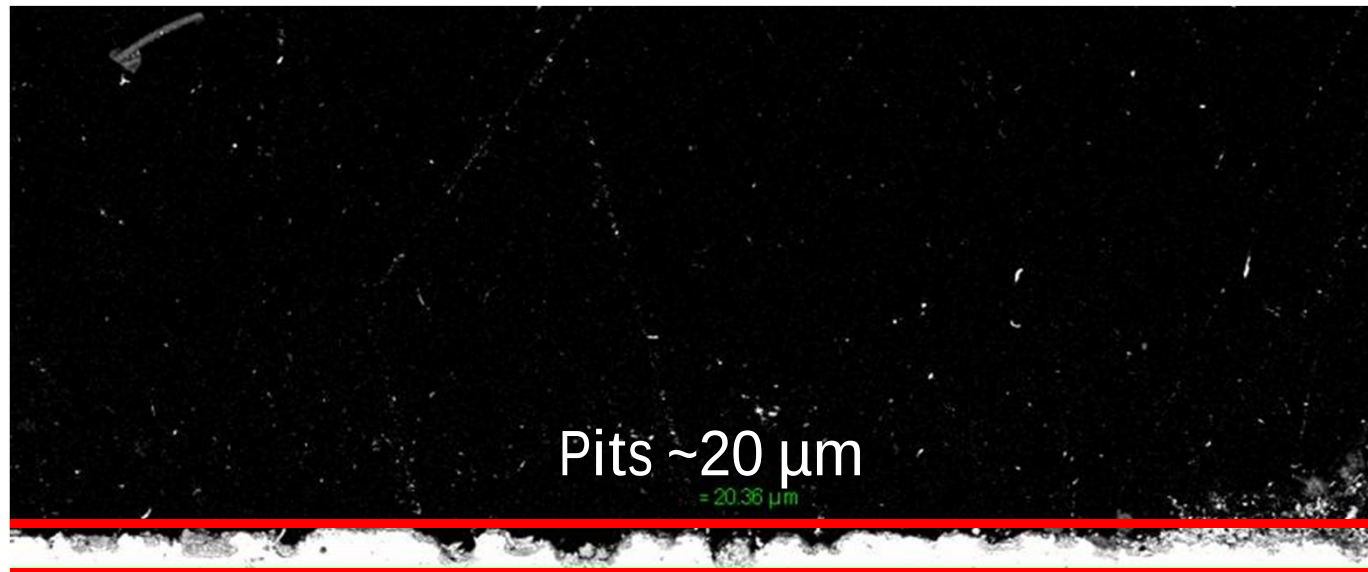
down



Again areas
without
corrosion
downwards



811h exposure "normal" plant operation
+ boiler shutdown & water wash totally
1124h



- No chlorine or sulfur found in the corrosion layer after the water wash

30 μm
LEO 1530

Mag = 196 X
WD = 13 mm

EHT = 20.00 kV
Signal A = QBSD

Aperture Size = 60.00 μm
Image Pixel Size = 598.9 nm

Date :1 Nov 2012



SEM results Sample 6. Pit corrosion. No traces of chlorine in pits.

Corrosion results

Exposure time	Operation	Ring temperature	Ring Weight Loss (mg)	Avg. Corrosion Layer Thickness (μm)	Calculated Avg. Corrosion (mm/yr)
2 h	Normal	80 °C	0	0	
2 h	Normal	75 °C	0	0	
811 h	Normal	90 °C	22	2*	0.02
1124 h	Normal + water wash	90 °C	72	6**	0.05

*Pit corrosion, pits ~10 μm deep

**Pit corrosion, pits ~20 μm deep

Measurements during oil burning

- Dew point and SO_3 were measured during oil burning
- A 2h probe (90 °C) study was also made



Flue gas composition during oil burning

Date 19.10.2012

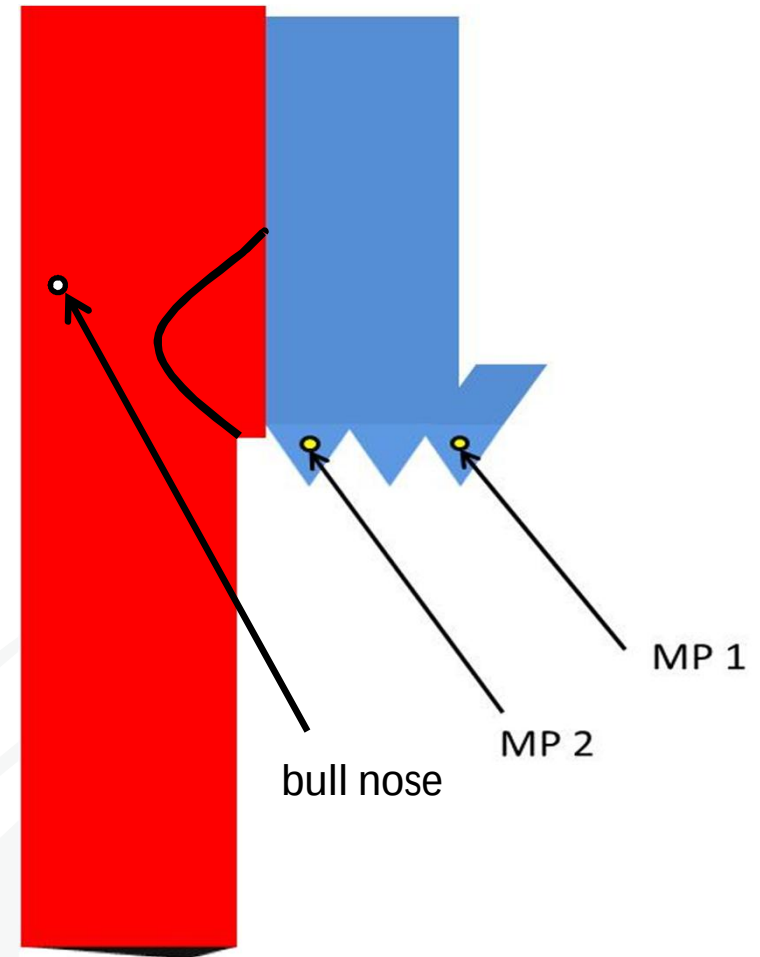
Time	Oil (t/h)	O ₂ (%)	SO ₂ (ppm)	SO ₂ (ppm 0% O ₂)	Air Ratio (λ)	Calculated Water Dewpoint (°C)
9:36	1.8	19.4	38	507	13.4	19
11:57	3.9	17.9	83	574	6.9	25

- Calculated Fuel Oil Sulfur Content 0.8% (based on flue gas analysis)

Sampling positions and SO₃ results

Date	Time	MP	SO ₃ /H ₂ SO ₄ (ppm)	Temp (°C)	Oil burners
18.10	19:20- 19:50	b.n.	1	240	2
19.10	10:05- 10:35	1	1	150	2
	12:15- 12:35	1	1	165	4
	16:27- 16:37	2	3	240	4
	16:53- 17:13	2	2	240	4

b.n.: bull nose



- No acid dewpoint was found in the dewpoint measurement

Ring after 2h exposure during oil burning

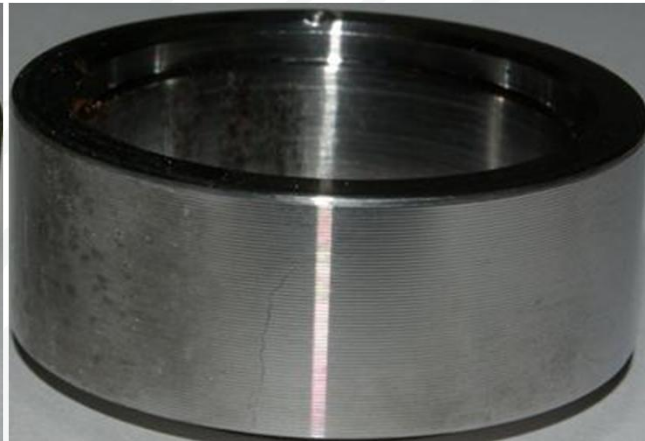
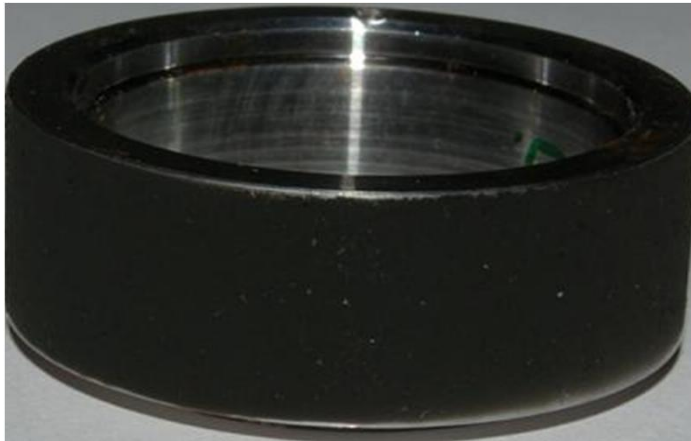
up

uncleaned ring

water+aceton+paper



down



Conclusions

- No significant corrosion seen under normal operation or after the water wash
- No acid dew point seen during oil burning
 - In part due to the extremely high dilution
- More heat can be removed from the flue gas without fear of acid dewpoint corrosion under normal operation



LIITE 10

**SKYREC/LTR: Probe Study of Corrosion in the Economizers of a Kraft
Recovery Boiler – draft report 16.12.2012**



Draft Report: Probe Study of Corrosion in the Economizers of a Kraft Recovery Boiler

Nikolai DeMartini, Tor Laurén, Emil Vainio, Mikko Hupa

Åbo Akademi University

17 December 2012

Contents:

<i>Summary</i>	<i>3</i>
<i>1. Introduction</i>	<i>4</i>
<i>2. Method</i>	<i>5</i>
<i>3. Results</i>	<i>7</i>
<i>4. Conclusions</i>	<i>13</i>

Summary

Long term probe studies (~1000h) were carried out at the Rauma mill in the economizers to study corrosion in the economizers. The air cooled probes were kept at 90 °C, above the water dew point, but well below an H_2SO_4 dew point. One was pulled out after 811h of normal operation and the second was pulled out after 1124h of normal operation plus the water wash. Negligible corrosion was seen in both cases. No acid dew point corrosion was seen indicating that modern mills can recover more heat from flue gases.

In addition, the dew point, SO_3 and corrosion (2h probe study) were measured during oil burning. Conditions during oil burning were special in that a very high air-to-fuel ratio was used. While up to 4 ppm of SO_3 was measured, no acid dew point or corrosion was seen. Further work has been proposed to see if corrosion would be seen during start up of a Kraft recovery boiler on oil.

1. Introduction

The objective of this work was to better understand the cause of corrosion on the flue gas side of heat transfer tubes in the economizer section of a recovery boiler. In particular this work was to clarify the conclusion of the dew point measurements at Rauma and Heinola in a previous study that indicated that there is no H_2SO_4 acid dew point, Figure 1.

The question then came up, why some mills see corrosion in the economizers. One subsequent hypothesis was that corrosion was promoted during the water wash. This long term probe test was designed to help clarify these earlier findings and questions.

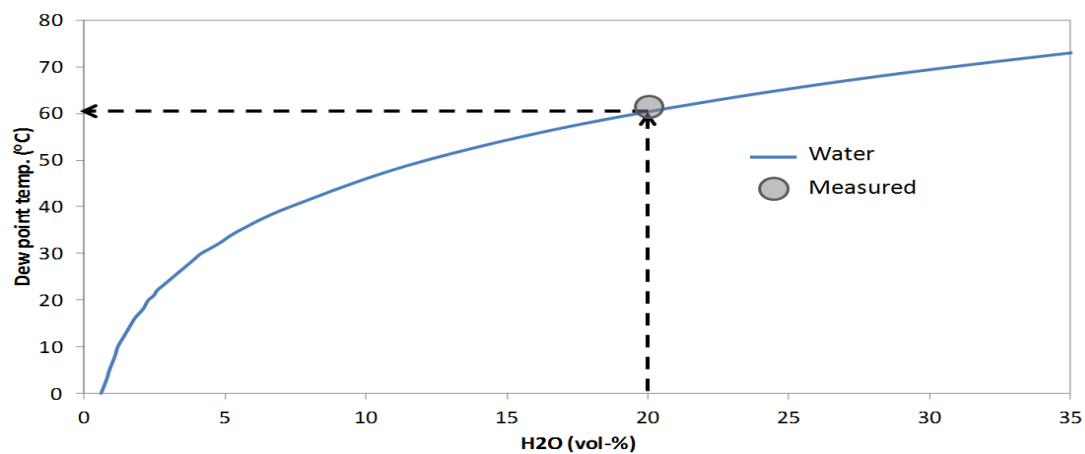


Figure 1. Water dew point temperature vs. flue gas water content. Measured dew point was for Rauma.

2. Method

Two probes were inserted into the economizer section at Rauma at the same time. Both probes were kept at 90 °C by air cooling. One was pulled just prior to the planned recovery boiler shutdown and the second was pulled after the water wash. A temperature of 90 °C was chosen because it is well above the water dewpoint, even in the presence of HCl and salt, but below a H_2SO_4 dewpoint, Figure 2. It is also well above the temperature water is absorbed by the salt due to the hygroscopic nature of salts such as Na_2SO_4 , Figure 3. The hygroscopic nature of salt is shown for both Na_2SO_4 and NaHSO_4 in Figure 3, but only NaHSO_4 is not present in the dust in Rauma. The presence of Na_2SO_4 is expected to result condensation at temperatures a few degrees °C above the water dew point. The choice of 90 °C was confirmed by two 2h probe studies, one at 80 °C and one at 75 °C. The schedule for the probe studies are given in Table I.

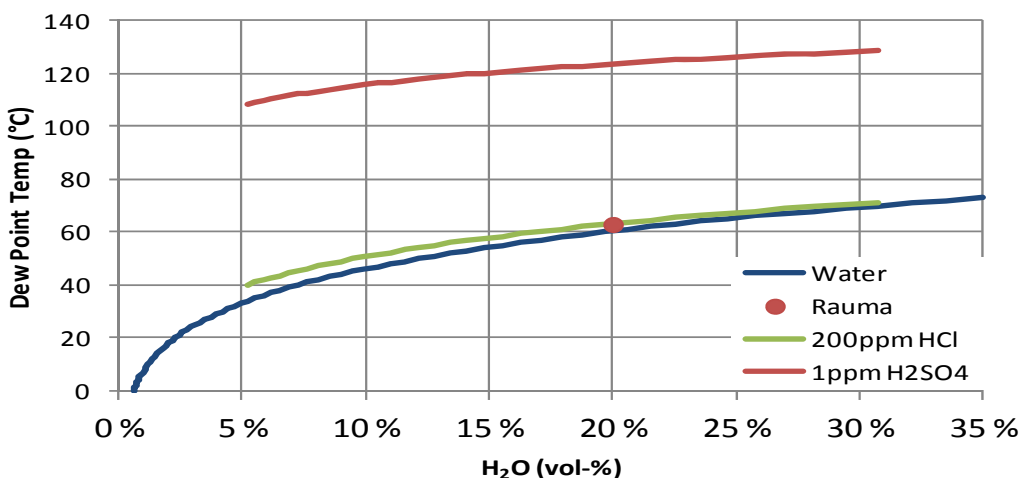


Figure 2. Water dew point and acid dew points based on 200 ppm HCl or 1 ppm H_2SO_4 as well as the measured dew point at Rauma.

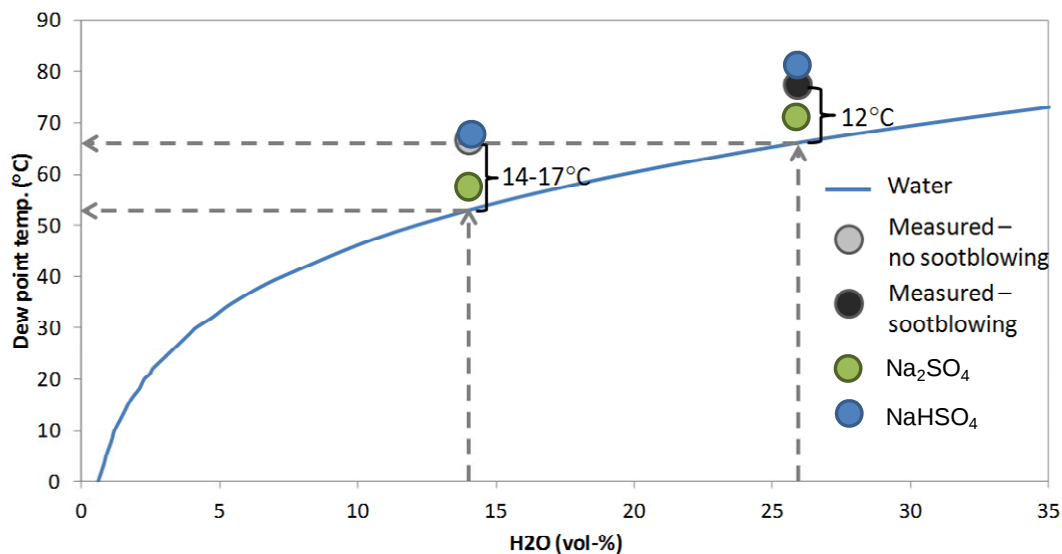


Figure 3. Effect of the salts NaHSO_4 and Na_2SO_4 on dew point. Dew points were measured at Heinola with and without sootblowing.

Additionally, SO_2 and SO_3 were measured in the flue gas and short term probe corrosion tests during oil firing in the recovery boiler. The oil firing was carried out under very special circumstances in which very high air-to-fuel ratios resulting in a flue gas with comparatively low SO_2 and low levels of H_2O .

Table I. Schedule for the probe studies.

Date In	Date Out	Probe Temp.	Comments
31.8.2012	31.8.2012	80 °C	2h probe test
31.8.2012	31.8.2012	75 °C	2h probe test
31.8.2012	4.10.2012	90 °C	811h probe test, probe pulled before water wash
31.8.2012	17.10.2012	90 °C	1124h probe test, probe pulled after water wash, but before oil firing
19.10.2012	19.10.2012	90 °C	2h probe test during oil firing

3. Results

The flue gas temperature in the economizers was about 150 °C and did not drop below about 110 °C during normal operation, Figure 4. The probes were isothermal at 90 °C. The data logger did not record the temperature for one of the probes for the first few days, but the conditions were the same for both probes.

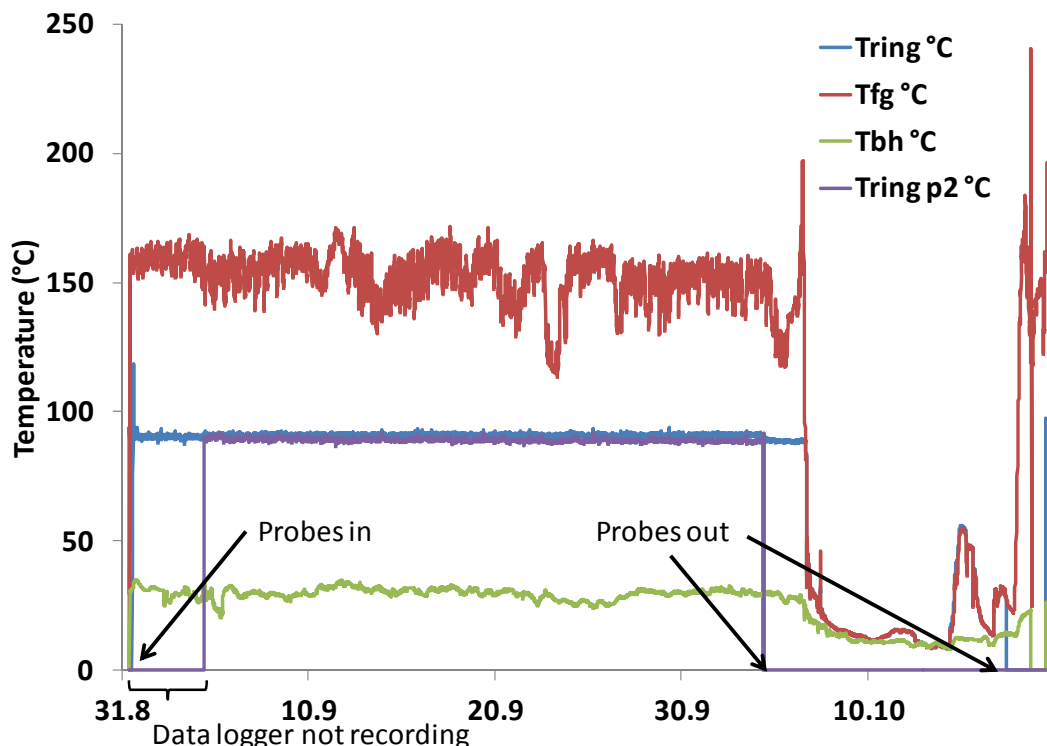


Figure 4. Temperatures of the probes (Tring and Tring p2), flue gas (Tfg) and boiler house (Tbh).

After 811h of normal operation the probe was covered in ash, Figure 5. There was virtually no corrosion on the probe, Figure 6. What little corrosion occurred was found on the top of the probe, but not on the bottom-most edge of the probe. The probe was placed in one of the lower turns in the economizers and it is not clear which were the windward and leeward sides of the probe. The corrosion layer was pitting up to approximately 10 μm , Figure 7. In some spots of the corrosion layer, the chloride was not balanced by alkali indicating iron chloride and chloride induced corrosion. One explanation for the combined observations of corrosion being present on the top but not bottom and the presence of chloride in the corrosion layer is that a small amount of water is dropping on the probe from the sootblowers. This would dissolve NaCl in the salt resulting in a chloride containing solution until the water evaporates. The negligible amount of corrosion seen along with the lack of sulfur in the corrosion layer indicated clearly that there is no acid dew point corrosion.

The probe that was pulled out after the water wash, Figure 8, had more corrosion than the probe pulled out before the water wash, but there was still virtually no corrosion, Figure 9. Again, the bottommost

edge was not corroded. The average corrosion for the two probes estimated on an annual basis was 0.02 and 0.06 mm/year for the probes pulled out before and after the water wash respectively, Table II.



Figure 5. Probe after 811h of Normal Operation

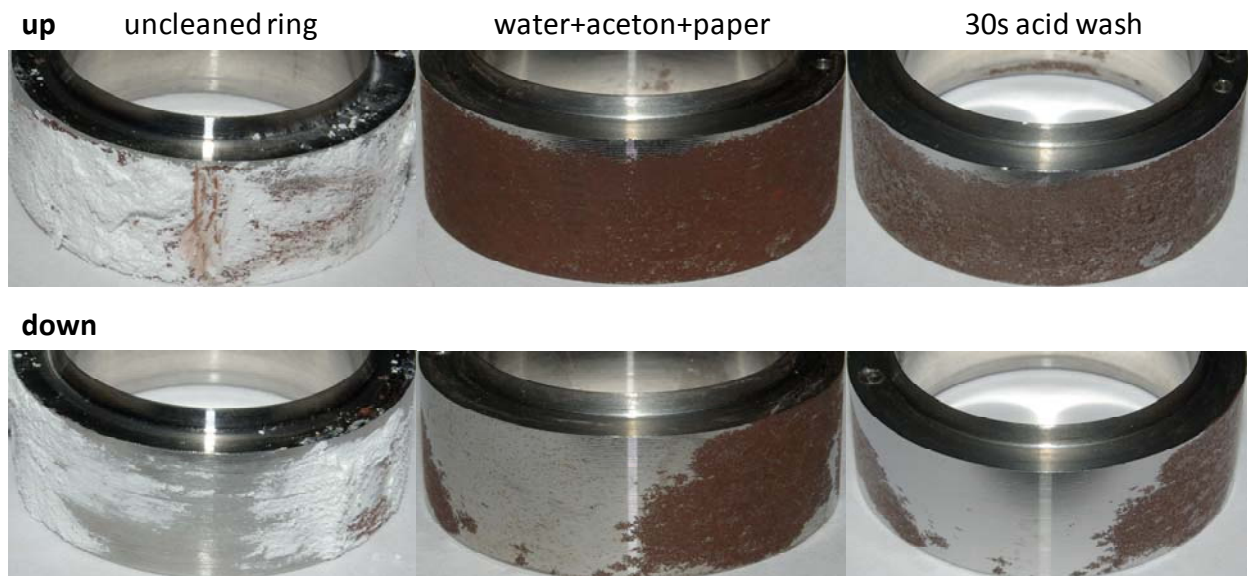


Figure 6. Ring after 811h normal operation. No iron oxide was found on the bottom edge of the probe.

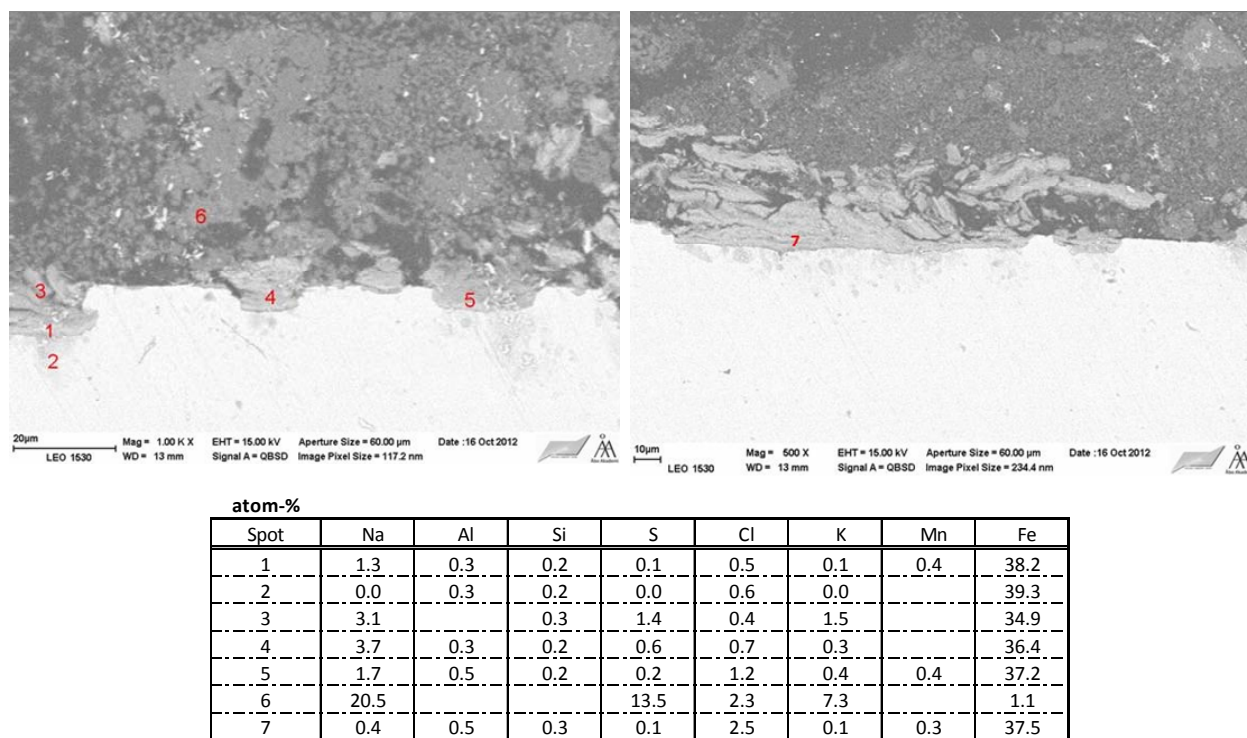


Figure 7. Spot analysis of corrosion layer from probe pulled out after 811 hours of normal operation (before water wash). In spots 2 and 7, the Cl is not balanced by Na or K.

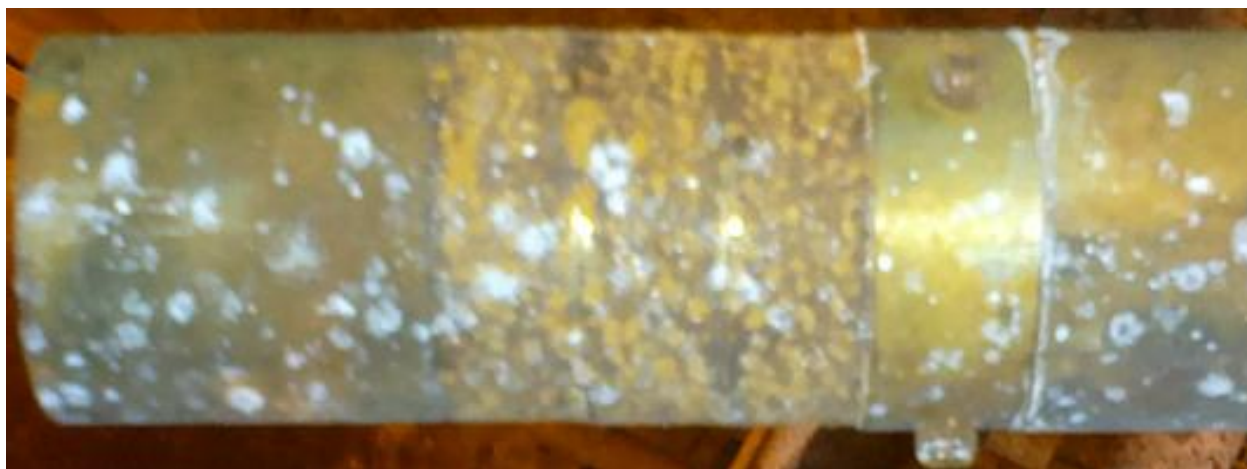


Figure 8. Probe after water wash - 1124h total (811h "normal" operation + water wash)

up uncleaned ring



water+aceton+paper



down



Figure 9. Ring after 1124h. Not that there are some areas without corrosion downwards on the bottom edge of the ring.

Table II. Corrosion layer thicknesses for the rings in the different probe studies. *Pit corrosion, pits ~10 μm deep. **Pit corrosion, pits ~20 μm deep.

Probe Time	Probe Temperature	Ring Weight Loss (mg)	Avg. Corrosion Layer Thickness (μm)	Calculated Avg. Corrosion (mm/yr)
2 h	80 °C	0	0	
2 h	75 °C	0	0	
811 h	90 °C	22	2*	0.02
1124 h	90 °C	72	6**	0.05
2 h	90 °C (oil)	0	0	

After the water wash and after acid washing the inside of the tubes, oil was burned in the boiler. The air ratio used was extremely high, resulting in a flue gas with a high oxygen content and low H₂O and SO₂ content due to the high level of dilution, Table III. Dew point and SO₃ were measured during oil burning at three different points, the bull nose and two different points in the economizer, Figure 10. No acid dew point was measured. The highest SO₃ level measured was about 3 ppm when four burners were firing oil, Table IV.

A 2h probe (90 °C) study was also made in the economizers. The probe study was carried out at the same time the measured SO₃ level was highest, but no corrosion was seen on the rings, Figure 11. There was clearly no acid dew point, but it is not clear why no acid dew point was seen even when SO₃ neared 3 ppm. Had there been an acid dew point, corrosion would have been expected in the two hour probe study.

Table III. Flue gas composition during oil burning. Date 19.10.2012. Calculated Fuel Oil Sulfur Content 0.8% (based on flue gas analysis). No acid dewpoint was found in the dewpoint measurement.

Time	O ₂ (%)	SO ₂ (ppm)	SO ₂ (ppm 0% O ₂)	Air Ratio (λ)	Calculated Dewpoint (°C)
9:36	19.4	38	507	13.4	19
11:57	17.9	83	574	6.9	25

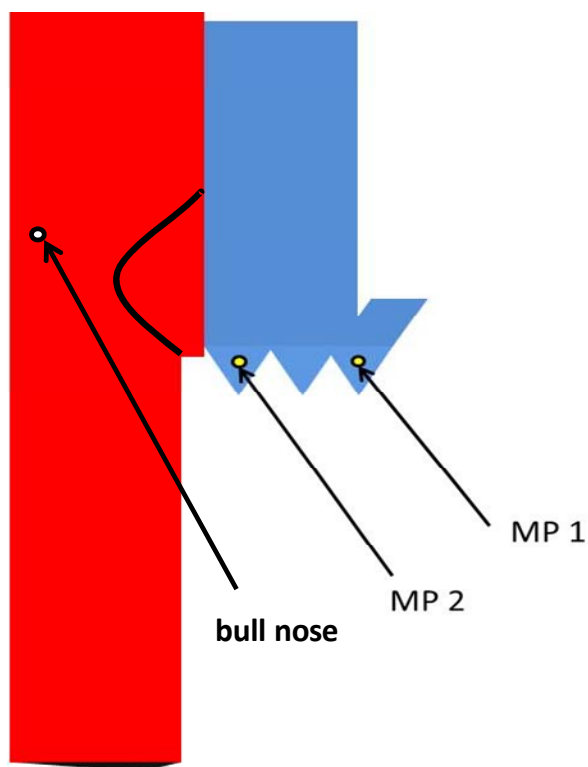


Figure 10. Measurement points for the SO₃ measurements.

Table IV. Sampling positions and SO₃ results. b.n.: bull nose.

Date	Time	MP	SO ₃ (ppm)	Temp (°C)	Oil burners
18.10	19:20-19:50	b.n.	1	240	2
19.10	10:05-10:35	1	1	150	2
	12:15-12:35	1	1	165	4
	13:10-20	1	3	165	4
	16:27-16:37	2	3	240	4
	16:53-17:13	2	2	240	4

Figure 11. Ring after 2h exposure during oil burning.

up

uncleaned ring

water+aceton+paper



down



4. ***Conclusions***

No significant corrosion seen under normal operation or after the water wash for the probes held at 90 °C. It was clear that there was no acid dew point corrosion due to H_2SO_4 formation during normal operation and mills can take more energy out of the flue gas without dew point corrosion under normal operational conditions. There was also no dew point corrosion seen during the oil firing. This may be due to the high air ratios used in this instance, but the results clearly show no acid dew point corrosion during normal operation of a modern Kraft recovery boiler. A follow up study during start-up on oil could clarify if during start-up an acid dew point can be seen.

LIITE 11

Teollisuuden Vesi Oy: Kirje hallitukselle 11.12.2012

Soodakattilayhdistys
puheenjohtaja
Timo-Pekka Veijonen

ref: Puhelinkeskustelu Veijonen/Vidqvist marraskuu 2012

Hyvä Soodakattilayhdistyksen hallitus,

Teollisuuden Vesi on uusimassa nettisivuja tämän loppuvuoden ja ensi vuoden alun aikana. Teemme sivuille katsauksia myös erilaisiin referensseihimme ja olemme ajatelleet, että yksi referensseistä olisi v. 2011 tehty vesiohjearviotyö nimeltään ”Suomen Soodakattilayhdistys, Vesikemian ohjearviot, 9.12.2011”.

Referenssistä julkaistaan perustietoja, kuten mikä oli perusteena työn teettämiselle, mitä hyötyjä sillä saavutettiin ja miten työ teidän suunnastanne katsottuna onnistui. Lisäksi tehdään lyhyt haastattelu, jossa Soodakattilayhdistyksestä valittu henkilö voi kertoa, miten työ sujui ja antaa kommentteja.

Kattilavesikemia ja lisäveden valmistuksen osaaminen on toimintamme yksi avainalueita ja tekemämme työ kasasi vedenkäsittelyyn liittyvää tietoa samoihin kansiin. Tästä syystä katsomme tärkeäksi, että voisimme kertoa työstä myös yhdistyksen ulkopuoliselle tekniikan ammattilaisille.

Toivon, että otatte tämän asian esille seuraavassa kokouksessanne. Antaessanne luvan referenssitiedon julkaisemiseen teemme jutusta lyhyen tekstiversion ja annamme sen teille kommentoitavaksi ennen julkaisua. Lisäksi tehtävää haastattelua varten tarvitsemme nimen yhteyshenkilöstä.

Kunnioittaen,

Maija Vidqvist

Teollisuuden Vesi Oy
Toimitusjohtaja