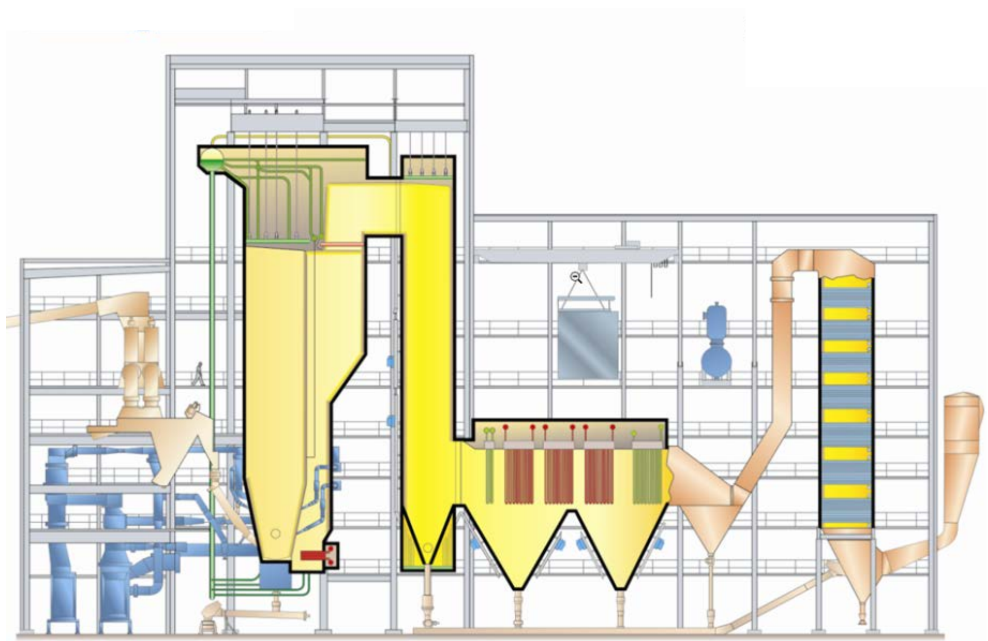
KME711

Combating superheater corrosion by new materials and testing procedures - Corrosion experiments in the waste fired CFB boiler P15 at Händelö



CONSORTIUM MATERIALS TECHNOLOGY

The High-Temperature Corrosion Center

KME720

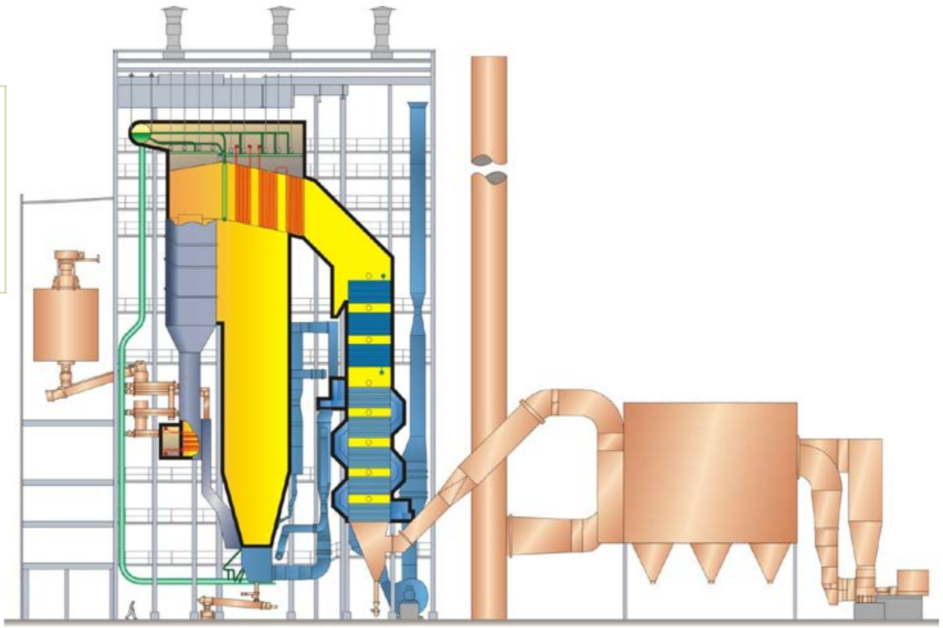
The effect of increased fractions of waste wood on water wall- and superheater corrosion - Combating corrosion by new materials and improved material selection

amec foster wheeler

kraftringen

SANDVIK

MH Engineering



Goal of the projects

Improve plant economy by enabling an increased green electricity production and optimum material selection

Correlating corrosion ➔ Flue gas

Quantifying corrosion rates for different materials and coatings

Verifying corrosion test in horizontal designed boiler

Comparing different corrosion testing methods

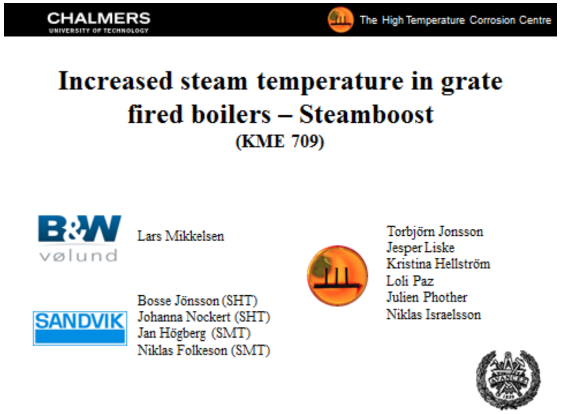
Project Plans

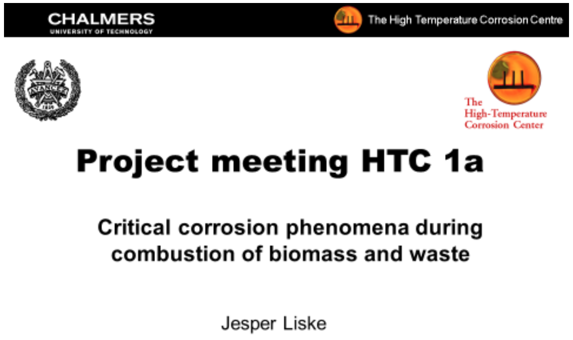
	1	2	3
KME711	Investigate corrosion of the superheaters in a **boiler with horizontal design** using 3 different corrosion testing methods	How does the corrosivity of **flue gas varies** depending on its temperature and chemistry?	Test **usability of FeCrAl alloys and coatings** and comparison towards state-of-the-art SS and conventional SS and steels
KME720	Investigate corrosion of the superheaters in a **boiler with horizontal design** using clamp testing	How does the corrosivity of **flue gas varies** with fuel mix and with stepwise increase of waste wood	Test **usability of FeCrAl alloys and coatings** and comparison towards state-of-the-art SS and conventional SS and steels

Test usability of FeCrAl alloys and coatings and comparison towards state-of-the-art SS and conventional SS and steels

- ✓ FeCrAl-Alloys
- ✓ High performance stainless steels
- ✓ Coatings

New coating technology: HVAF



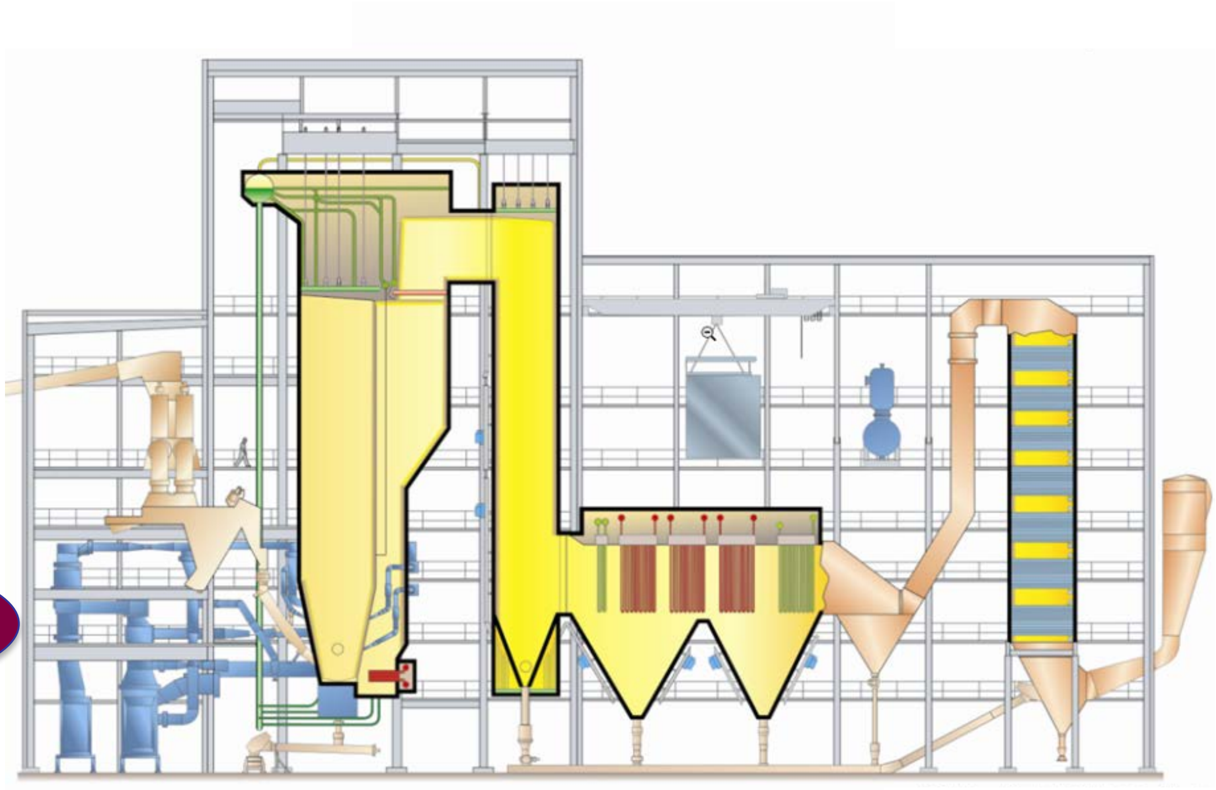


Investigate corrosion of the superheaters in a boiler with horizontal design using 3 different corrosion testing methods

KME711

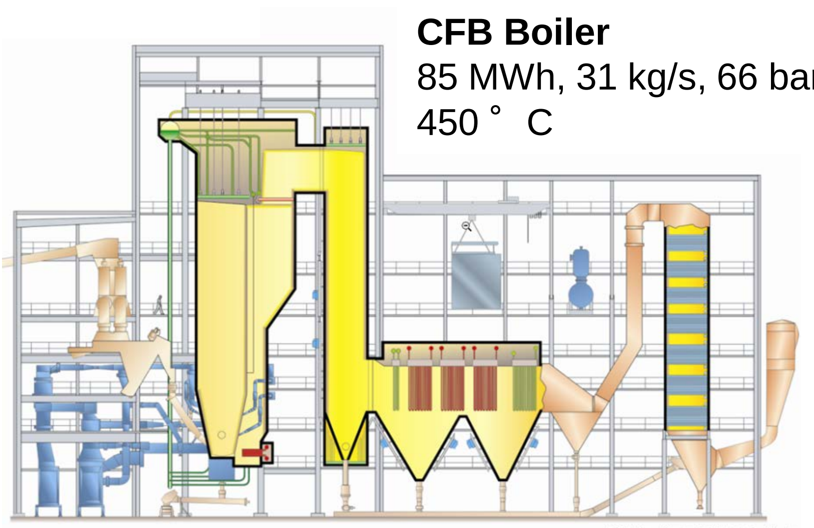
Corrosion testing methods

- Probes
- Coils/tubes
- Clamps



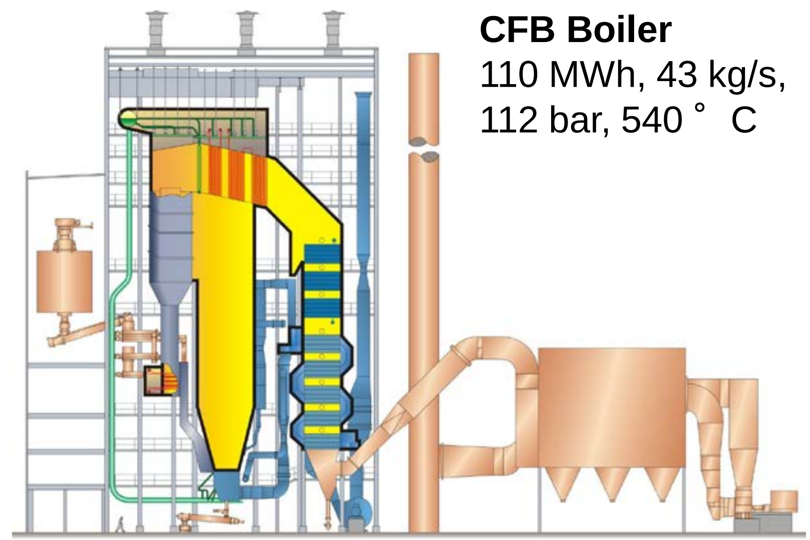
A great overlap between KME720 and KME711

- Same boiler manufacturer, SH in a horizontal design
- Clamp testing, aiming at investigate same materials at same temperatures in the two projects
- Two different fuel mixes



CFB Boiler
85 MWh, 31 kg/s, 66 bar, 450 ° C

KME711 waste boiler



CFB Boiler
110 MWh, 43 kg/s, 112 bar, 540 ° C

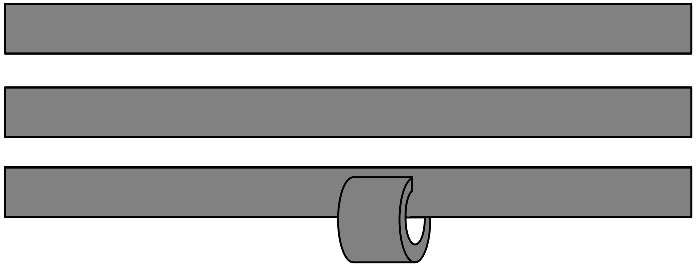
KME720 biomass/waste wood boiler

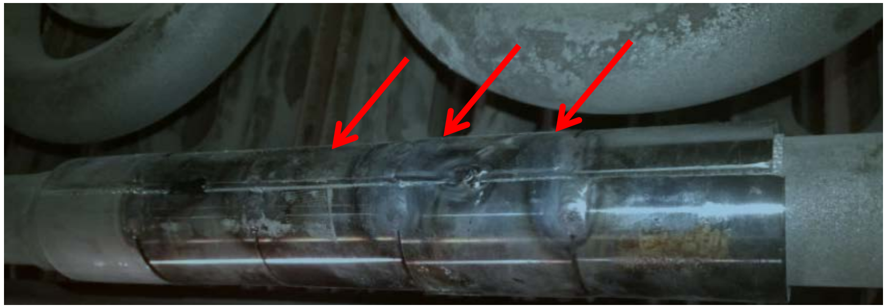
Measurement campaigns in the two projects

Clamps

Technique developed by Foster Wheeler

KME711
KME720





Measurement campaigns in the two projects

Technique developed by Foster Wheeler

Clamps

KME711
KME720

Effect of startup sequence

Start exposure with pre-heated probes?

KME711

The effect of startup sequence

Conclusions

- ✓ The startup sequence seems to have only a minor effect on the initial stages of exposure.
- ✓ Regardless of the tested starting conditions the corrosion attack is in all cases very fast leading to thick oxide scales and formation of metal chlorides resulting in poor scale adhesion.
- ✓ Pre-heating and pre-oxidation of the sample lead to a slightly milder attack with decreased presence of metal chlorides.

Measurement campaigns in the two projects

Technique developed by Foster Wheeler

Clamps

KME711
KME720

Start exposure with pre-heated probes?

Effect of startup sequence

KME711

Short term probe exposures

Evaluating different corrosion prediction techniques

KME711
KME720

Evaluate different "corrosion prediction" tools

Thermodynamical model

IACM (alkali chloride levels)

In-situ corrosion probe

Corrosion & deposit probes, 24h + 144h

Waste

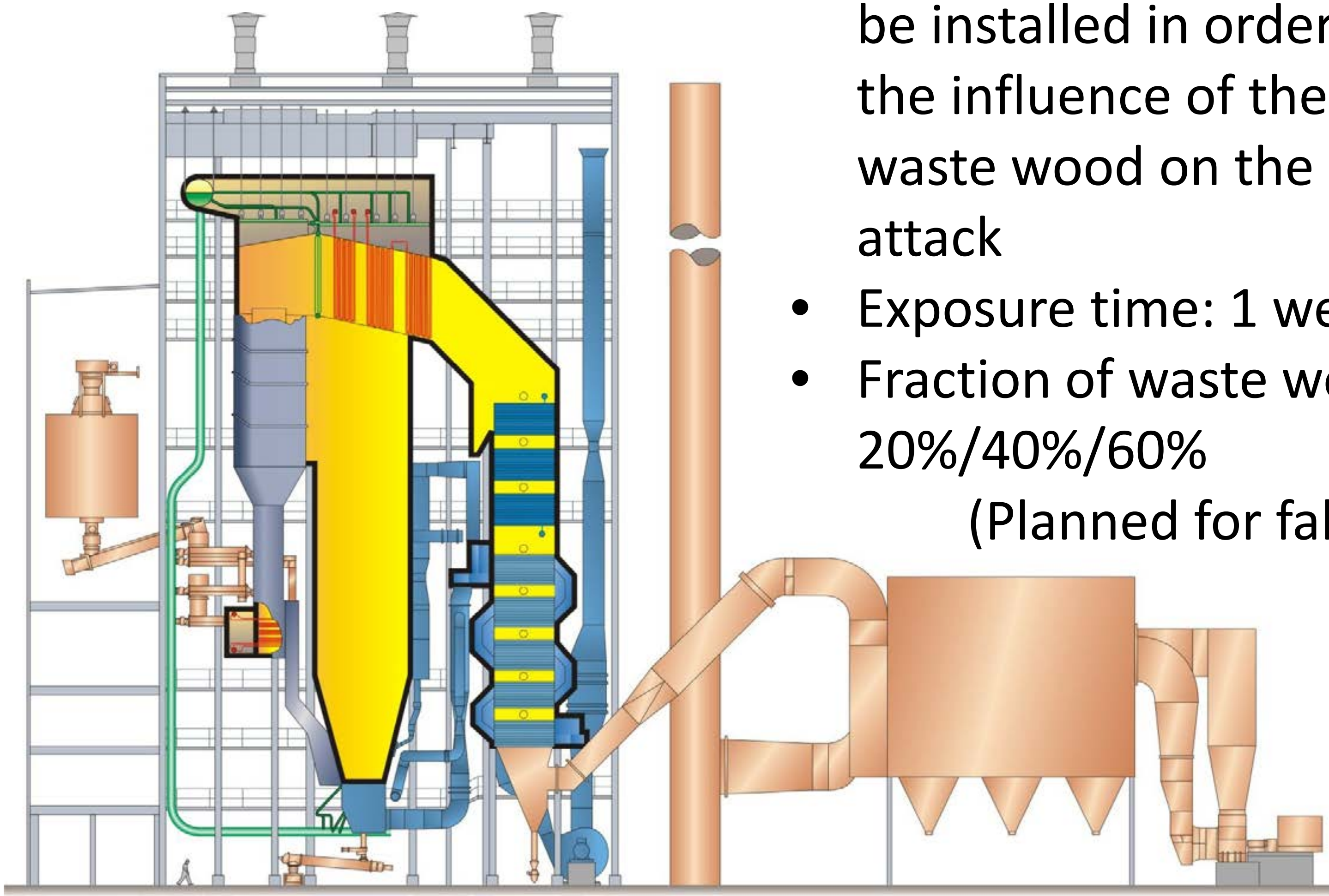
Waste + Ammoniumsulphate

New stainless steels and FeCrAl's

Mechanistic study of Cl penetration

Evaluate new materials

Water wall corrosion in KME720



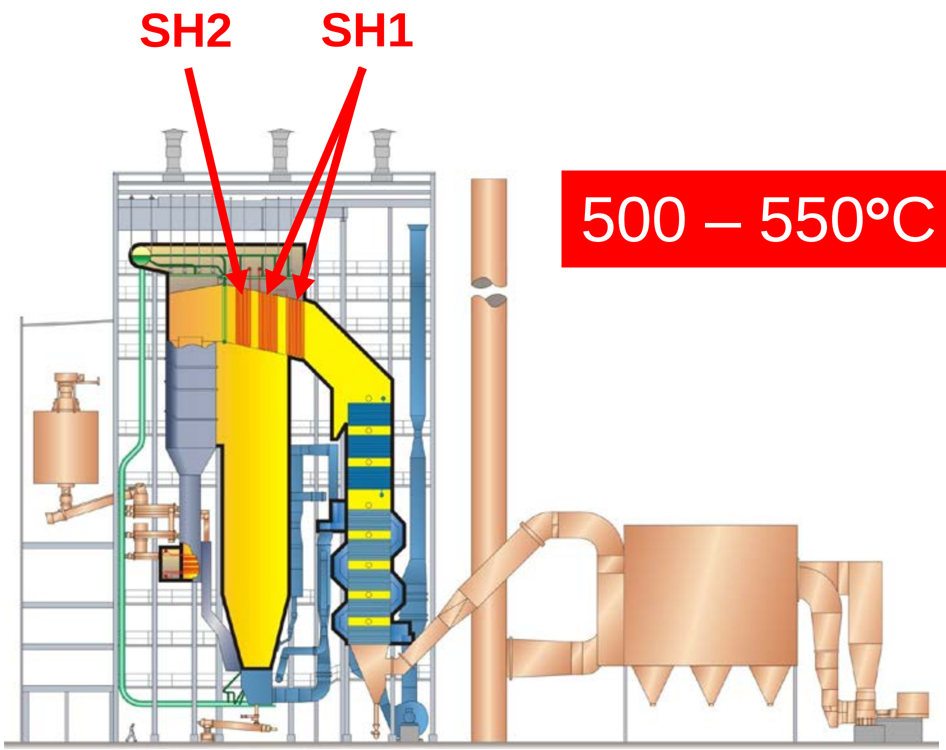
- Water wall corrosion probe will be installed in order to study the influence of the share of waste wood on the corrosion attack
- Exposure time: 1 week
- Fraction of waste wood: 20%/40%/60%

(Planned for fall 2017)

Measurement campaigns in the two projects

Technique developed by Foster Wheeler	Clamps	KME711 KME720
Start exposure with pre-heated probes?	Effect of startup sequence	KME711
Evaluating different corrosion prediction techniques	Short term probe exposures	KME711 KME720

Clamp exposures in KME720



500 – 550°C

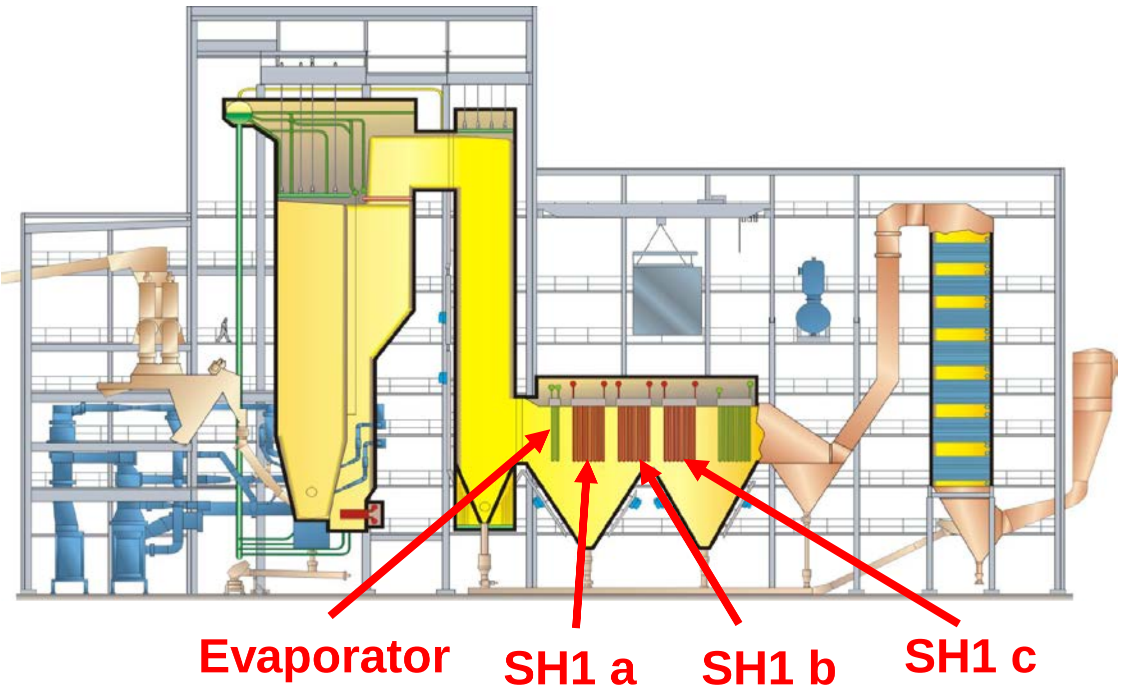
Materials

- 16Mo3
- 13CrMo4-5
- 10CrMo9-10 **(Only SH1)**
- X10CrMoVNb9-1 **(Only SH1)**
- 347H
- CorEr (In625)
- Sanicro 28

Measurement campaigns in the two projects

Technique developed by Foster Wheeler	Clamps	KME711 KME720
Start exposure with pre-heated probes?	Effect of startup sequence	KME711
Evaluating different corrosion prediction techniques	Short term probe exposures	KME711 KME720

Clamp exposures in KME711



- ✓ 3 sets of clamps installed in 2014
- ✓ 1 set removed during revision in 2015 **(analyzed)**
- ✓ 1 set removed during revision in 2016 **(under analysis)**
- ✓ One set will be removed during revision in summer 2017

500 – 550°C Expected

360-380°C Measured

Clamps (1st set 2015)

Materials

- 16Mo3
- 13CrMo4-5
- 10CrMo9-10 (Only SH´s)
- TP310H
- St 35.8 (Only Evaporator)
- Sanicro 28

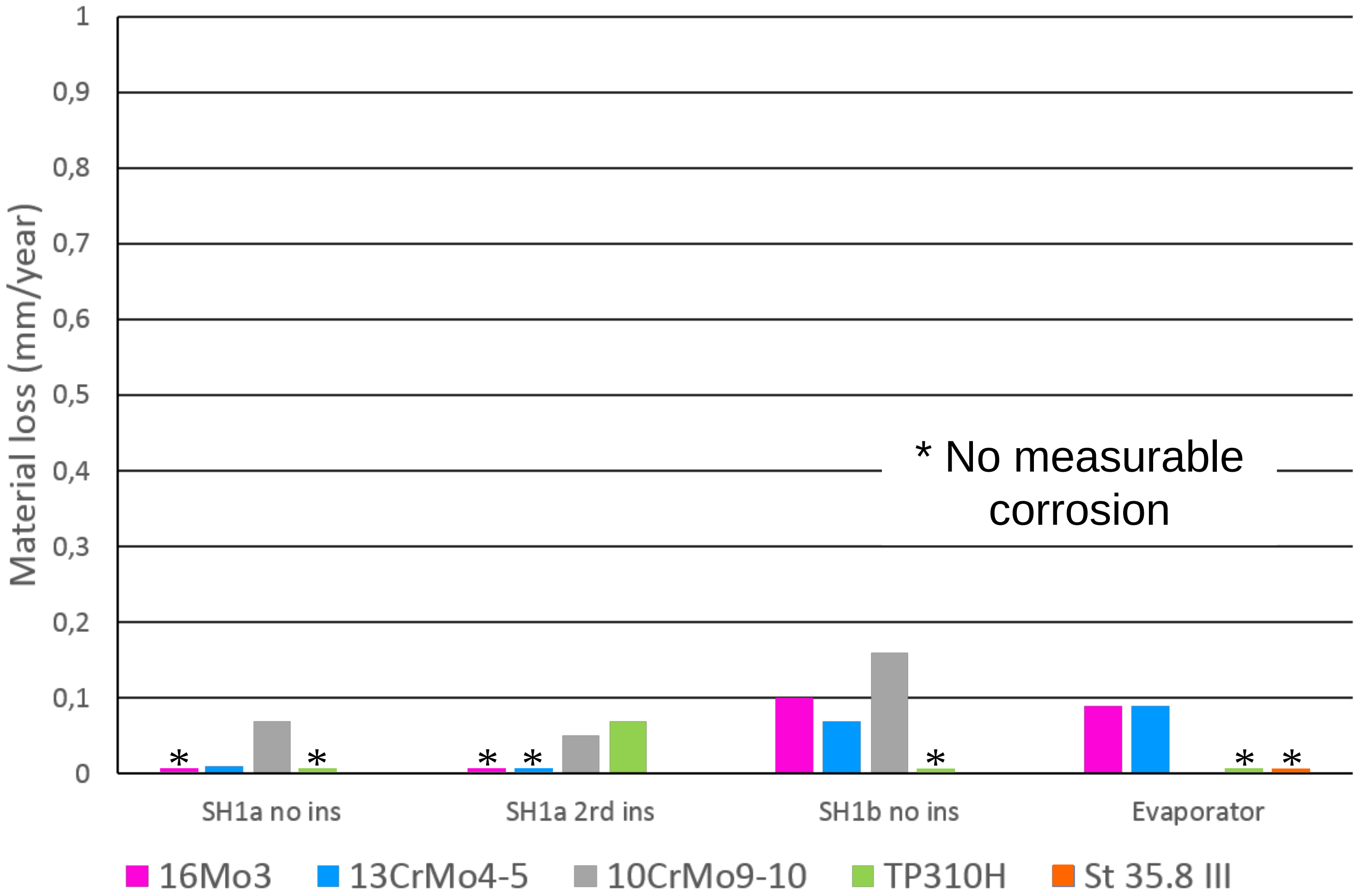
Positions

- SH1a no insulation
- SH1b no insulation
- SH1a 2 rounds of insulation
- Evaporator

✓ SEM/EDX

✓ Material loss

Clamps: Material loss (1st set after 1 year)



Clamps (2^{nd} set 2016)

Materials

- TP310H
- 16Mo3
- 13CrMo4-5
- 10CrMo9-10 (Only SH's)
- Sanicro 28
- St 35.8 (Only Evaporator)
- Esshete 1250
- IN625 overweld
- Kanthal

2015 (SH)

Positions

- SH1a no insulation
- SH1b no insulation
- SH1a 2 rounds of insulation
- Evaporator

✓ The samples were removed after **2 years**
✓ They are being prepared and checked with SEM/EDX

No significant corrosion has been detected

Measurement campaigns in the two projects

Technique developed by Foster Wheeler	Clamps	KME711 KME720
Start exposure with pre-heated probes?	Effect of startup sequence	KME711
Evaluating different corrosion prediction techniques	Short term probe exposures	KME711 KME720

Evaluate different “corrosion prediction” tools

Thermodynamical model

IACM (alkali chloride levels)

In-situ corrosion probe

Corrosion & deposit probes, 24h + 144h

Waste

Waste + Ammoniumsulphate

New stainless steels and FeCrAl’s

Mechanistic study of Cl penetration

Evaluate new materials

UNIVERSITY OF BORÅS

Thermodynamic equilibrium modeling of solid waste combustion in the CFB boiler

Farzad Moradian
Anita Pettersson

Aim

- Model to calculate chemical composition flue gas leaving the furnace:
  - Determination the corrosivity of the flue gas (based on chemistry of fuel mix, sulfur-containing additive, and bed temperature)
- Focus will remain on the concentrations of alkali chlorides, HCl and SO_2 in the flue gas
- IACM measurements will be used to evaluate the accuracy and validity of the model

Plan & Progress

Chemical fractionation

+ FactSage

- ✓ Samples of solid waste and ash fractions received
- ✓ Chemical fractionation in progress

Evaluate different "corrosion prediction" tools

Thermodynamical model

IACM (alkali chloride levels)

In-situ corrosion probe

Corrosion & deposit probes, 24h + 144h

Waste

Waste + Ammoniumsulphate

New stainless steels and FeCrAl's

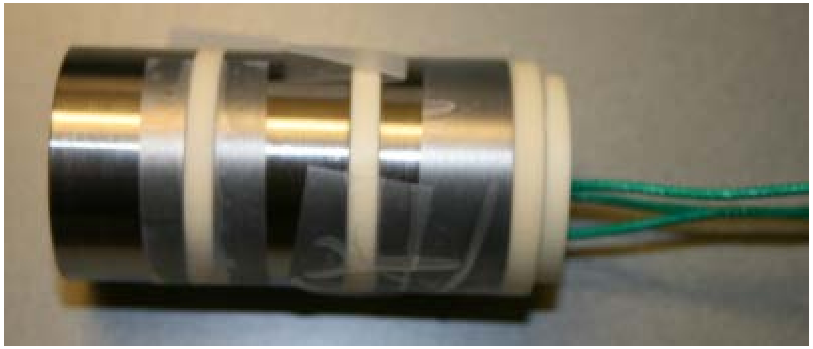
Mechanistic study of Cl penetration

Evaluate new materials

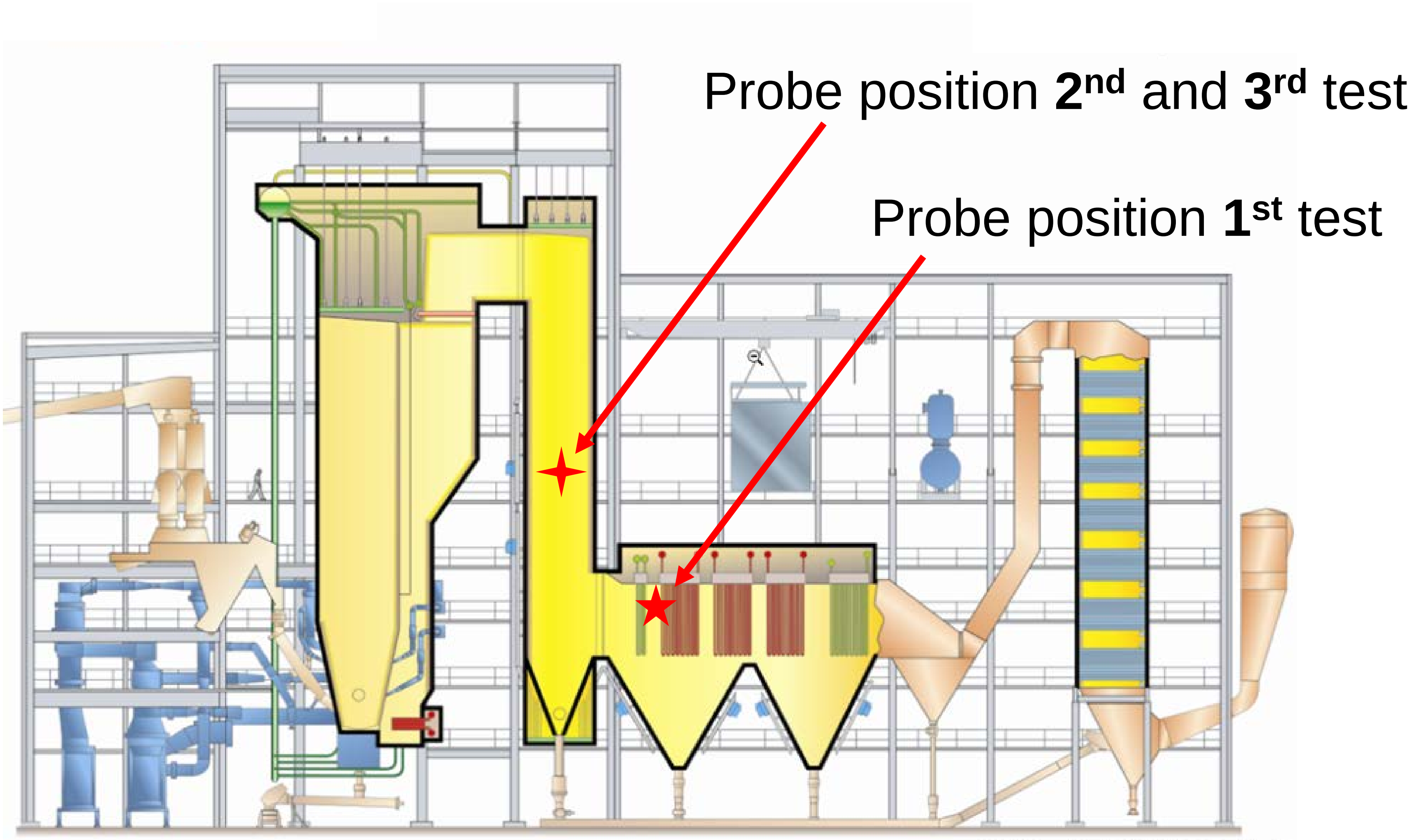
In-situ corrosion probe

Introduction in-situ corrosion probe

- Online corrosion probe (MECO™) system
  - Based on LPR (Linear Polarization Resistance) method
  - Three measurement electrodes, electrically connected to the measuring circuit. Ceramic insulation between the measurement electrodes.
    - W1, test material 1
    - R, reference electrode, same material as W1 or W2.
    - W2, test material 2



Results in-situ corrosion probe test



Results in-situ corrosion probe test

1st in-situ corrosion probe test

Probe installed at horizontal pass (2013-2014)

- Low flue gas temperature
- Low corrosion

2nd in-situ corrosion probe test

Probe installed at empty pass, higher flue gas temperature (2014-2015)

- High corrosion values measured
- Malfunctions in remote connection

3rd in-situ corrosion probe test

Probe installation (20161102)

- To be analyzed

Evaluate different "corrosion prediction" tools

- Thermodynamical model
- IACM (alkali chloride levels)
- In-situ corrosion probe

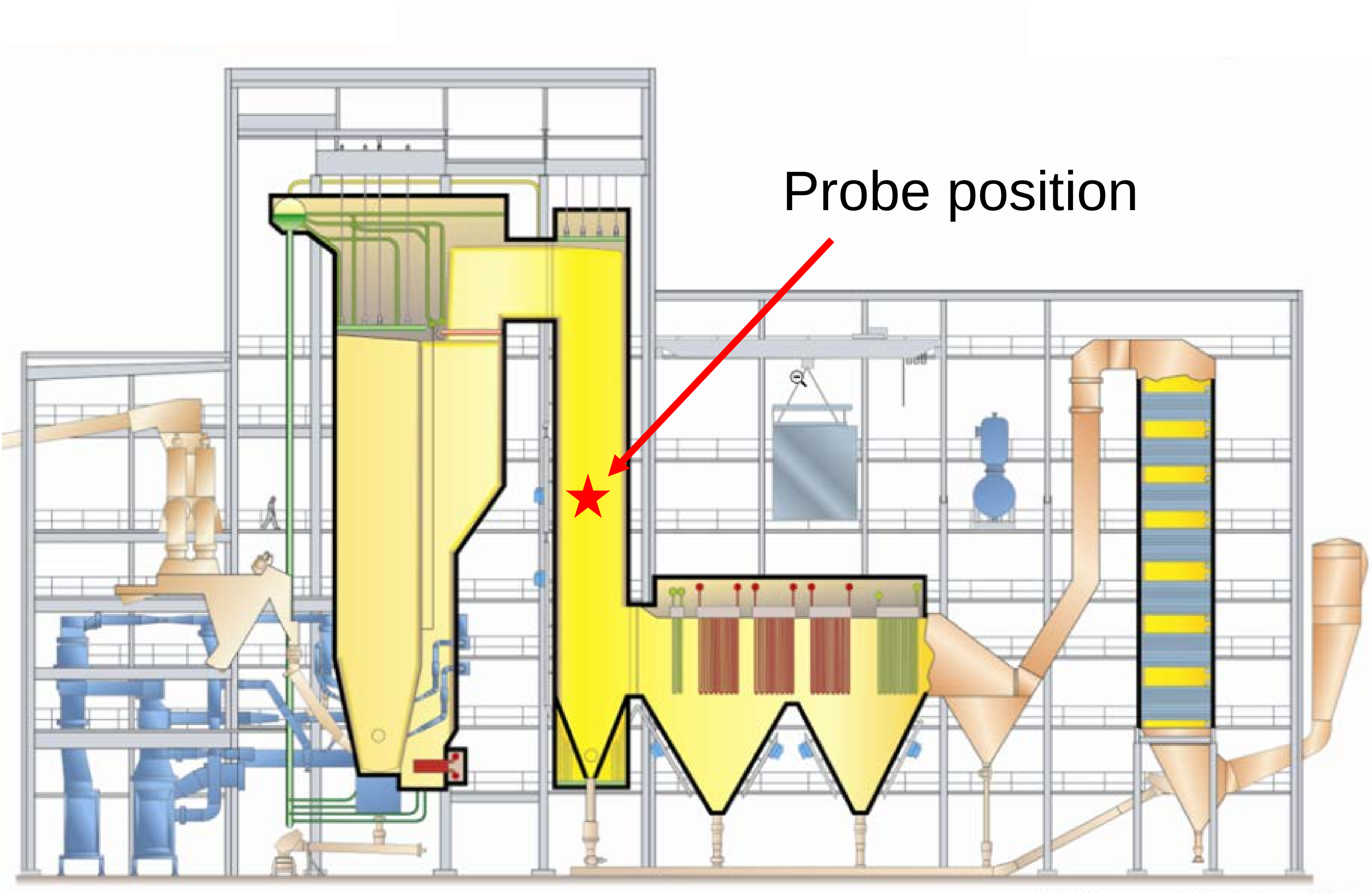
Corrosion & deposit probes, 24h + 144h

- Waste
- Waste + Ammoniumsulphate

- New stainless steels and FeCrAl's
- Mechanistic study of Cl penetration

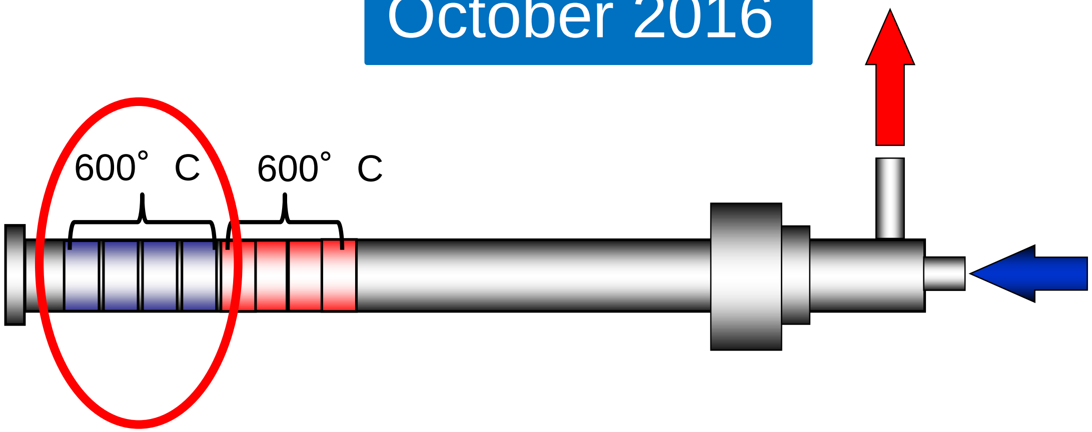
Evaluate new materials

Short term probe tests in empty pass



Boiler exposures
Reference (waste)

October 2016

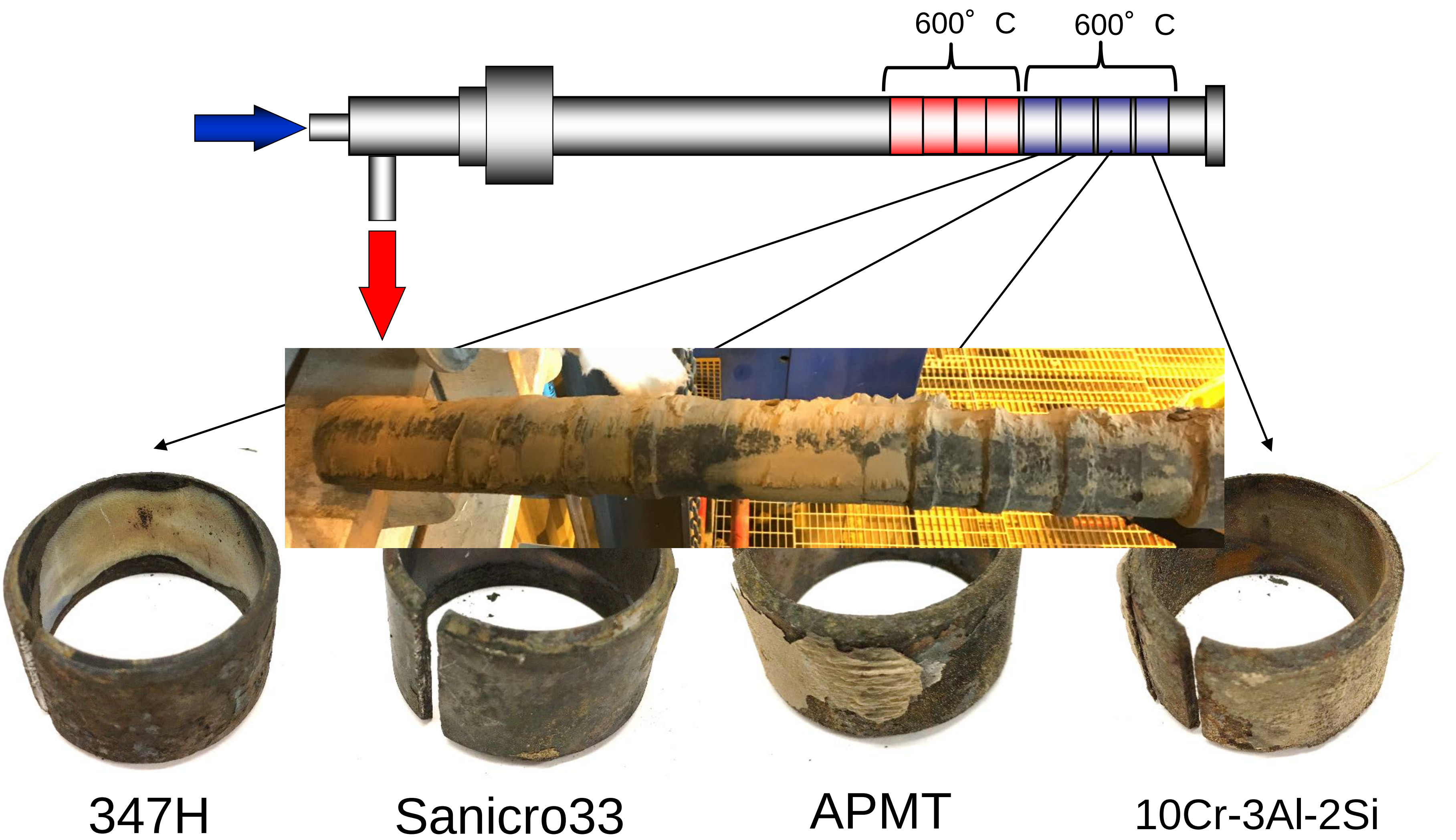


- 10Cr-3Al-2Si
- Sanicro 33
- APMT
- 347H

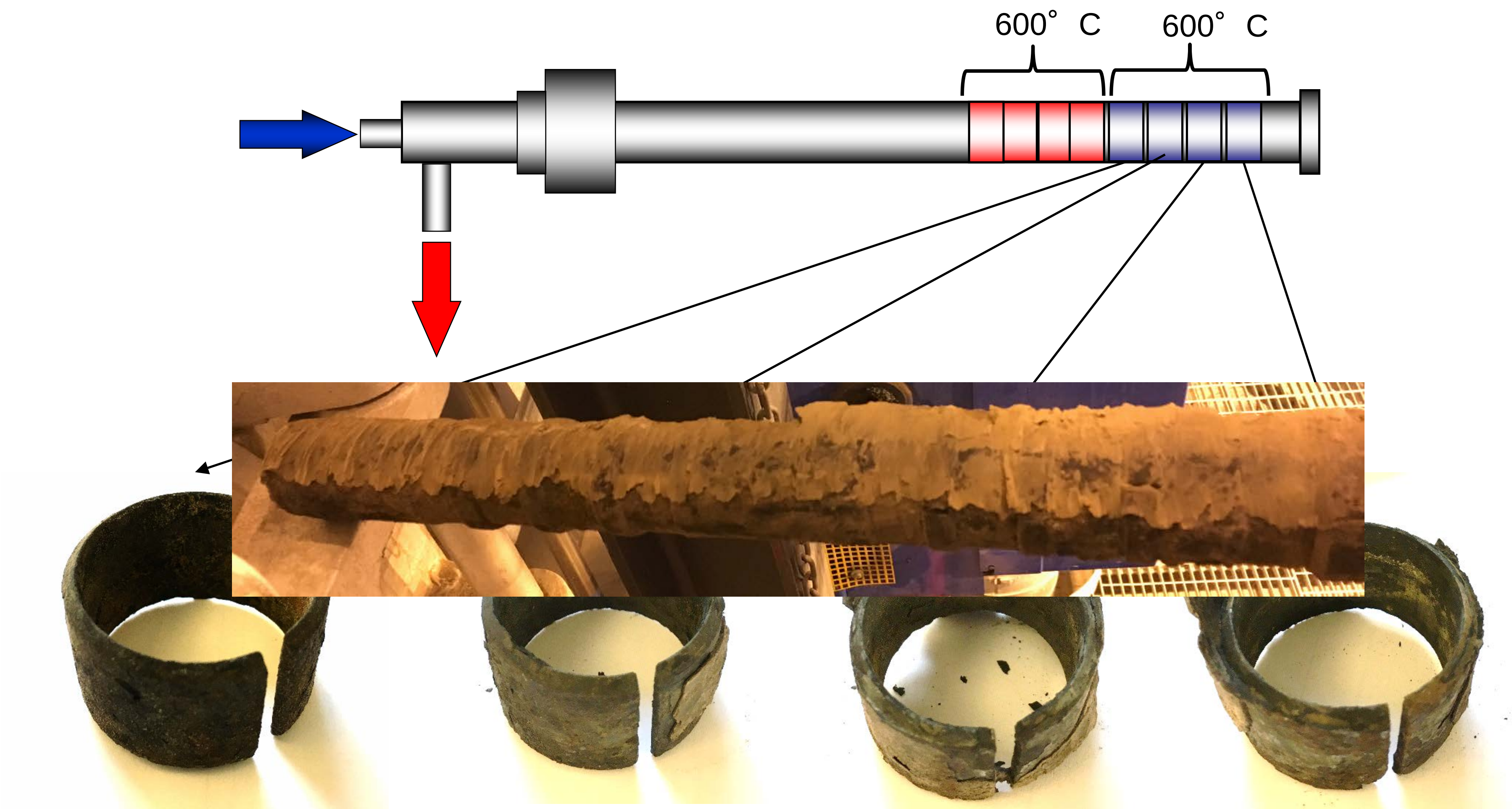
- T22
- T22 pre-ox
- 347H
- 347H pre-ox

24 h waste + 144 h waste
(8+8 samples)

Reference (waste) 24 h



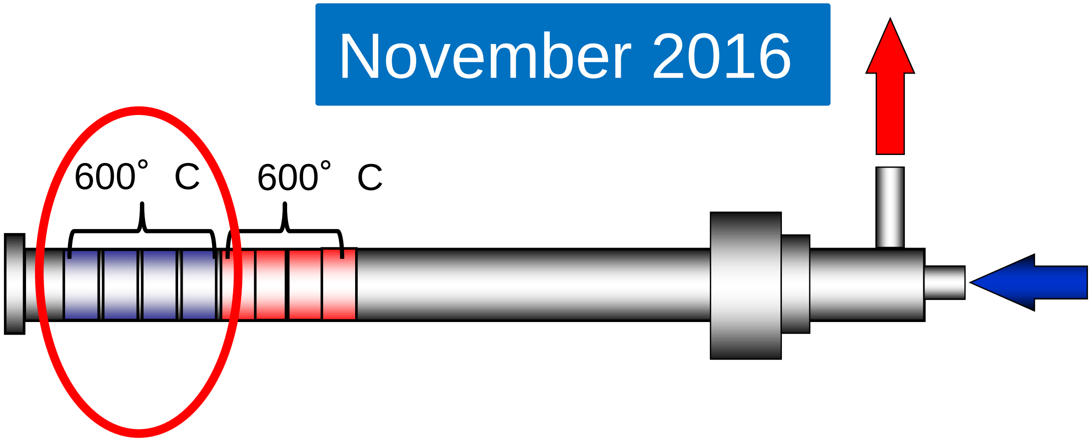
Reference (waste) 144 h



347H Sanicro33 APMT 10Cr-3Al-2Si

Boiler exposures
Ammonium sulfate additive

November 2016

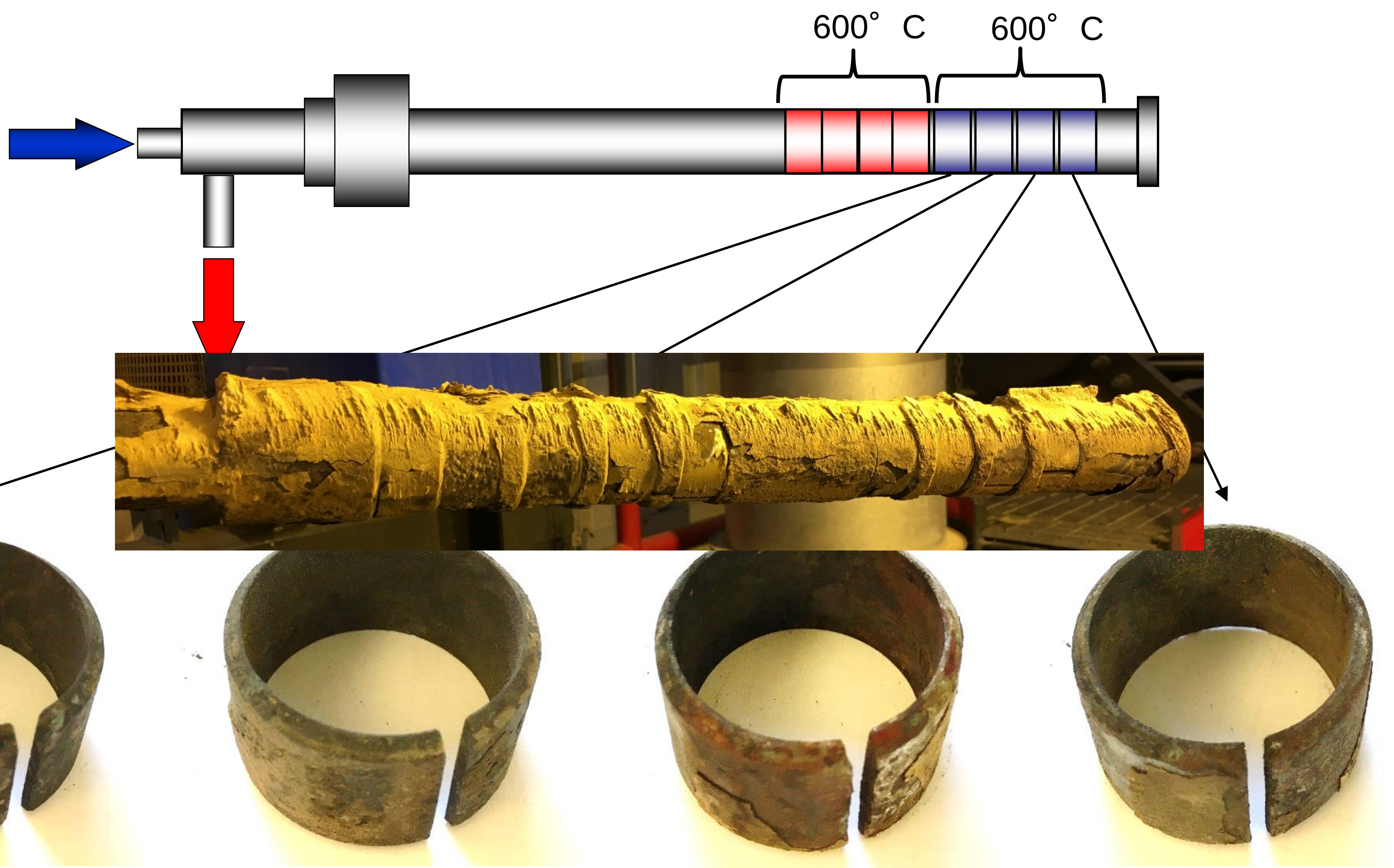


- 10Cr-3Al-2Si
- Sanicro 33
- APMT
- 347H

- T22
- T22 pre-ox
- 347H
- 347H pre-ox

24h ammonium sulfate + 144 h ammonium sulfate (8+8 samples)

Boiler exposures
Ammonium sulfate additive 24h



347H Sanicro33 10Cr-3Al-2Si 10Cr-3Al-2Si

Optical overview

24h waste

347H

Sanicro33

APMT

10Cr-3Al-2Si

144h waste

347H

Sanicro33

APMT

10Cr-3Al-2Si

24h Ammonium-sulfate

347H

Sanicro33

10Cr-3Al-2Si

10Cr-3Al-2Si

Evaluate different “corrosion prediction” tools

Thermodynamical model

IACM (alkali chloride levels)

In-situ corrosion probe

Corrosion & deposit probes, 24h + 144h

Waste

Waste + Ammoniumsulphate

New stainless steels and FeCrAl’s

Mechanistic study of Cl penetration

Evaluate new materials

The
High-Temperature
Corrosion Center

Mechanistic study of chlorine penetration of oxide scales

Andrea Olivas

How are different oxides affected by a corrosive environment?

Initiation

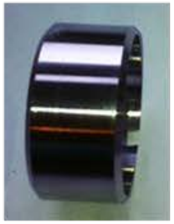
Propagation

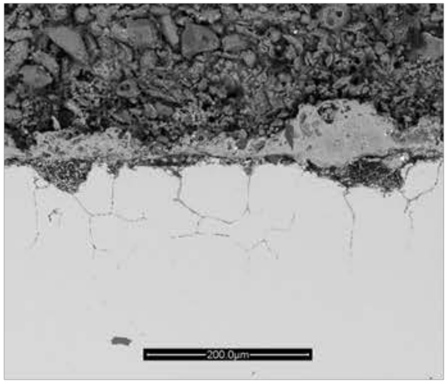
0 s

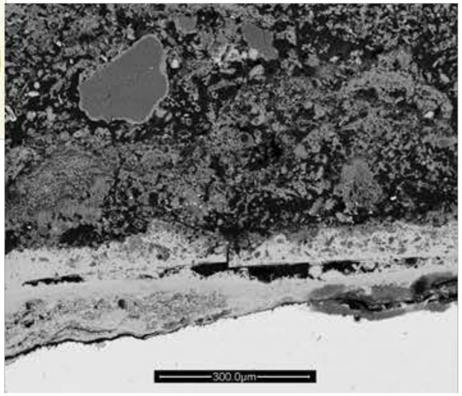
24 h

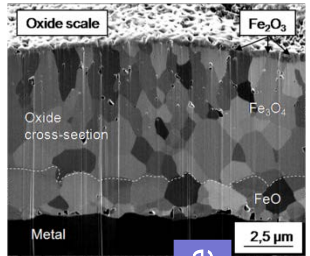
1000 h

? h

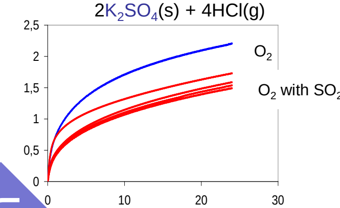








$2SO_2(g) + O_2(g) + 4KCl(s) + 2H_2O(g) \rightarrow 2K_2SO_4(s) + 4HCl(g)$



Knowledge

Validation

Knowledge

Intelligent exposures

Understanding of corrosion mechanisms

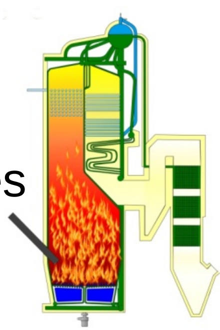
Multiple analytical approach

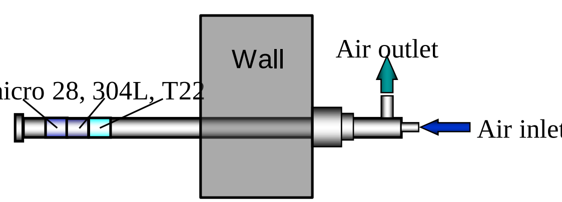
Knowledge

Validation

Knowledge

Field exposures





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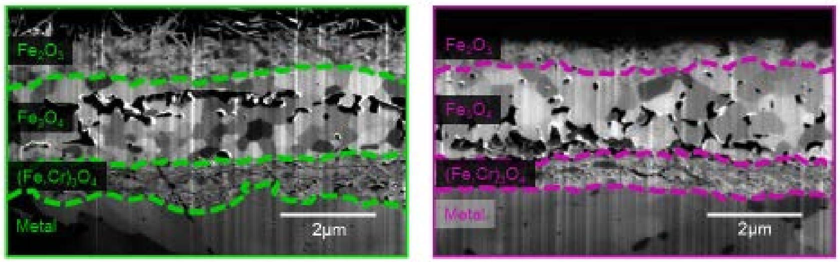
The High Temperature Corrosion Centre

Pre-Oxidation	
$5\%O_2+20\%H_2O+N_2$	
500 °C 12 h	600 °C 40 min



Oxides with different microstructures → Different effect of Cl?

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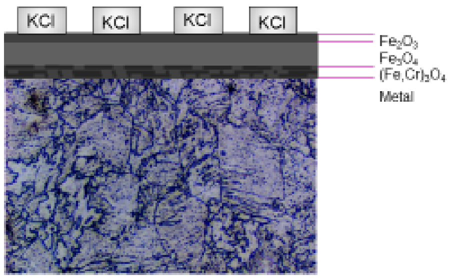
Experimental

$0,1 mg/cm^2$ KCl



$5\%O_2+20\%H_2O+N_2$

400 ° C

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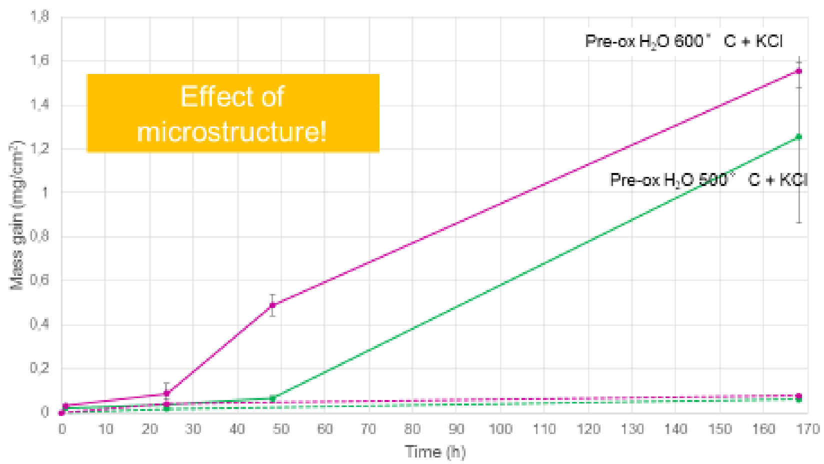
KCl exposure of Pre-Oxidized T22 at 400 ° C



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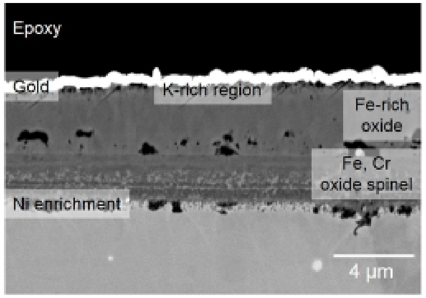
Influence of KCl and HCl: experimental starting conditions

Step 1: Pre-oxidation



Alloy	Fe	Cr	Ni	Mn	Si	C
347H	Bal	17.6	10.1	1.6	0.6	0.05

Oxidation time: 168 hours
Temperature: 600 ° C
Evironment: 5%O_2+N_2+1.35µmol K^+/cm^2 in form of K_2CO_3

Breakdown of protective oxide

½ $Cr_2O_3(s) + K_2CO_3(s) +$ ¾ $O_2(g) \leftrightarrow K_2CrO_4(s) + CO_2(g)$

*Stability of the potassium chromate formed has earlier been reported to be low and after 168 hours it is seldom detected

Formation of K-rich area

$Fe_2O_3(s) + K_2CO_3(s) \leftrightarrow 2KFeO_2(s) + CO_2(g)$

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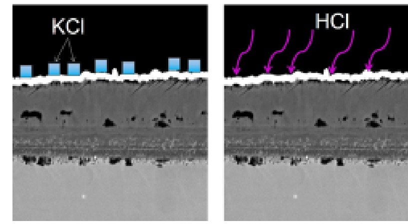
Influence of KCl and HCl: experimental starting conditions

Exposure time: 24 hours
Temperature: 600 ° C

5%O_2+20%H_2O+N_2+0.1mg/cm² KCl



5%O_2+20%H_2O+500ppmHCl+N_2

Step 2: Exposure in presence of chlorine

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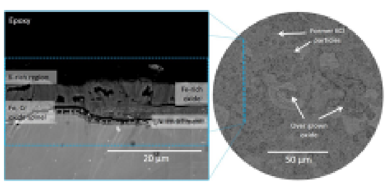
Influence of KCl and HCl: exposures in presence of Cl

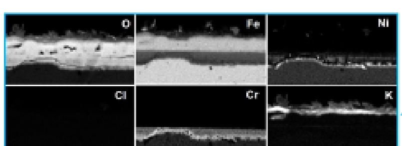
Results: KCl(s)



Oxide layers similar to pre-oxidation

No spallation

KCl evaporation
$KCl(s) \leftrightarrow KCl(g)$



$Fe_2O_3(s) + K_2CO_3(s) \leftrightarrow KFeO_2(s) + CO_2(g)$

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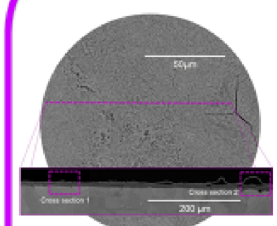
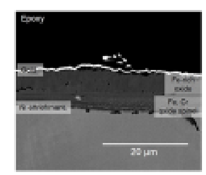
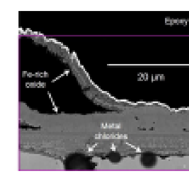
Influence of KCl and HCl: exposures in presence of Cl

Results: HCl(g)

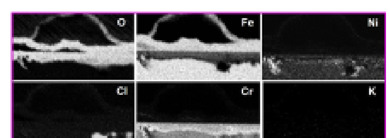




Cross section 1



Cross section 2



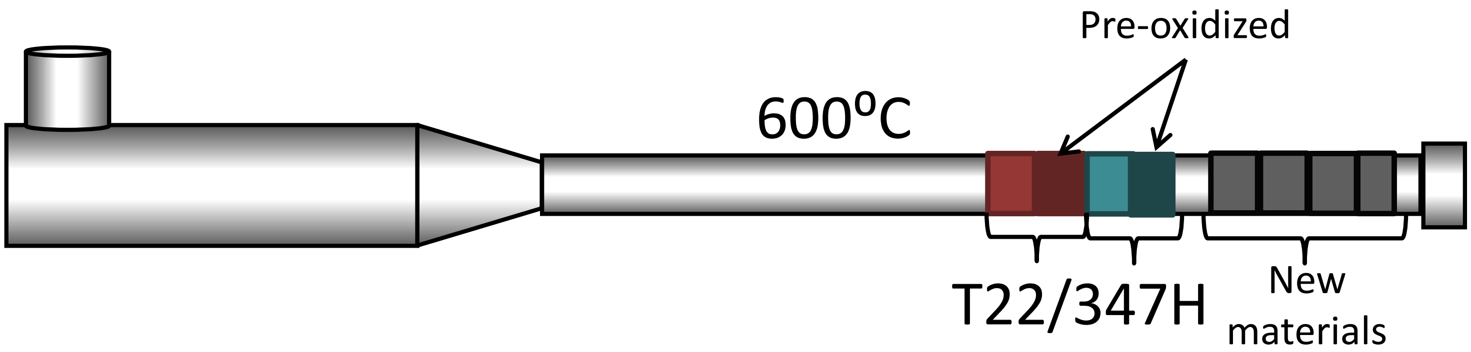
Presence of chlorine was detected at the oxide/metal interface beneath a region with blisters.

$2HCl(g) + KFeO_2(s) \leftrightarrow Fe_2O_3(s) + KCl(s) + H_2O(g)$

$KCl(s) \leftrightarrow KCl(g)$

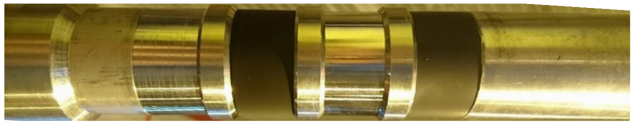
*According to the XRD results, weak signals of iron and chromium chlorides were detected.

Laboratory exposures vs Field exposures



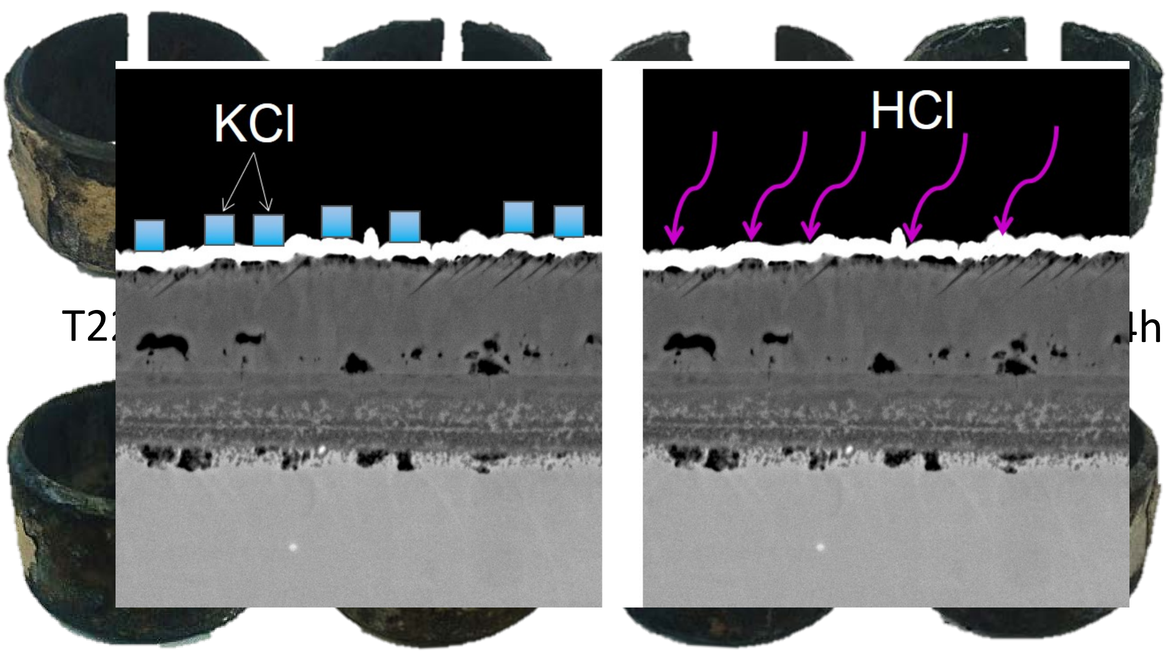
<table>
<tr><th colspan="8">Reference</th><th colspan="8">With Amonium Sulphate</th></tr>
<tr><td colspan="4">24 hours</td><td colspan="4">144 hours</td><td colspan="4">24 hours</td><td colspan="4">144 hours</td></tr>
<tr><td colspan="2">347H</td><td colspan="2">T22</td><td colspan="2">347H</td><td colspan="2">T22</td><td colspan="2">347H</td><td colspan="2">T22</td><td colspan="2">347H</td><td colspan="2">T22</td></tr>
<tr><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td><td></td><td>Pre-Ox</td></tr>
<tr><td colspan="16">600 °C</td></tr>
</table>

Laboratory exposures vs Field exposures



Starting conditions

After 24 hours exposure



347H 24h 347H PO 24h 347H 144h 347H PO 144h

SEM/EDX

Summary KME711

- Investigated the startup effect of probes – presented at the 22FBC conf 2015
- 3 years clamp exposures ongoing (1 and 2 years are removed and are being analyzed)
- Investigating mechanistic laboratory findings in field (penetration of Cl)
- Short and long term testing of novel materials (SS and FeCrAl) and coatings (HVAF)
- Evaluation of "corrosion prediction" tools (TD model, IACM, In-situ corrosion probe)
- The project follows the project plan and budget

Summary KME720

- Yearly clamp exposures are ongoing (first set are removed and are being analyzed, second set is being exposed)
- Long term testing of novel materials (SS and FeCrAl) and coatings (HVAF)
- Short term probe testing planned for spring 2017
- The project follows partly the project plan and budget
  - A delay of water wall exposures due to risk of boiler shutdown