

Sulfur recirculation and improved material selection for high temperature corrosion abatement – Investigating different aspects of corrosion memory (KME 714)



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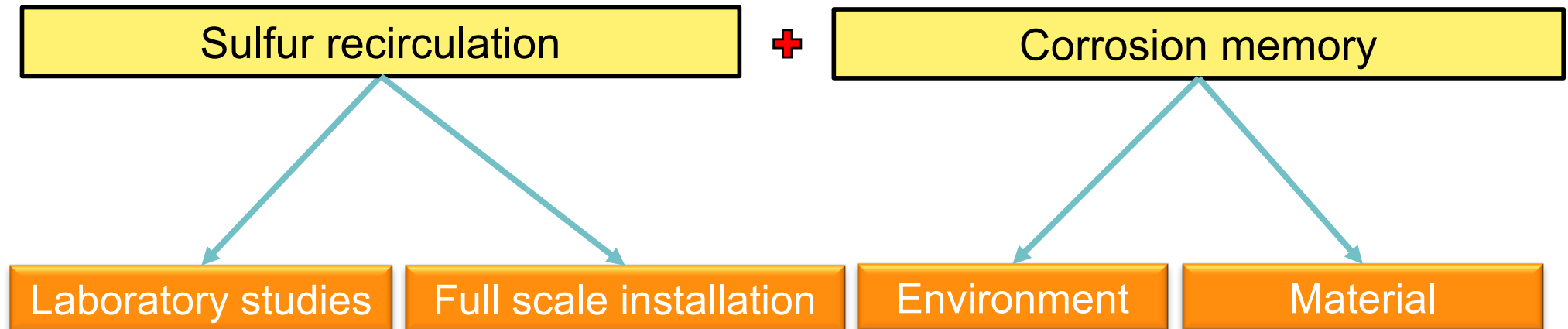
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Julien Phother



Kristian Vinter Dahl
Melanie Montgomery
Yohanes Malede

Overall Goal of KME714

- Research strategy and correlation to KME goals



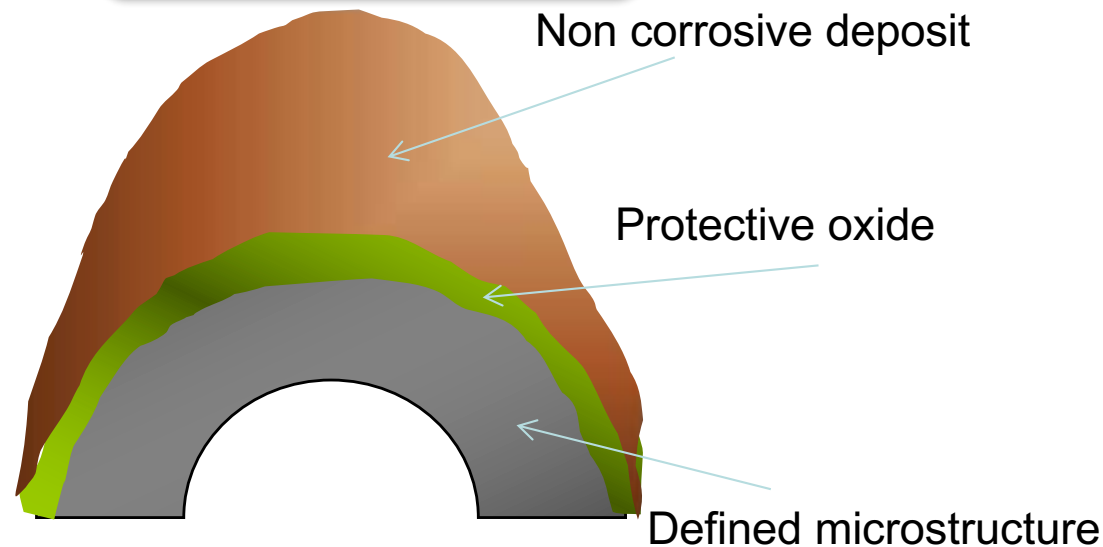
KME goals:

- Increase green electricity production from combustion of biomass and waste
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- Improved material design/selection

Corrosion memory – definition

Oxide scales, alloy microstructure and thick deposits from the past influencing future corrosion attack.

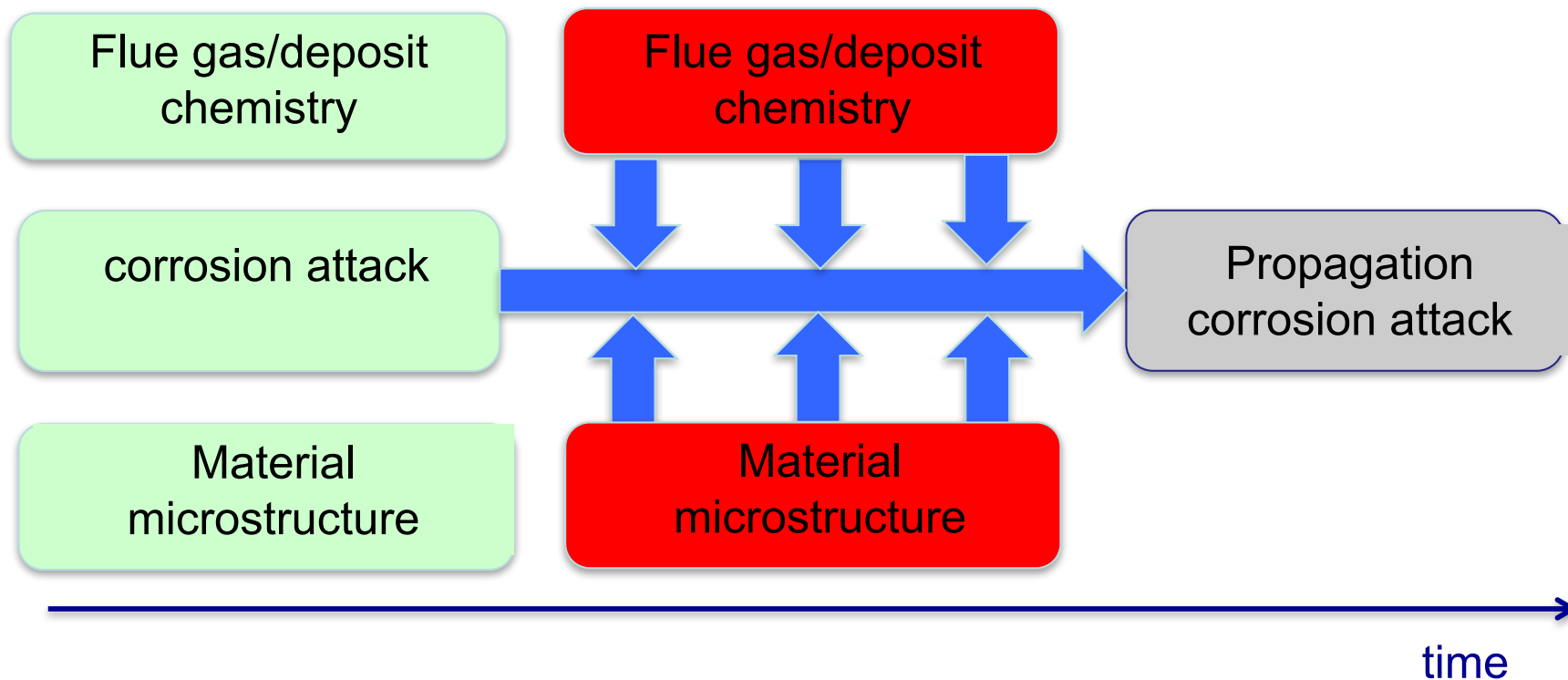
Flue gas from non-corrosive fuel



Flue gas from a corrosive fuel

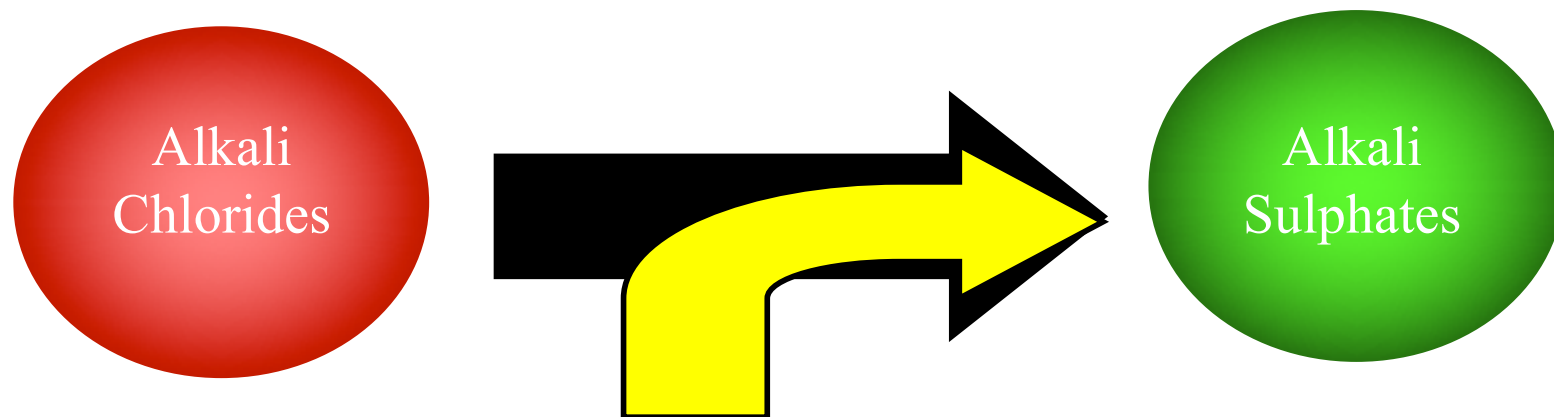


What are the challenges in studying the propagation?



A strategy for mitigating the alkali induced corrosion of high temperature steels

Change the fireside environment by means fuel additives

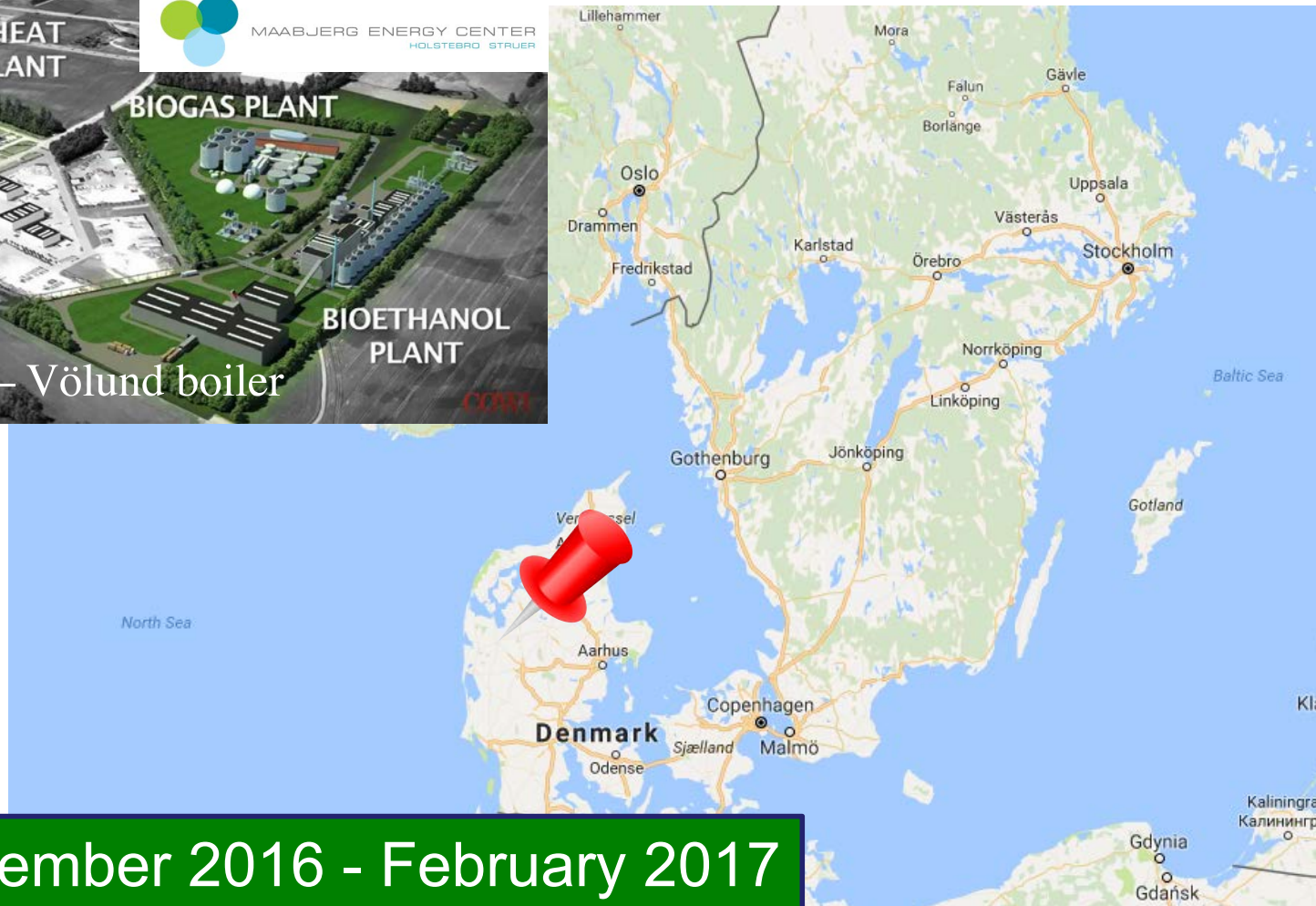


Adding sulfur or sulfur-rich fuels

- Elemental sulfur
- Ammonium sulphate
- Sulfur recirculation
- Municipal sewage sludge

Autumn-Winter 2016/17

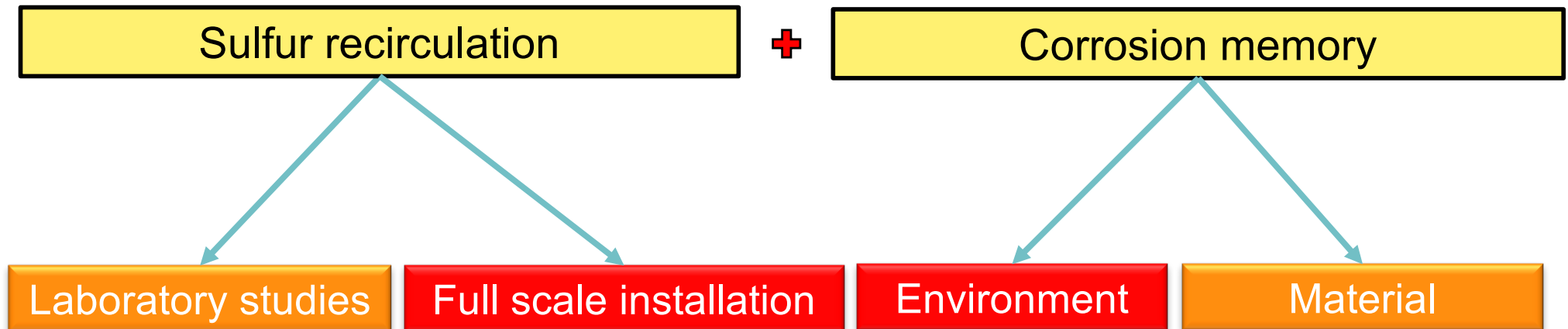
Field exposures



November 2016 - February 2017

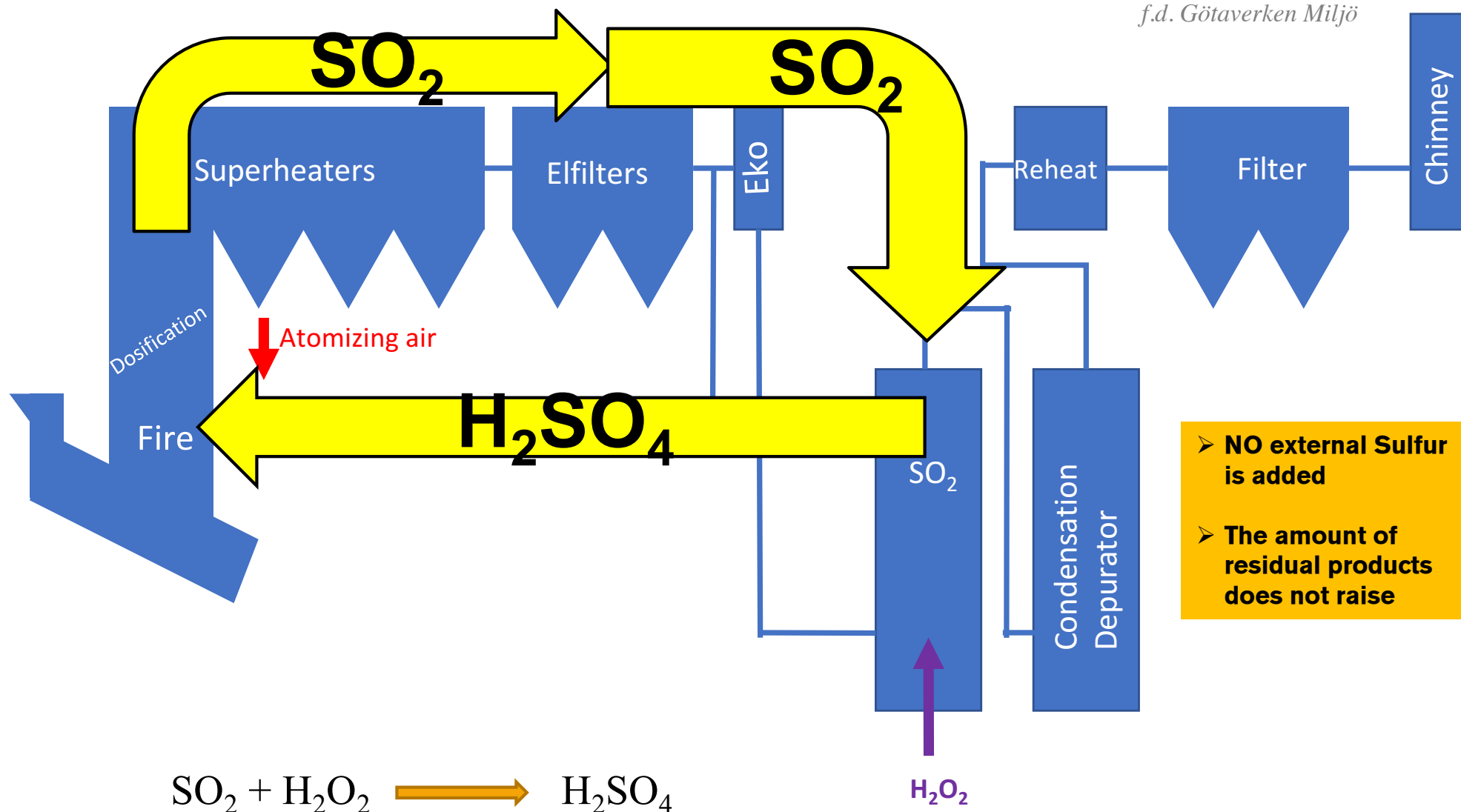
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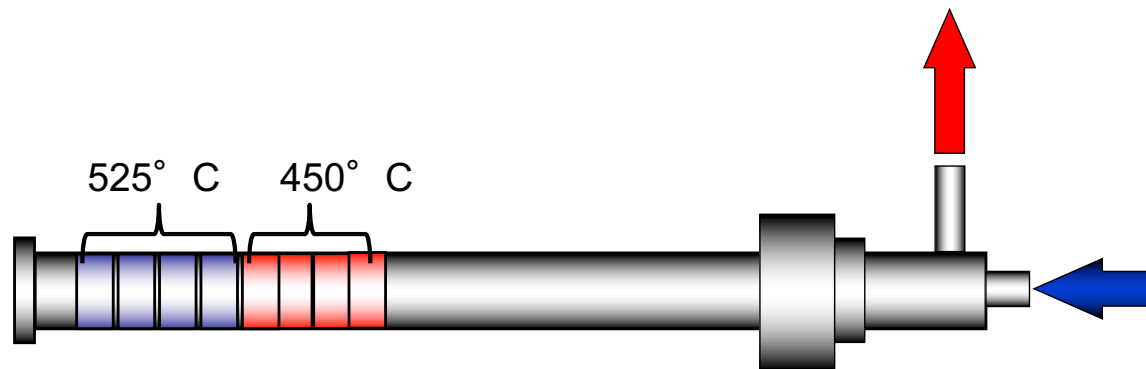
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Experimental matrix Materials

November 2016 – February 2017



- 13CrMo4-5
- Sanicro 28
- 310
- 347H

525°C

- 13CrMo4-5
- Sanicro28
- 310
- 347H

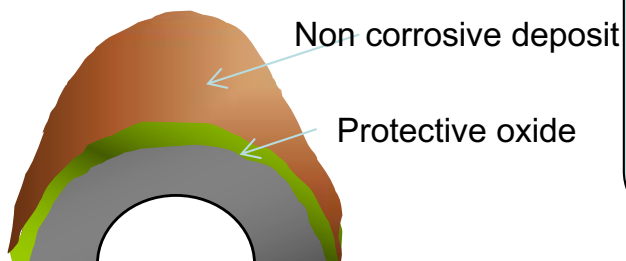
450°C

Moderate
(Sulfur m

Corrosive
added)



Reference
probe



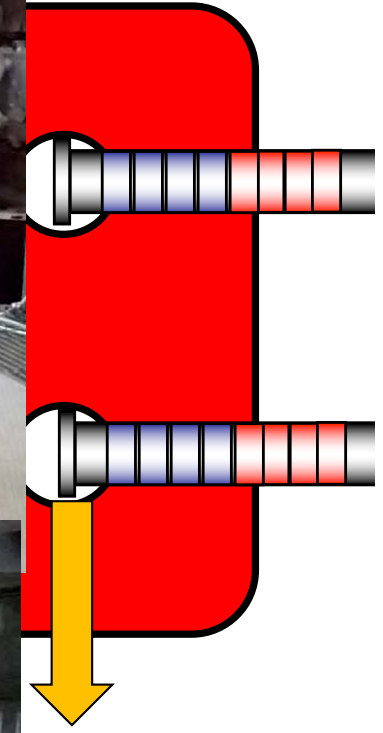
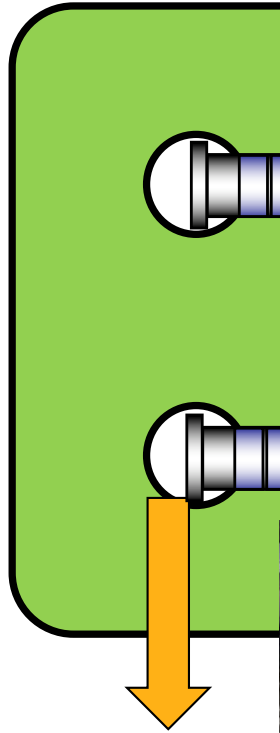
- TP347H (reference)
- 310
- Sanicro 28
- 13CrMo 4-5

Reference
probe



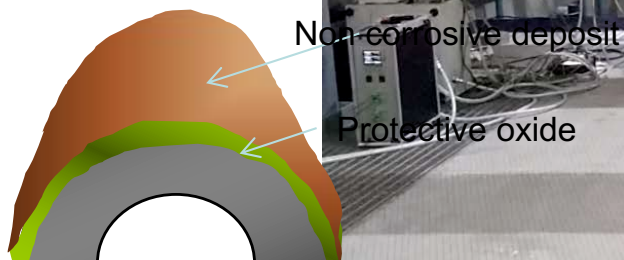
Moderate corrosive
(Sulfur recirculation)

Highly corrosive
(No-sulfur added)

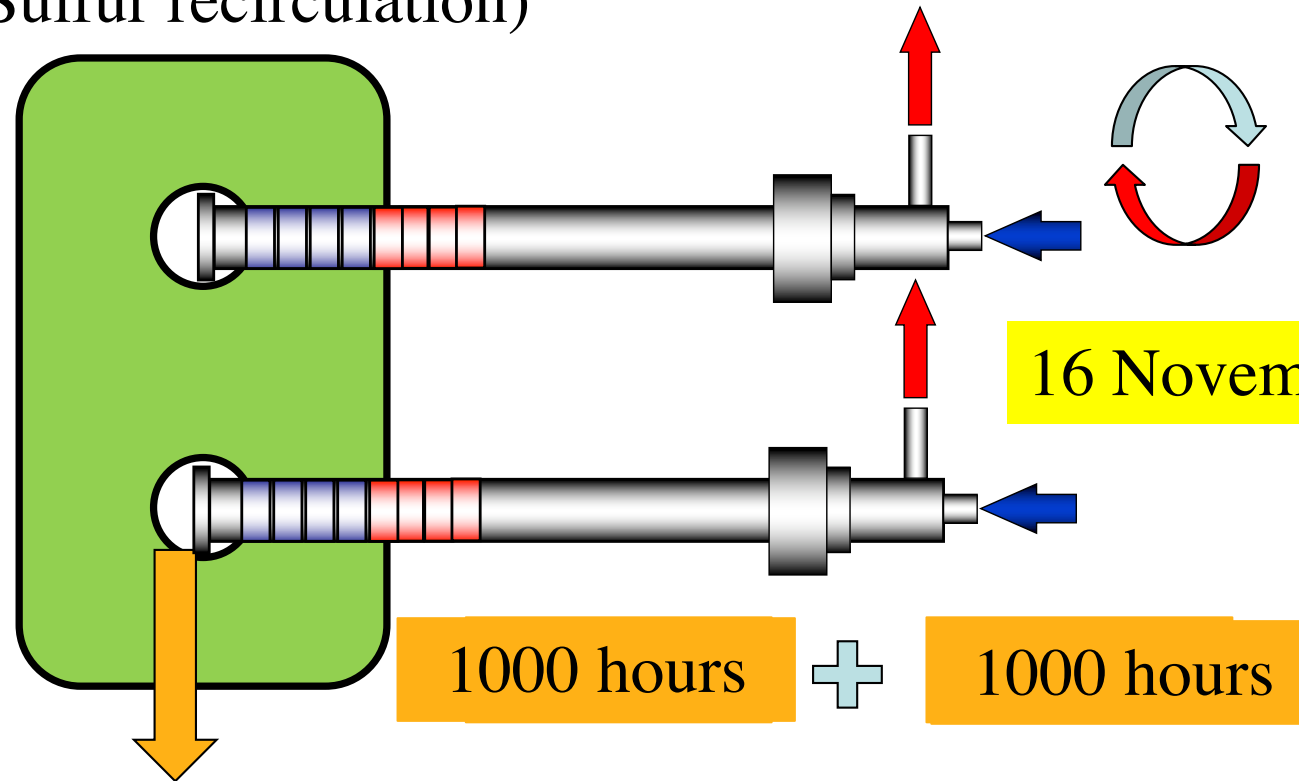


Reference
probe

Reference
probe



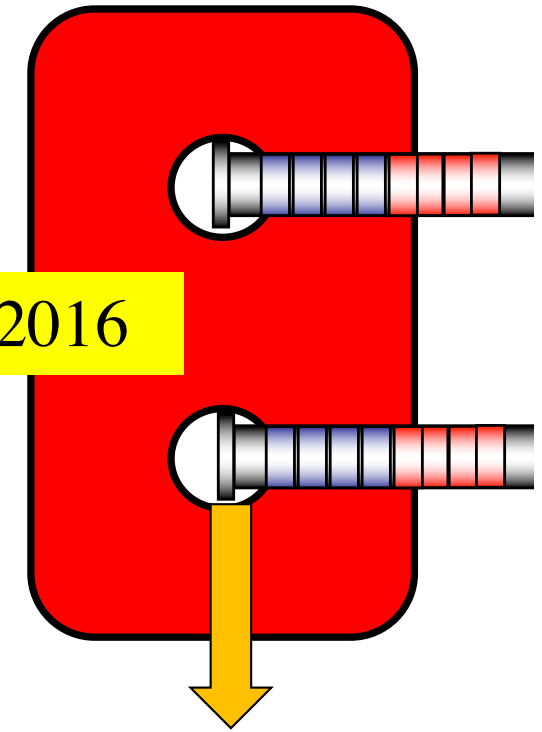
Moderate corrosive
(Sulfur recirculation)



Reference
probe

28 December 2016

Highly corrosive
(No-sulfur added)



Reference
probe

8 February 2017

Characterization

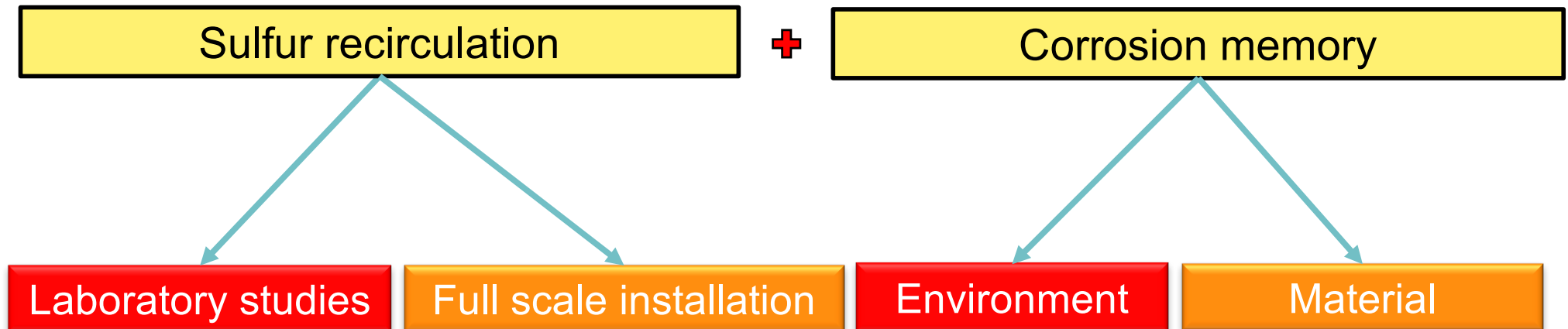
- Ion Chromatography (IC)
- Material loss
- SEM/EDX
- XRD

Ongoing



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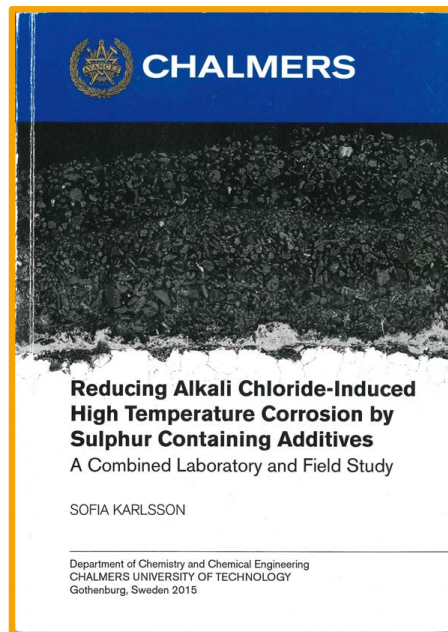
KME goals:

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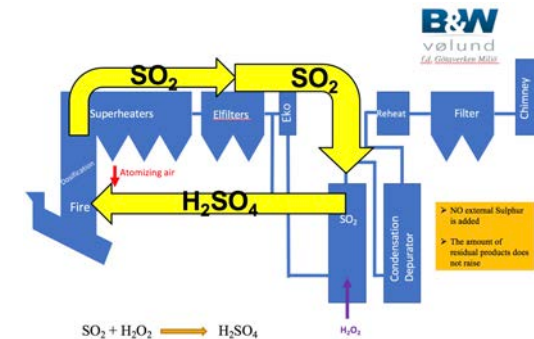
Research strategy

Fundamental research

Corrosion
mechanisms



Fundamental
understanding of
the corrosion
process in boilers



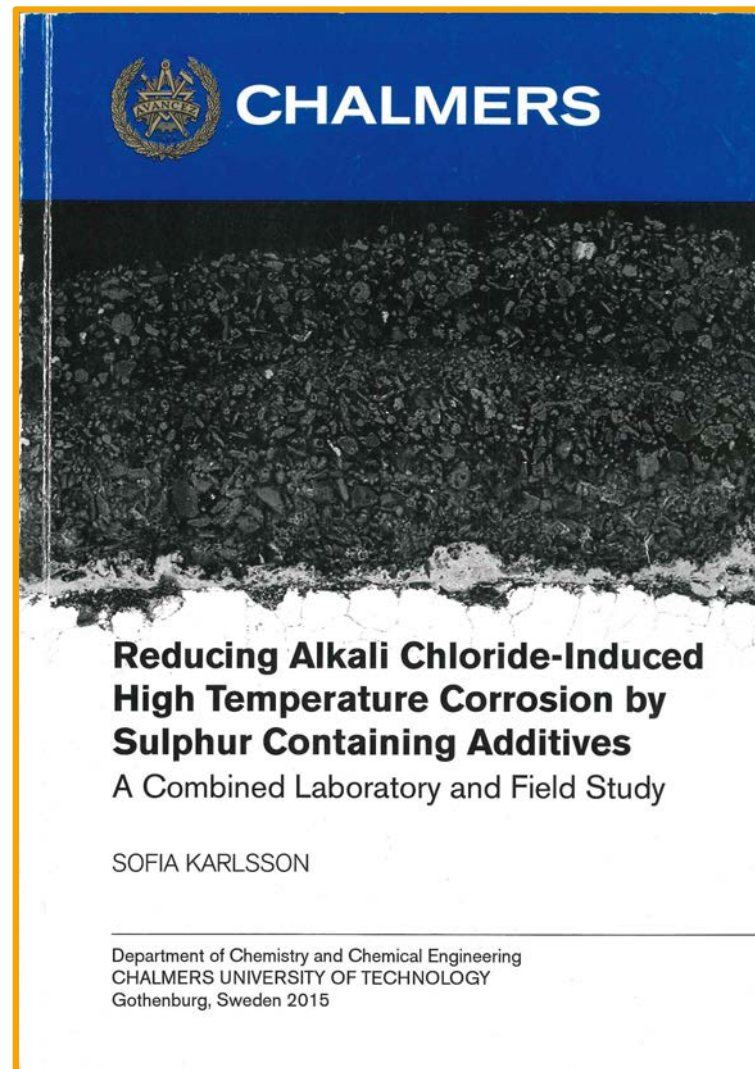
Effects of
corrosion

Applied research

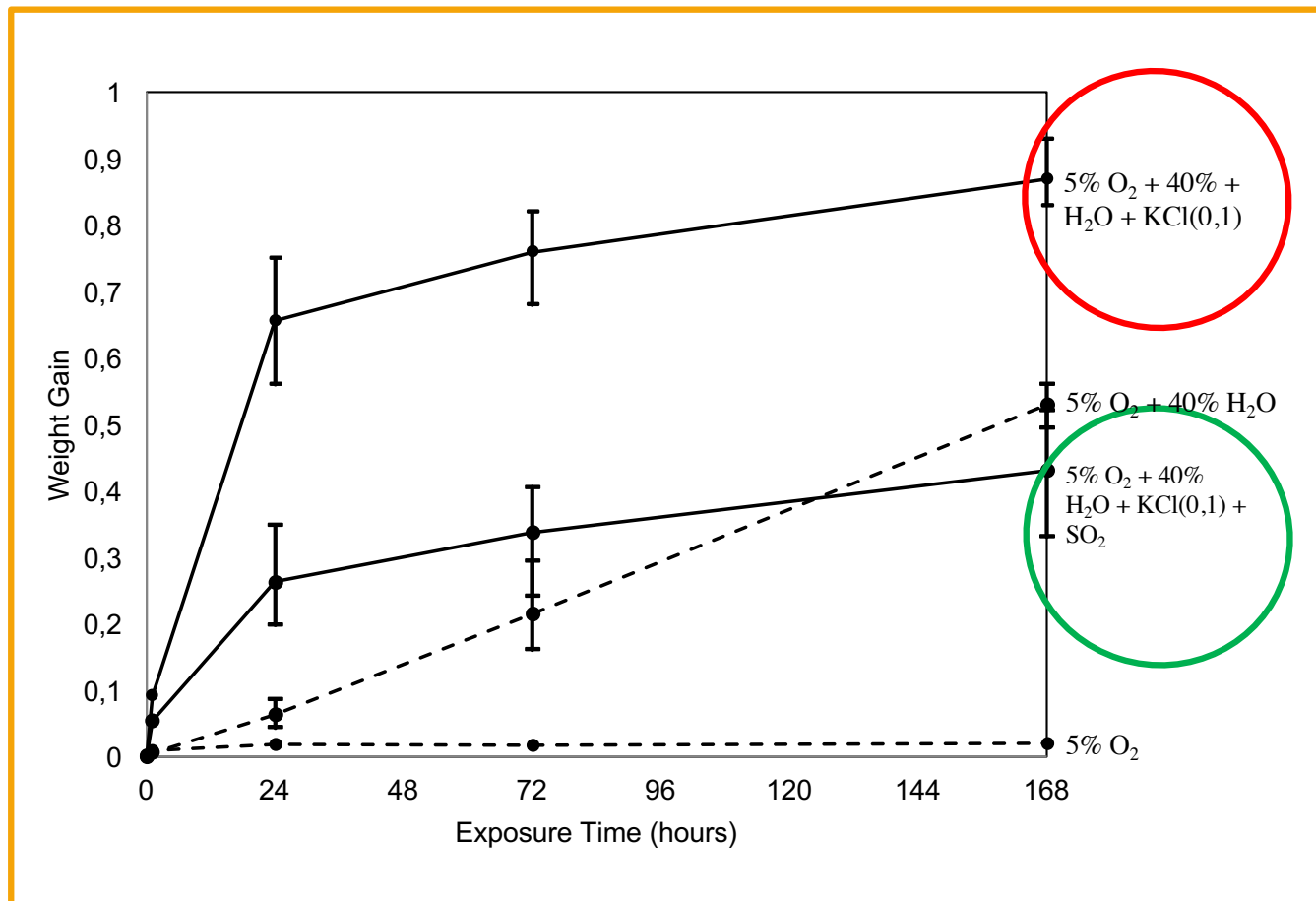
Laboratory
studies

Field
studies

The effect of SO₂ on KCl induced high temperature corrosion of stainless steel



The effect of SO_2 on KCl induced high temperature corrosion of stainless steel

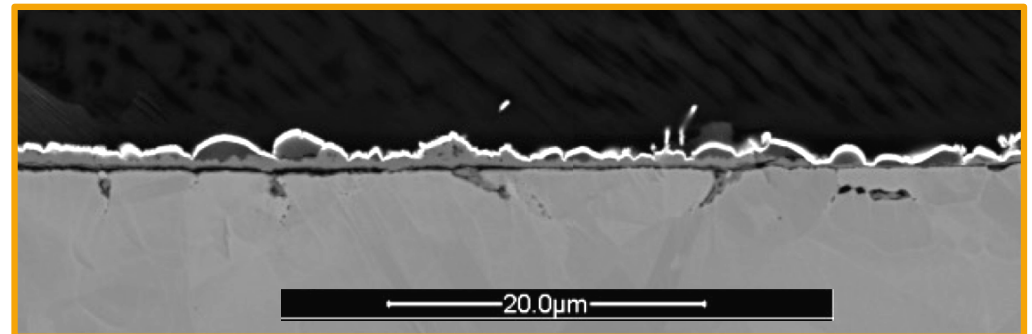
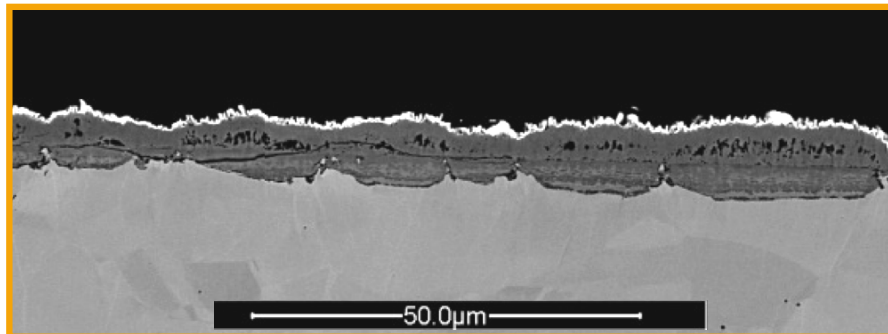


The effect of SO_2 on KCl induced high temperature corrosion of stainless steel

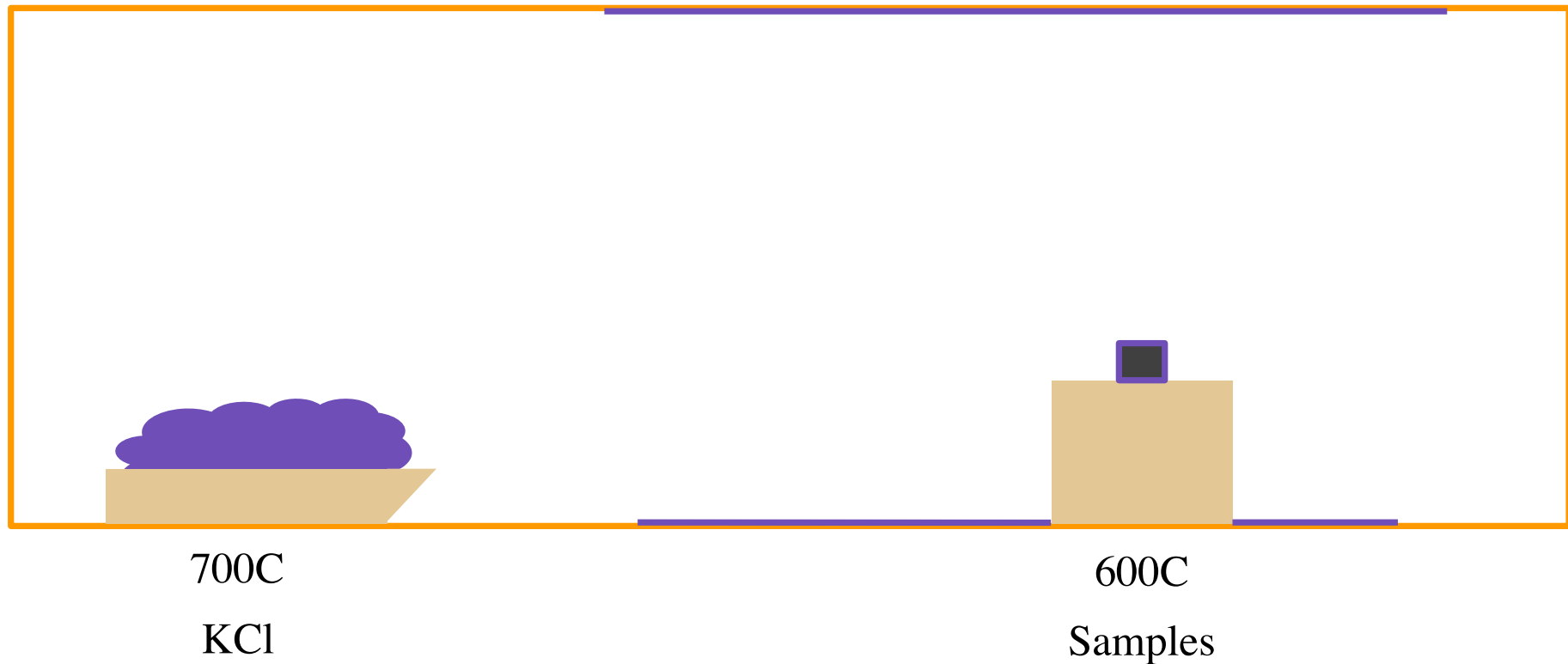
Without SO_2

Cross section BSE

With SO_2



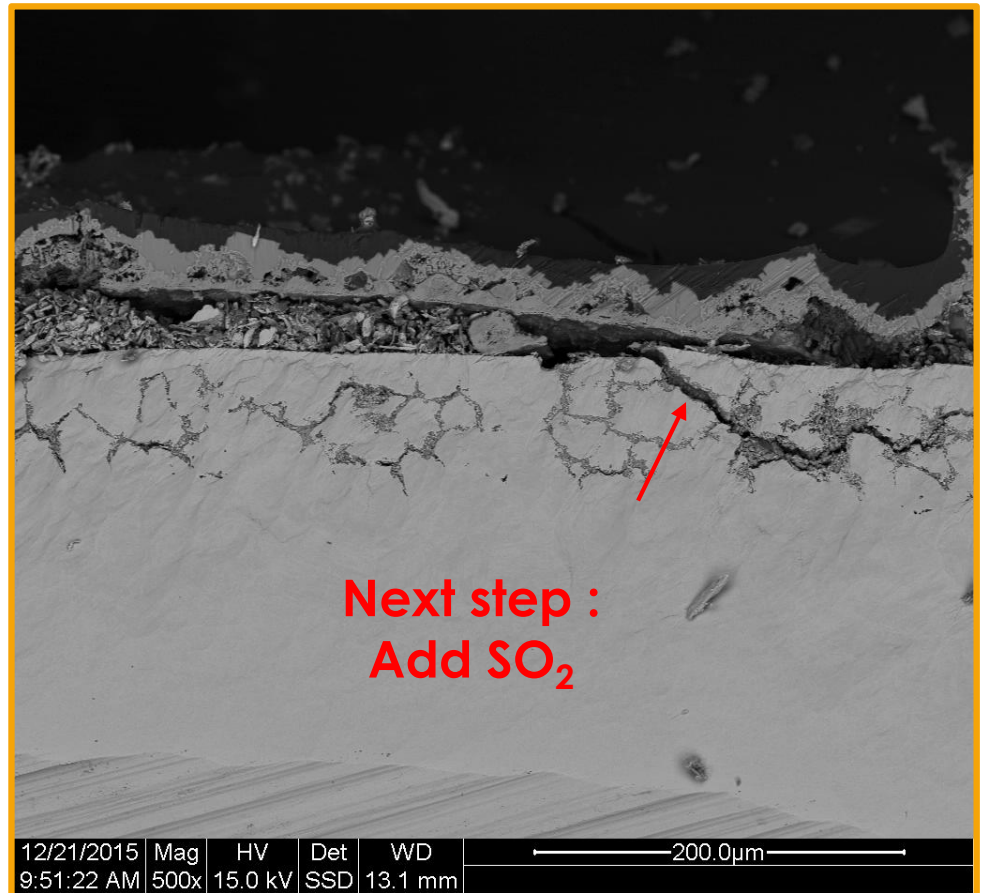
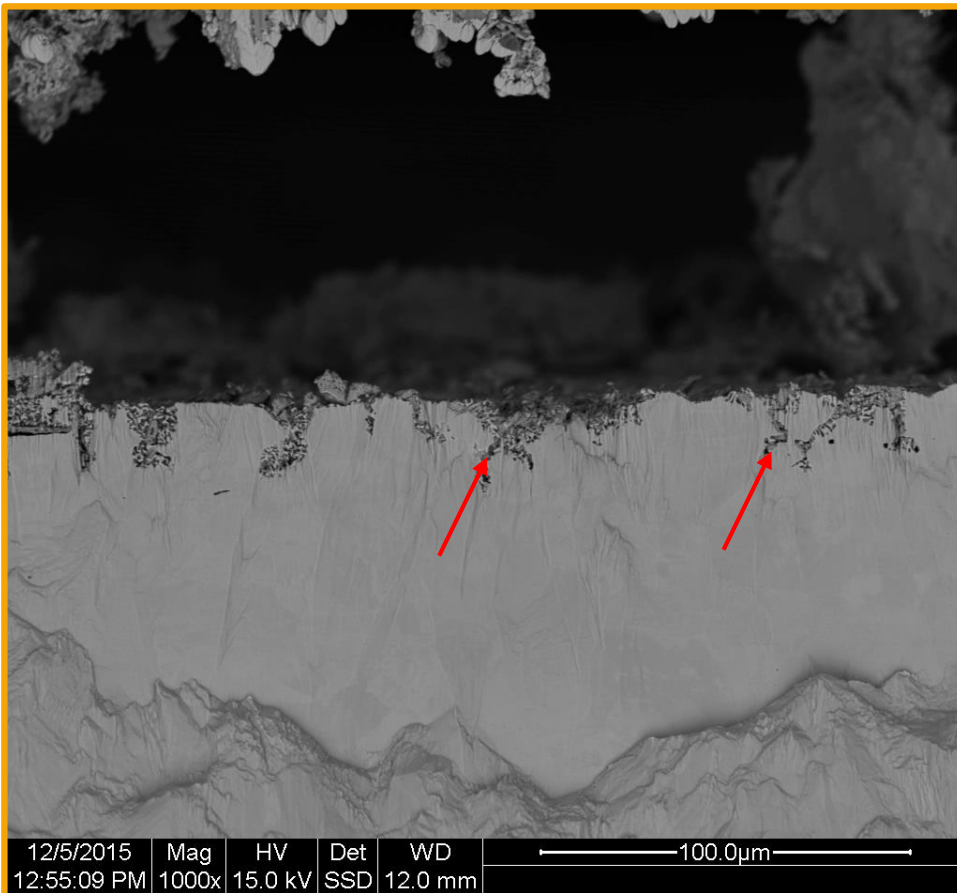
KCl added continuously



Regions with large amounts of KCl

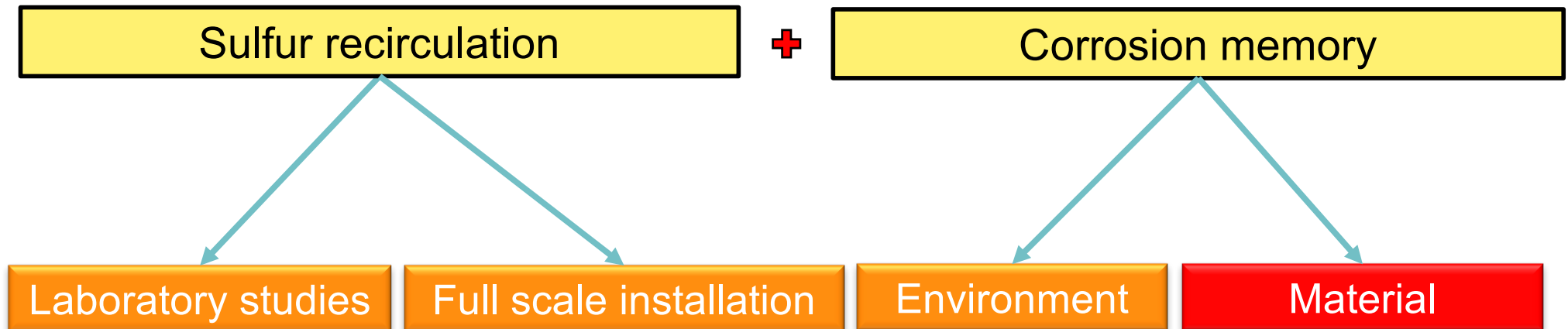


Cross-section



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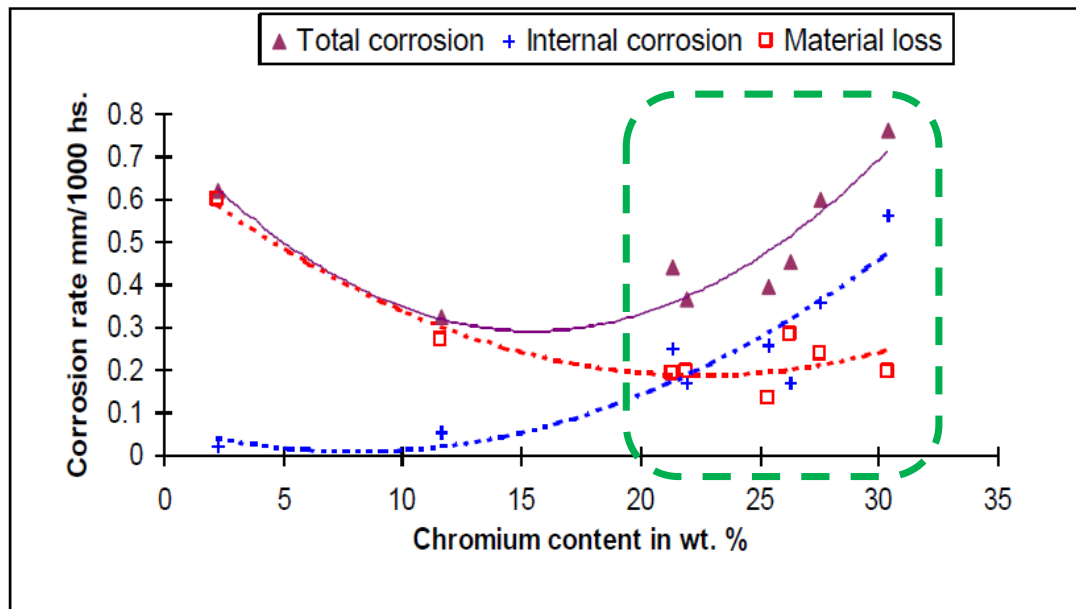
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Corrosion and steel microstructure

Controlled laboratory investigations (DTU), Investigation of field samples (DTU/DONG)

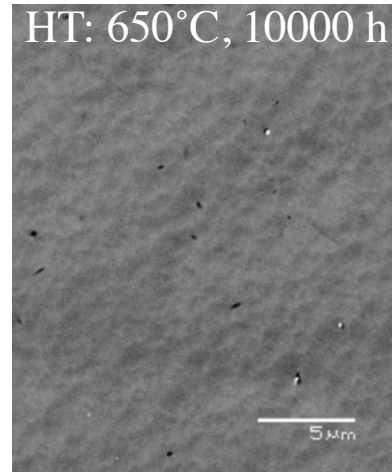
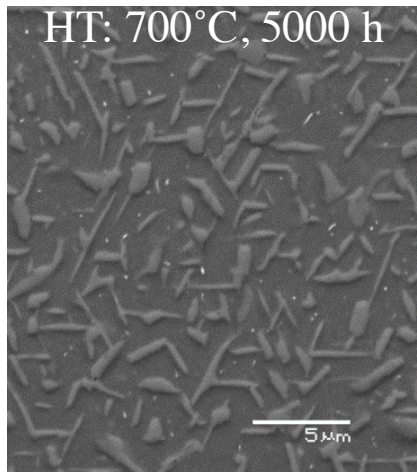
Background: Findings for corrosion rates of materials with different Cr-content



- **High Cr** content increases **internal corrosion** (blue line).
- **Low Cr** content gives high **material loss** (red line).
- Minimum in total corrosion lies at 15-18wt% Cr (purple line)

Is the increased internal corrosion only due to Cr-content or also the distribution of Cr?
(at high Cr content extensive precipitation can occur)

Controlled laboratory corrosion exposures of modified AISI310 (24 wt% Cr) steel in different heat treatment conditions



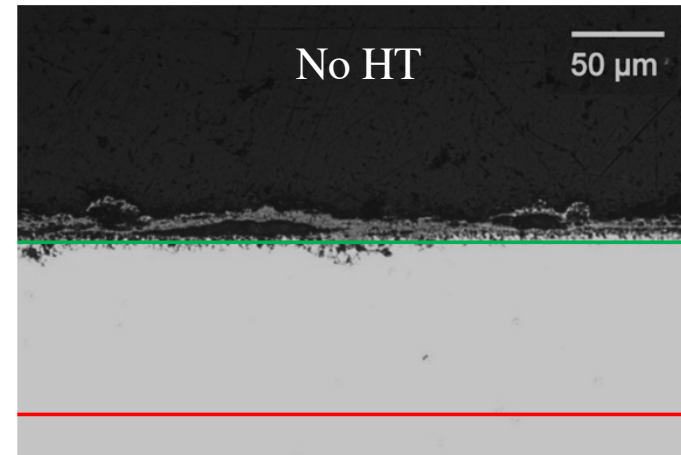
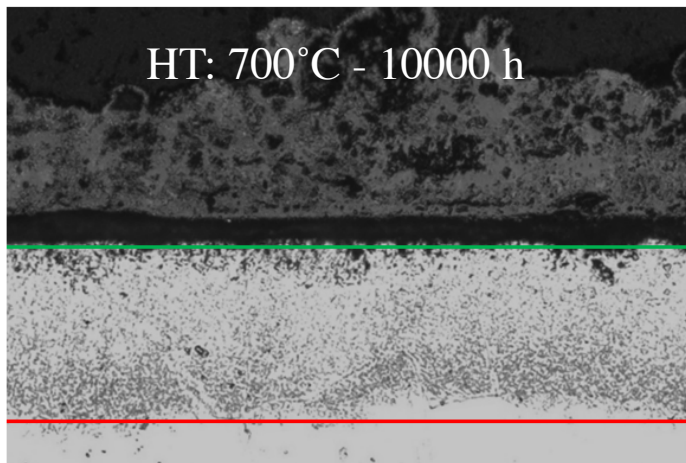
Heat treatment at 700°C leads to heavy σ -phase precipitation. At slightly lower temperature no precipitation occurs even after longer exposure times



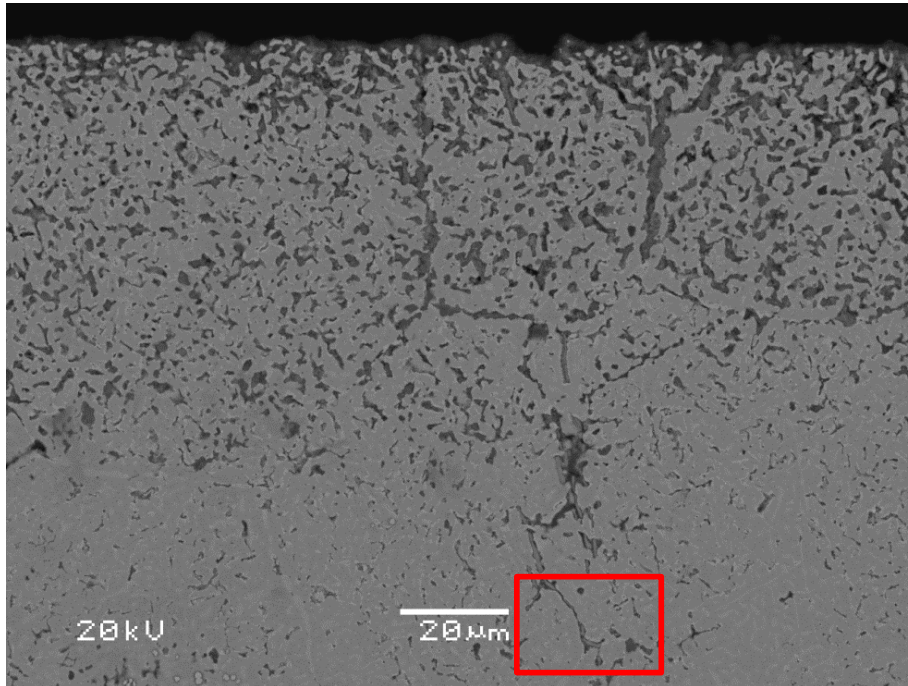
Possibility to corrosion test the same material below 650°C with very different precipitate distribution

Corrosion testing:

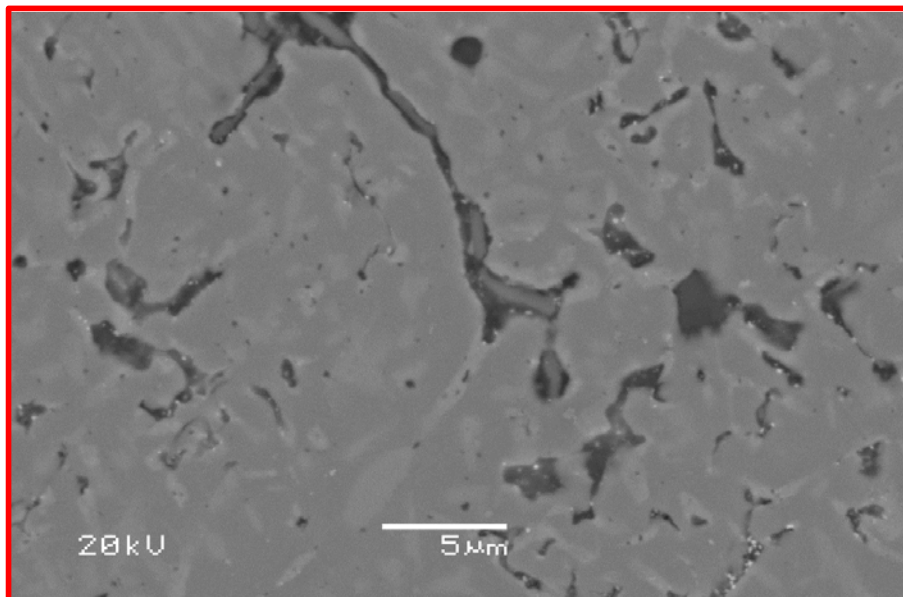
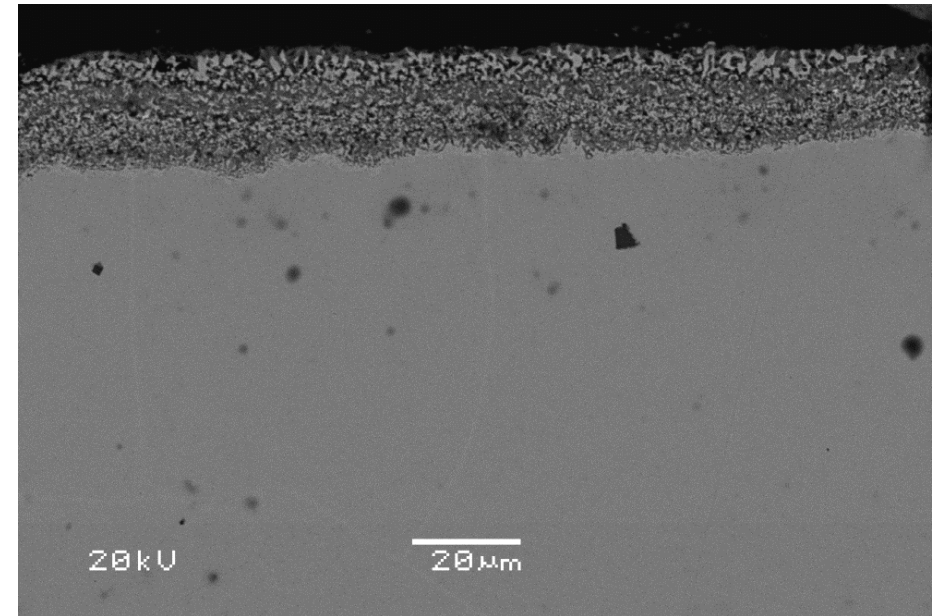
Exposure: 15 % H₂O, 5 % O₂ and balance N₂, 600°C, 168h, KCl Deposit



HT: 700°C - 10,000 h



No HT



Clear influence of microstructure on corrosion attack

Heat treated material (Cr-rich σ phase) =>
Higher internal corrosion rate

Next steps:

In depth microstructural characterization

Laboratory exposure of TP347 in both aged and
as received conditions

Investigation of field samples

Fynsværket, unit 8, SH4:

different specimens with different temperature profiles – TP347H vs .Tempaloy AA1. Inlet and outlet,
17,000 hours

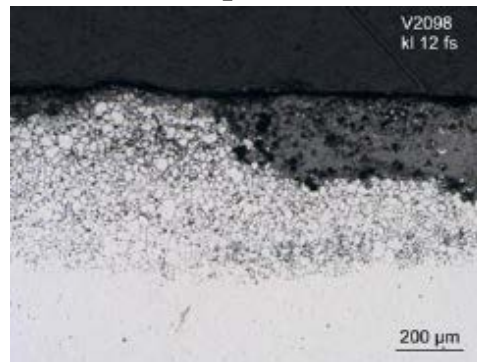
Amagerværket 1:

Test section with different specimens 304H, 310, as well as 347H, **30,000 hours**

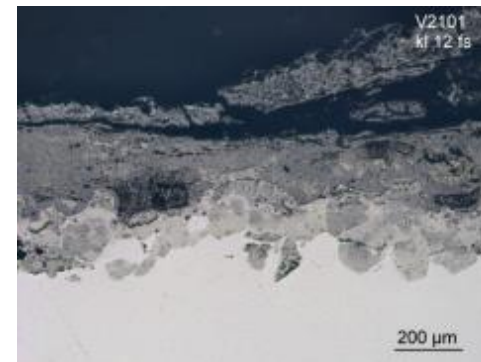
TP 347H FG



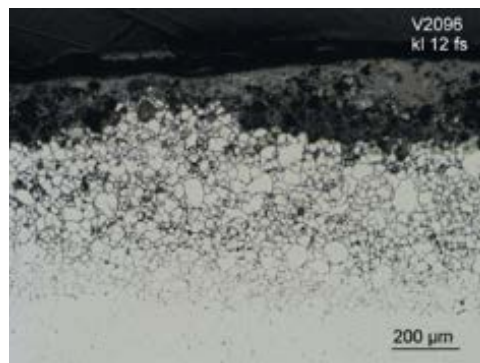
DMV Super 304H



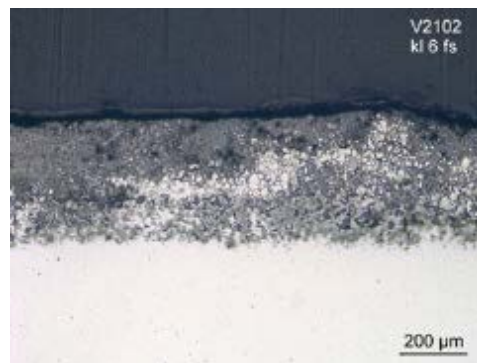
DMV 310N



DMV 347H FG



TX304HB

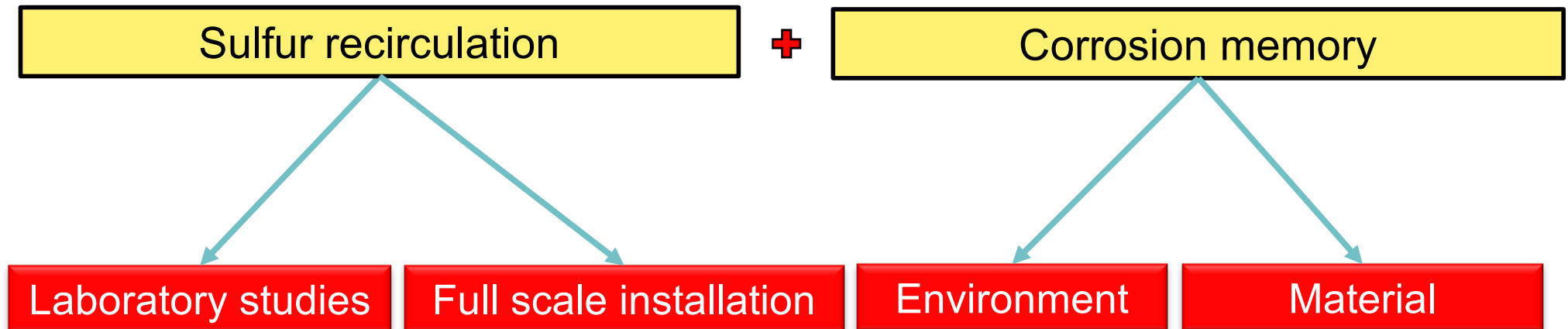


Work to be done:

- Comparison of microstructure for different steels and exposures in etched condition.
- Select specimens for more SEM analysis to understand corrosion attack.
- More advanced microscopy at areas at the corrosion front (FIB lift out and TEM).

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