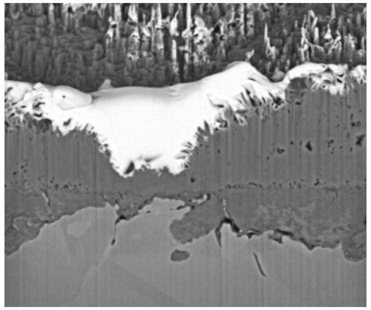
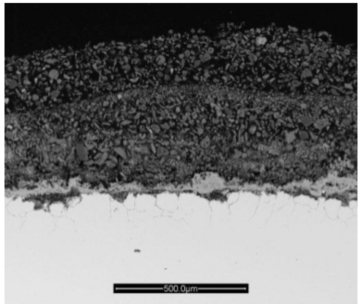
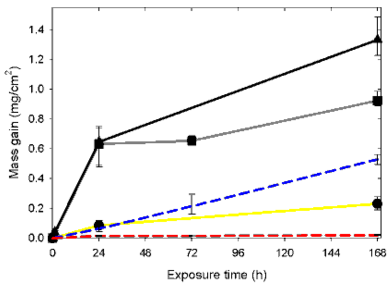
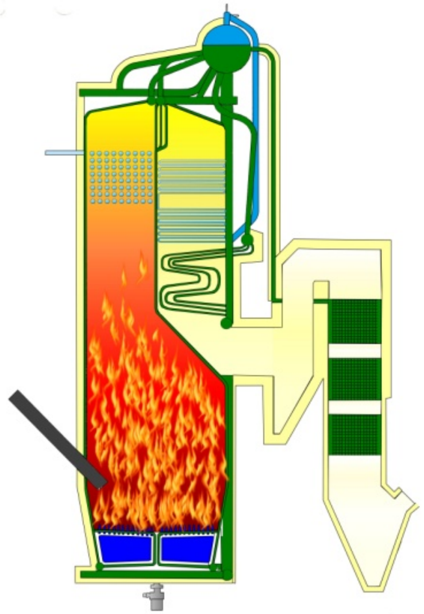
# Why High Temperature Corrosion research?

The
High-Temperature
Corrosion Center







# Chain of events – HTC/KME research

**Corrosion problems**

Defined by industry and academia in collaboration

**Corrosion mechanism**

Generic results from the projects

**Corrosion solutions**

The obtained knowledge is implemented by the industry

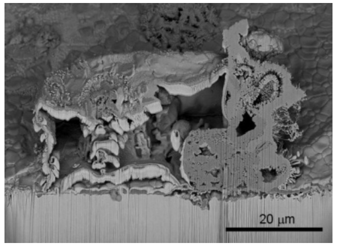
# Chain of events – HTC/KME research

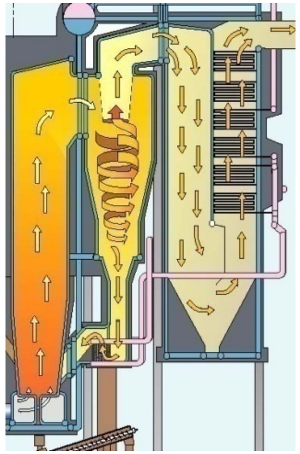
Corrosion problems

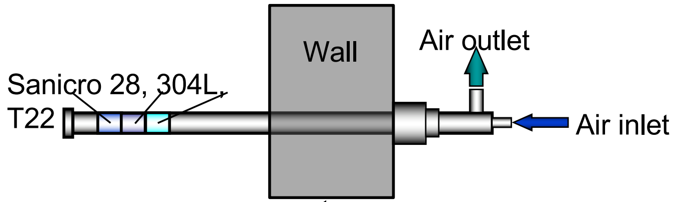
Defined by industry and academia in collaboration

**Fundamental research**

Corrosion mechanisms





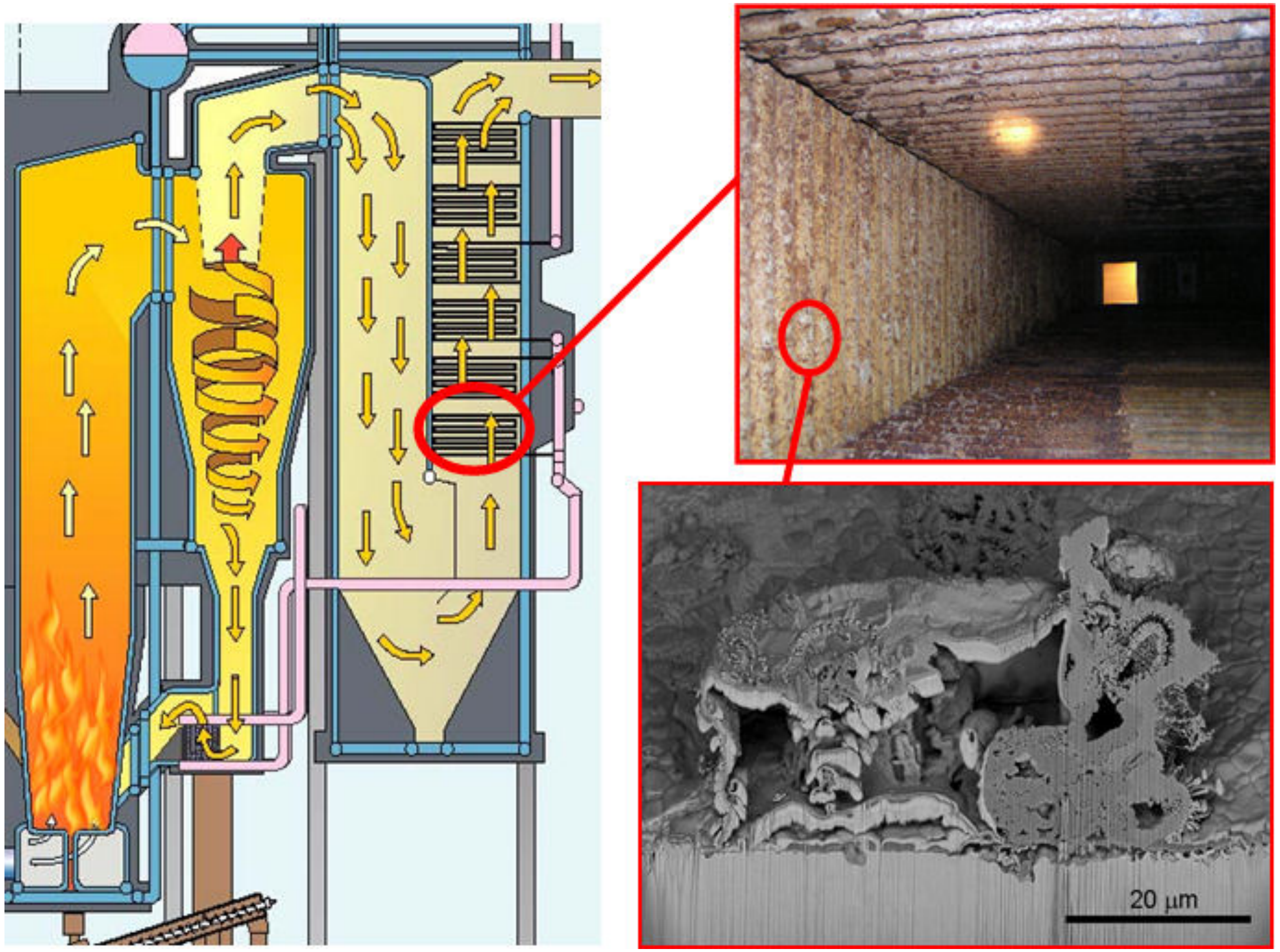

Effects of corrosion

**Applied research**

Laboratory studies

Field studies

# What is the problem?




Material degradation reduces the lifetime of the superheaters.

As consequence, the biomass and waste fired boilers are operated at lower temperatures with decreased electrical efficiency, compared to coal fired boilers.

# Fossil fuel *vs.* biomass and waste

The long term goal is to replace fossil fuels by biofuel. However, the corrosion rates is higher…

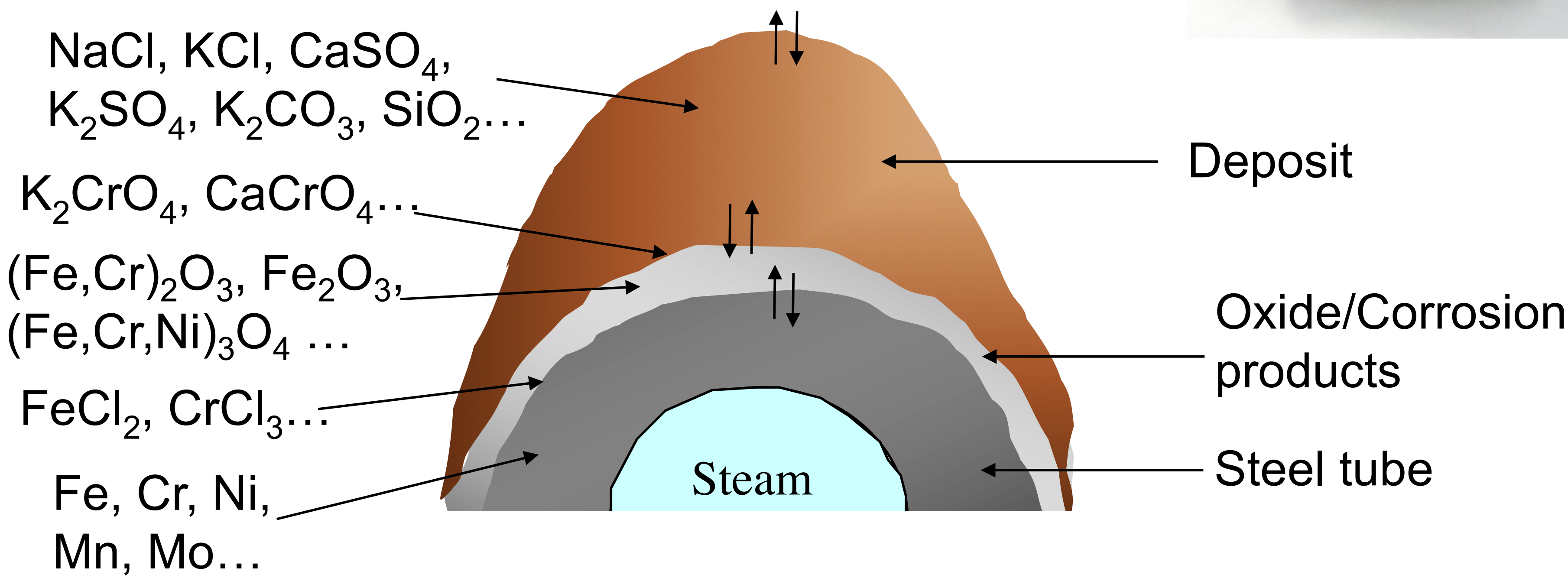
| | Fossil-fuel (Coal) | Biomass (Wood) | Biomass (Agriculture) | Waste |
|---|---|---|---|---|
| $pO_2$ | ~3% | ~5% | ~5% | 6-11% |
| $pH_2O$ | ~10% | 20-25% | 20-25% | 20-25% |
| Reactive alkali | Low | Medium | High | High |
| $pSO_2$ | High | Low | Low | Low |
| $pHCl$ | High | Low | Medium | High |
| Steam temperature (state-of-the-art) | 630°C | 520°C | 450°C | 420°C |

The electricity efficiency depends on the steam temperature!

# The fireside environment in a biomass/waste fired boiler

The chemical environment at the superheater is very complex!

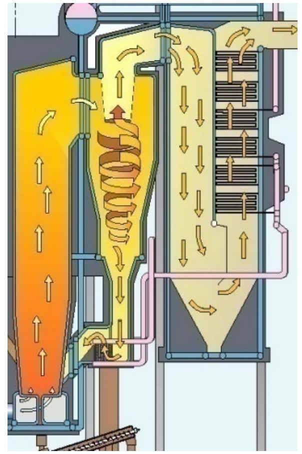
$CO_2$, $H_2O$, $O_2$, HCl, $SO_2$, $NO_x$ and particles…



# Chain of events – HTC/KME research

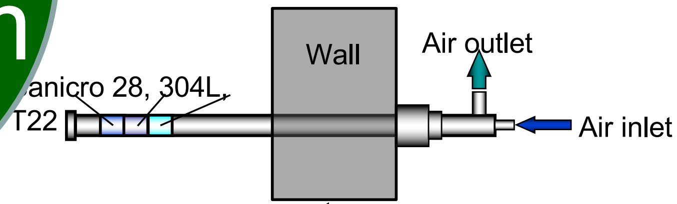
**Fundamental research**

Corrosion mechanisms



Corrosion problems

Corrosion mechanism

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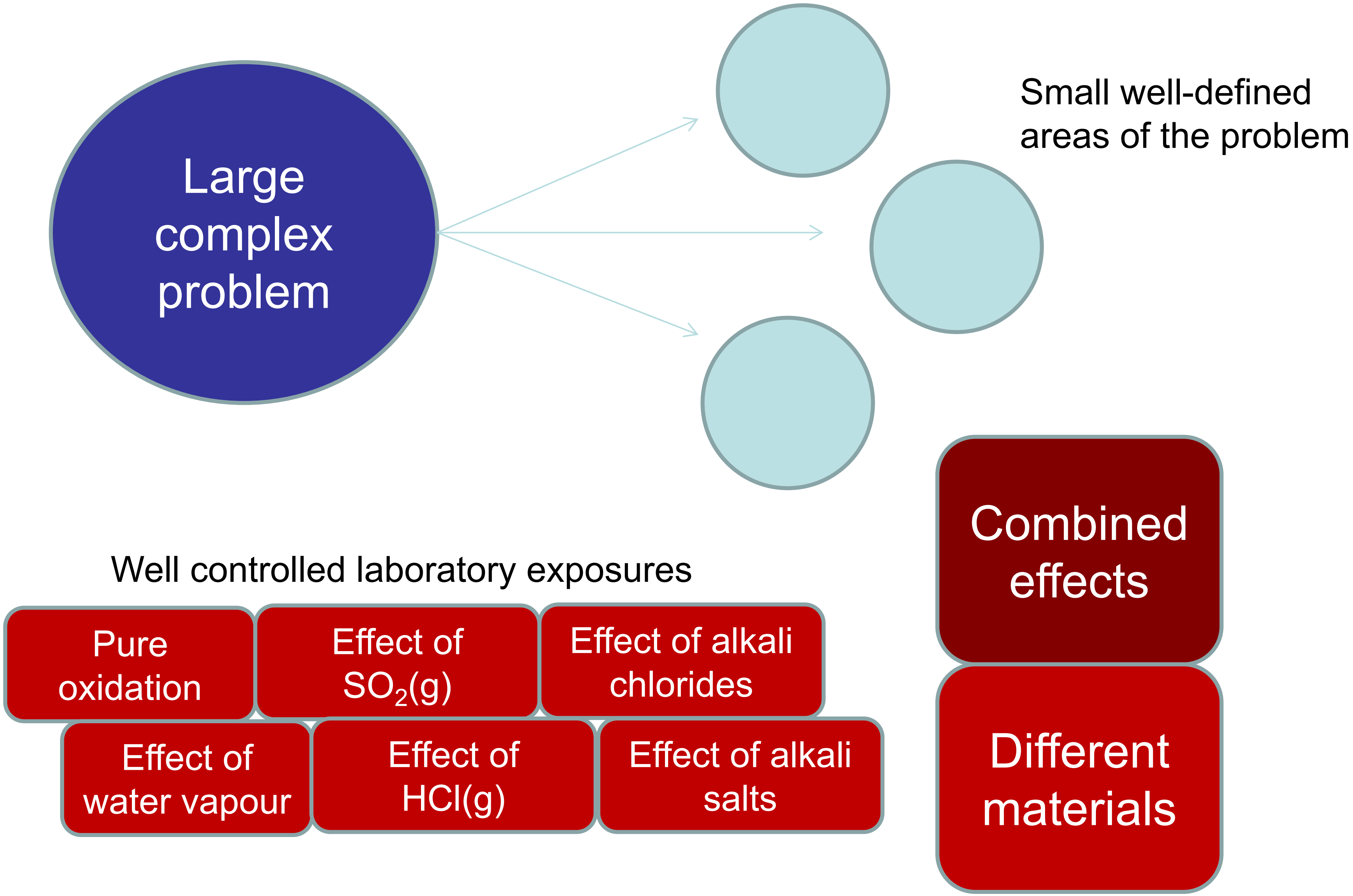

Large complex problem
Small well-defined areas of the problem
Well controlled laboratory exposures
Pure oxidation
Effect of $SO_2(g)$
Effect of alkali chlorides
Effect of water vapour
Effect of HCl(g)
Effect of alkali salts
Combined effects
Different materials

# What causes the corrosion problems on stainless steels?

- The corrosion resistance of stainless steels comes from their ability to form a chromium rich oxide film that grows slowly and protects the material from further oxidation.

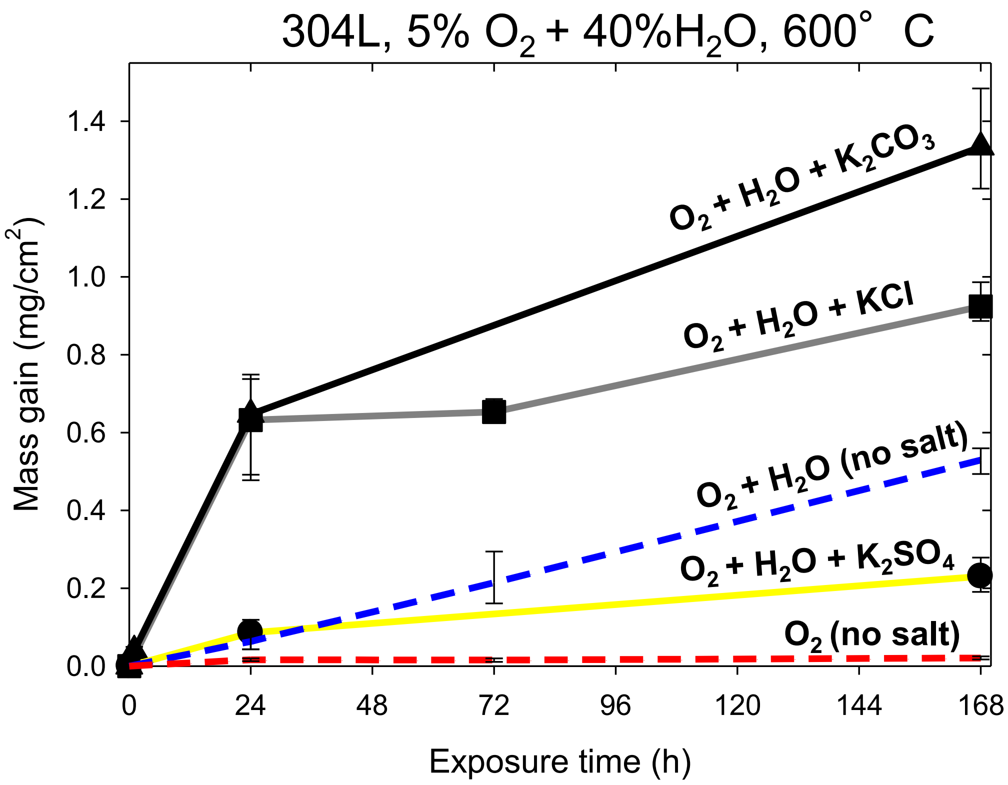
- The oxide usually consists of a corundum type solid solution with Cr and Fe, $(Cr,Fe)_2O_3$, where the Cr to Fe ratio determines whether it is protective (as chromia, $Cr_2O_3$) or poorly protective (as hematite, $Fe_2O_3$).

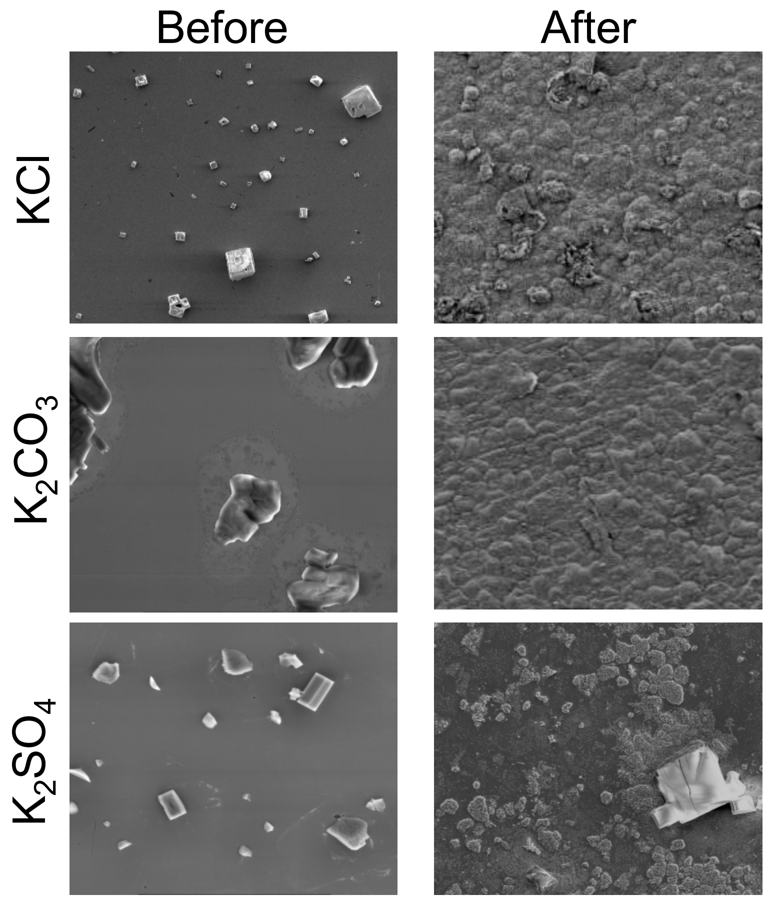
$$Cr_2O_3 \longleftrightarrow (Cr,Fe)_2O_3 \longleftrightarrow Fe_2O_3$$

**Protective** ↔ **Poorly protective**
**Slow growing** ↔ **Fast growing**

$$(Cr,Fe)_2O_3 \xrightarrow{O_2 + H_2O(g)} Fe_2O_3 + CrO_2(OH)_2(g)$$

# The effect of chromium depletion on chromia forming steels




Chromate formed

Chromate formed

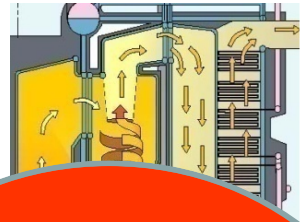
No chromate formed

$$(Cr,Fe)_2O_3 \xrightarrow{O_2 + H_2O + K_2CO_3} Fe_2O_3 + K_2CrO_4 + CO_2$$

# Chain of events – HTC research

Fundament … arch

Corrosion
mechanism



Corrosion problems

Corrosion mechanism

Corrosion solutions

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# New ways to increase the $SO_2$ content of the flue gas: Recirculation of sulphur

GÖTAVERKEN
MILJÖ

**Reference exposure:**

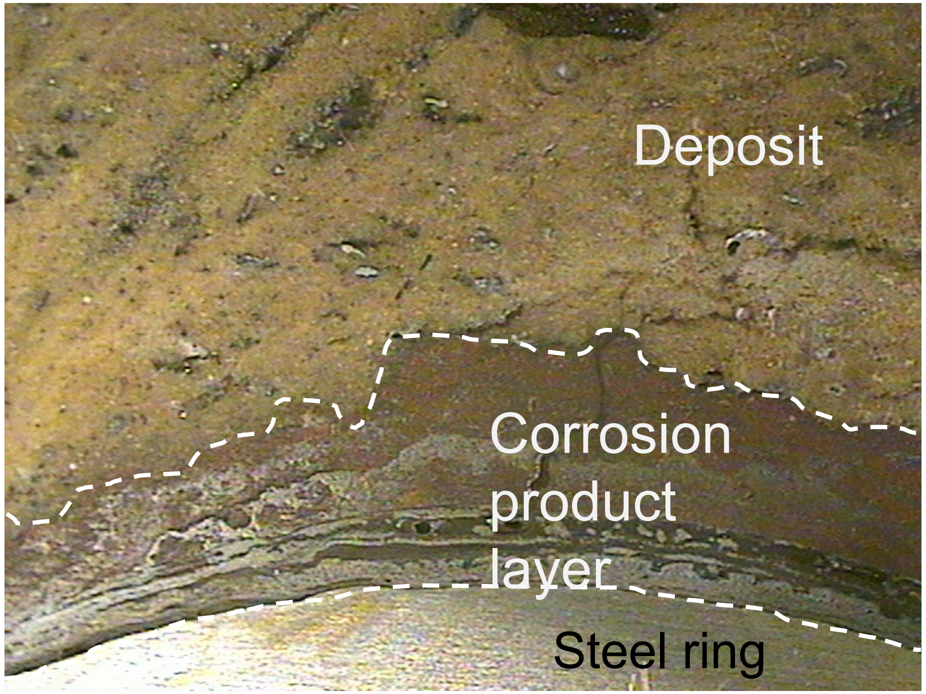
**$p$HCl =300 ppm**
**$pSO_2$ = 90 ppm**

**Sulphur recirculation:**

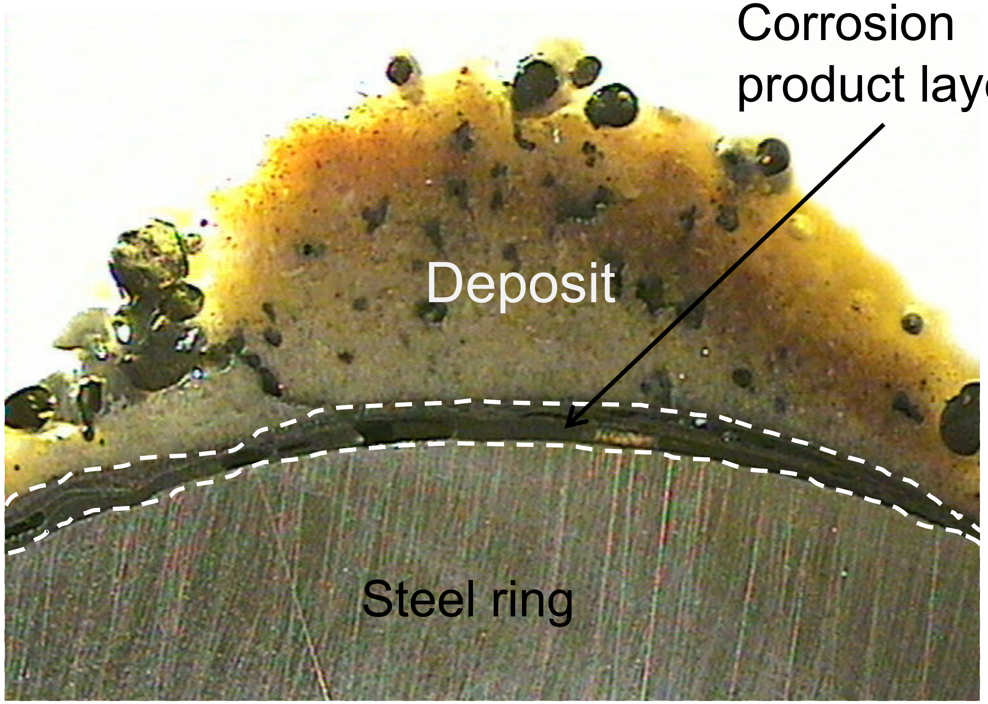
**$p$HCl =400 ppm**
**$pSO_2$ =270ppm**

# Outtake of corrosion probes after 1000 hours exposure without sulphur recirculation

# The beneficial effect of sulphur recirculation on 16Mo3



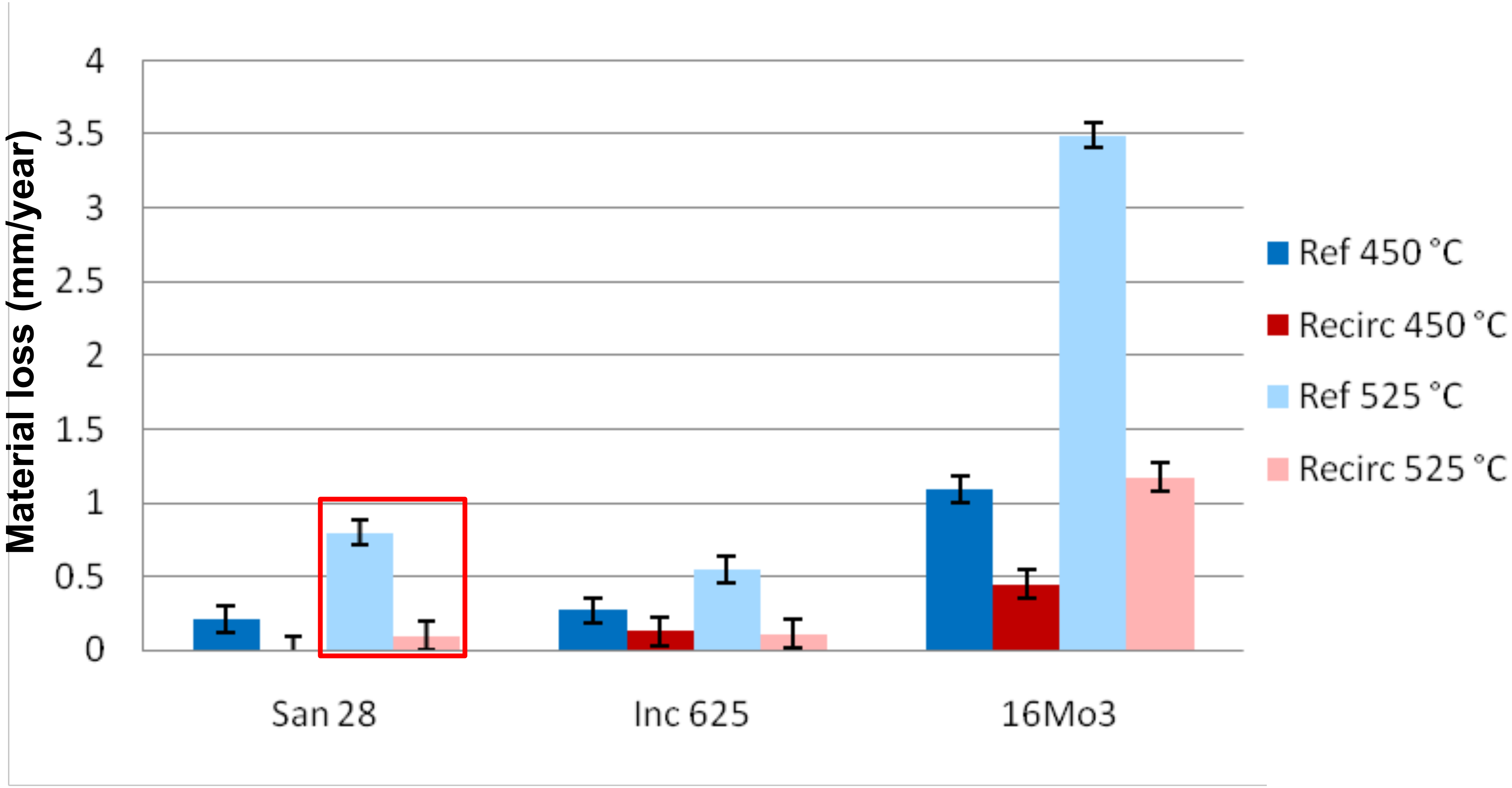

Reference exposure, 525° C, 1000h




Sulphur recirculation exposure, 525° C, 1000h

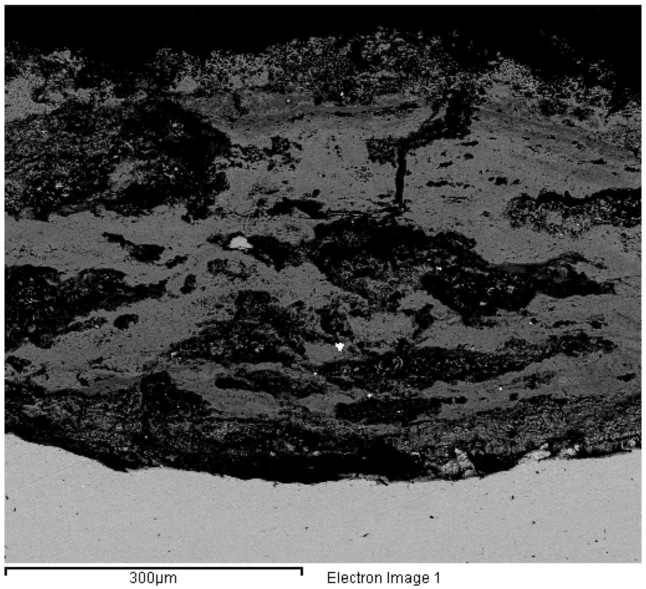
# Long term effect of sulphur recirculation on corrosion

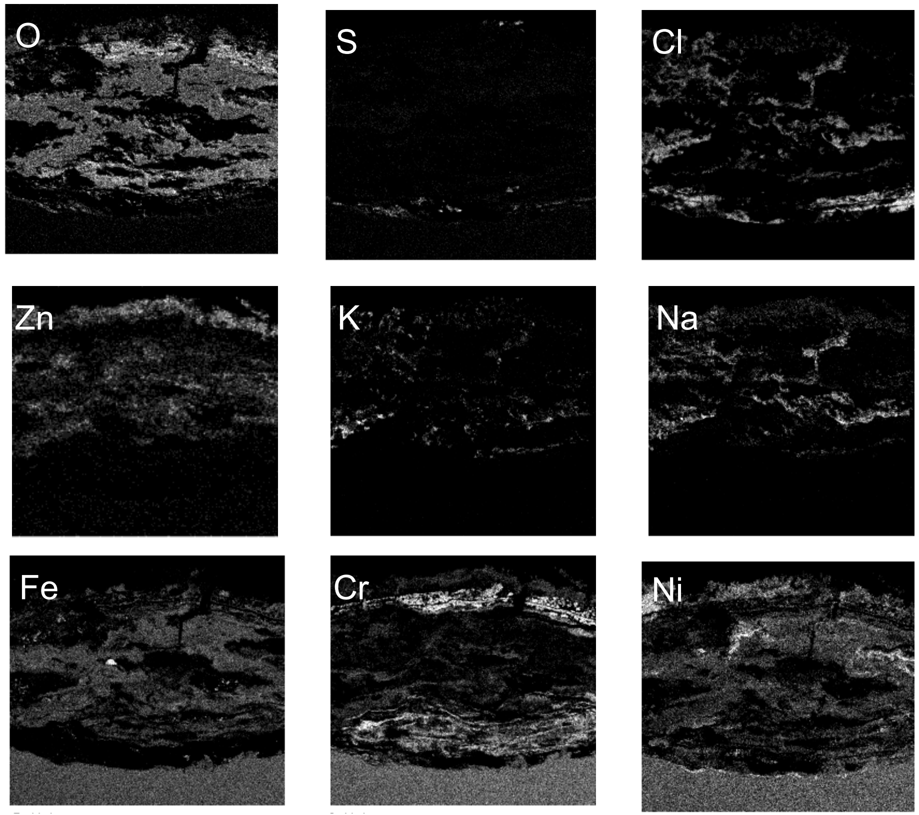
Exposure time: 1000 hours



# The effect of sulphur recirculation on corrosion

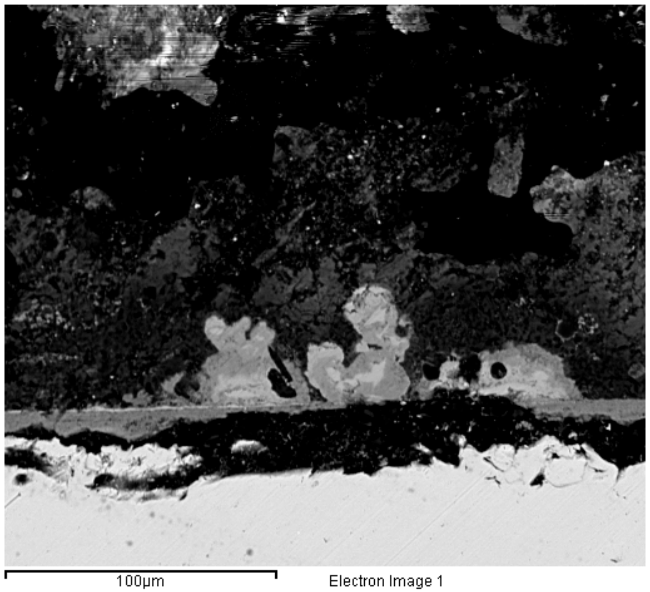
## Sanicro 28 exposed for 1000 hours at 525°C without sulphur recirculation

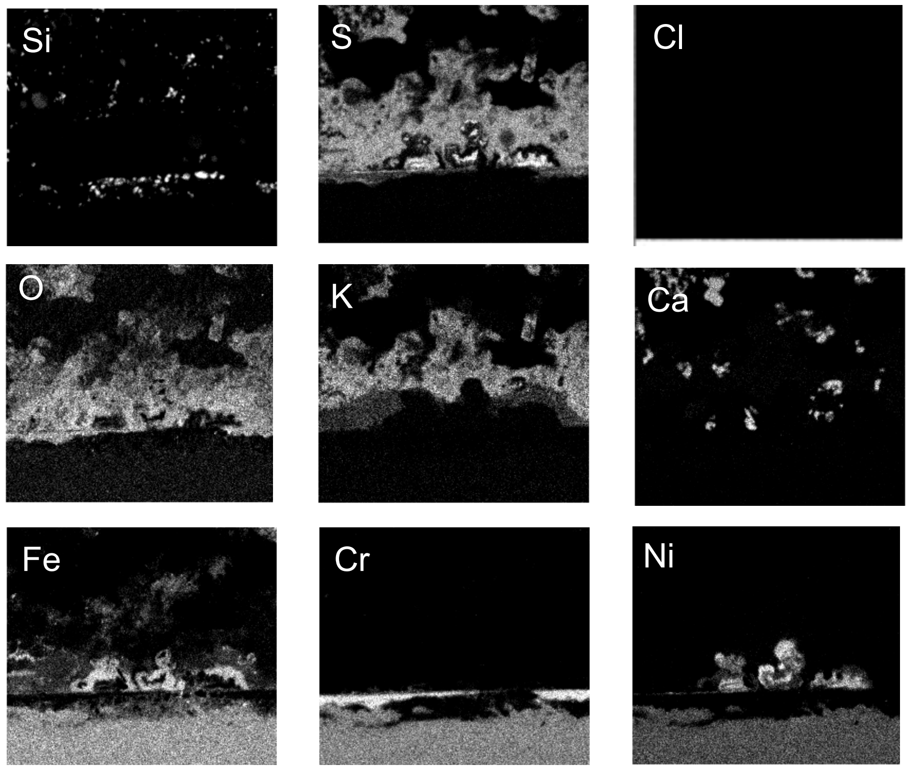


# The effect of sulphur recirculation on corrosion

## Sanicro 28 exposed for 1000 hours at 525°C with sulphur recirculation



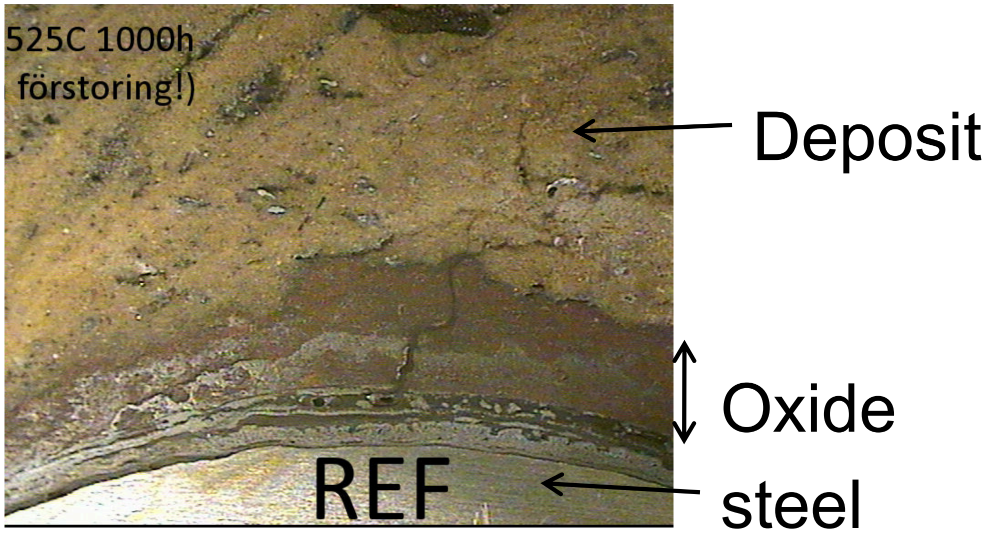



# What's special about HTC/KME

- Often short time between research results and application in reality

**Sulfur additions in high alkali environments**

| | |
|---|---|
| 2008 | Lab studies |
| 2009/2010 | Large scale test in Savenäs |
| 2014 | Commercial product |
| 2016 | First installation (DK) + Research project |



# New opportunities within HTC/KME

## Team up Experimental And Modeling Work on Oxidation Reaction Kinetics

**TEAMWORK**

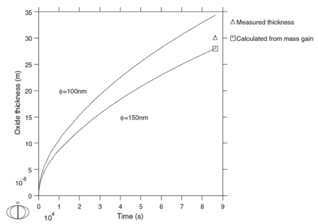
*T. Jonsson,* CTH, L. Mikkelsen, B&W Völund, T. Helander, SHT, M. Lundberg, SMT, J-E. Svensson, CTH, A. Persdotter, CTH, L. Paz, CTH, H. Larsson, KTH, J. Ågren, KTH, L. Höglund KTH, J. Jeppsson, TC, B-Å. Andersson, Eon, J. Liske CTH

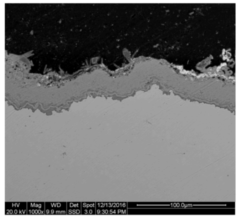
**Project support: R. Pettersson Jernkontoret**

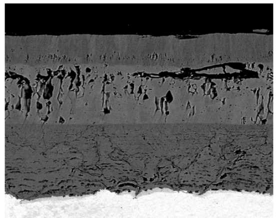
## Projektets mål

**Nya simulerings- och modelleringsverktyg**

i) *som ett FoU-hjälpmedel*
ii) för livstidsprediktering
iii) optimering av driftstemperatur





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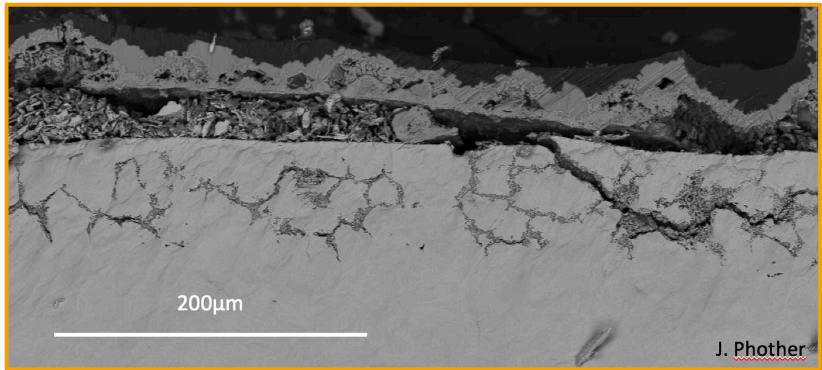
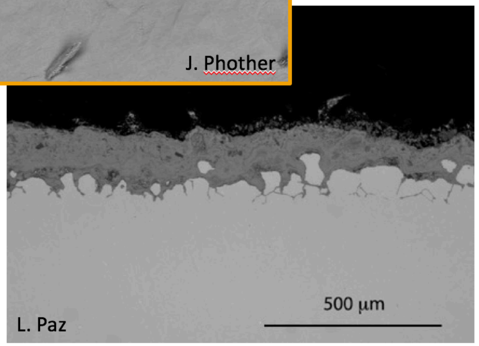
## Example FIB/SEM – 3D



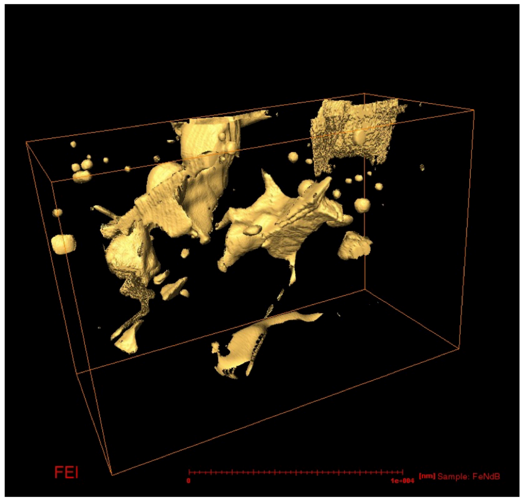




Challenge:
- K and/or Cl present at the corrosion front?
- Voids?
- Precipitates in the alloy?
- ***2D image of 3D structure.***

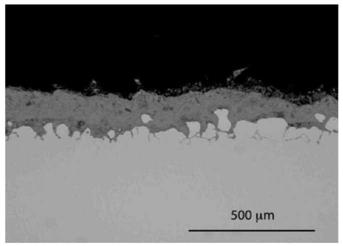


## Example FIB/SEM – 3D

3D information



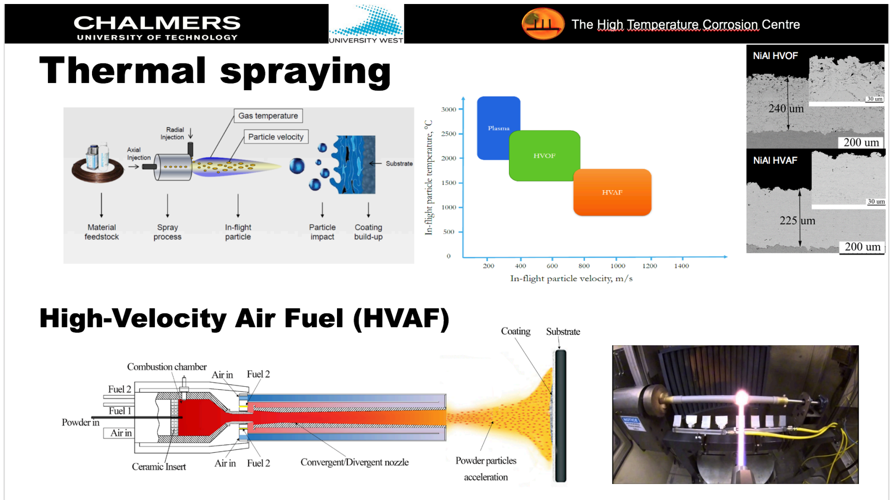

Particles
Voids
Elemental distribution
Crystal structure
...



# Corrosion solutions – New materials

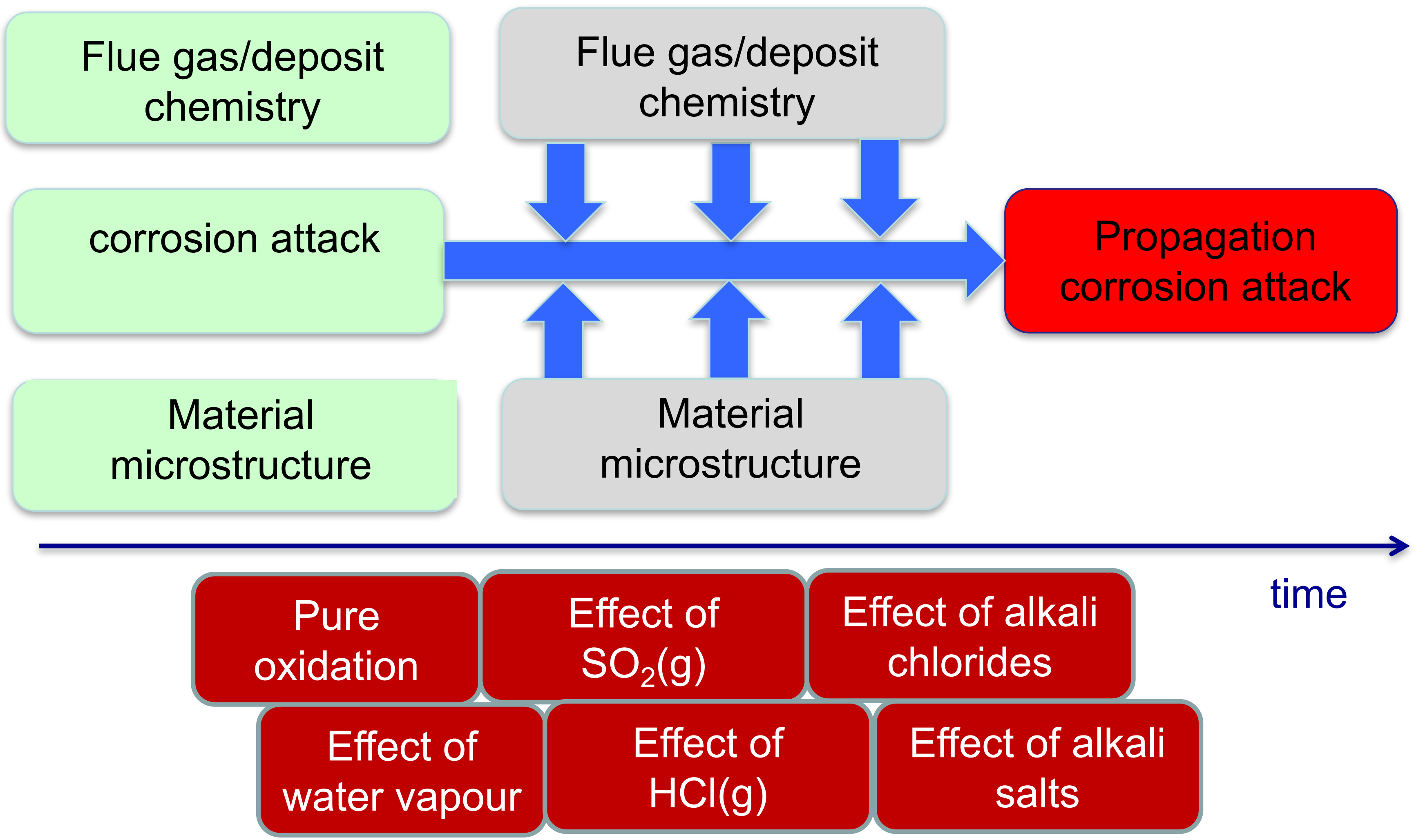

New alloy development in collaboration Sandvik

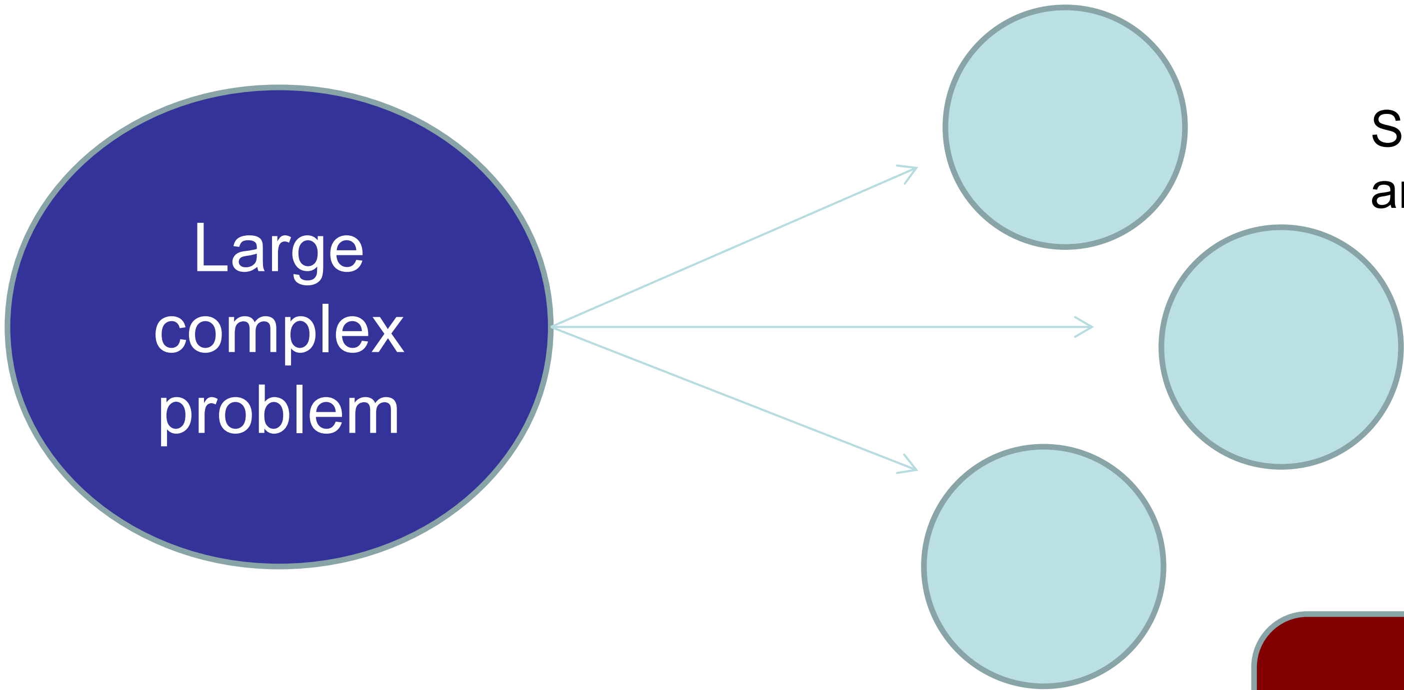
New coatings




SANDVIK

# Corrosion solutions – boiler operation






Small well-defined areas of the problem

Well controlled laboratory exposures

- Pure oxidation
- Effect of $SO_2$(g)
- Effect of alkali chlorides
- Effect of water vapour
- Effect of HCl(g)
- Effect of alkali salts

Combined effects

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