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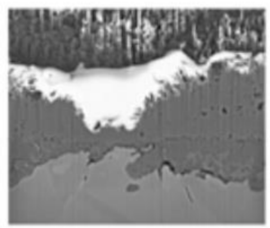
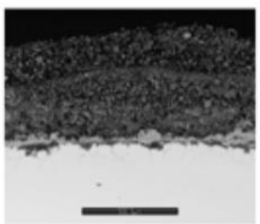
UNIVERSITY OF TECHNOLOGY
The High Temperature Corrosion Centre

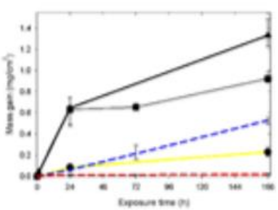
HTC: Critical corrosion phenomena
KME: 709, 711, 714, 720

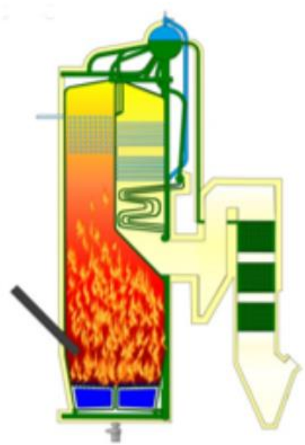
The High-Temperature Corrosion Center

Amanda Persdotter, Andrea Olivas, Christine Geers, Erik Larsson, Jan-Erik Svensson, Jesper Liske, Johan Eklund, Julien Phother, Lars-Gunnar Johansson, Loli Paz, Mohammad Sattari, Torbjörn Jonsson









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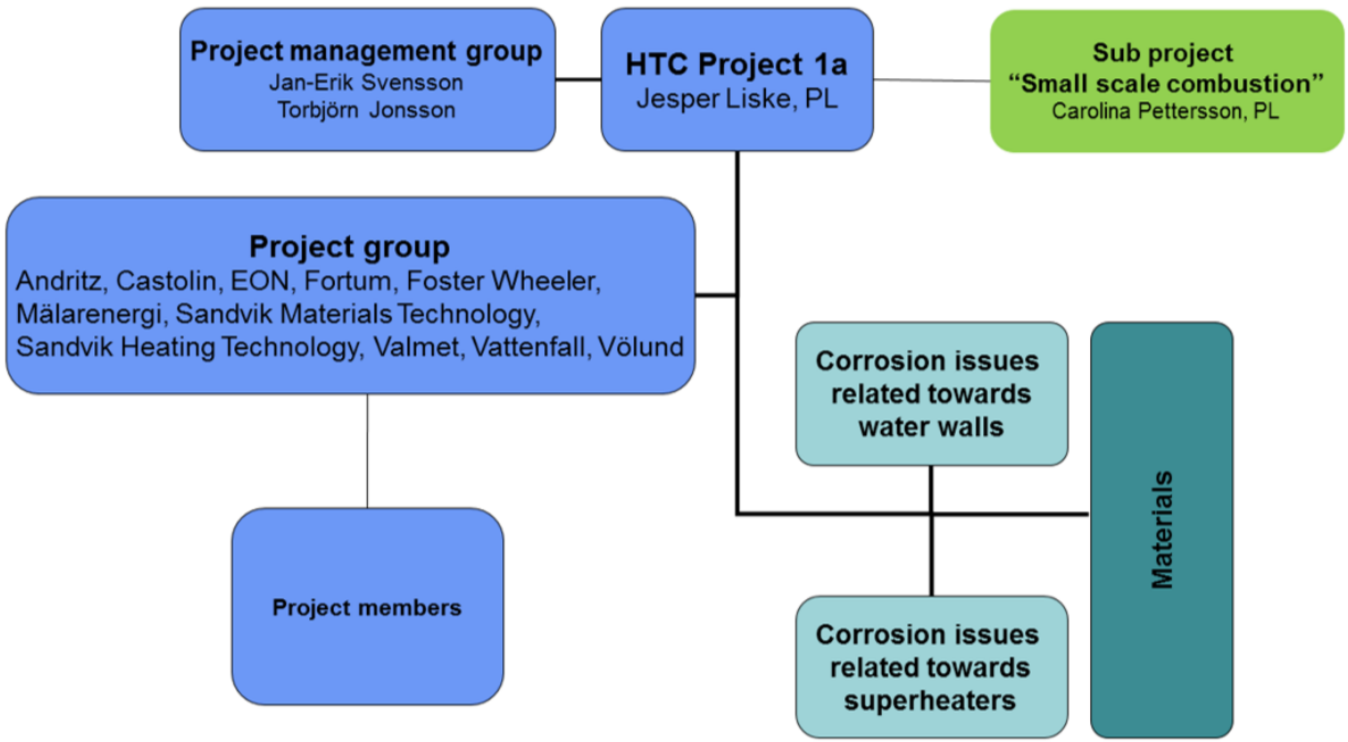
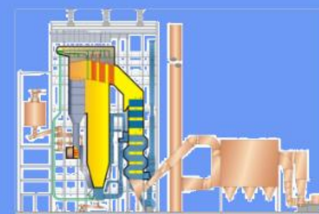
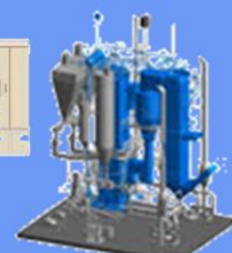
Critical corrosion phenomena in the combustion of biomass and waste



The Member Companies



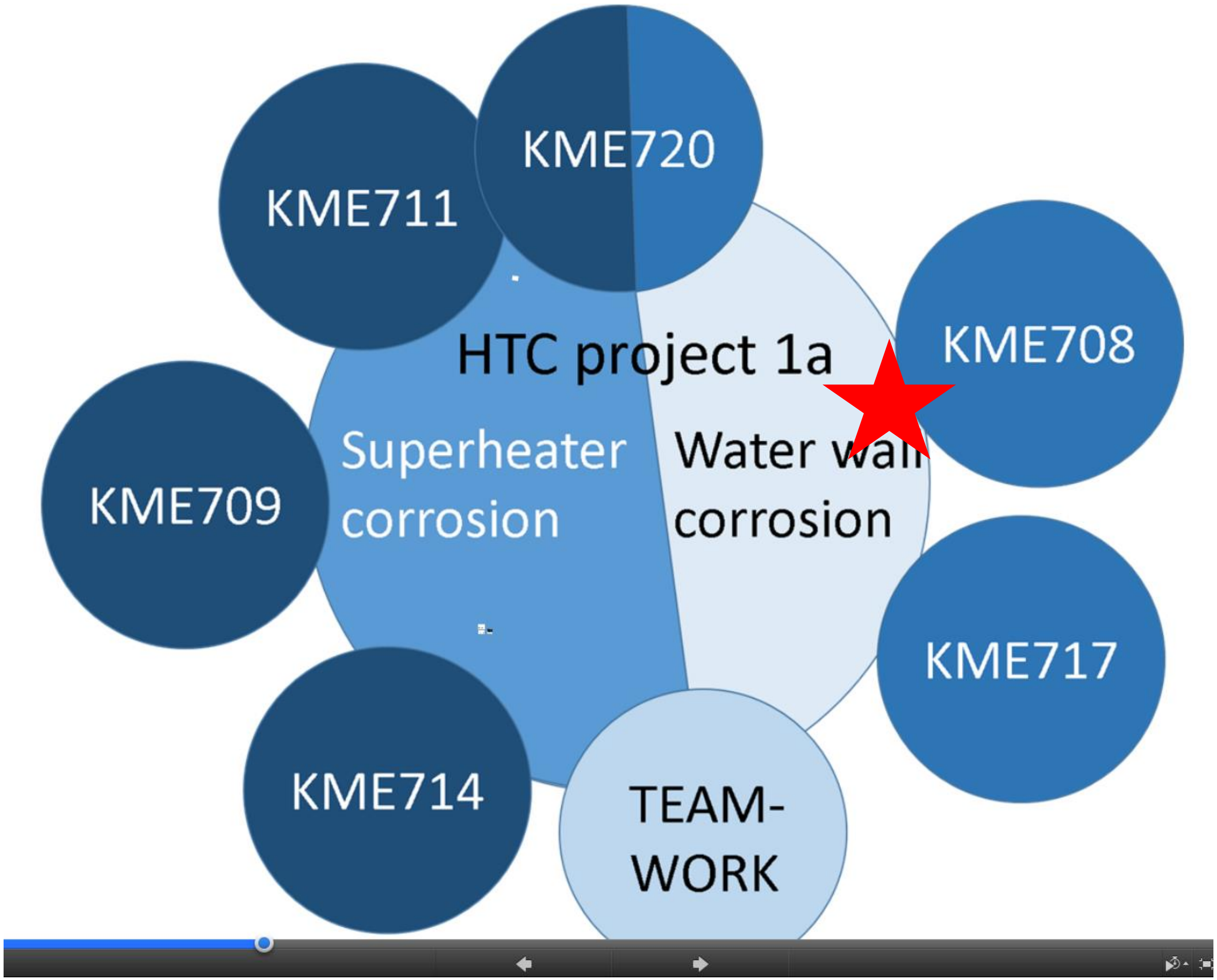





- Sandvik Materials Technology
- Sandvik Heating Technology
- Castolin

- Valmet
- Foster Wheeler
- Völund
- Andritz

- Vattenfall
- EON
- Fortum
- Linköping Tekn. V
- Mälarenergi
- Göteborg Energi


KME711
KME720
KME708
HTC project 1a
Superheater corrosion
Water wall corrosion
KME709
KME717
KME714
TEAM-WORK

Results from KME508 & 708

Deposit analysis in atomic %

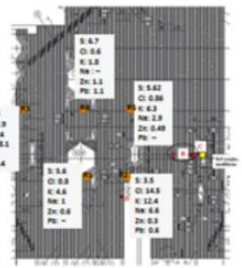
On right wall

Medium corrosion

Widely varying composition, depending on location

High Cl associated with high K, and vice versa

Sidovägg motorvägsida
(sedd inifrån eldstaden)



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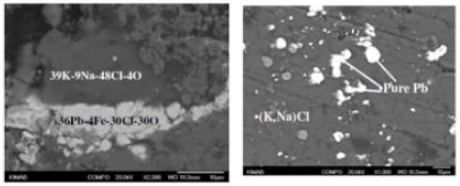
Confidentiality - None

VATTENFALL

Front wall – cross-sections of deposits

- Lead observed both as pure lead and Pb-Cl-O mixture



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Confidentiality - None

VATTENFALL

Deposit analysis Conclusions

•Not much spread in chemical composition results within individual deposi samples, but, chemical composition of deposit varies somewhat with positior on the furnace wall.

•Cl was found in all the deposit samples. Sometimes very high amounts (3(wt%). Generally higher amounts of Cl found on front and back walls where corrosion is highest.

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•Zn-Cl, pure Pb and Pb-Cl-O correlations. Will use XRD for more information

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Confidentiality - None

VATTENFALL

Test coupons after testing

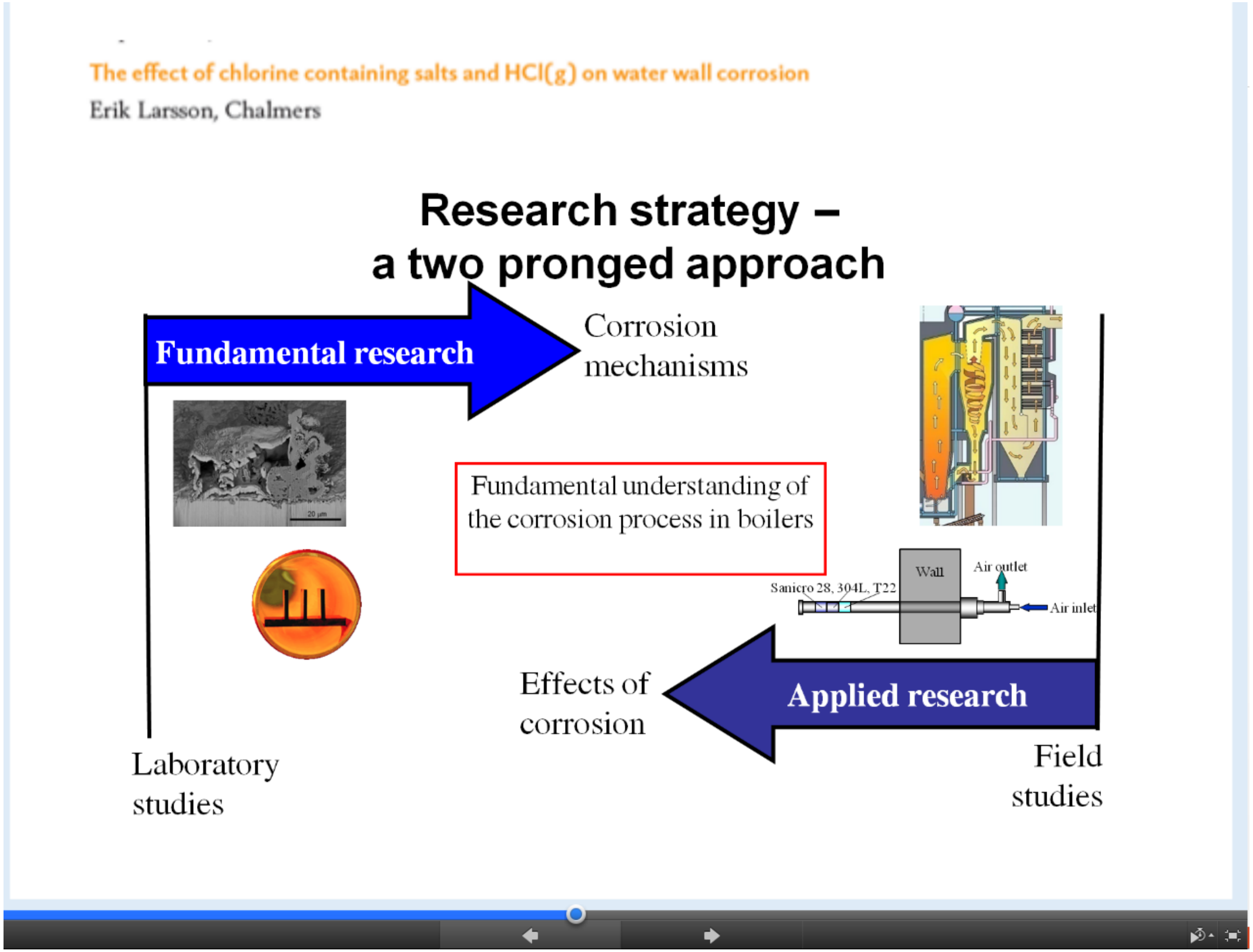
amec foster wheeler

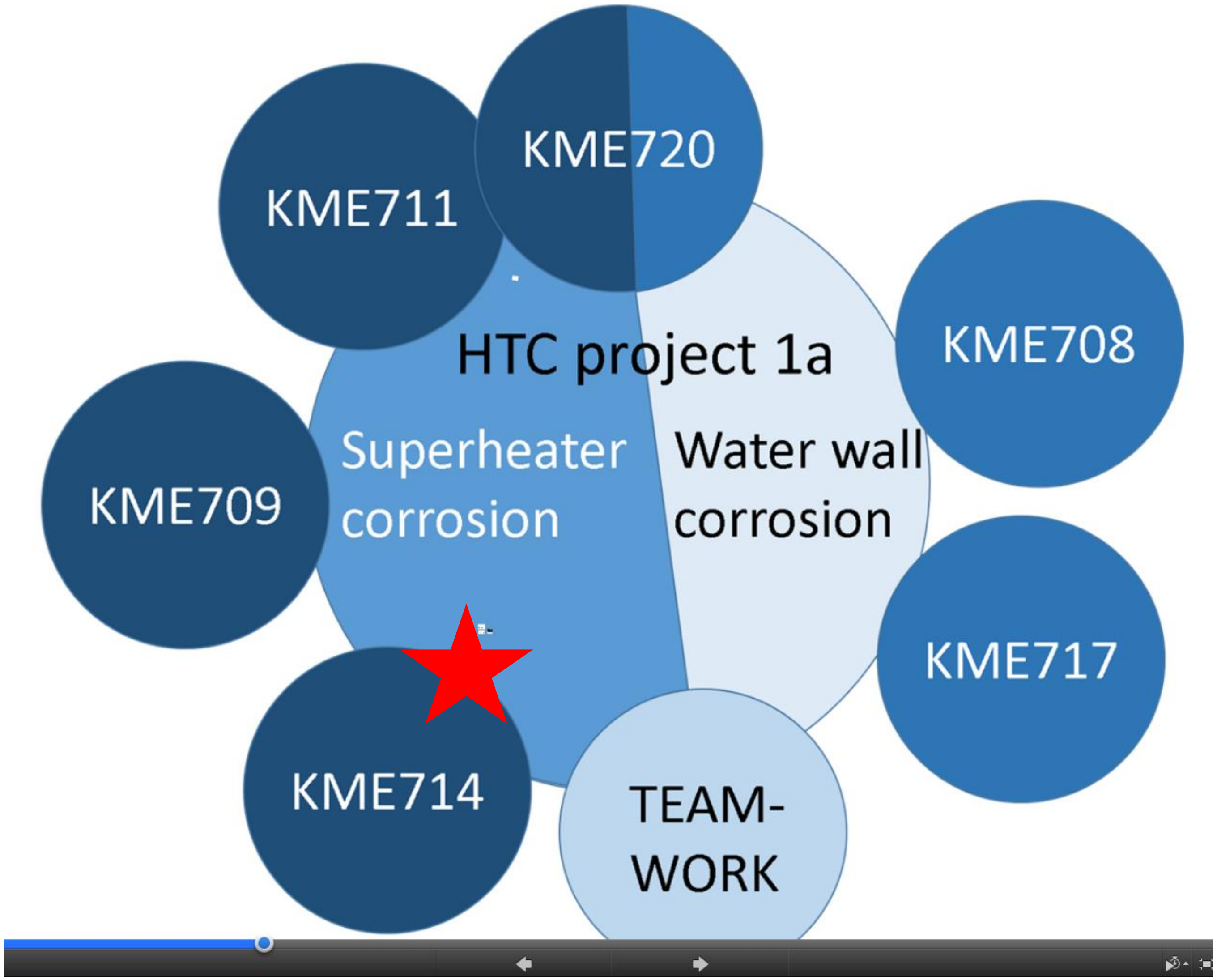
T=330C T=360C

C-steel, 16Mo3 and 13CrMo4-5

Waste fired CFB boiler, P15 in Norrköping

7


The effect of chlorine containing salts and HCl(g) on water wall corrosion
Erik Larsson, Chalmers
Research strategy –
a two pronged approach
Fundamental research
Corrosion mechanisms
Fundamental understanding of the corrosion process in boilers
Wall
Air outlet
Sanicro 28, 304L, T22
Air inlet
Effects of corrosion
Applied research
Laboratory studies
Field studies


KME720
KME711
HTC project 1a
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Superheater corrosion
Water wall corrosion
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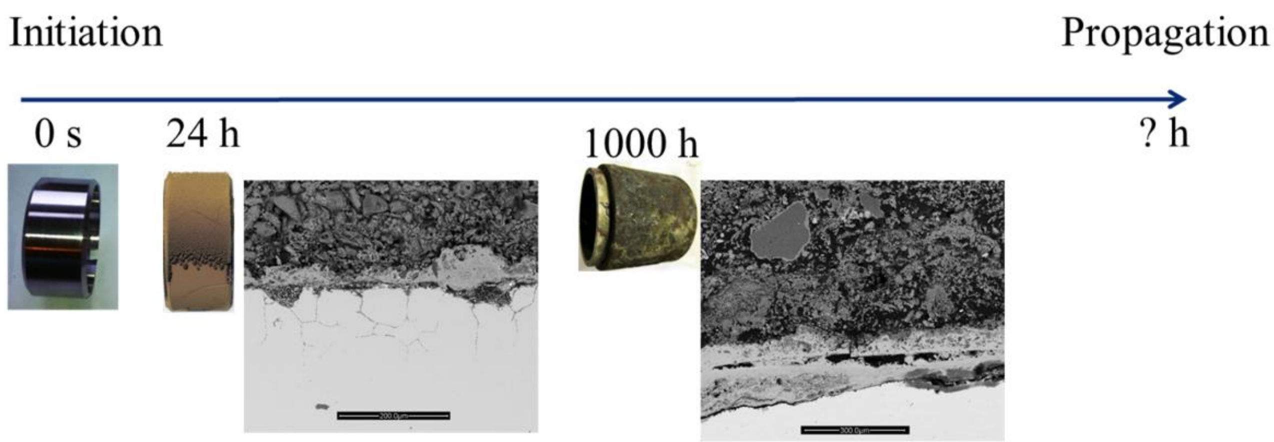
KME714
TEAM-WORK

How is the corrosion attack affected by the environment?



A stainless steel exposed in a waste fired boiler at 500 °C

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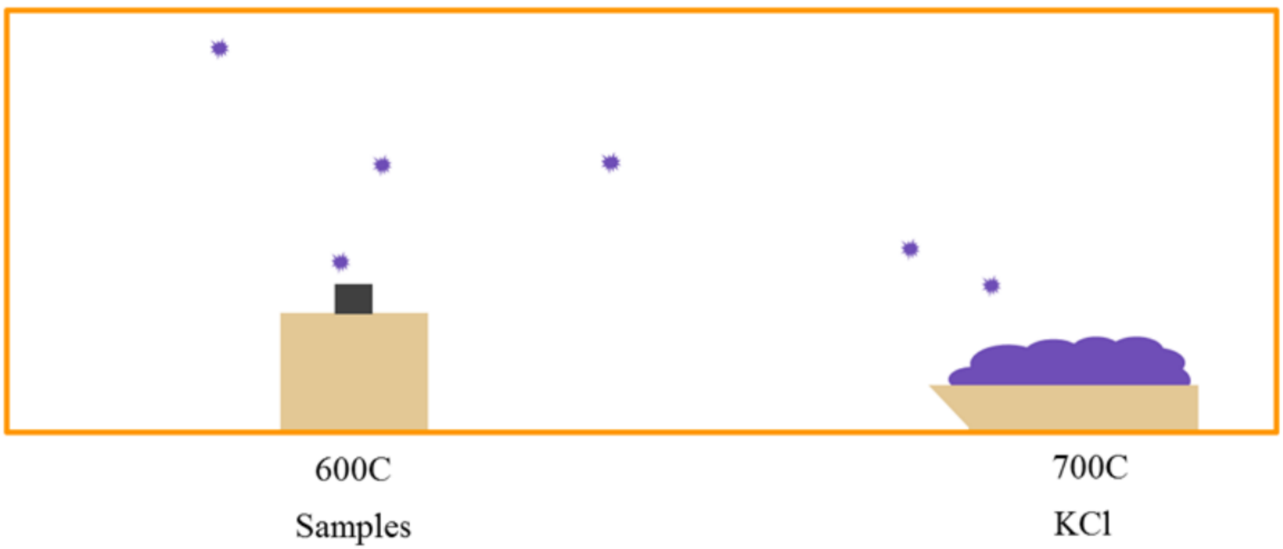
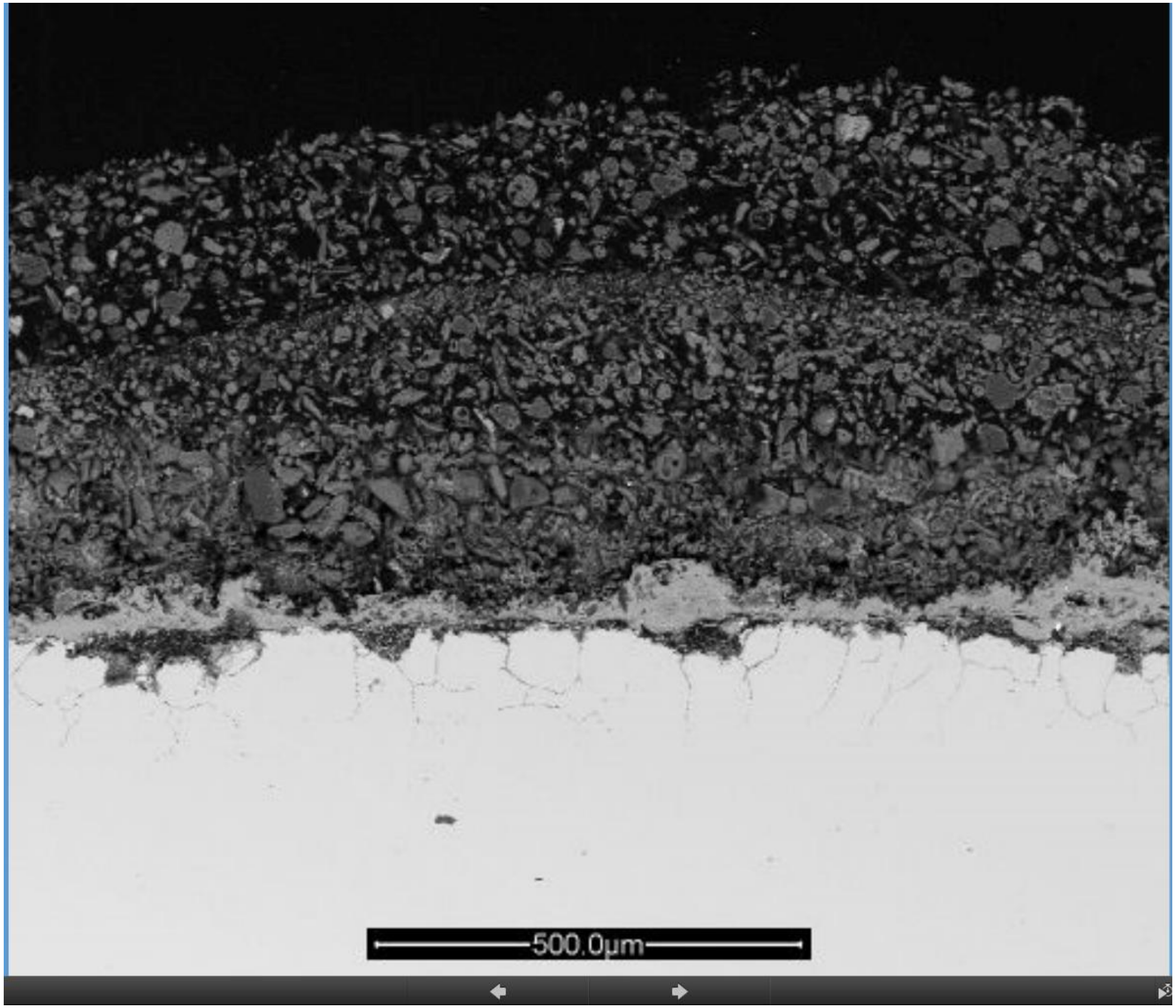
The High Temperature Corrosion Centre

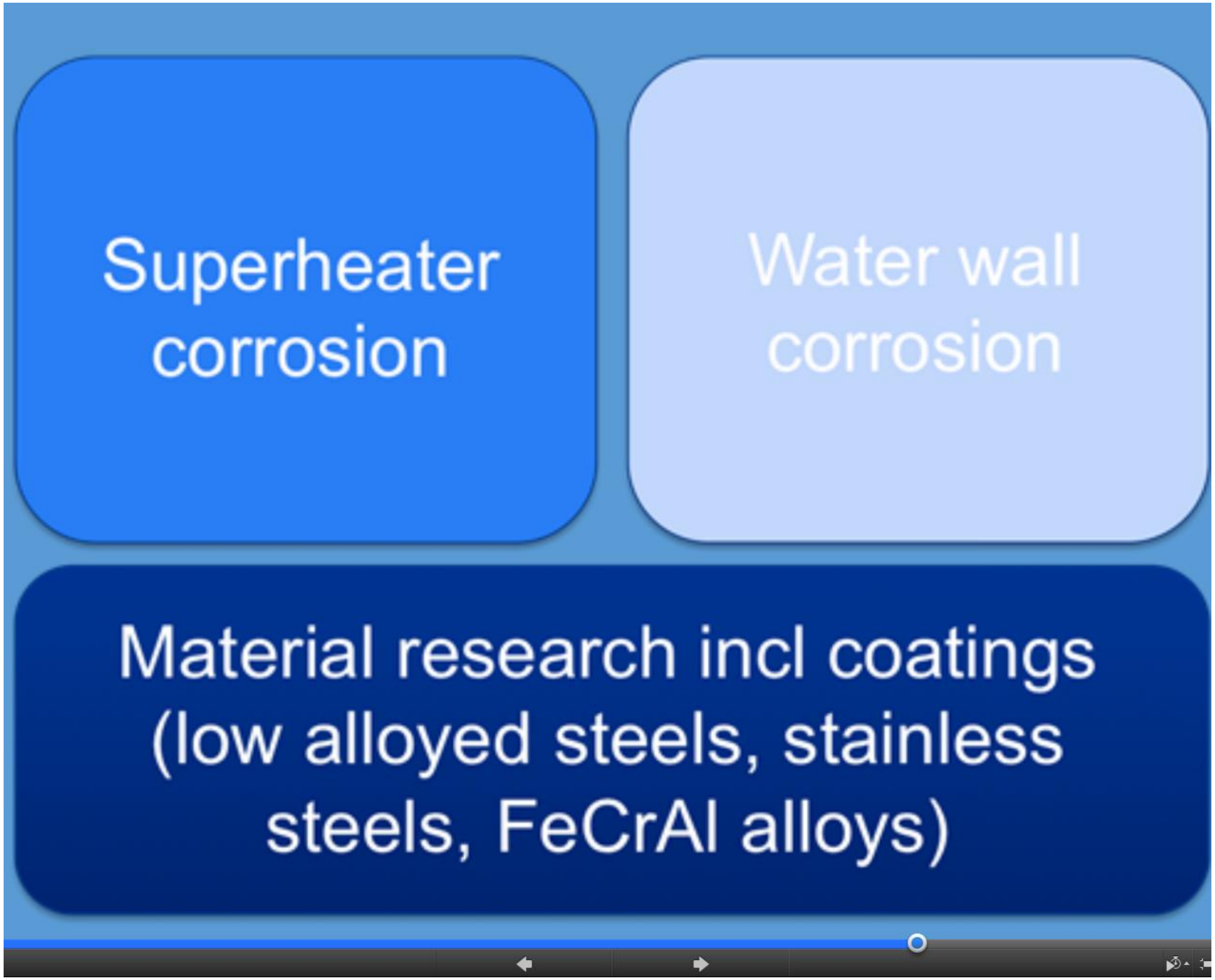
KCl added continuously

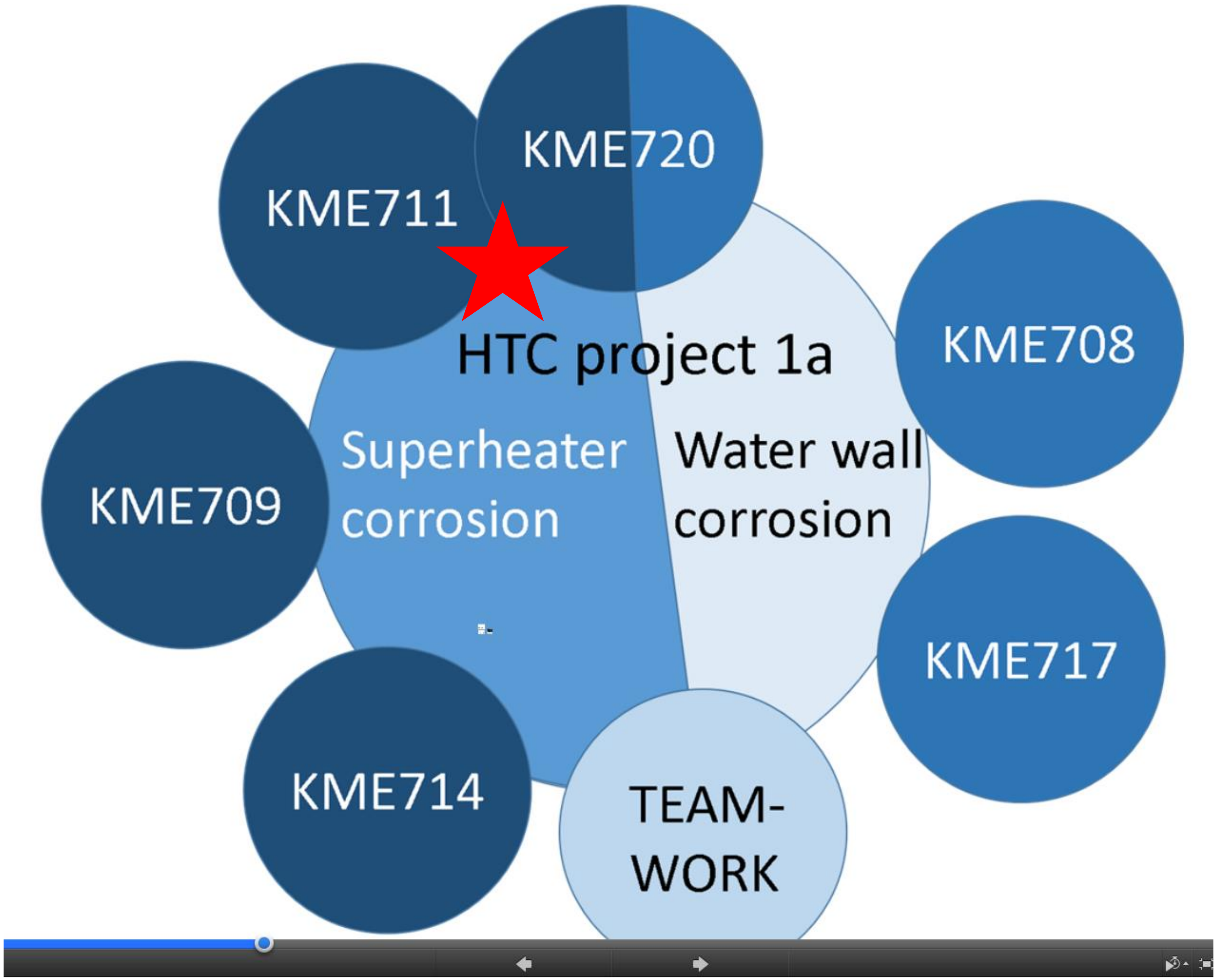
The effect of corrosive deposits and gases – KCl continuously deposited in laboratory exposures

Julien Phother, Chalmers




500.0µm


Superheater corrosion
Water wall corrosion
Material research incl coatings (low alloyed steels, stainless steels, FeCrAl alloys)


KME711
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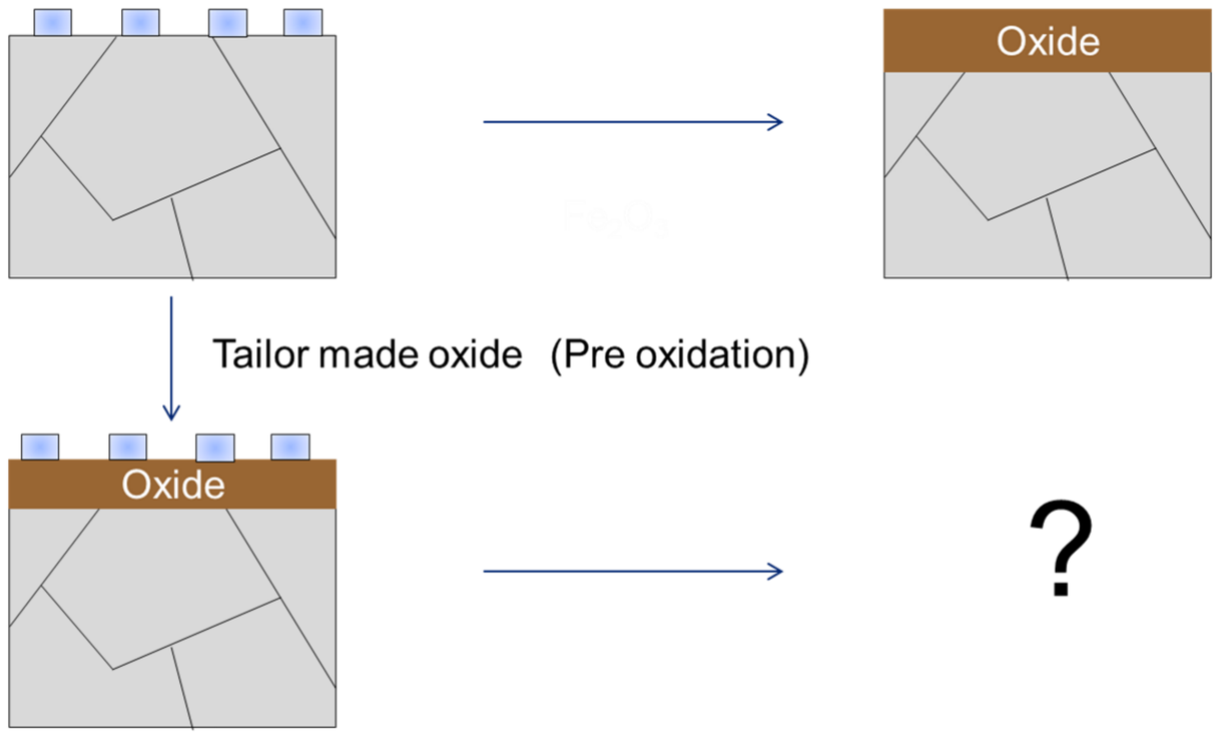
Change the starting condition



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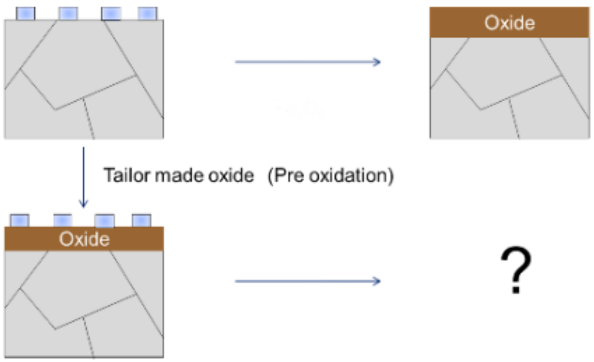
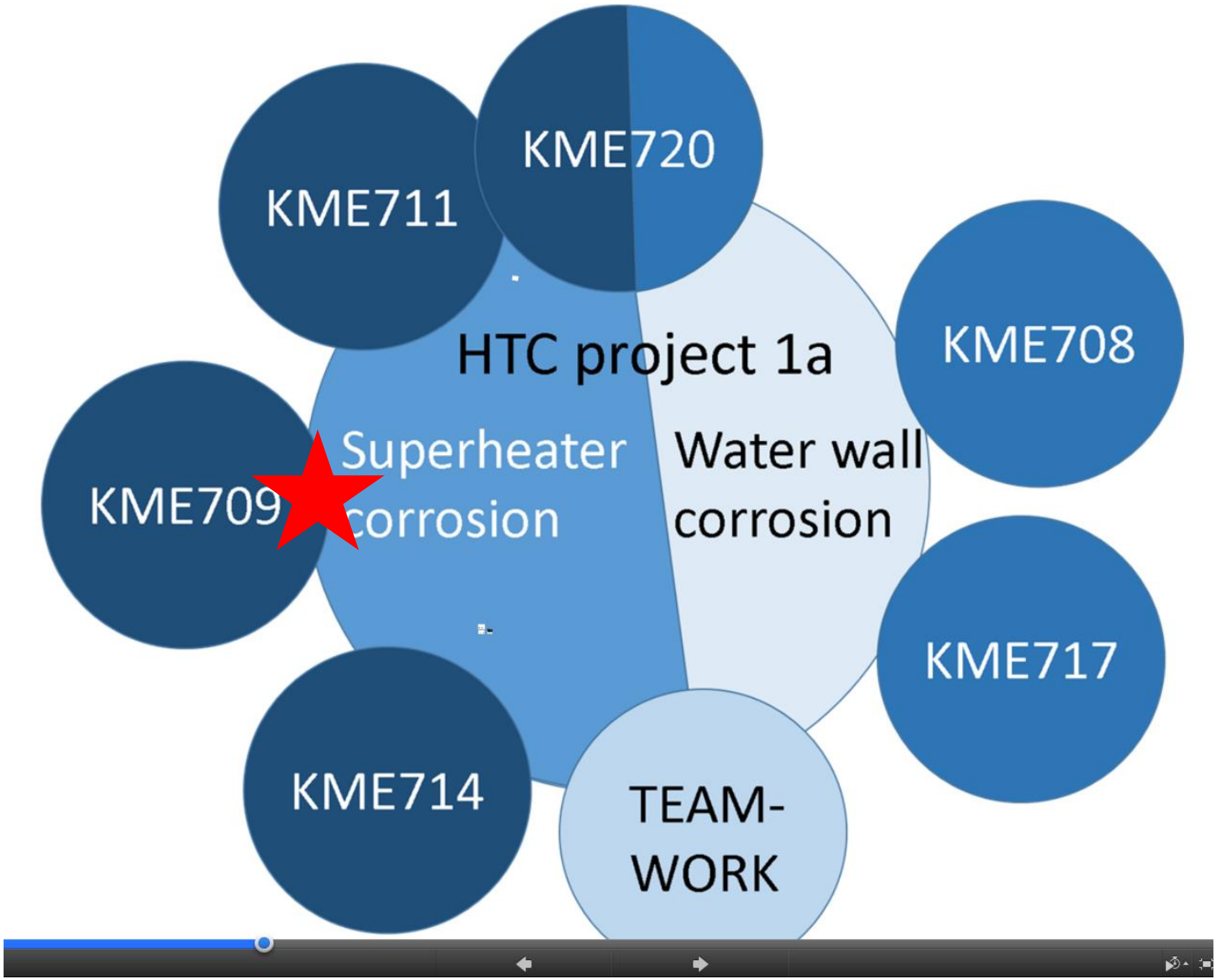


Mechanistic study of chlorine penetration of oxide scales

Andrea Olivas, Chalmers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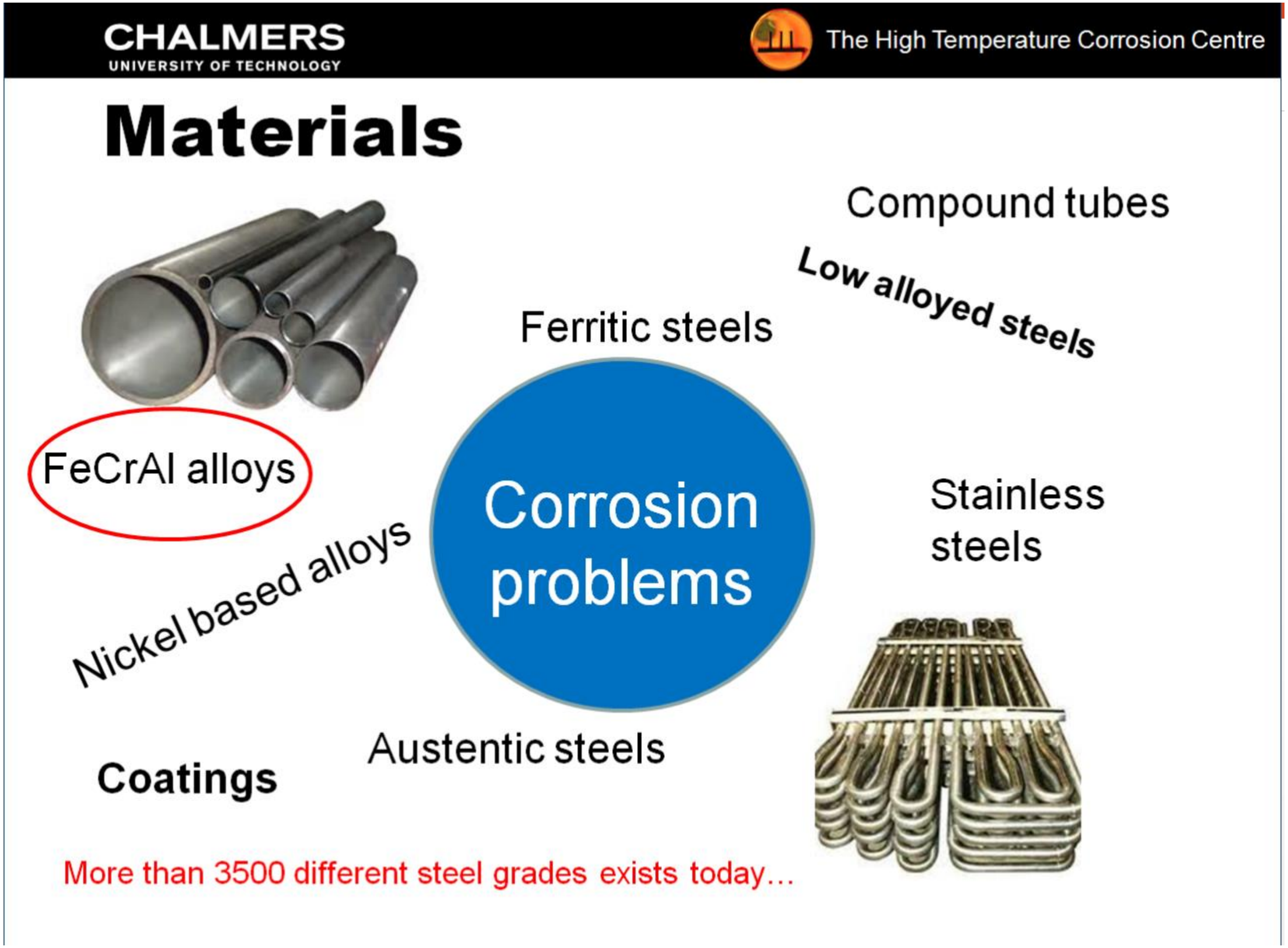
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The High Temperature Corrosion Centre
Materials
Compound tubes
Low alloyed steels
Ferritic steels
FeCrAl alloys
Corrosion problems
Stainless steels
Nickel based alloys
Austentic steels
Coatings
More than 3500 different steel grades exists today…

HTC: Critical corrosion phenomena
KME: 709, 711, 714, 720

The High-Temperature Corrosion Center

The effect of chlorine containing salts and HCl(g) on water wall corrosion

Erik Larsson

Results from KME508 & 708

Deposit analysis in atomic %

On right wall

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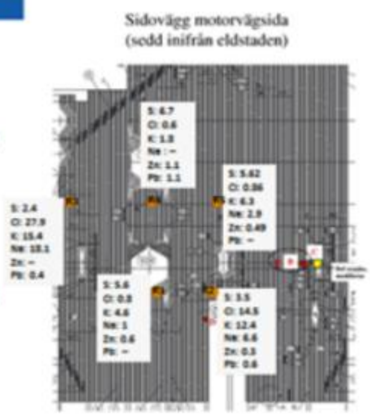

Front wall – cross-sections of deposits

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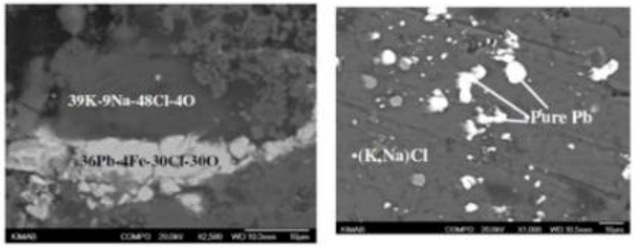

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Test coupons after testing

amec foster wheeler

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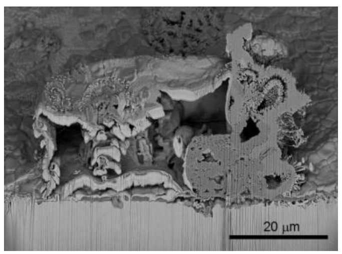
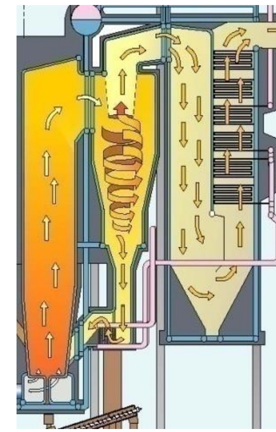
Waste fired CFB boiler, P15 in Norrköping

Research strategy

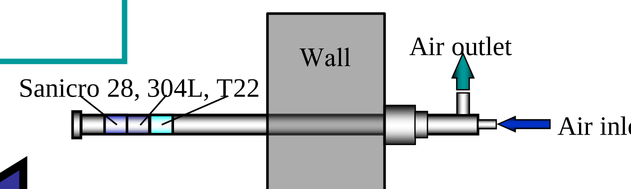
Fundamental research

Corrosion mechanisms





Fundamental understanding of the corrosion process in boilers



Effects of corrosion

Applied research

Laboratory studies

Field studies

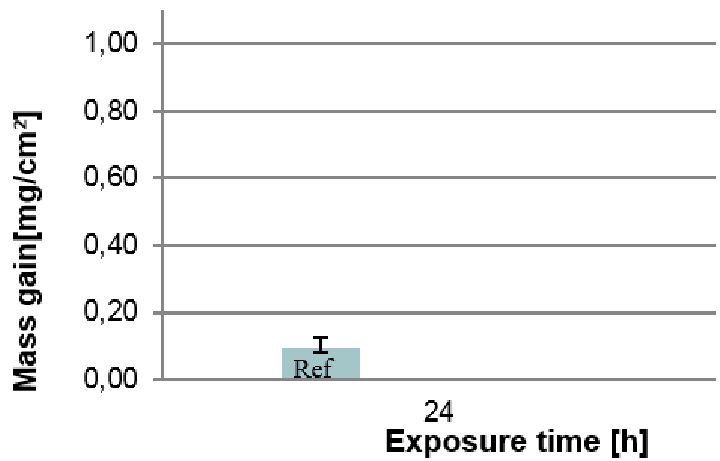
Material composition

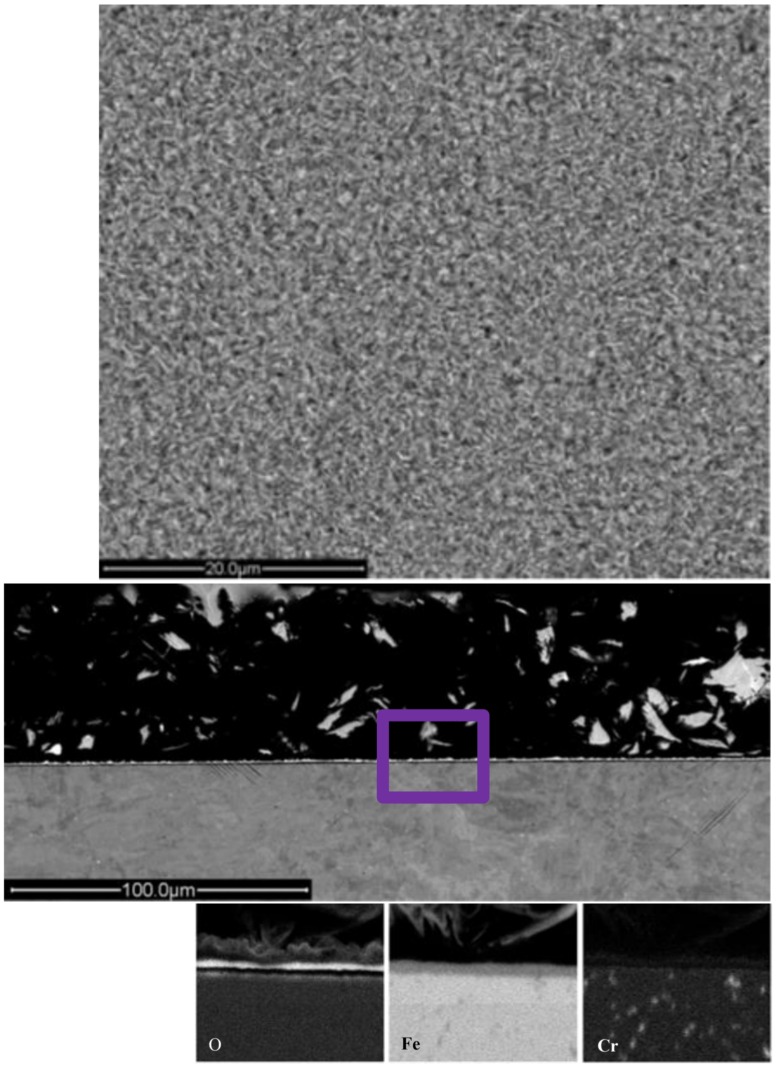
T22	Fe	Cr	Mn	Mo	Si	S	P	C
At%	96	2.2	0.5	0.9	0.3	0.01	0.01	0.09

Exposure conditions

- 400° C
- 5% O_2 + 20% H_2O, N_2 balance = **Reference (Ref)**

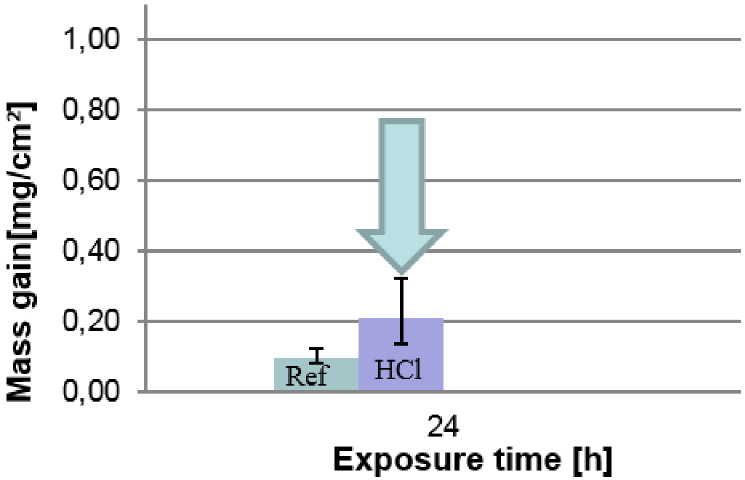
- **Ref** + 0.1 mg/cm^2 HCl(g)
- **Ref** + 0.1 mg/cm^2 KCl(s)
- **Ref** + 0.1 mg/cm^2 KCl(s) + HCl(g)
- **Ref** + 0.185 mg/cm^2 $PbCl_2$(s)

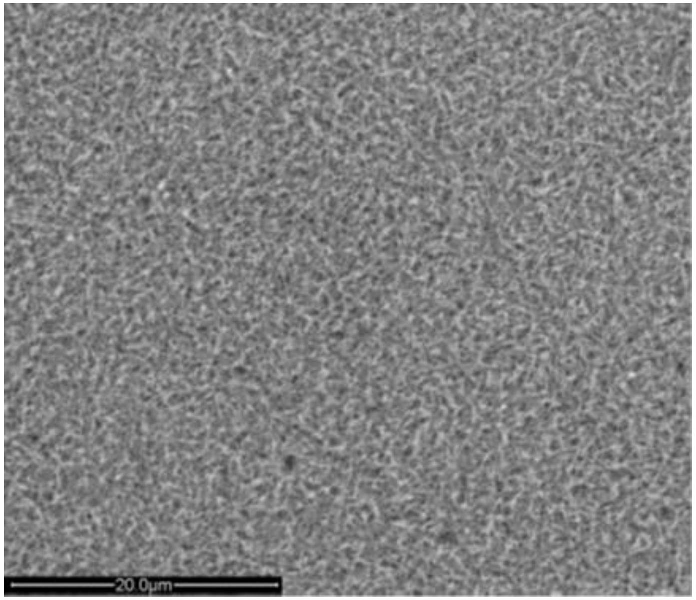




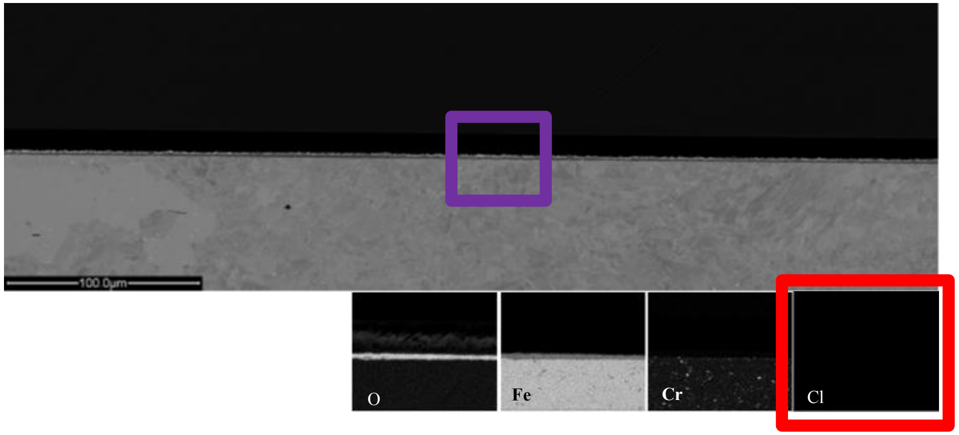
- Thin oxide
- Good adhesion
- No severe attack

Introduction of Cl in the form of HCl

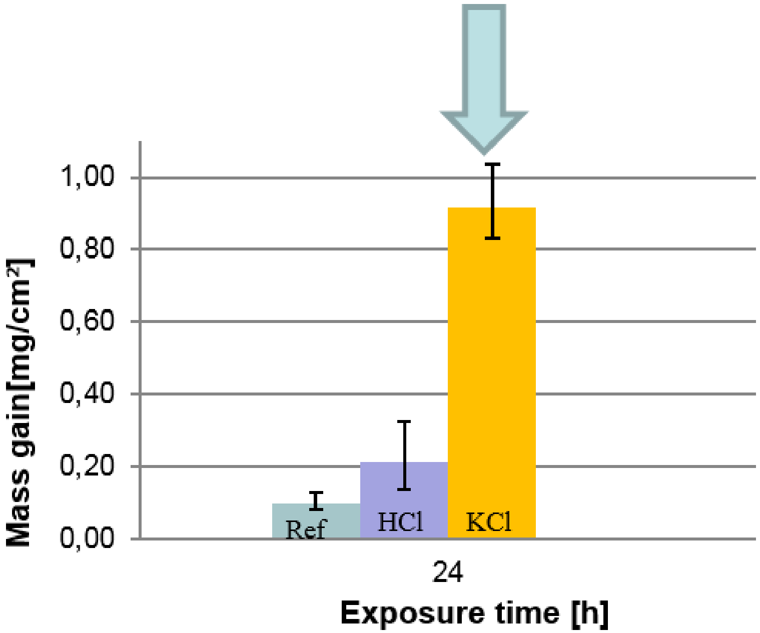


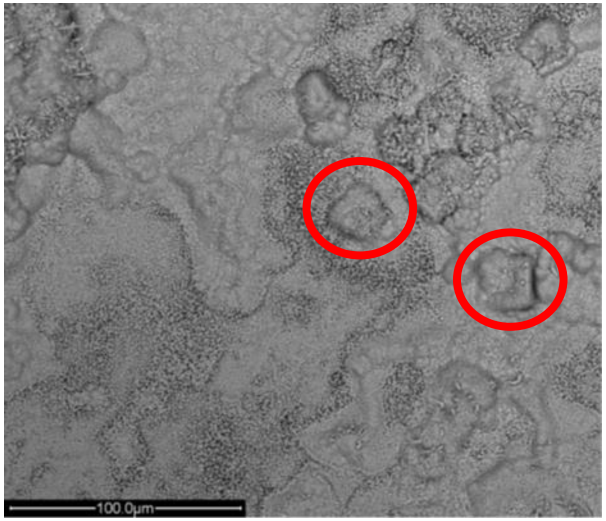


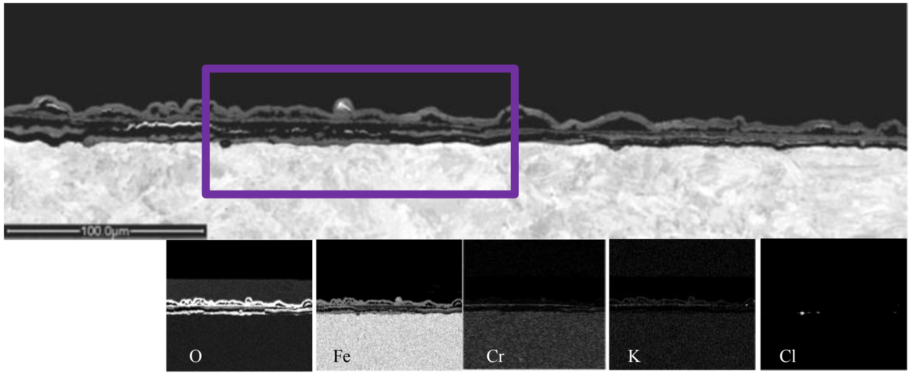
- Thin oxide, well adherent
- Slight increase in corrosion
- Cl has not penetrated the oxide



Introduction of Cl in the form of KCl

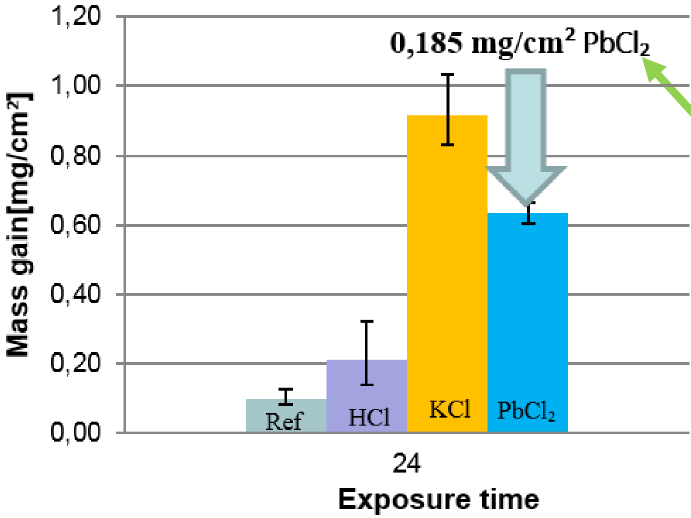






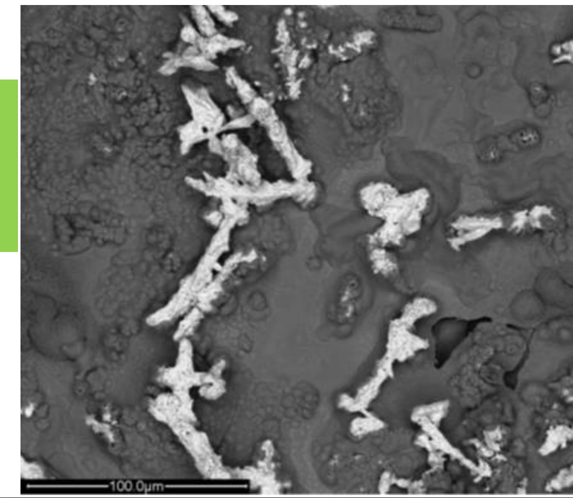
- Widespread attack
- KCl overgrown with oxide
- Layered thick oxide

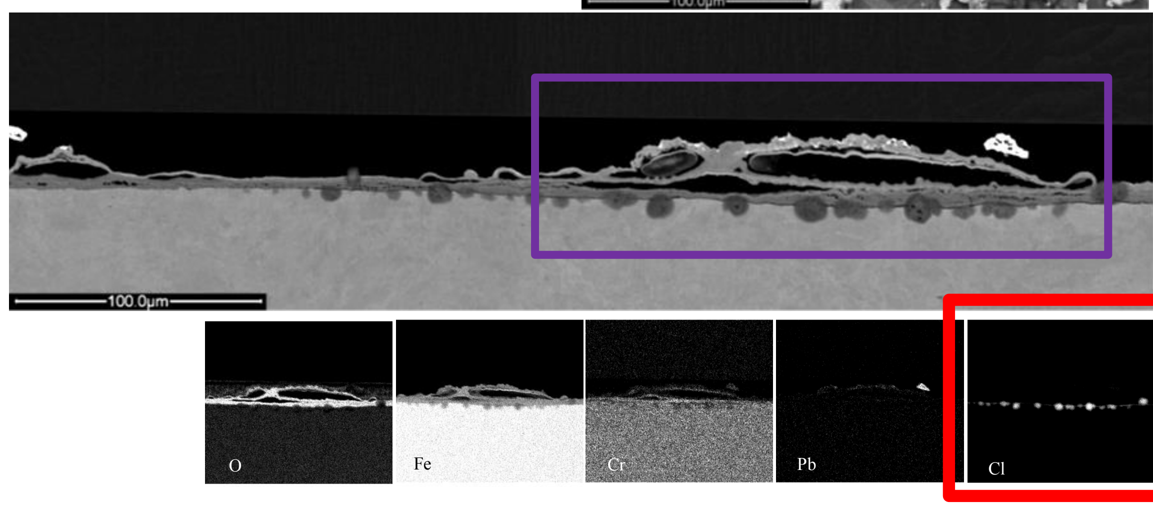
Introduction of Cl in the form of a heavy metal salt



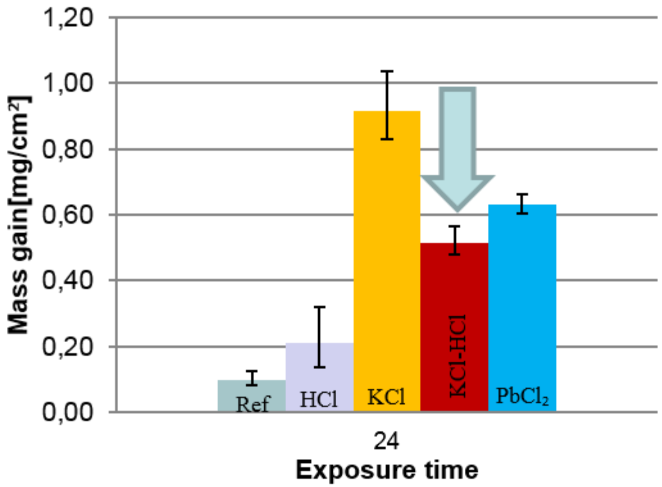
Equal moles of Cl

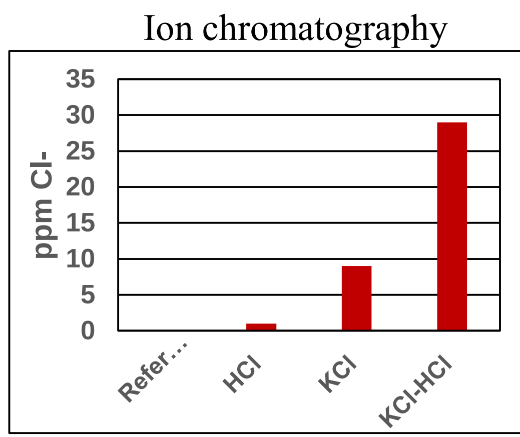
KCl 0,1 mg/cm^2 ↔ 0,185 mg/cm^2 $PbCl_2$

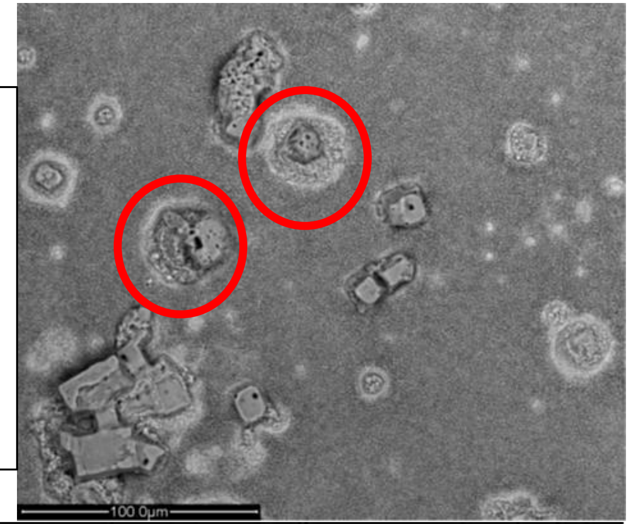


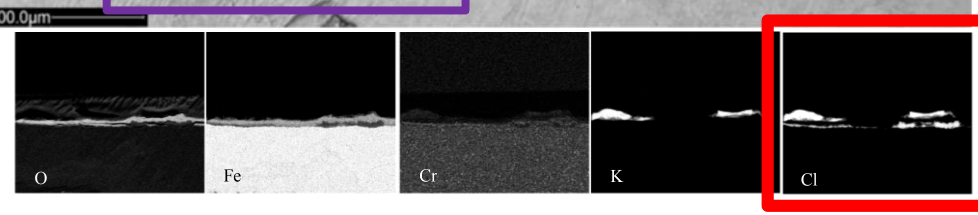


- Pb detected as PbO
- Localized attack
- Cl present at steel/oxide interface

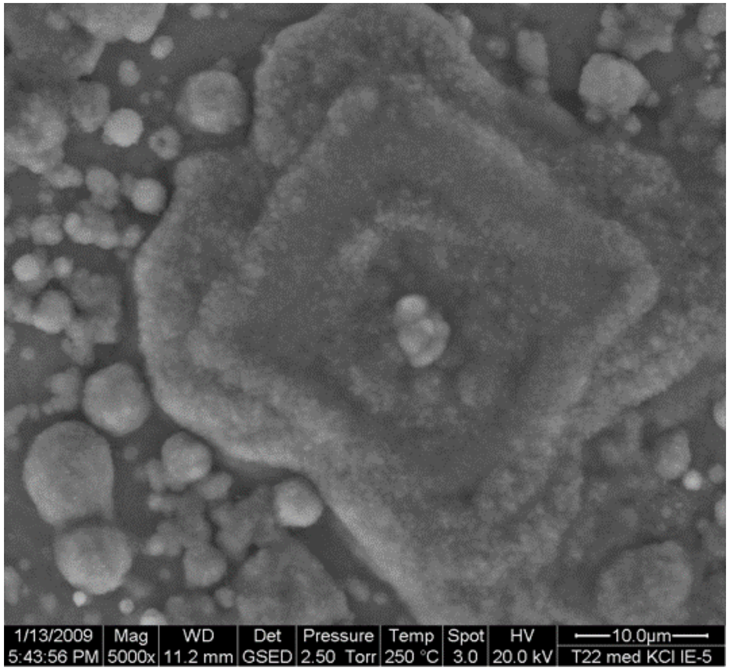








- Lower mass gain compared to KCl
- Localized attack in the vicinity of KCl
- Thick oxide around KCl
- Thin oxide between KCl
- Cl detected below KCl ⟹ thickest oxide



Early stages of exposure important

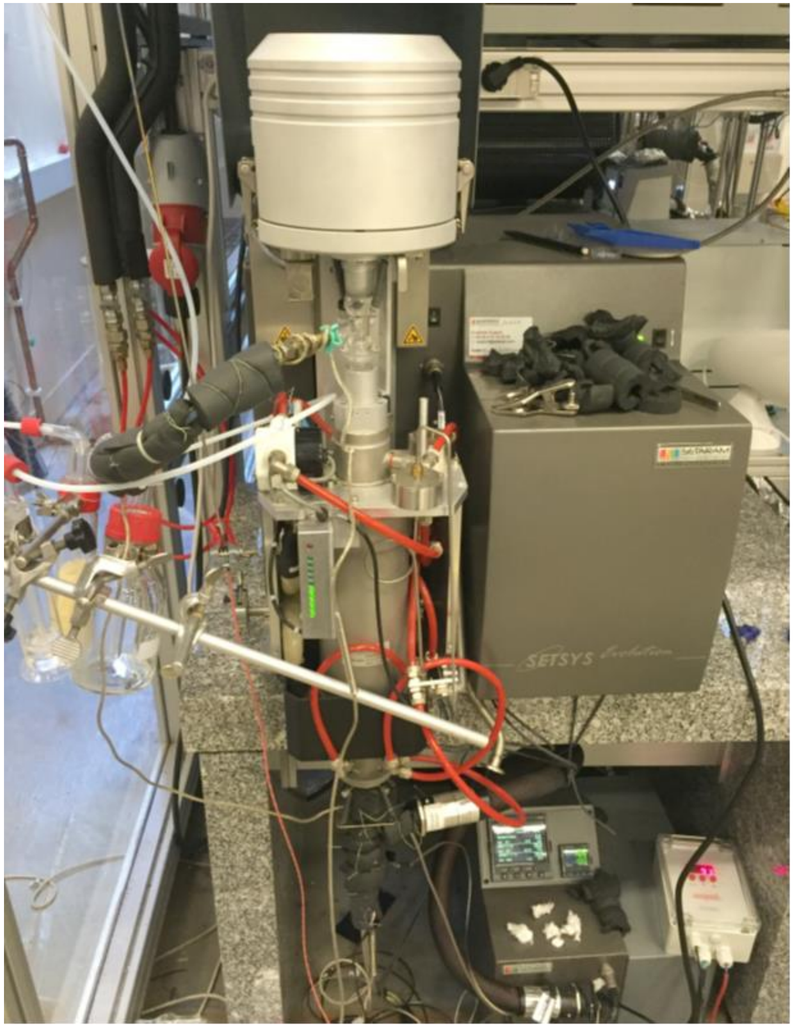
T22 KCl In situ ESEM study. N Folkeson, T Jonsson

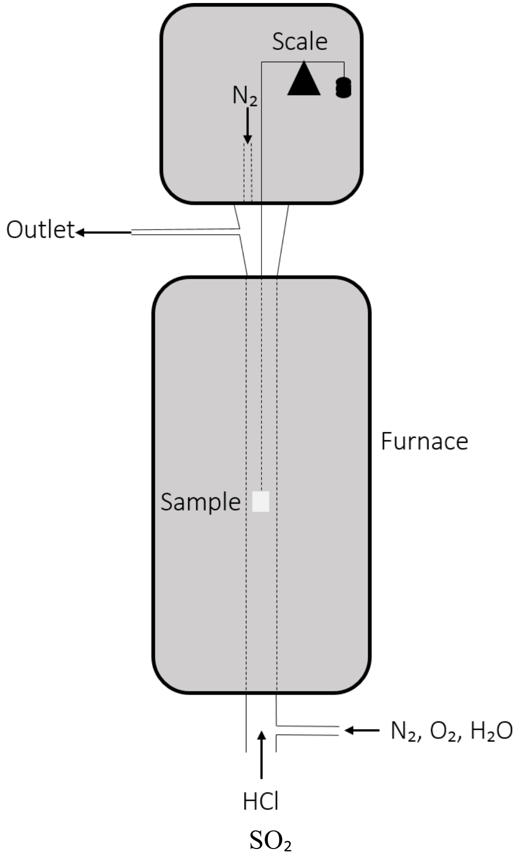
What happens during the early stages in the KCl-HCl exposures?

-Not possible to introduce HCl(g) into the ESEM

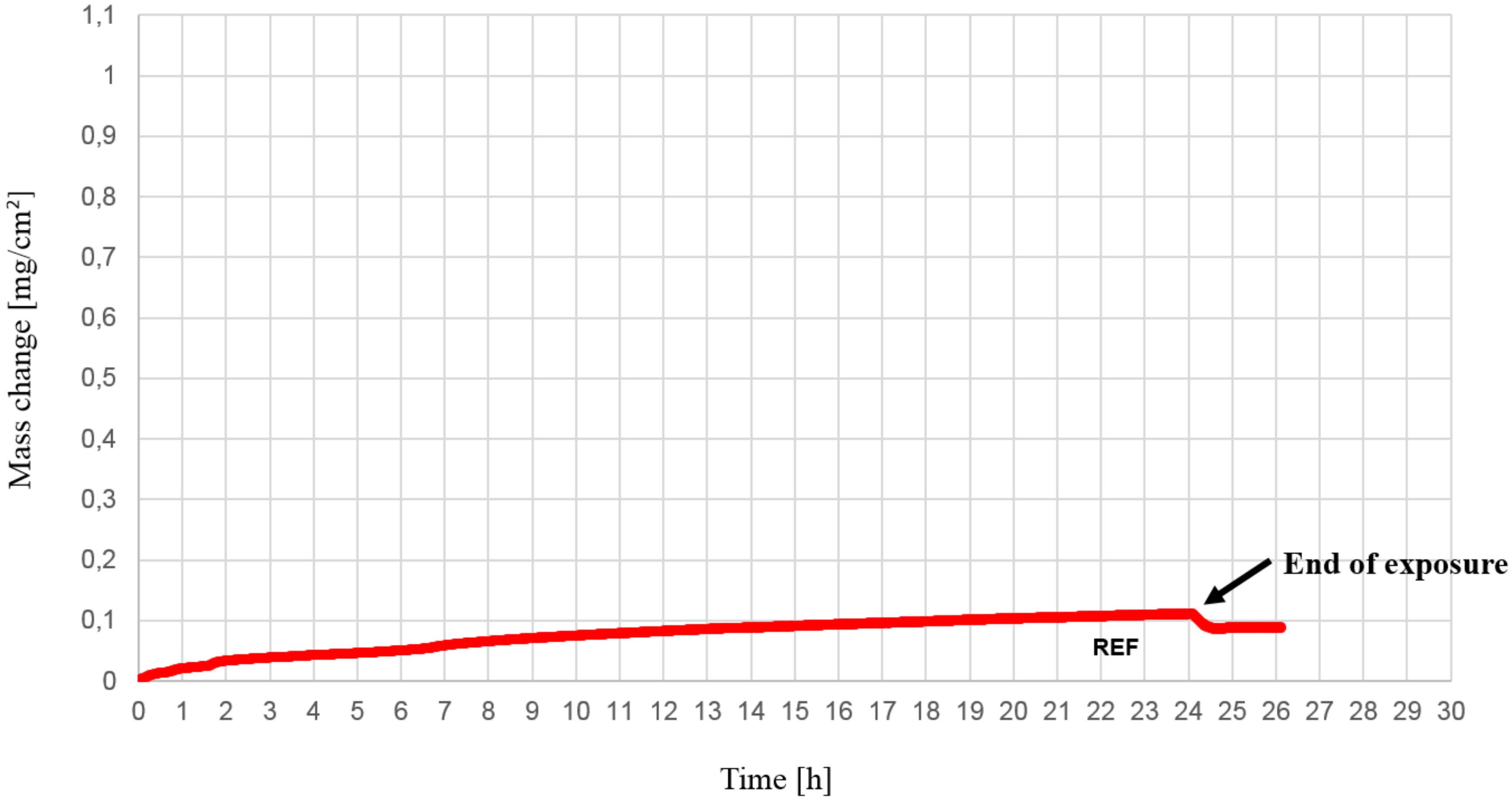
How can we study the initation?

Setaram Setsys Tg system





Oxidation kinetics



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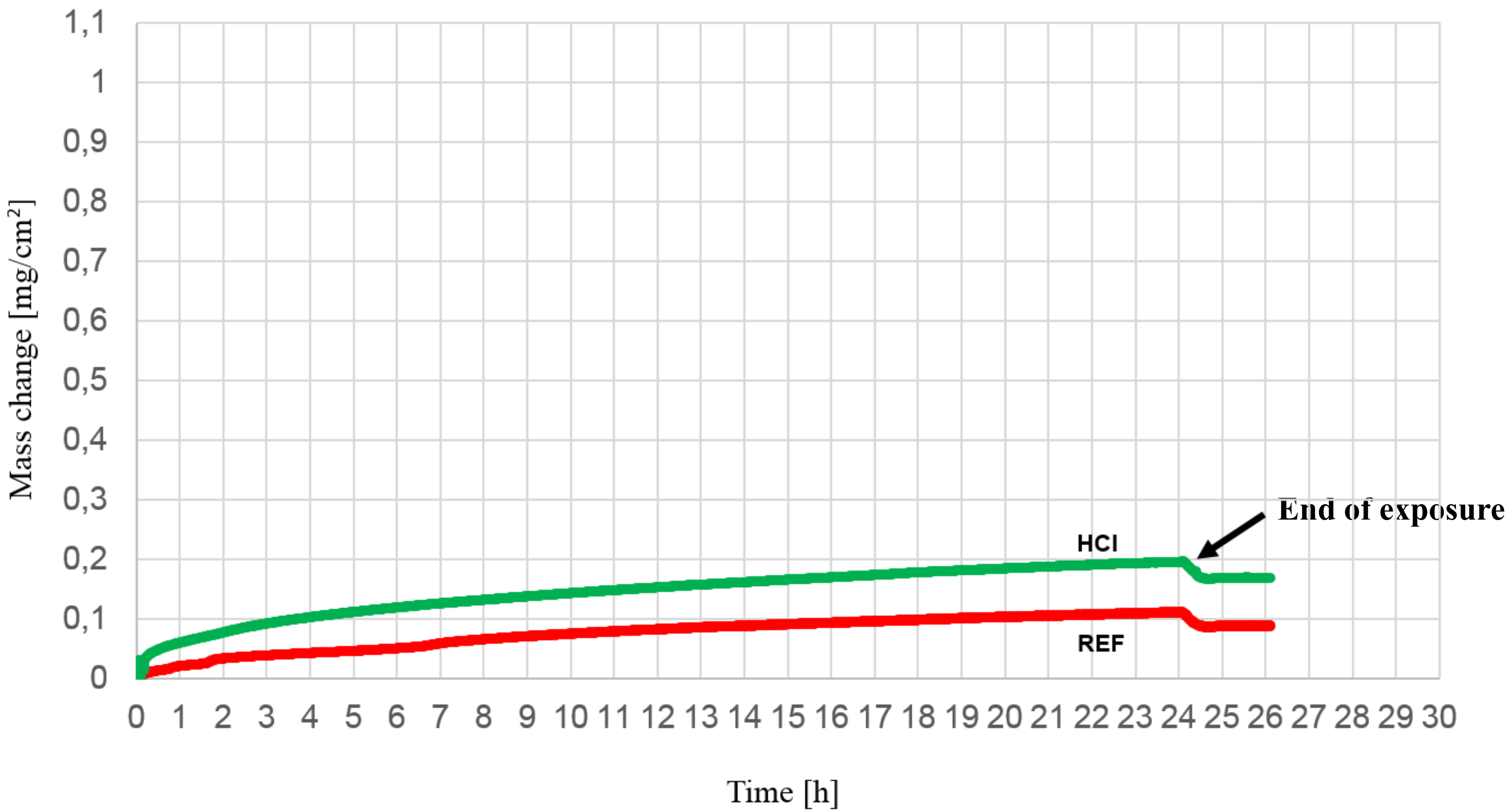
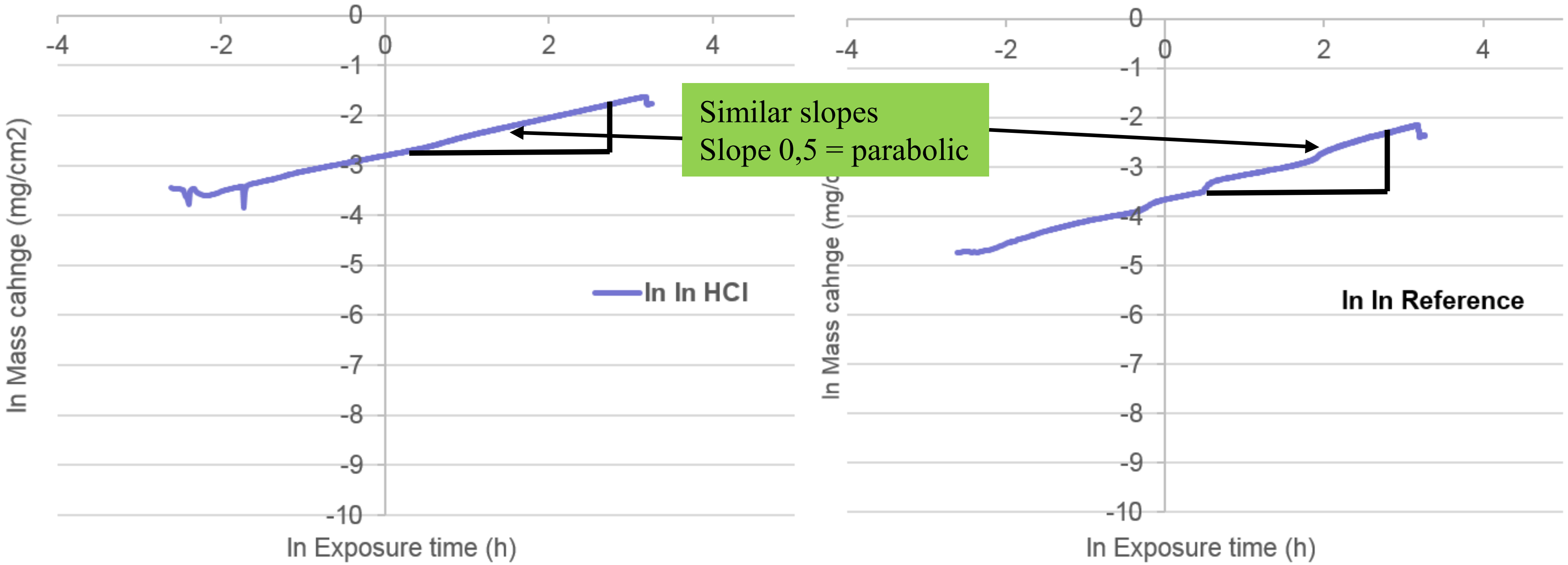


Interpretation of oxidation kinetics



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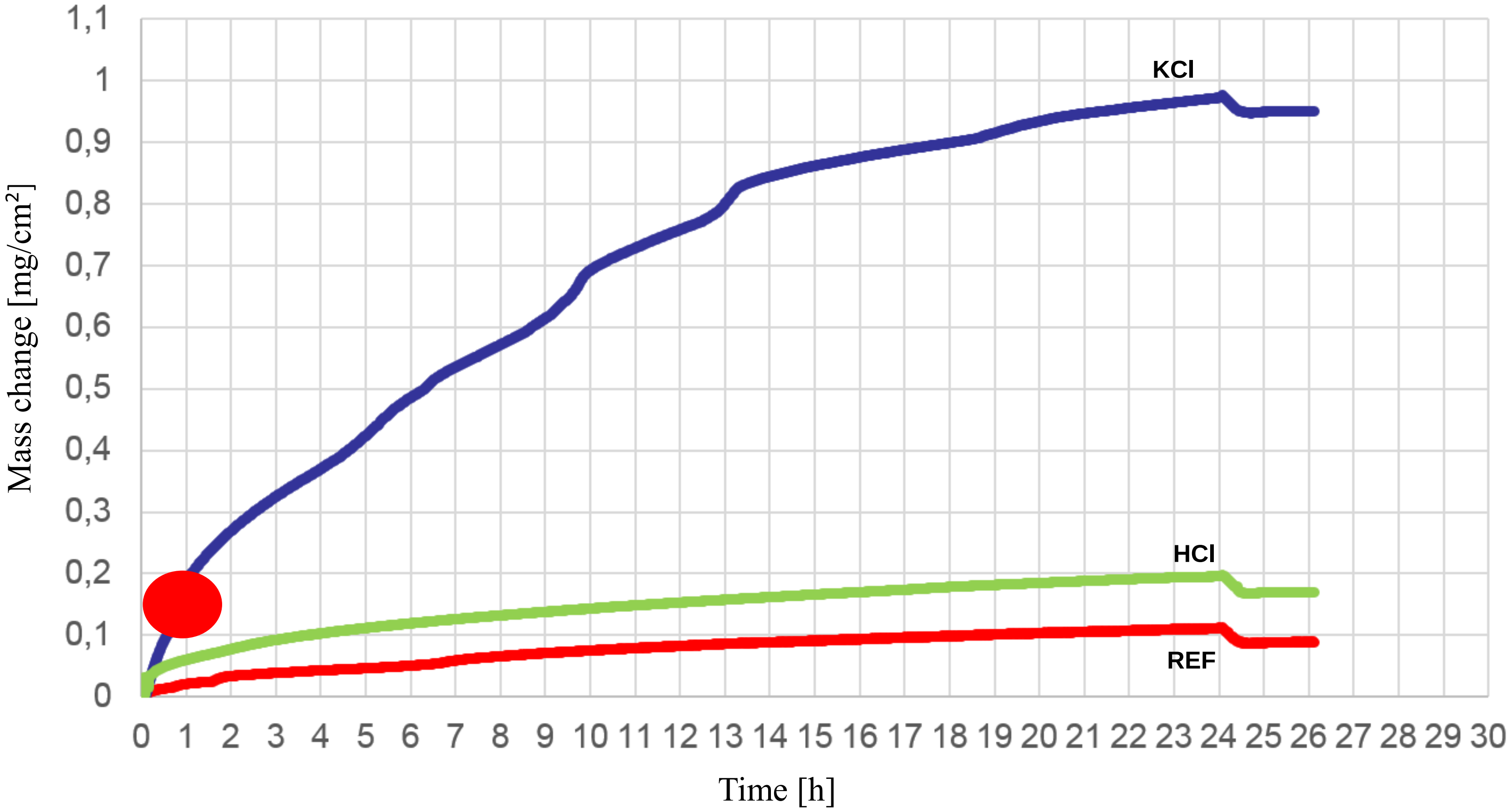

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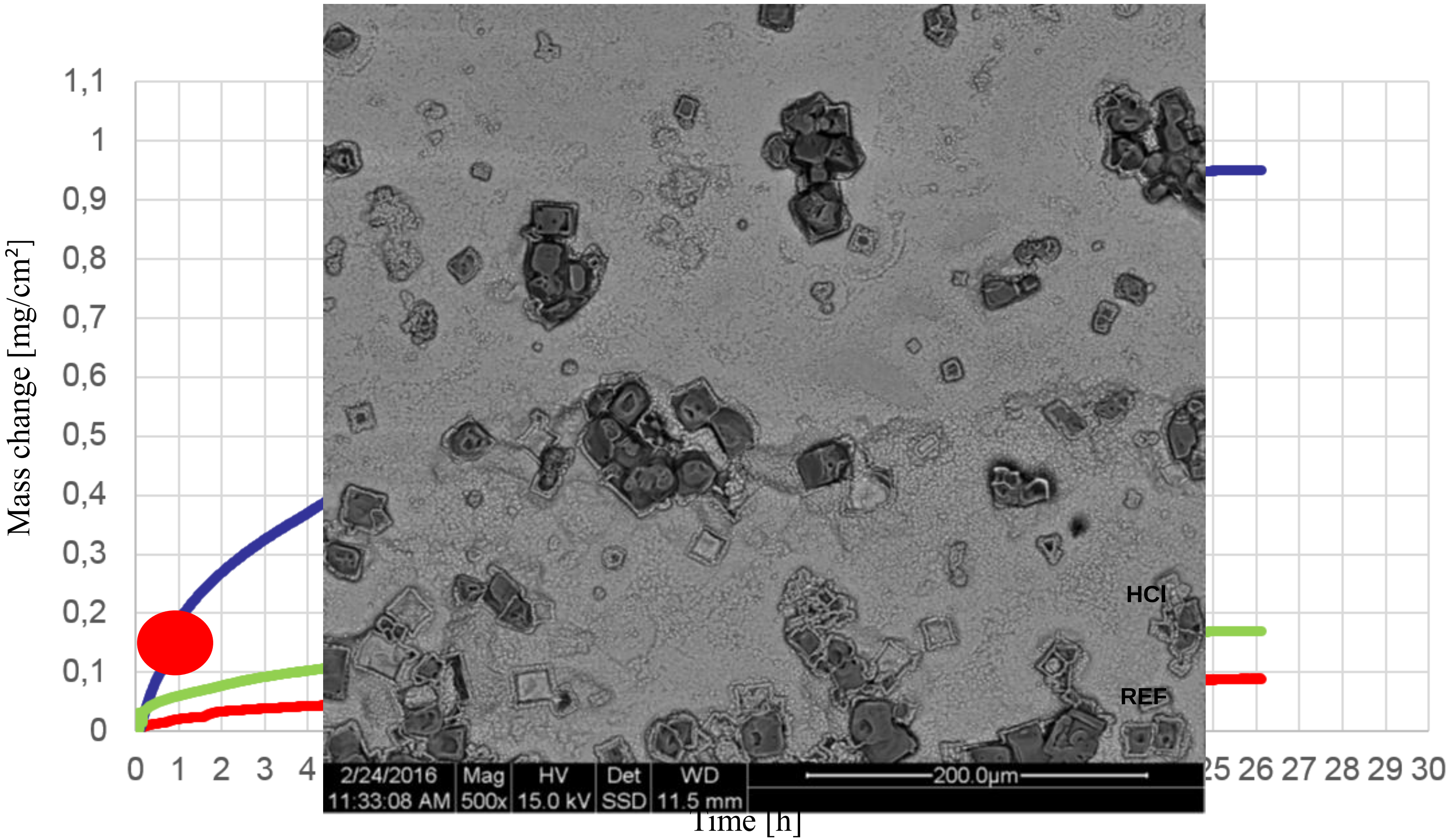

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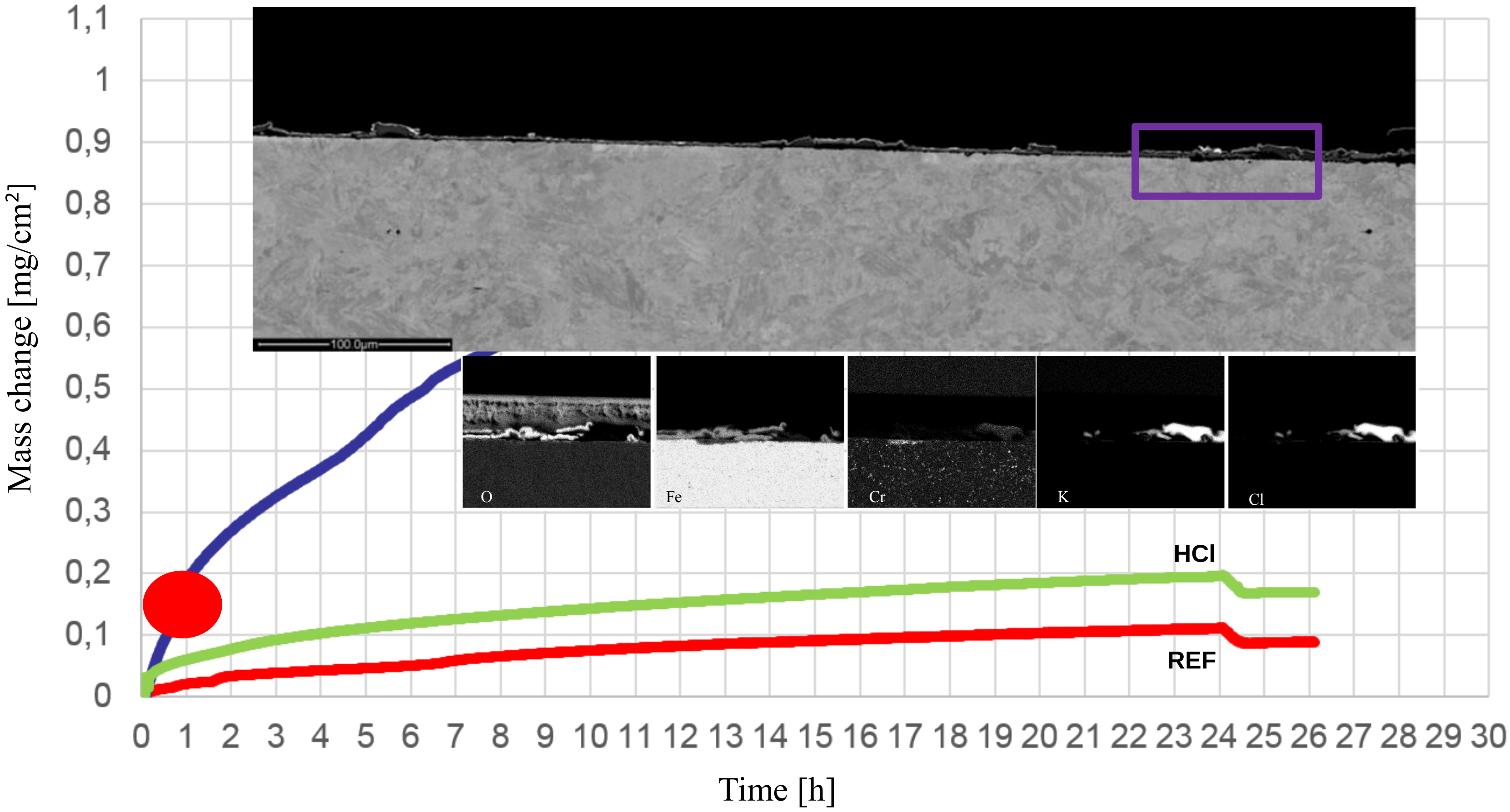

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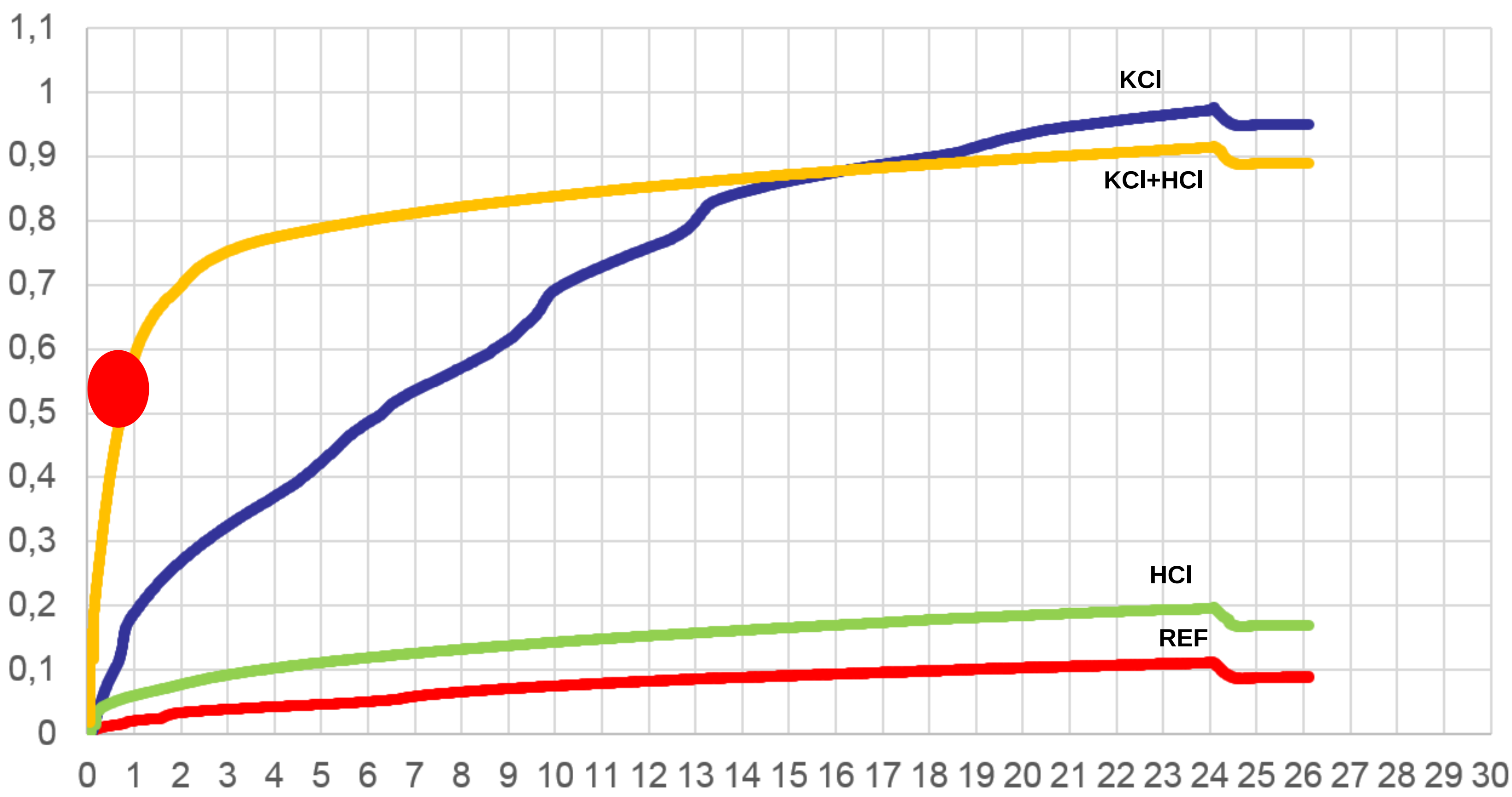

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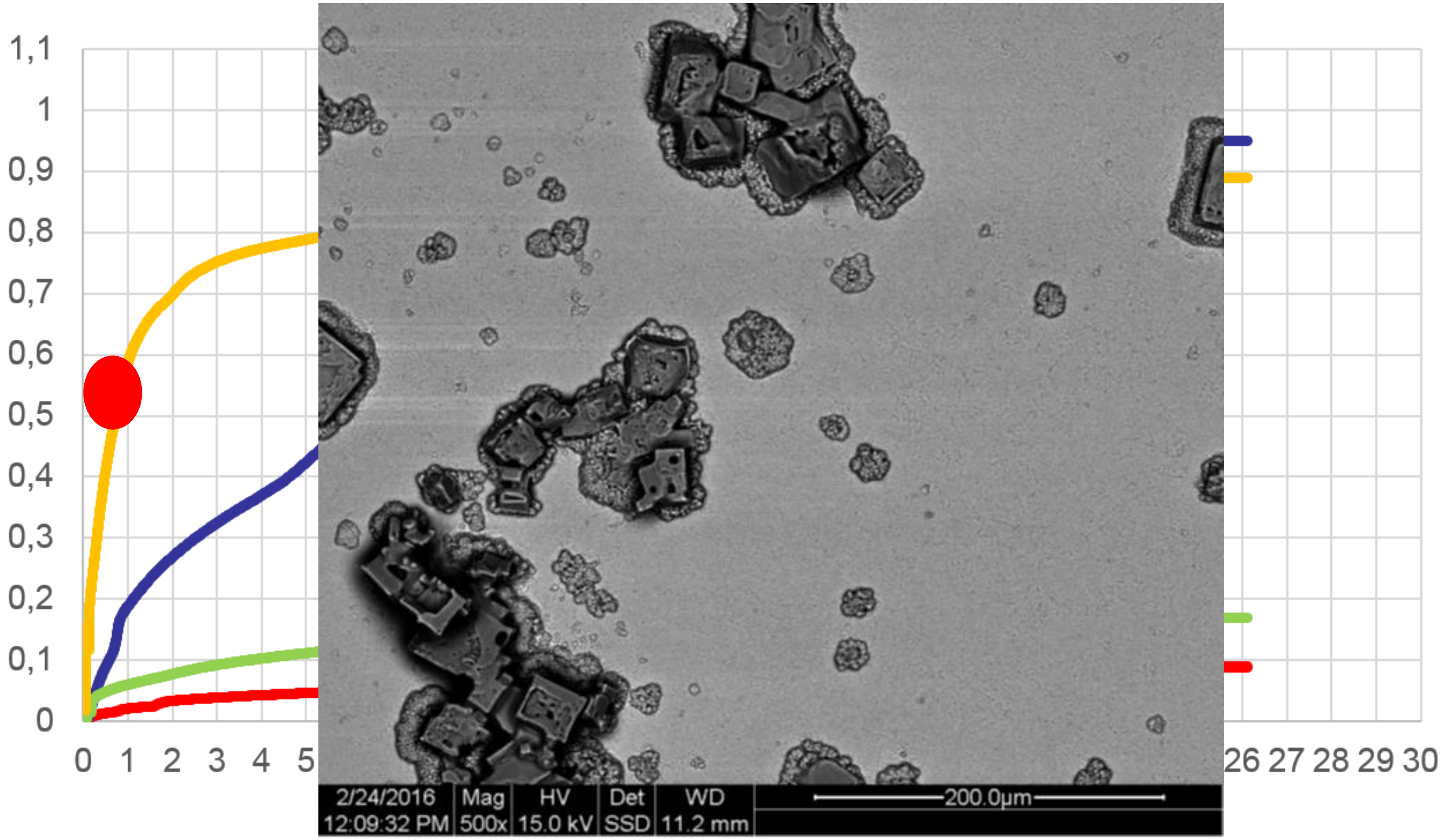

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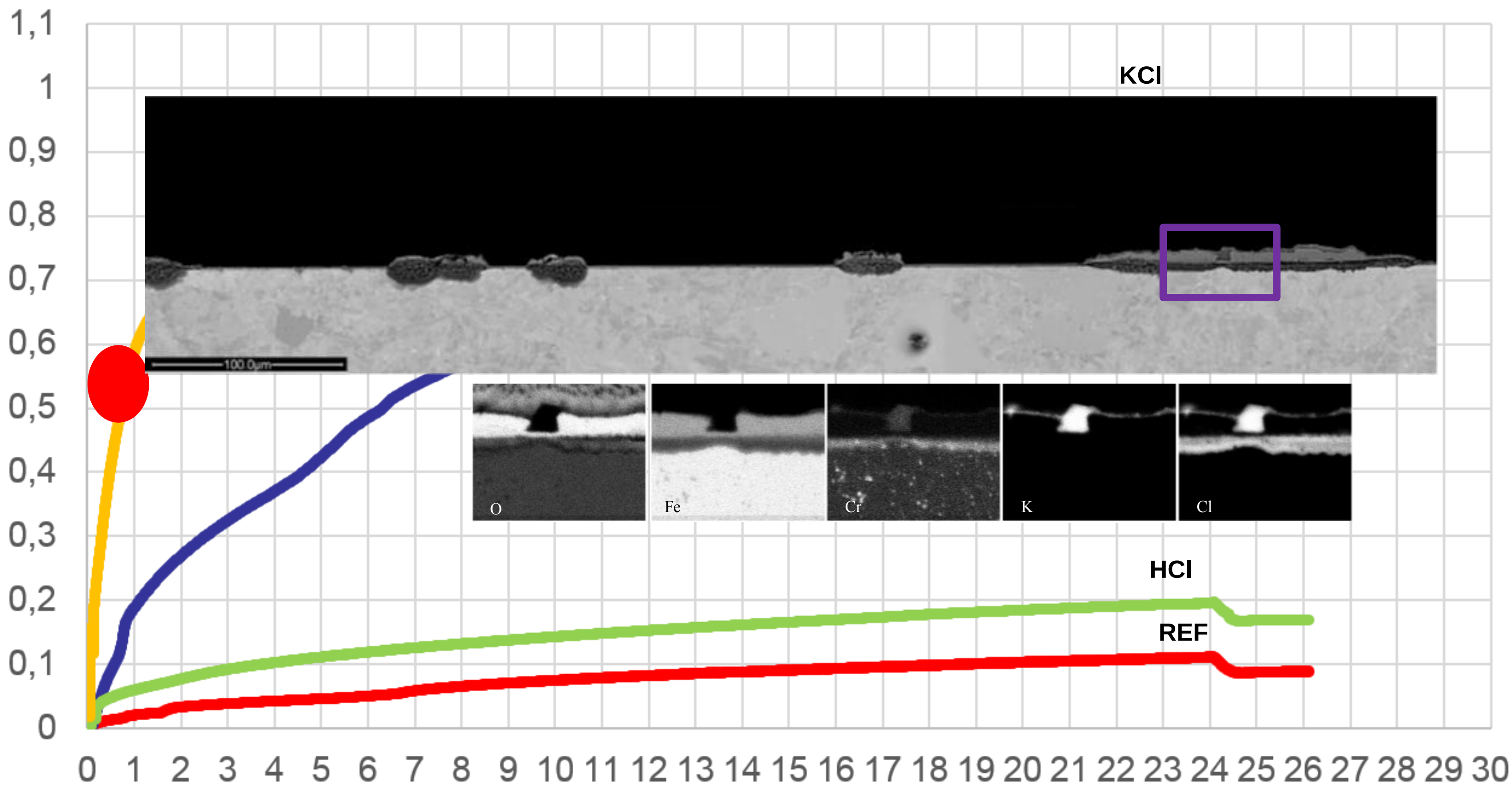
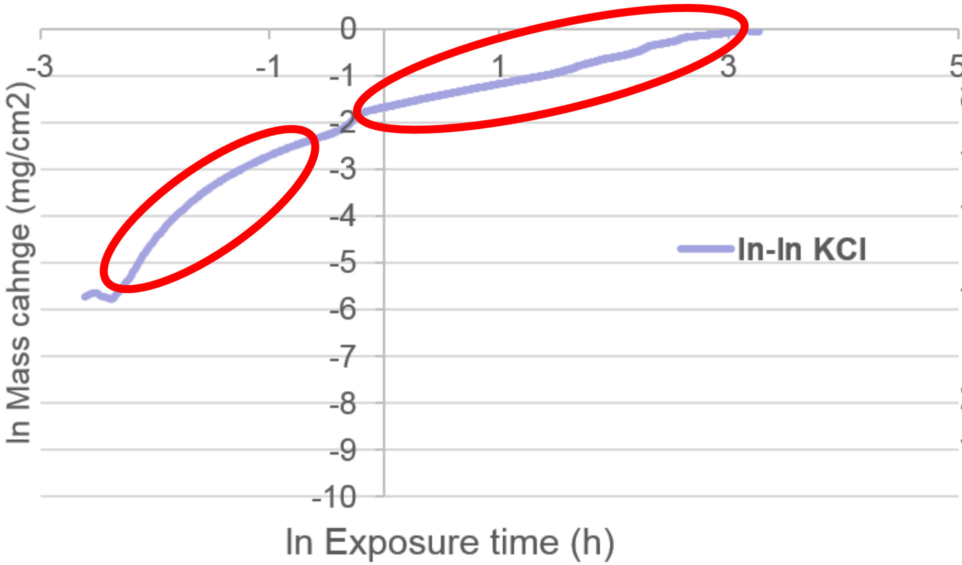
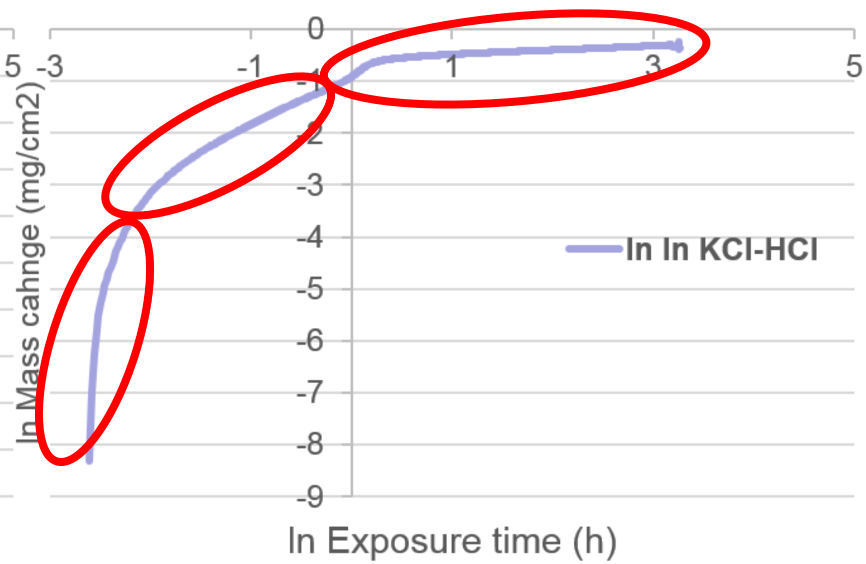


Interpretation of oxidation kinetics

Different reaction processes can be identified

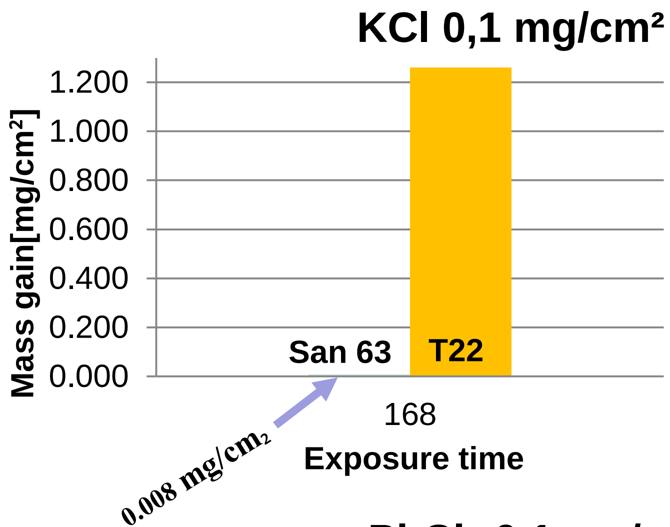
Corrosion rate has leveled off

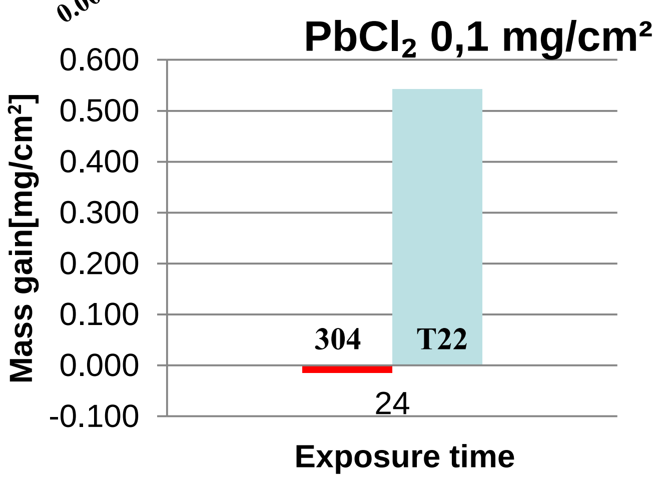




Preventative methods?

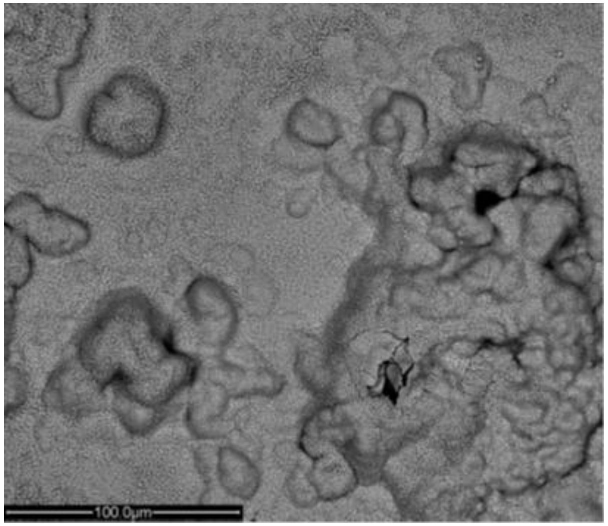
Change the material



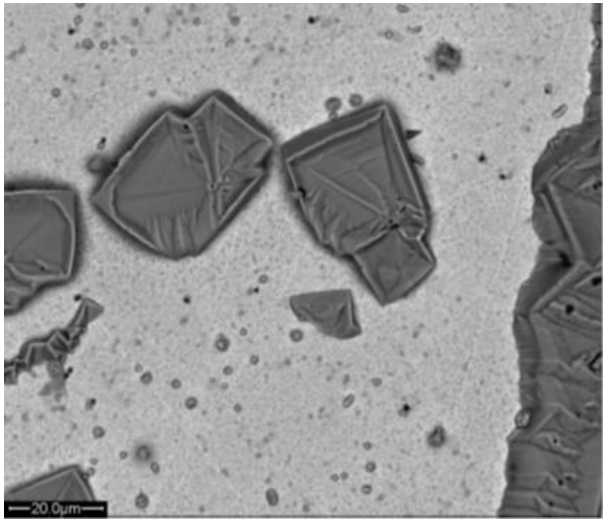


400 °C KCl, 168h

T22



Sanicro 63



Future work

- Further investigate the corrosion mechanism in the KCl-HCl exposures
- Continued $PbCl_2$ investigation with and without HCl
- Detailed microscopy investigation of corroded samples including advanced cross sectional techniques (e.g. FIB and BIB) and TEM analysis
- Investigate possible prevention methods e.g. use of new materials/coatings or change furnace environment e.g. active bed technology

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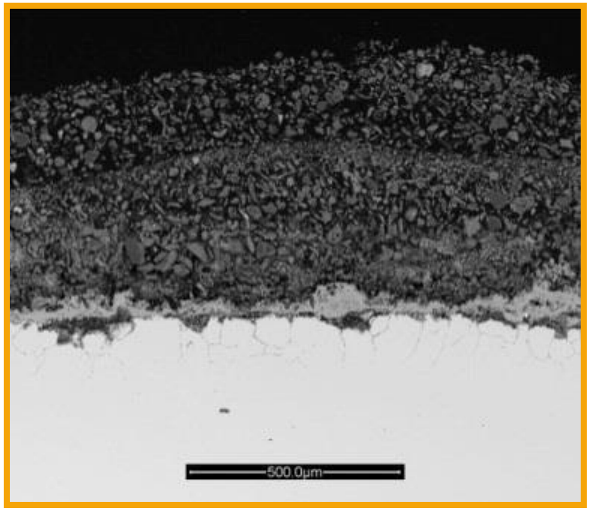
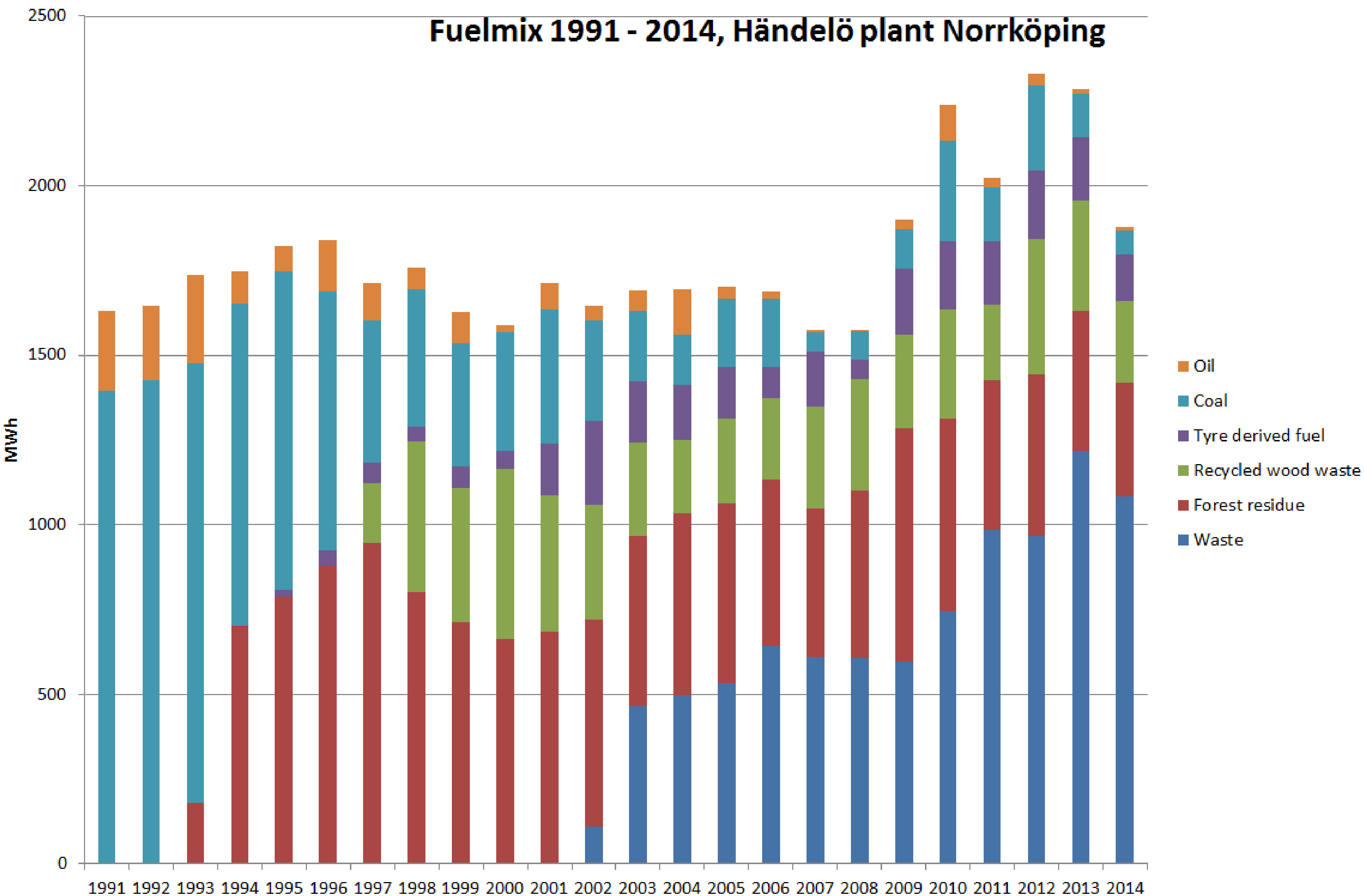
Corrosion Center

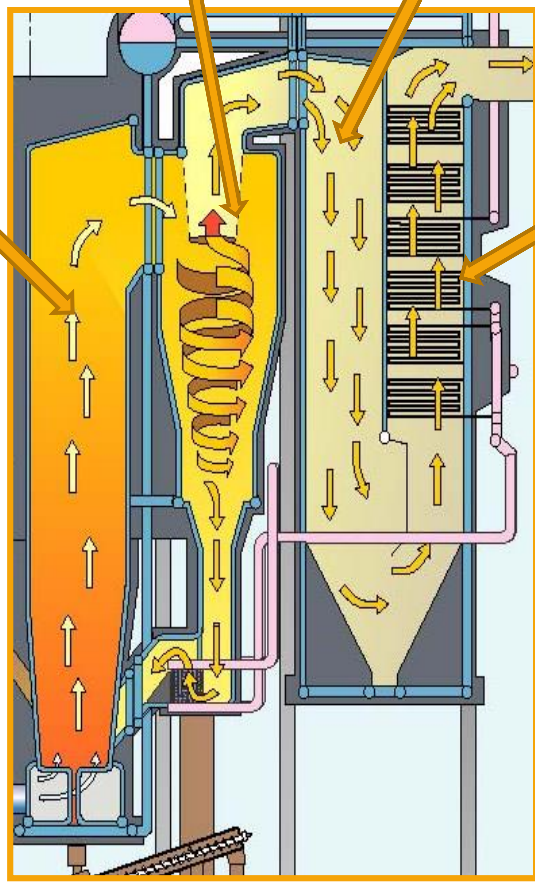
KCl induced high temperature corrosion of stainless steel



Julien Phother


Fuelmix 1991 - 2014, Händelö plant Norrköping
MWh
2500
2000
1500
1000
500
0
1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014
Oil
Coal
Tyre derived fuel
Recycled wood waste
Forest residue
Waste

Boiler and corrosion



Deposits and corrosion

Substance	Fossil fuel	Biomass and waste
pO_2	~1%	~5%
pH_2O	~10%	20-30%
Release of alkali compounds	low	high
pSO_2	high	low

- Corrosion resistance of stainless steels : Cr rich oxide film
- Depletion of Cr from the oxide :

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

$$(Cr,Fe)_2O_3 \xrightarrow[O_2 + KCl]{} Fe_2O_3 + K_2CrO_4$$

How are different oxides affected by a corrosive environment?

Initiation

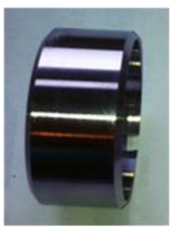
Propagation

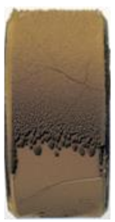
0 s

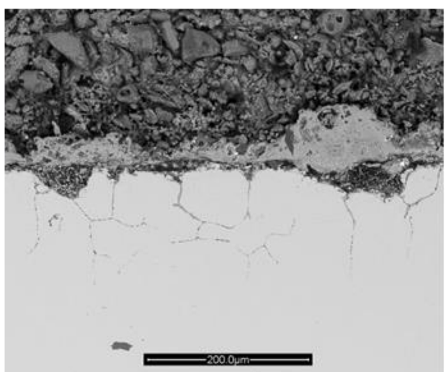
24 h

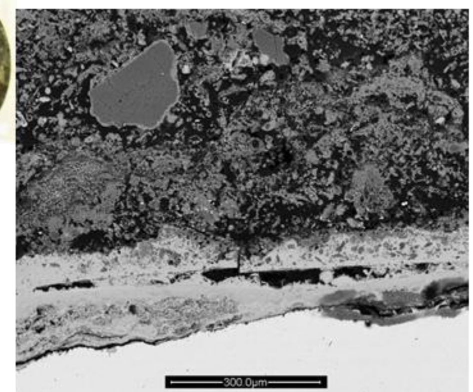
1000 h

? h









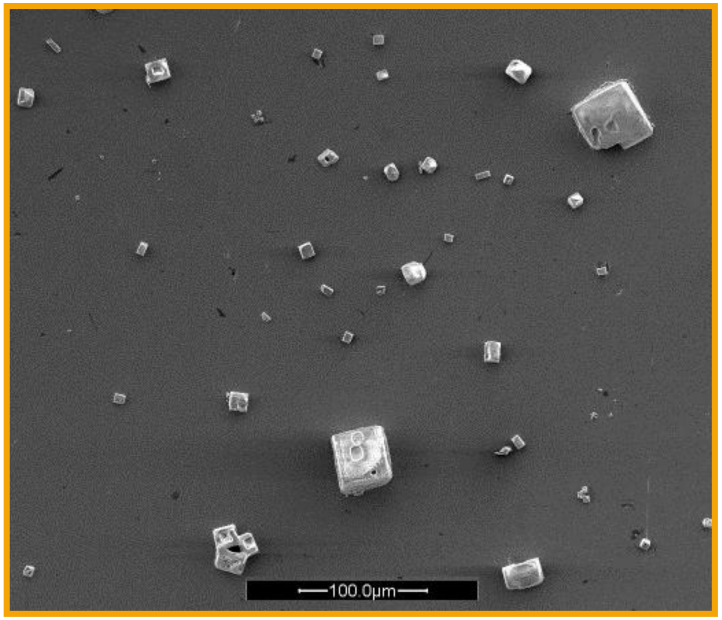
KCl lab exposures

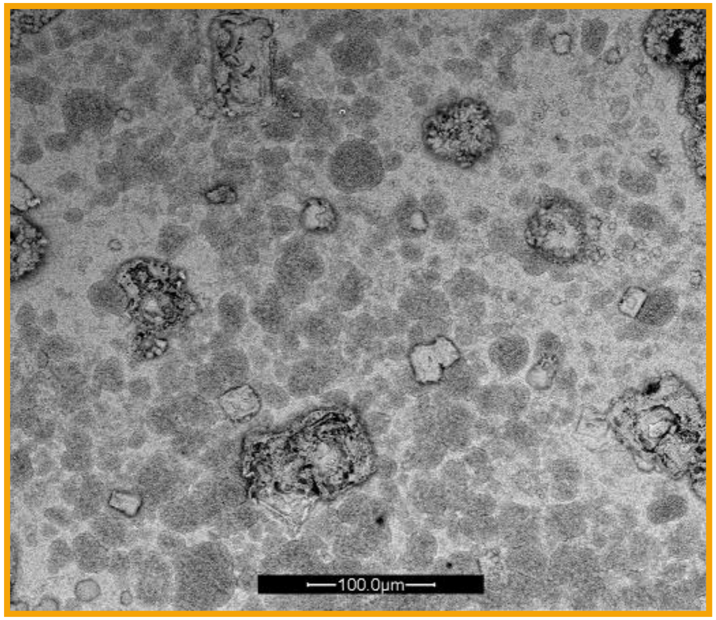
- What has been done before:
  - Initial spray of salt on samples : 0,1 or 1 mg/cm^2
  - Understand the effect of KCl on the initiation of corrosion

- Limitations :
  - KCl is quickly consumed
  - After 24H the massgain curve is not representative of real boilers conditions

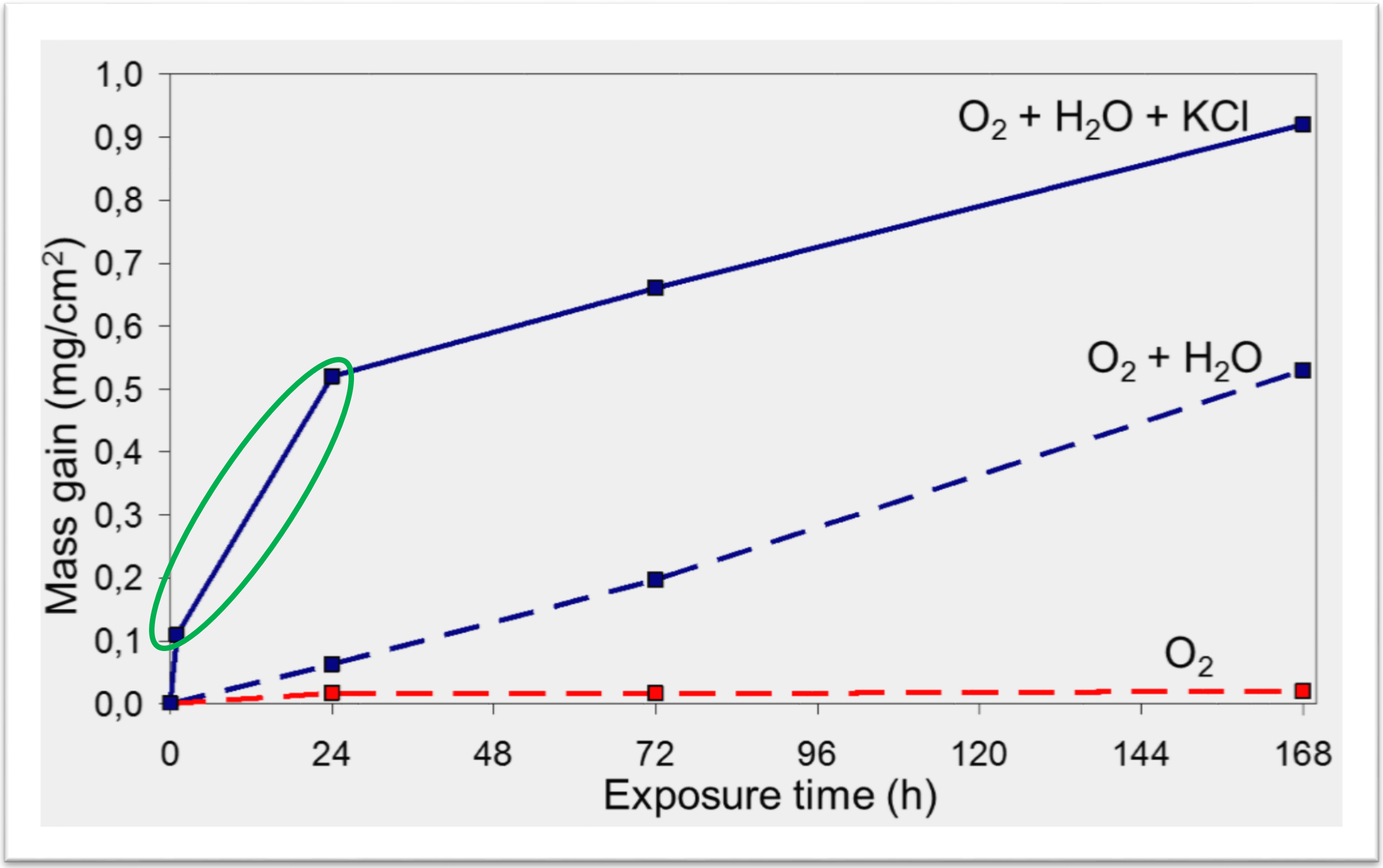
KCl lab exposures

- What has been done before:
  - Initial spray of salt on samples : 0,1 or 1 mg/cm²
  - Understand the effect of KCl on the initiation of corrosion





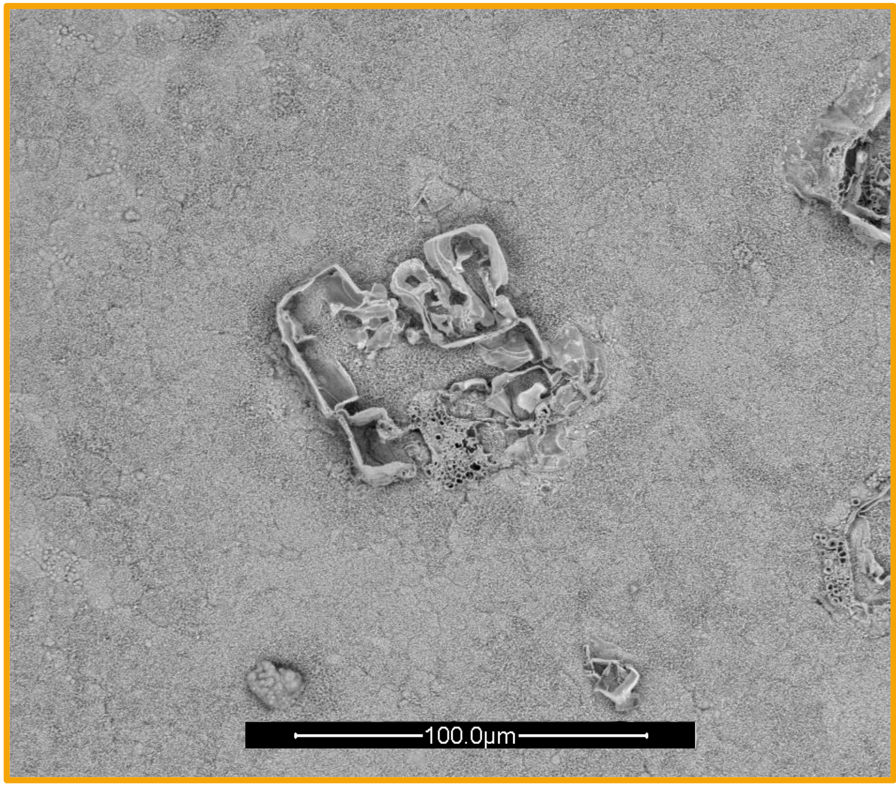
KCl lab exposures



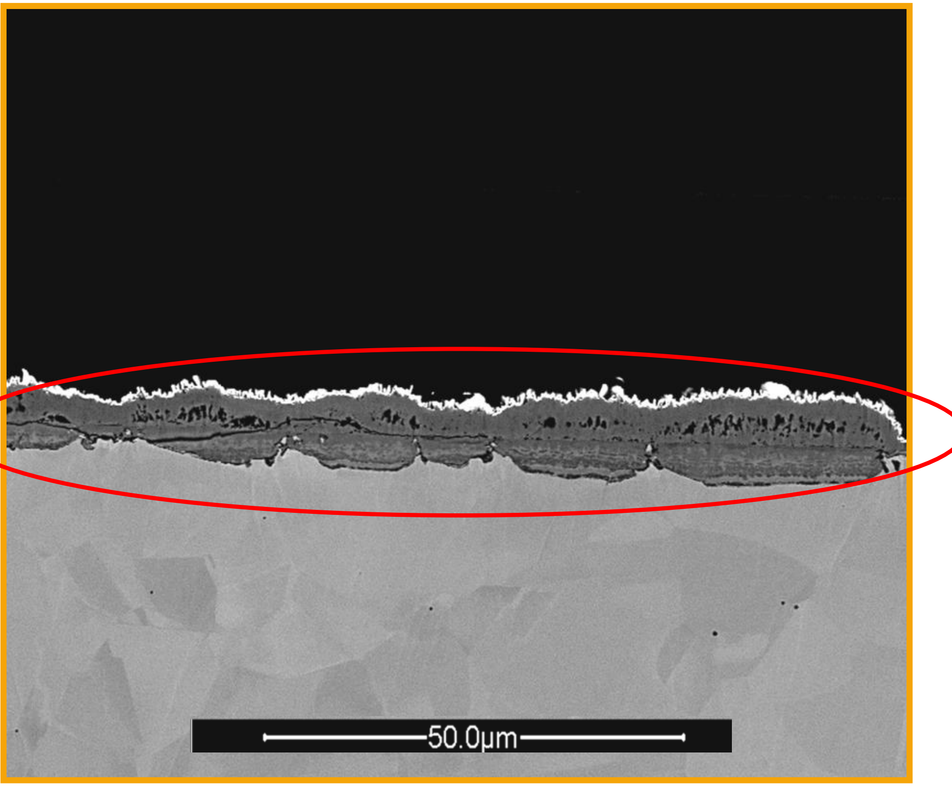
KCl lab exposures

24h – 40%H_2O – 5%O_2 - 600ºC - 0.1 mg/cm²

Plane view BSE



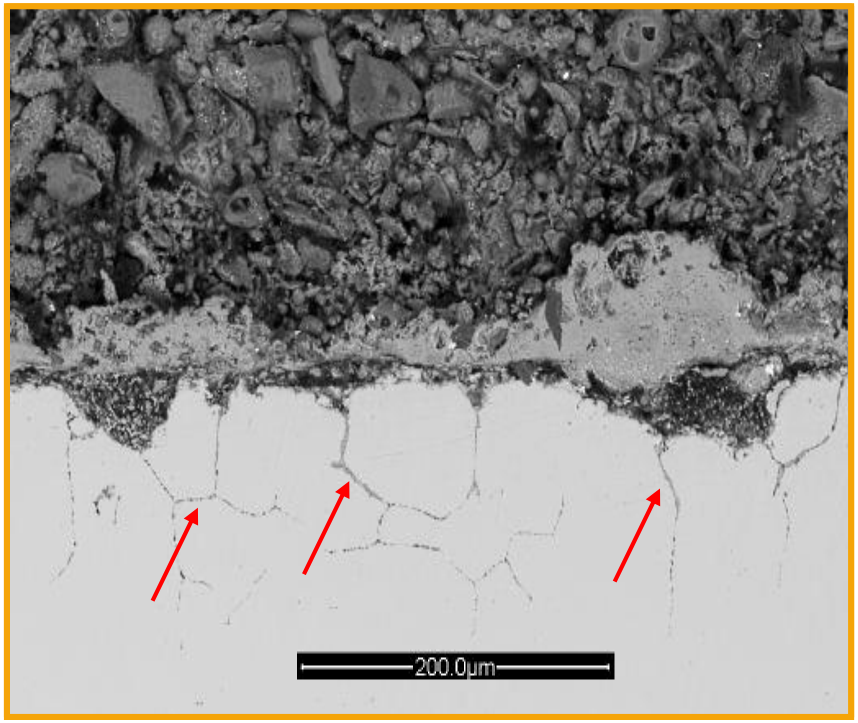
Cross section BSE



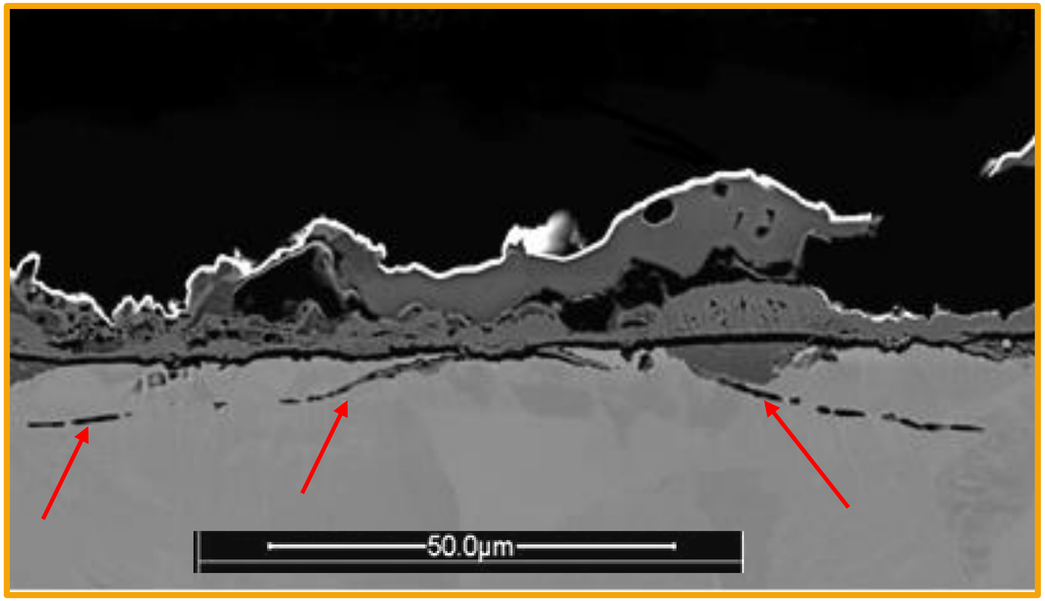
KCl lab exposures

24h – 40%H_2O – 5%O_2 - 600ºC - 1.0 mg/cm²

Plane view BSE

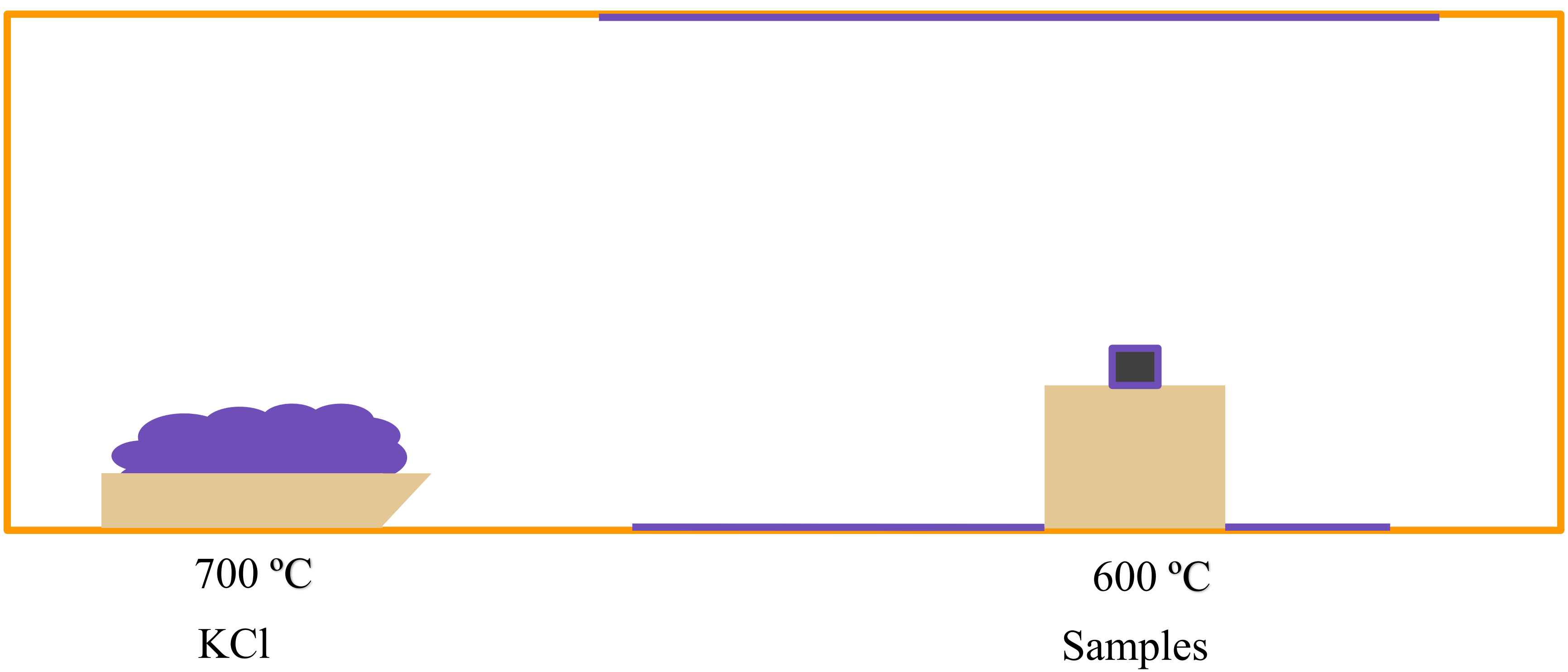


Cross section BSE



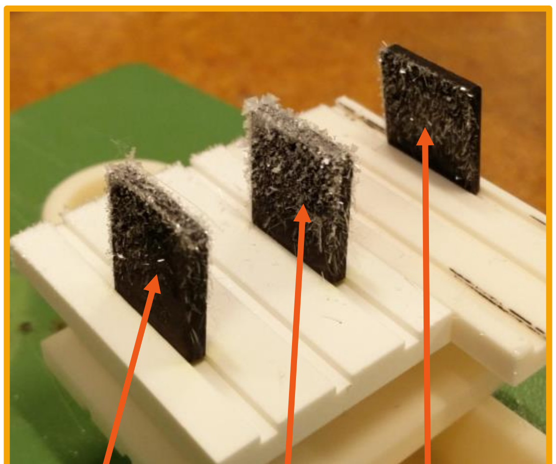
Next step :
KCl added continuously

KCl added continuously



Experiment

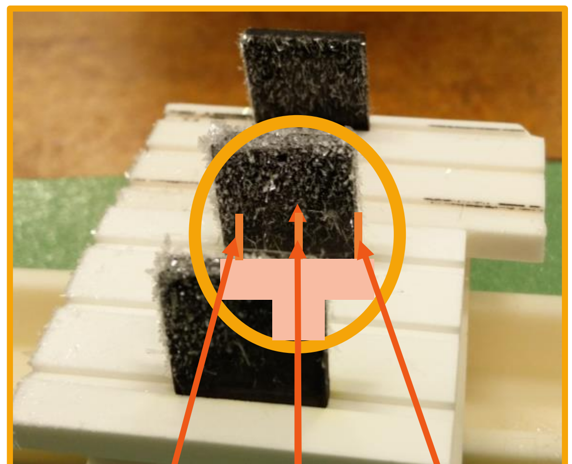
KCl1 : 24H – 20%H_2O - 600ºC



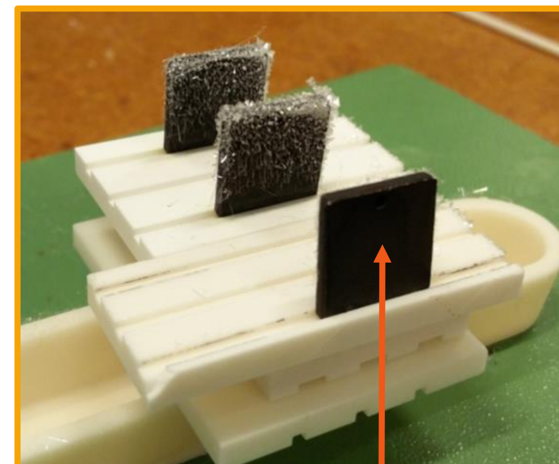
Left Side
LS

Middle
M

Right
Side
RS



Middle Left Side
M LS
« Most KCl
deposition »

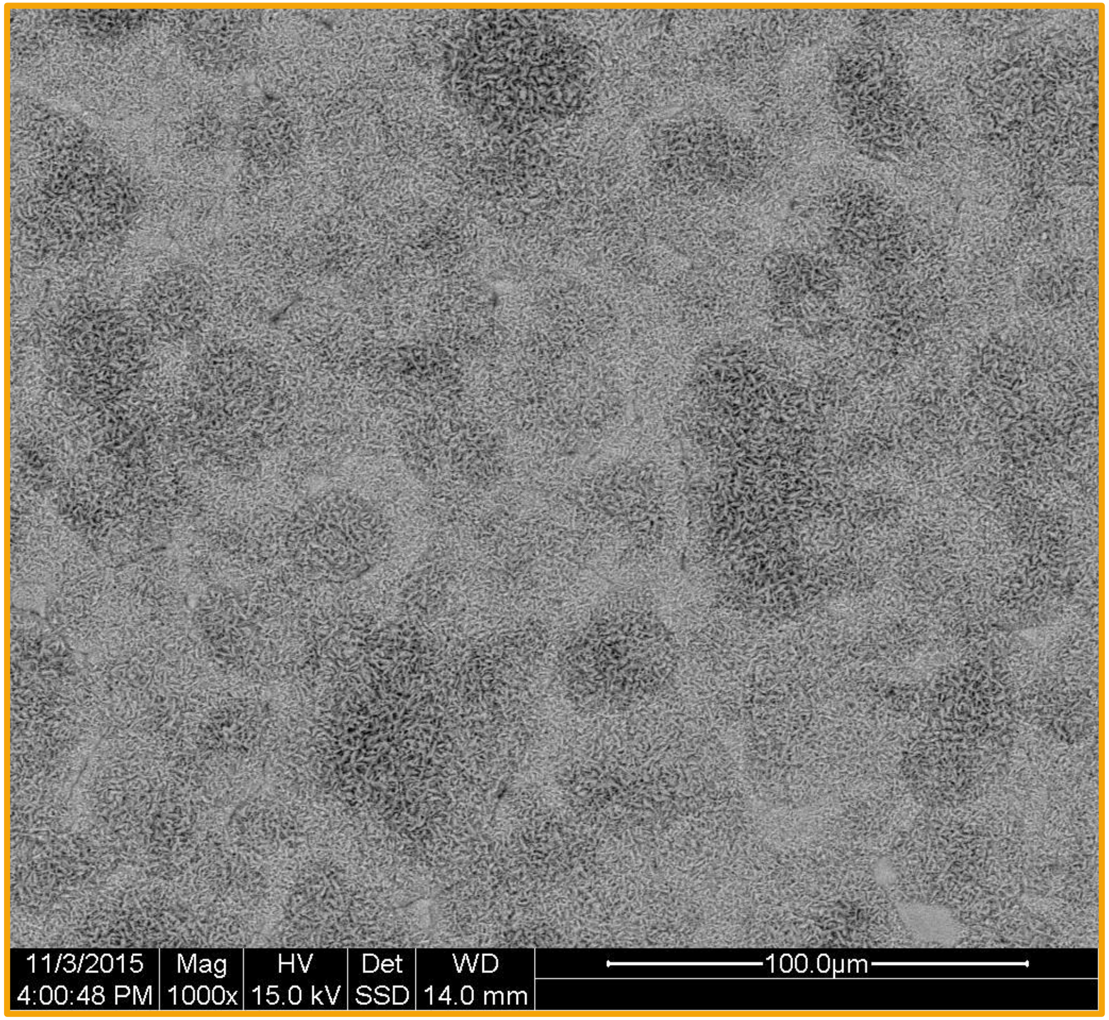


Right Side Wall Side
RS WS
« Least KCl depostion »

Least KCl

Plane view

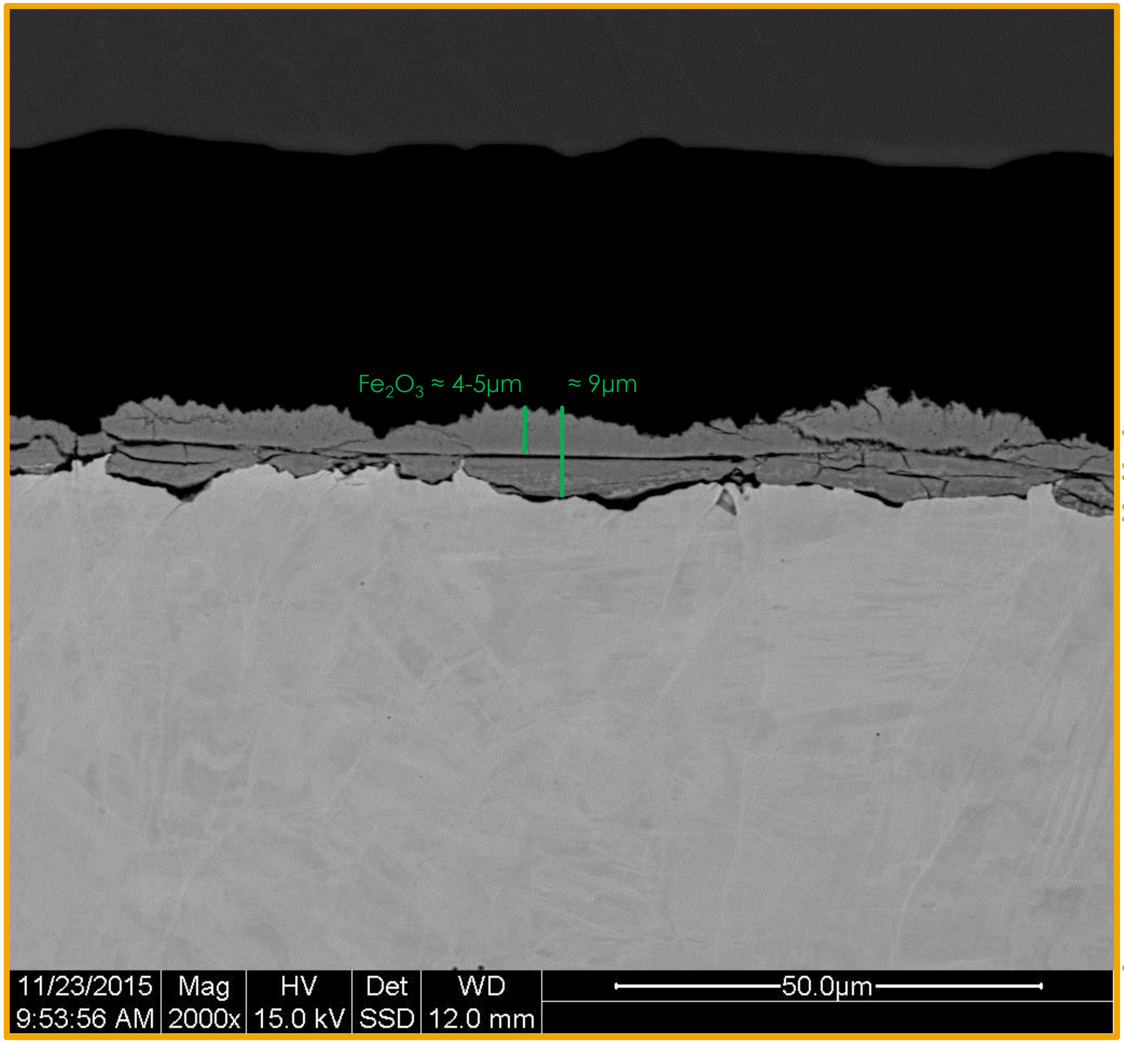
BSE



Least KCl

Cross-section

BSE



$Fe_2O_3 \approx$ 4-5µm

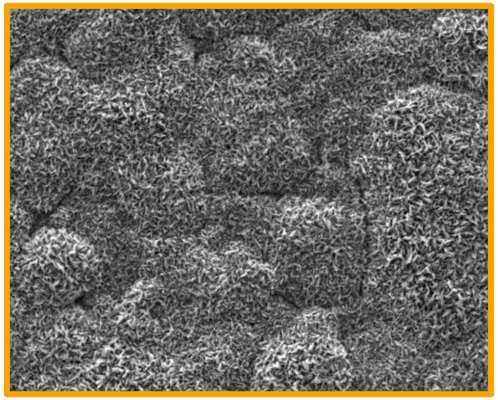
$(Cr,Fe,Ni)_3O_4 \approx$ 4-5µm

Bulk 304L

Summary

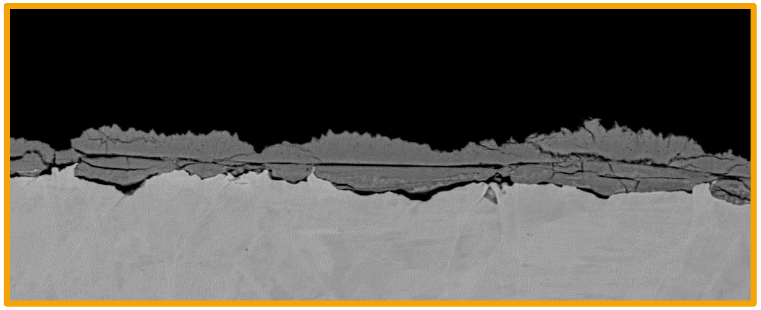
Least KCl deposition

- Plane view
  - Homogeneous surface
  - Usual Fe_2O_3 observed
- Cross-section
  - Oxide thickness : ≈ 9 - 15µm
  - Comparison : With 0,1mg/cm² of KCl initially sprayed ≈ 7 - 9µm



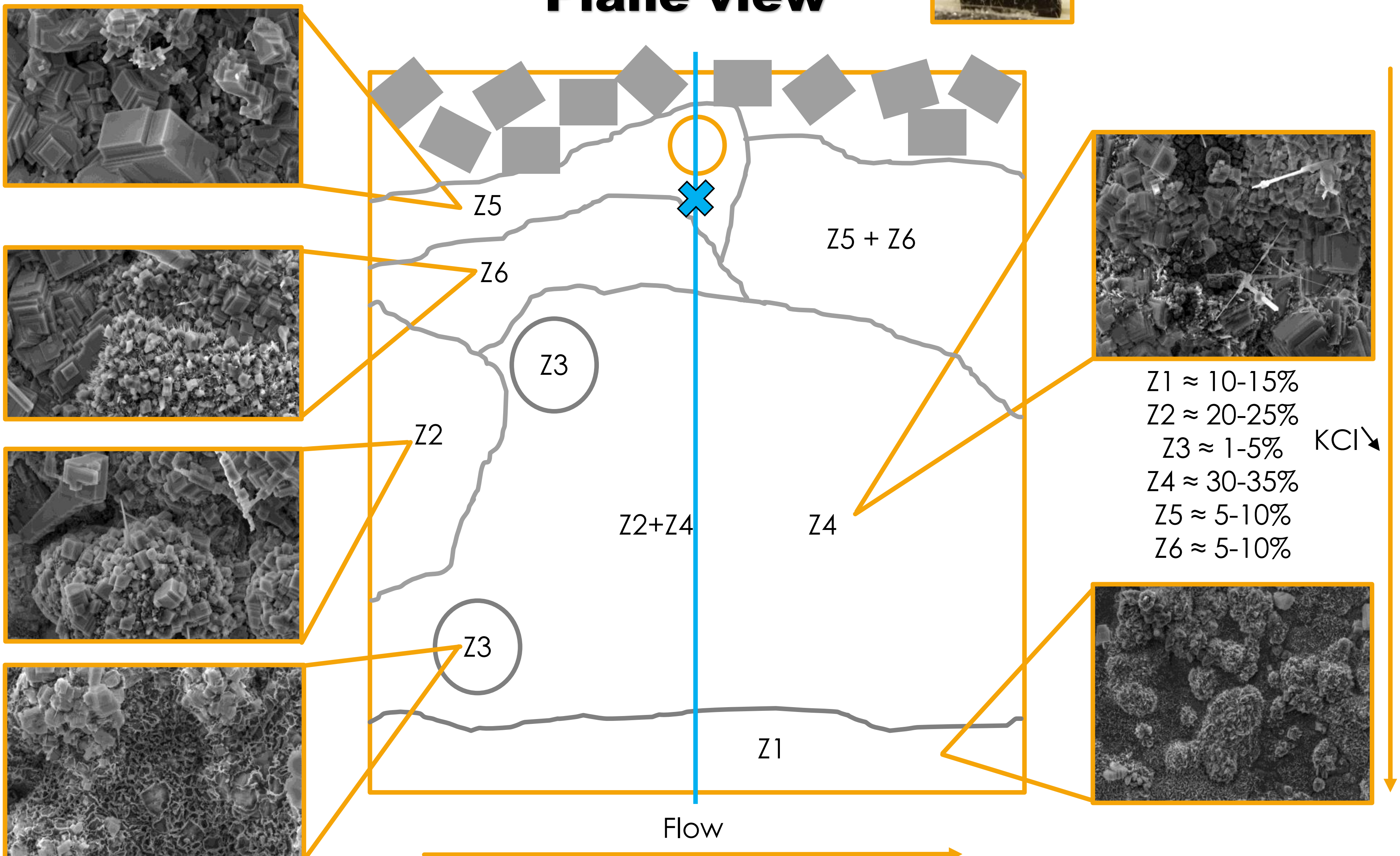
At least as corrosive as the former exposures

A little more corrosive



Most KCl

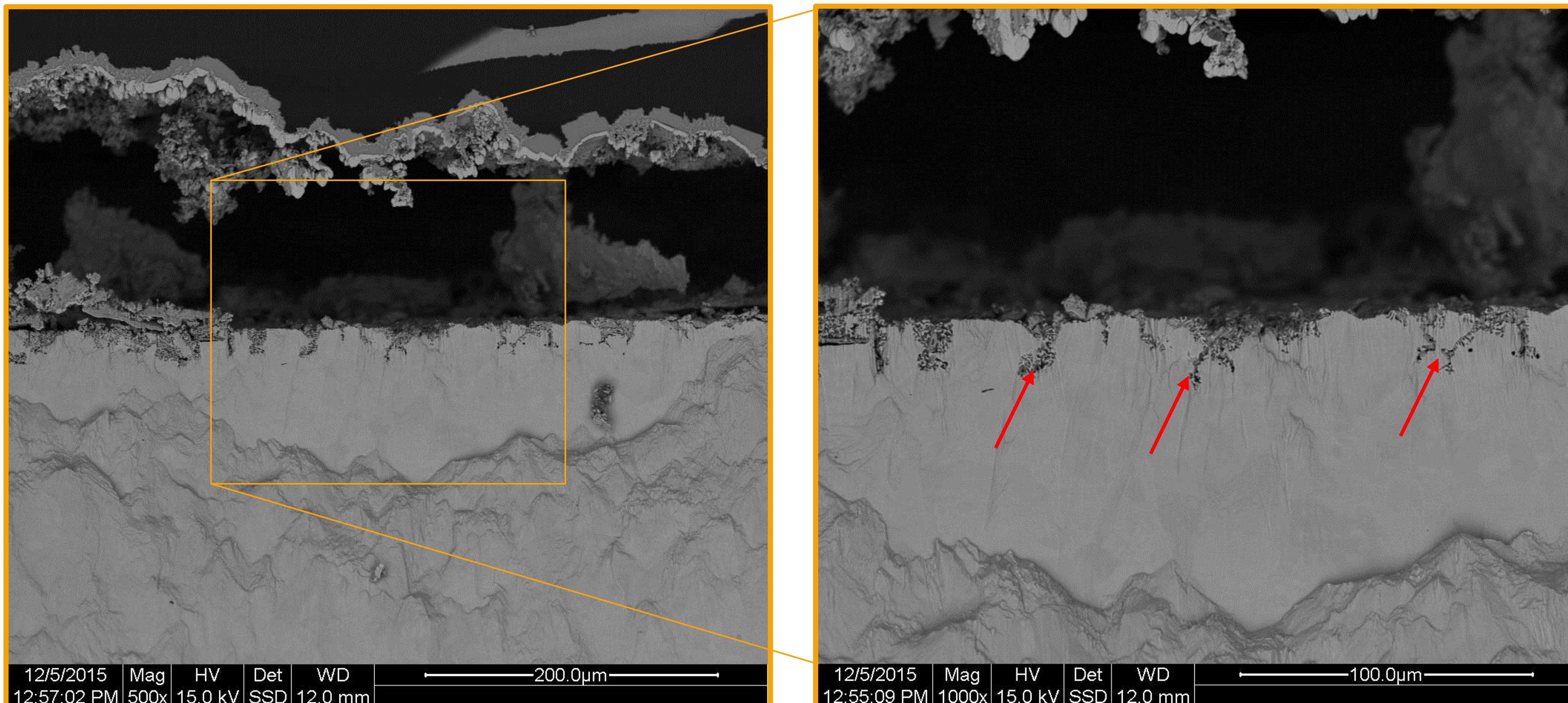
Plane view



Most KCl

Cross-section

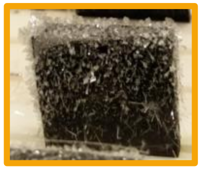
BSE

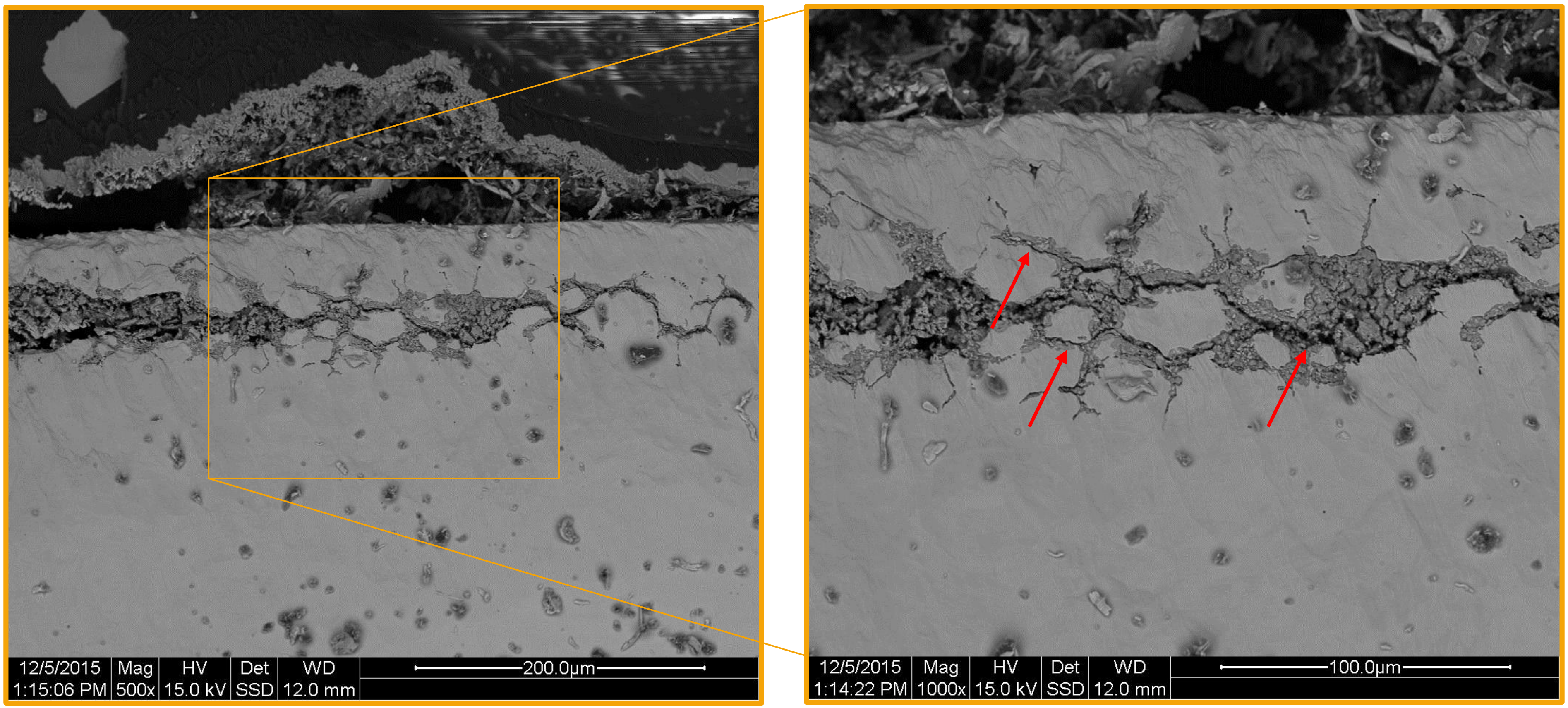


Most KCl

Cross-section

BSE

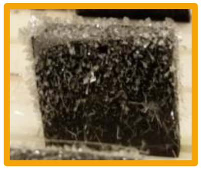


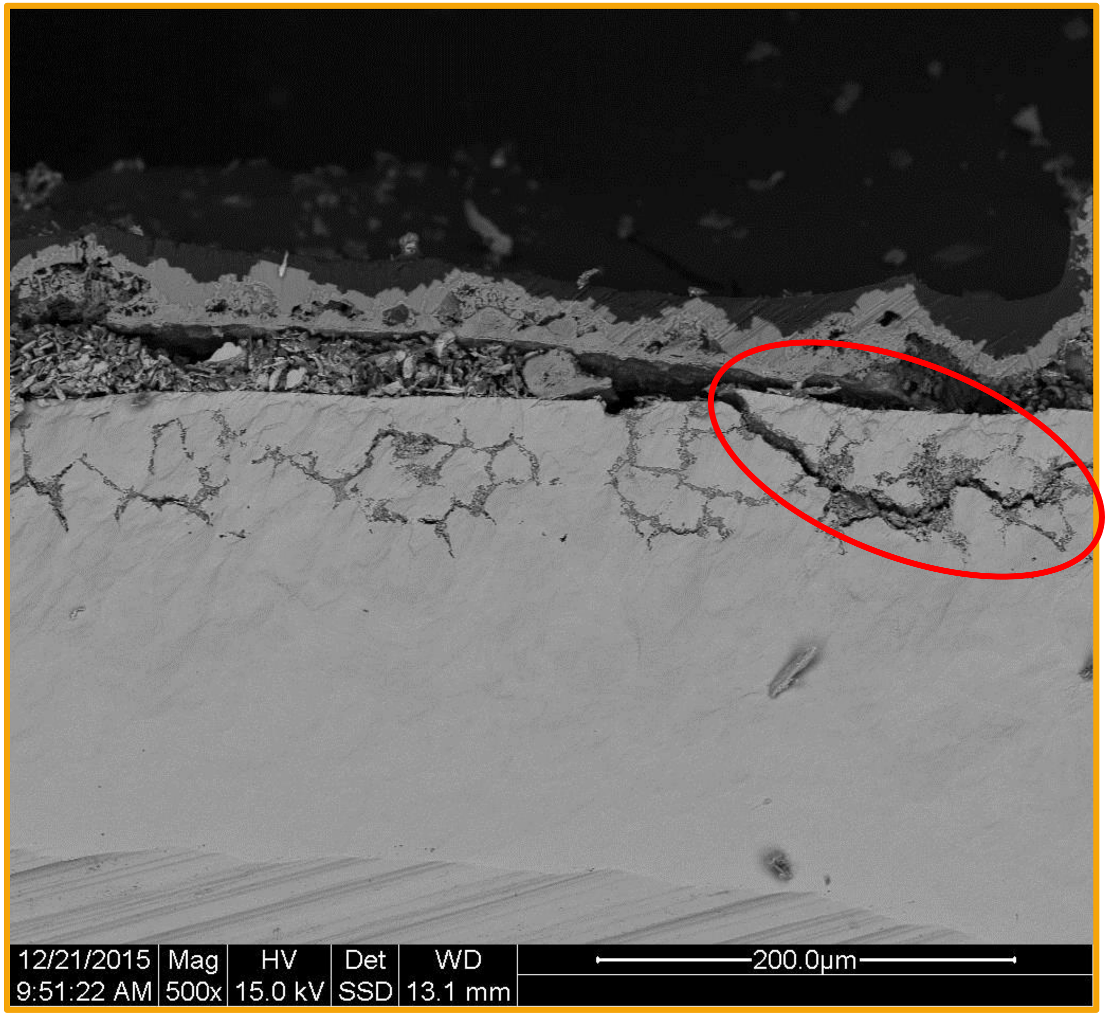


Most KCl

Cross-section

BSE

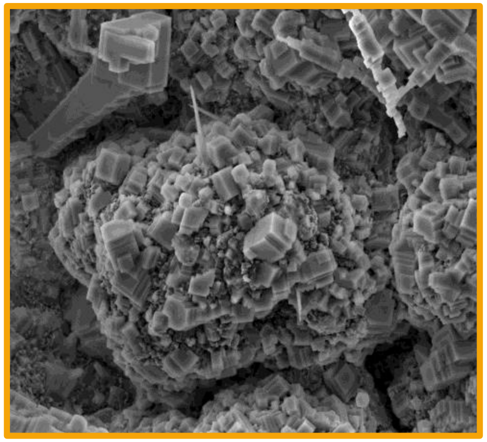




Summary

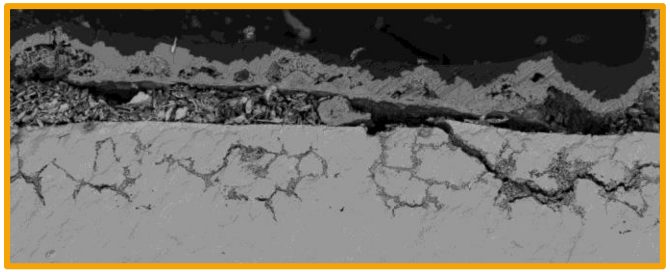
Most KCl deposition

- Plane view
  - Heterogeneous surface
  - Condensated KCl observed
- Cross-section
  - Grain boundaries attack
  - Can lead to spallation of the oxide AND of the bulk metal



A more corrosive environment

Corrosion features from the field can be observed



Next steps

- Run shorter exposures : 1H, 30 min, 10 min etc …
  - Understand the how the corrosion is triggered
- Run longer exposures :
  - Understand how the corrosion propagate
  - Compare different alloys
  - Corrosion memory effect

The
High-Temperature
Corrosion Center

Mechanistic study of chlorine penetration of oxide scales

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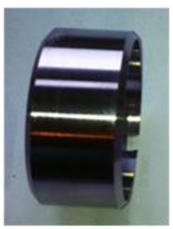
Environmental Inorganic Chemistry
Department of Chemical and Biological Engineering
Göteborg, Sweden

andrea.olivas@chalmers.se

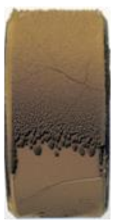
How are different oxides affected by a corrosive environment?

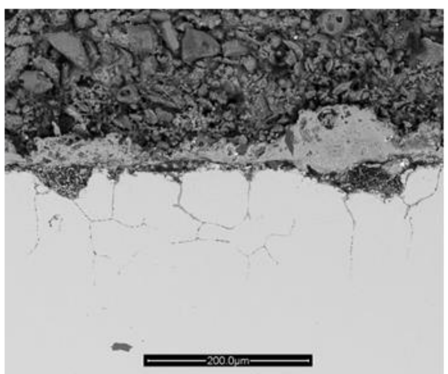
Initiation — Propagation

0 s

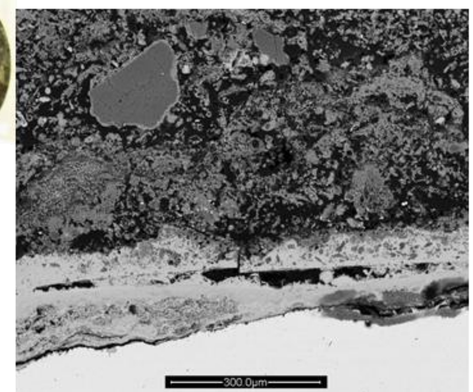


24 h



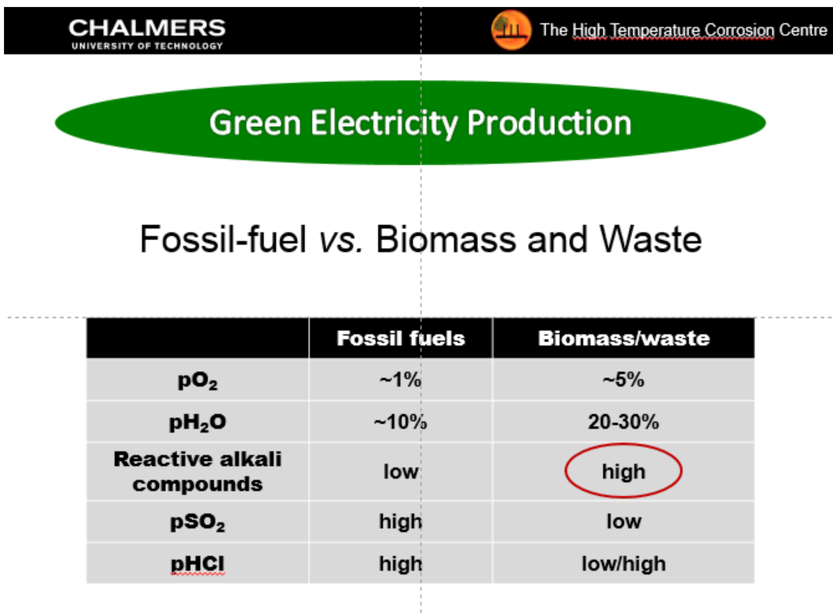


1000 h



? h

Influence of KCl



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The High Temperature Corrosion Centre

Green Electricity Production

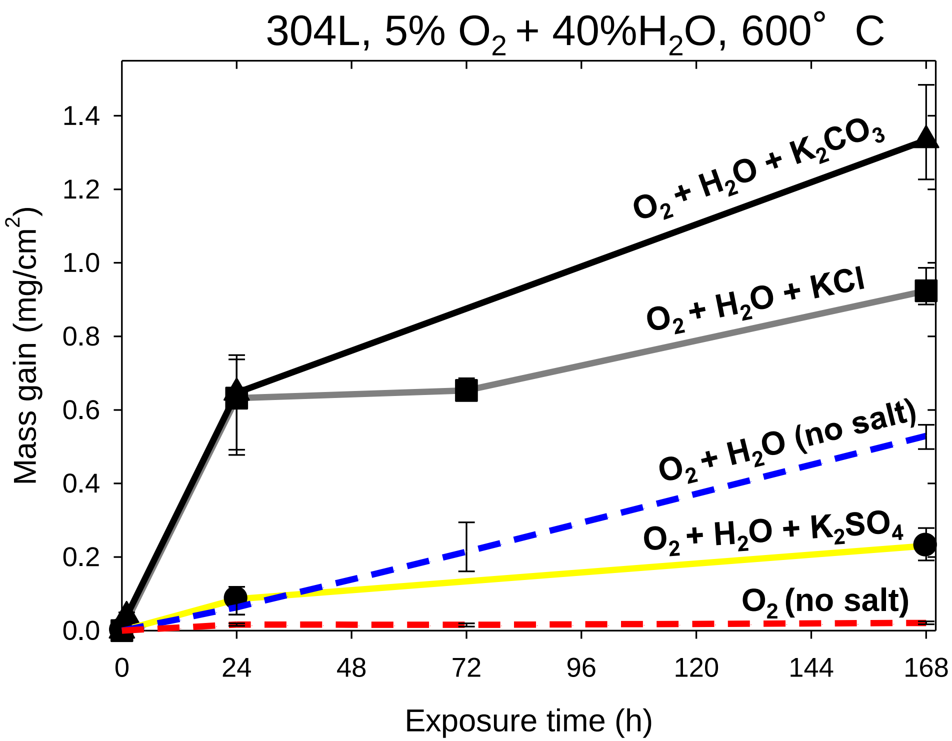
Fossil-fuel *vs.* Biomass and Waste

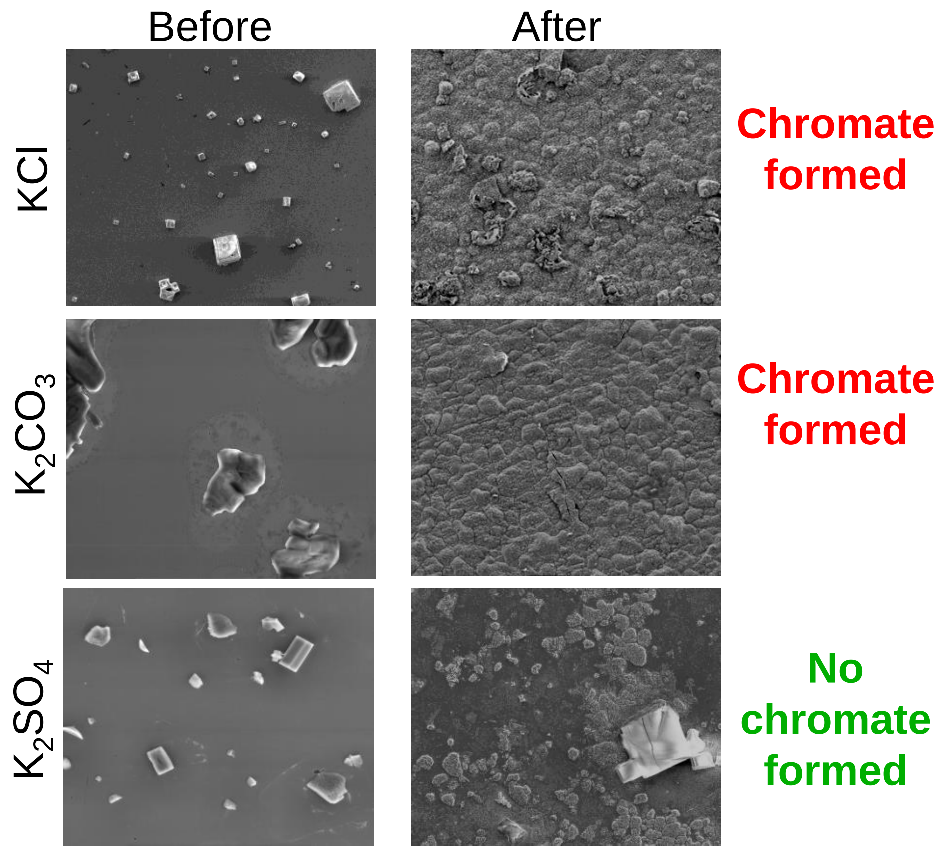
	Fossil fuels	Biomass/waste
pO_2	~1%	~5%
pH_2O	~10%	20-30%
Reactive alkali compounds	low	high
pSO_2	high	low
pHCl	high	low/high

Stainless Steel

Low alloyed steel

Influence of KCl - Chromium depletion on chromia forming steels





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

Influence of KCl

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Green Electricity Production

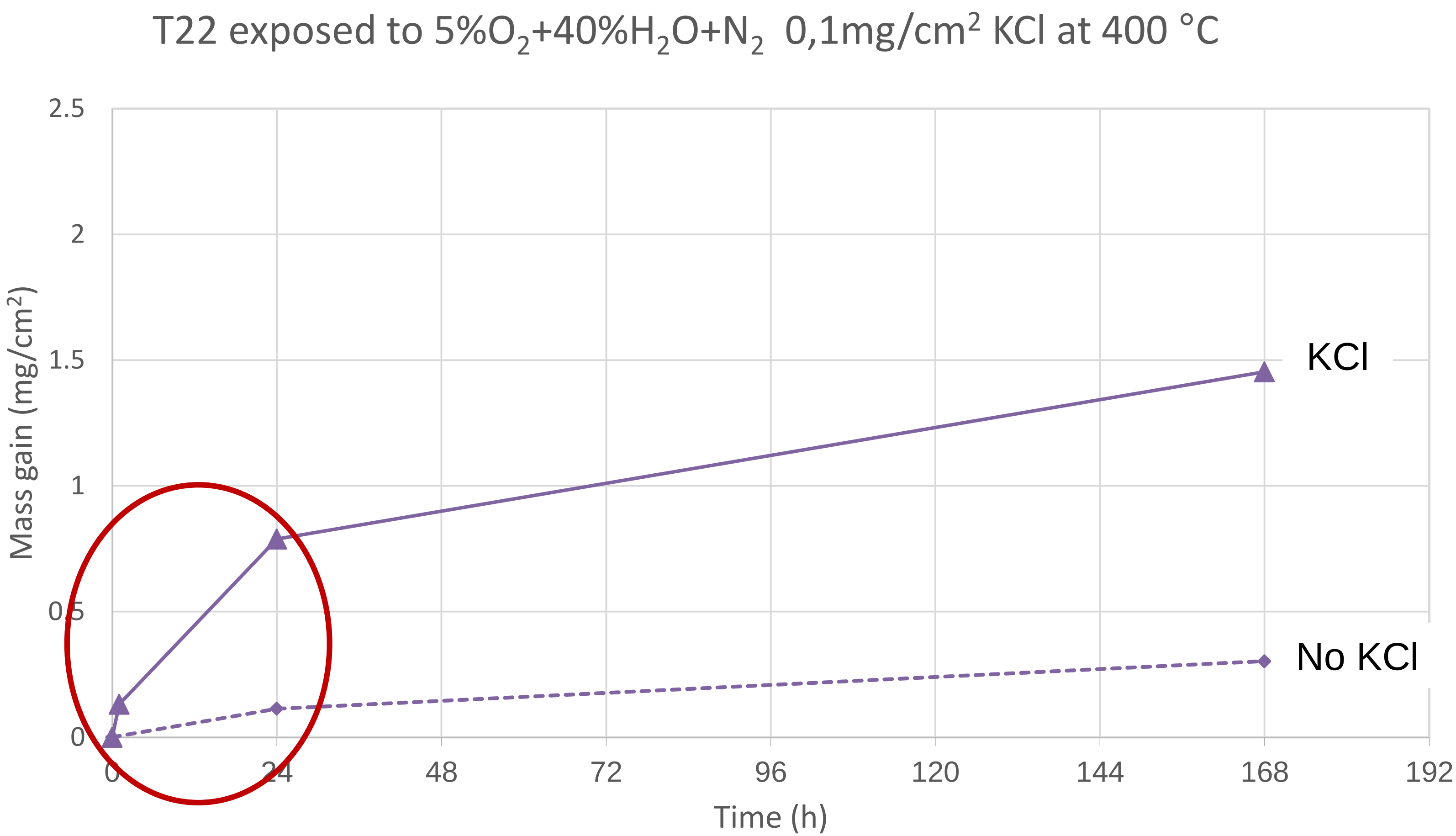
Fossil-fuel *vs.* Biomass and Waste

	Fossil fuels	Biomass/waste
pO_2	~1%	~5%
pH_2O	~10%	20-30%
Reactive alkali compounds	low	high
pSO_2	high	low
pHCl	high	low/high

Stainless Steel

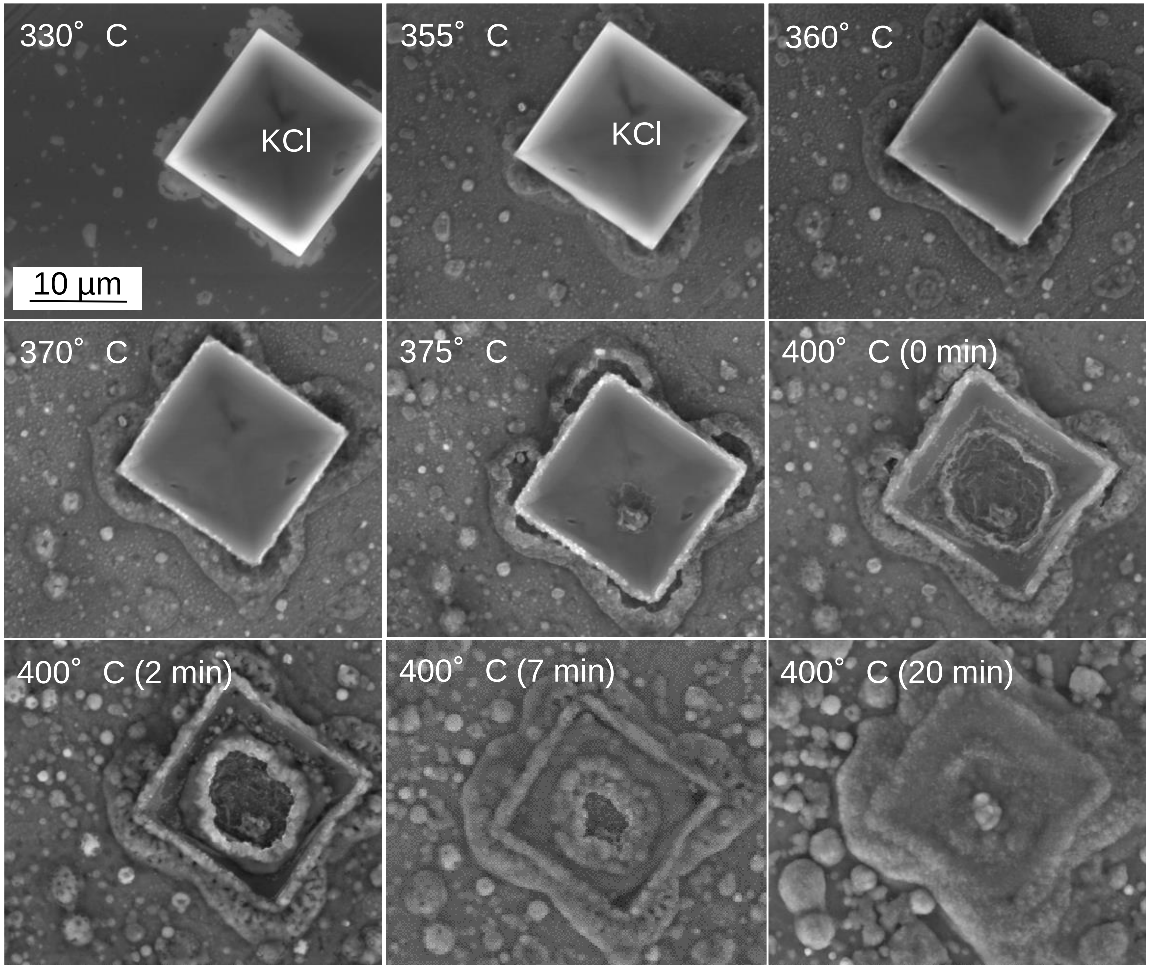
Low alloyed steel

Influence of KCl - Mass change



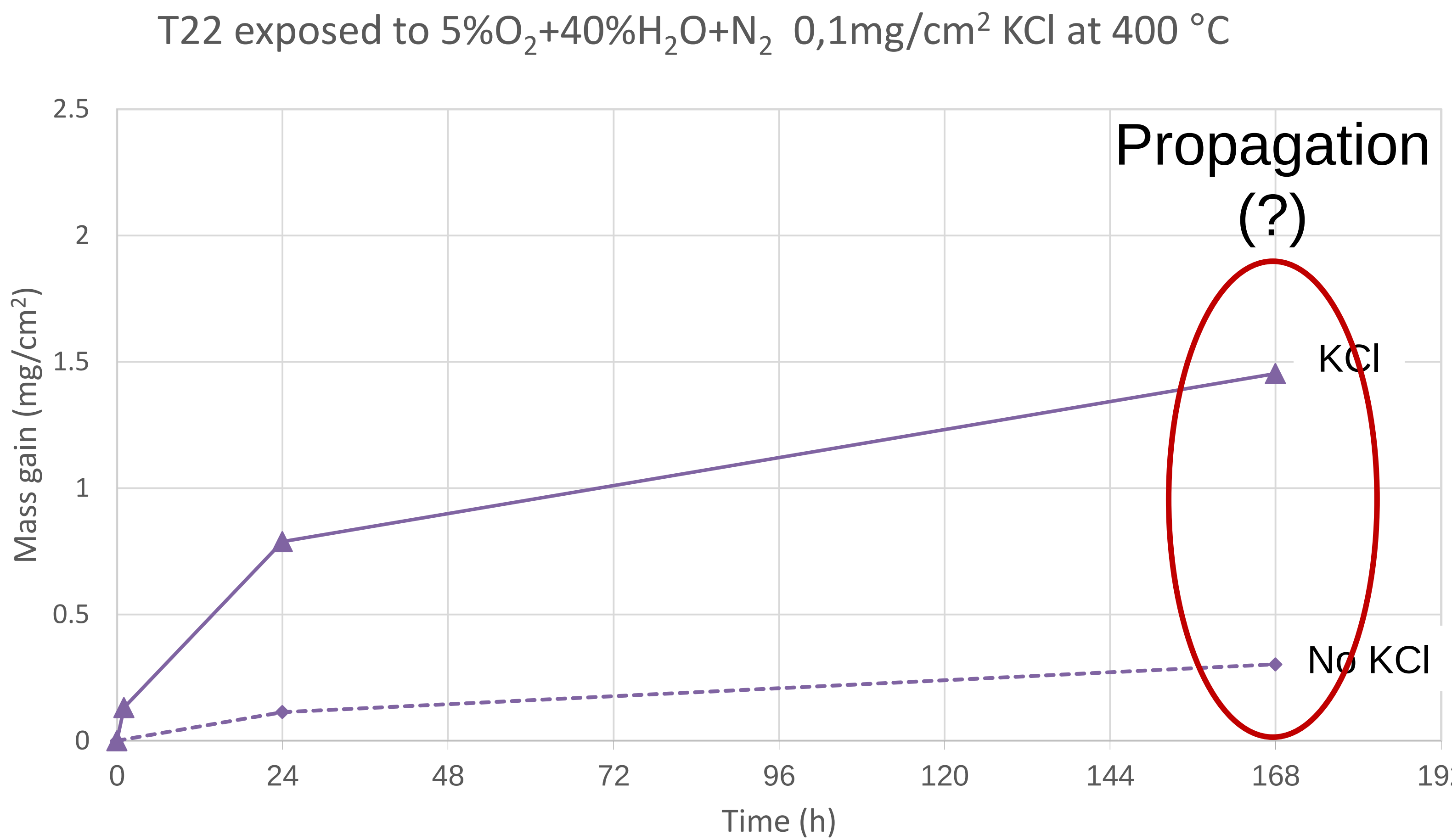
Folkeson, N., et al., *The influence of small amounts of KCl(s) on the high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 and 500 degrees C.* Materials and Corrosion-Werkstoffe Und Korrosion, 2011. **62**(7): p. 606-615.

Evolution of the corrosion scale – overview



Jonsson, T., et al., *An ESEM in situ investigation of initial stages of the KCl induced high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 degrees C.* Corrosion Science, 2011. **53**(6): p. 2233-2246.

Influence of KCl: Mass change



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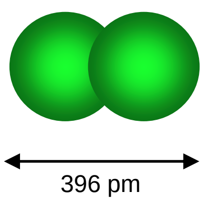
Influence of Chlorine

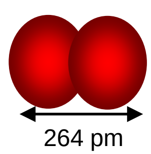
Active Oxidation – Chlorine Cycle

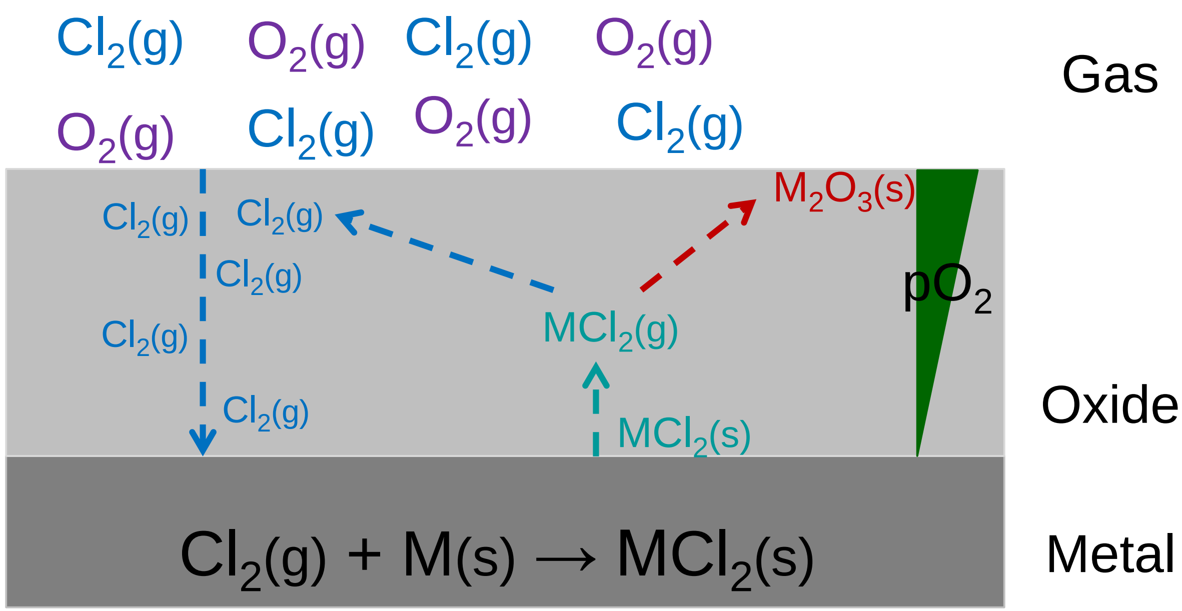
$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + Cl_2(g)$$

Cl_2



O_2





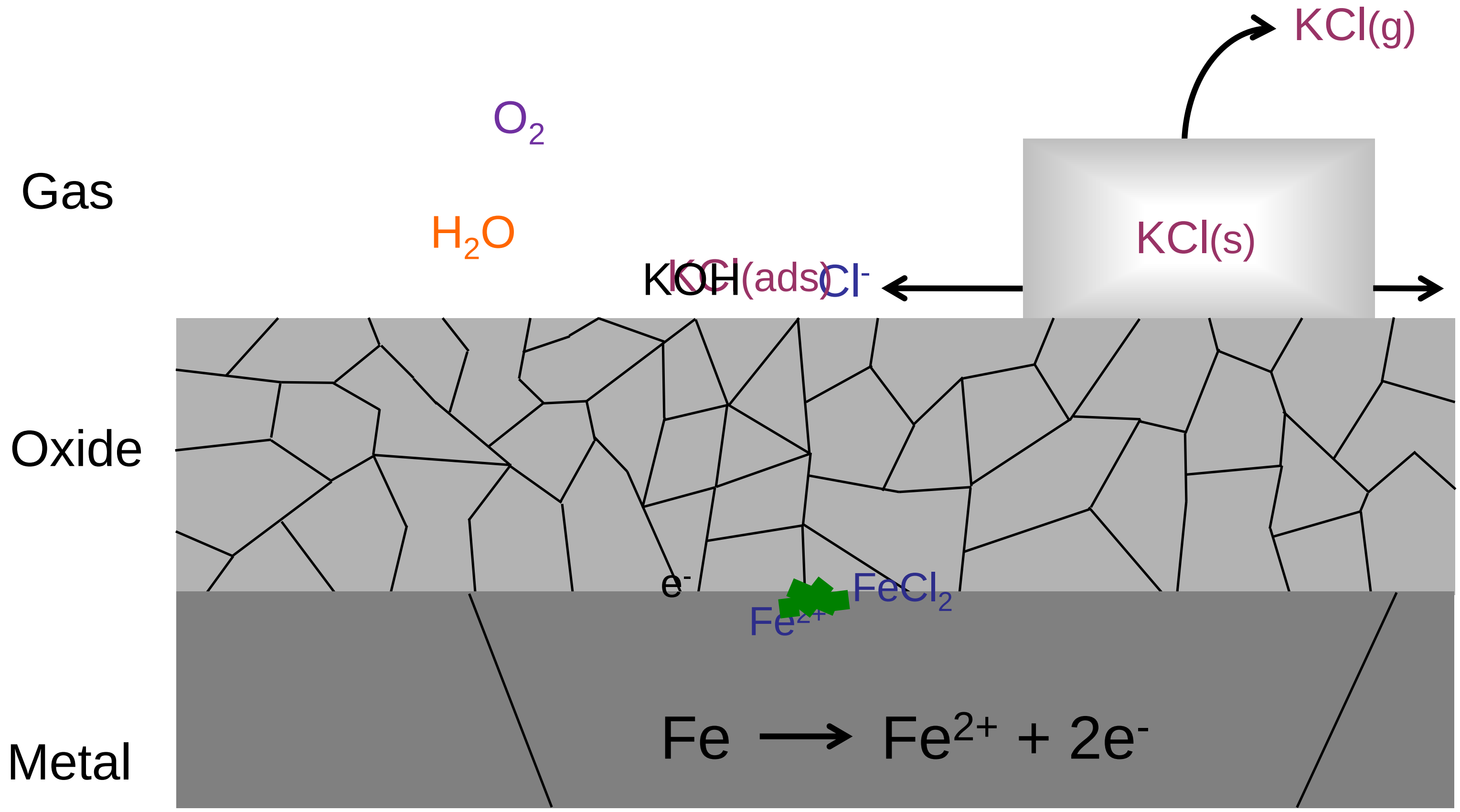
$$2MCl_2(g) + 1/2O_2(g) \rightarrow M_2O_3(s) + 2Cl_2(g)$$

Grabke, H.J., E. Reese, and M. Spiegel, *The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits.* Corrosion Science, 1995. **37**(7): p. 1023-1043.

Influence of Chlorine

Scheme of KCl-induced corrosion

$$KCl(ads) + 1/2O_2(g) + H_2O(g) + 2e^- \rightarrow 2KOH(g) + 2Cl^-(ads)$$



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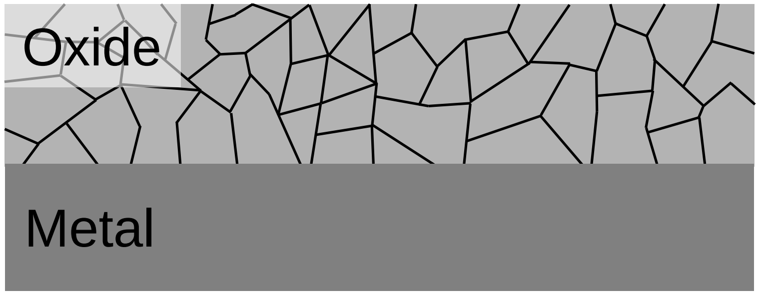
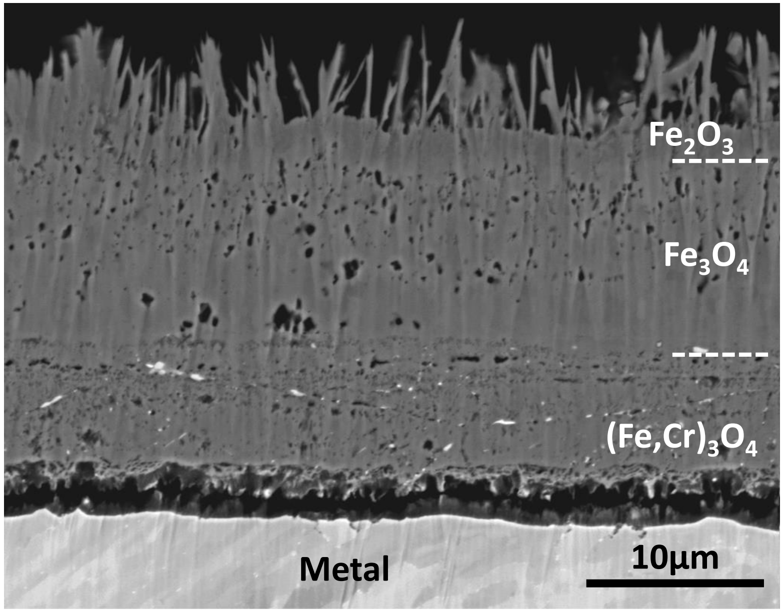
Schematic mechanism



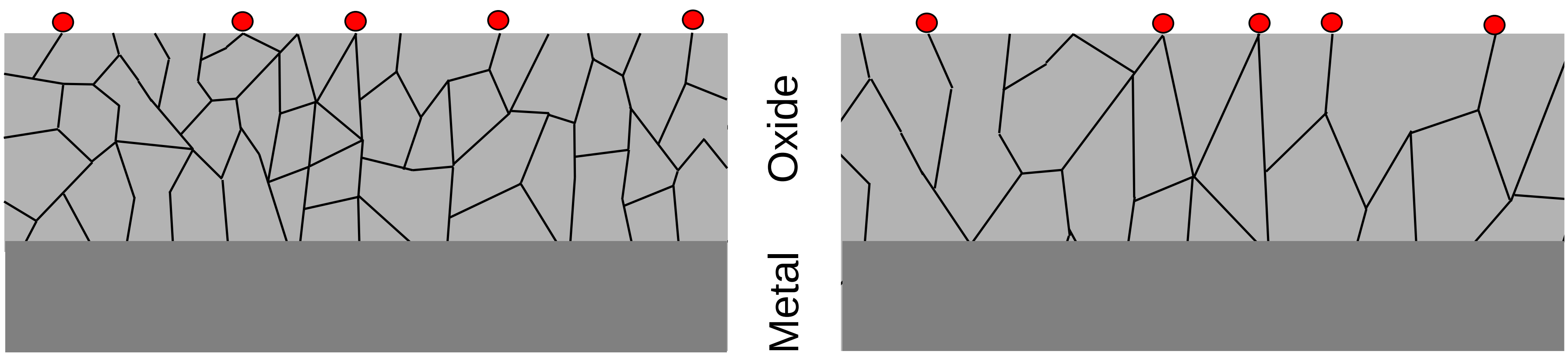
Reality



Low alloyed steel (T22) 500° C

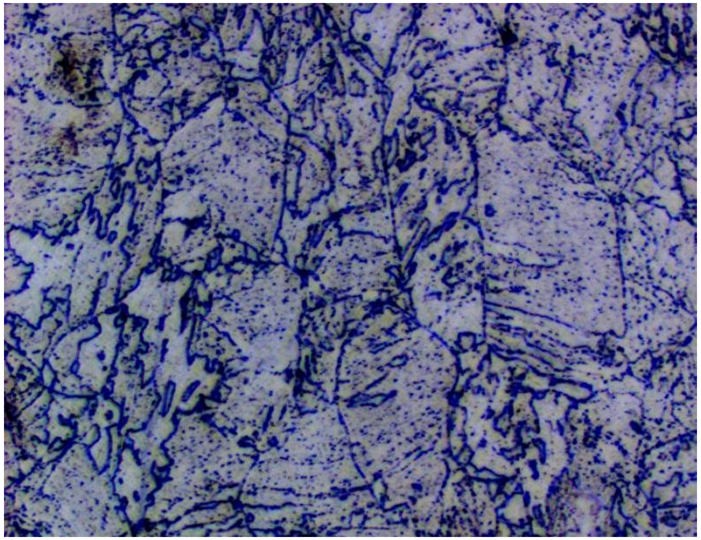
Folkeson, N., et al., *The influence of small amounts of KCl(s) on the high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 and 500 degrees C.* Materials and Corrosion-Werkstoffe Und Korrosion, 2011. **62**(7): p. 606-615.

Pre-Oxidation	
$5\%O_2+20\%H_2O+N_2$	
T1	T2



Oxides with different microstructures → Different effect of Cl?

Experimental: Starting conditions

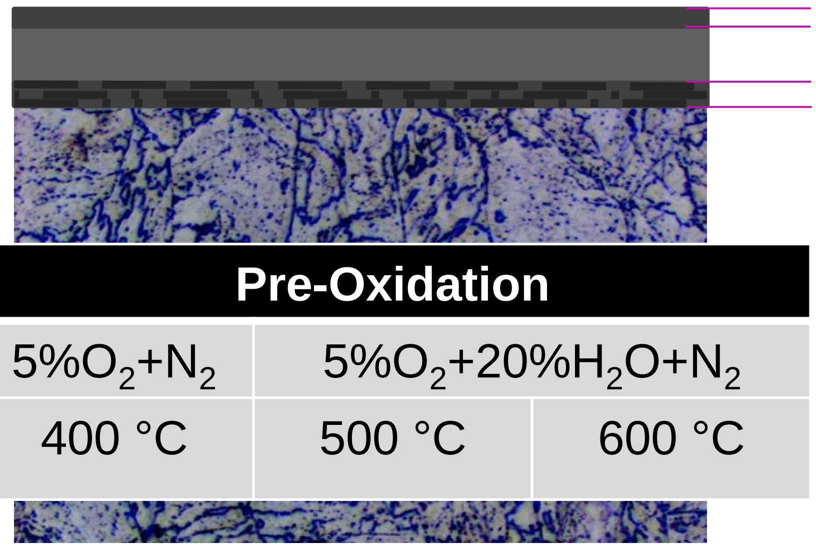


Low alloyed steel T22

Elemental composition in mass percent

Fe	Cr	Mo	Mn	Si	C	P	S
96.01	2.19	0.93	0.49	0.26	0.095	0.014	0.01

Experimental: Starting conditions



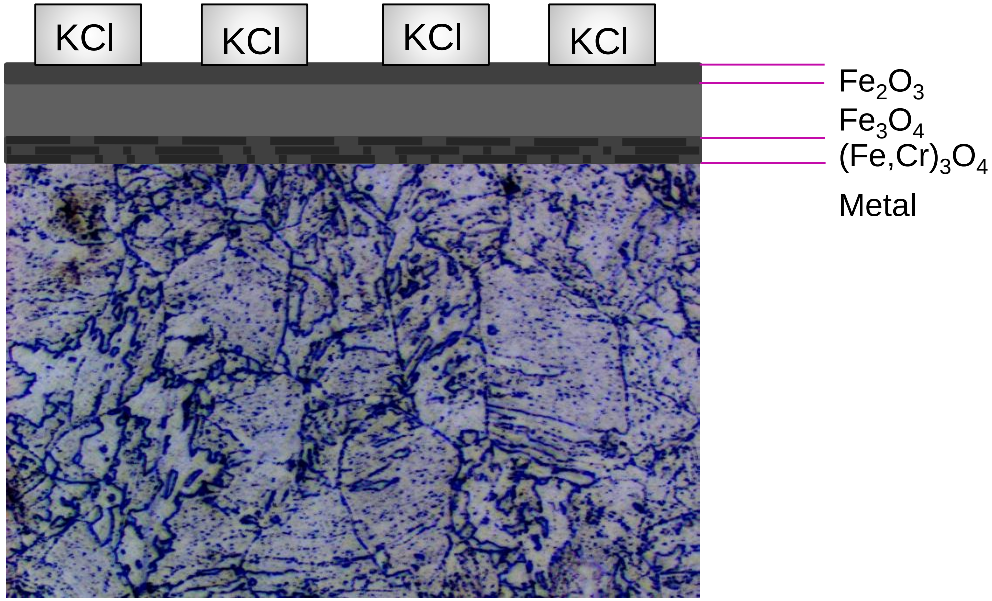
Pre-Oxidation		
$5\%O_2+N_2$	$5\%O_2+20\%H_2O+N_2$	
400 °C	500 °C	600 °C

Low alloyed steel T22
Elemental composition in mass percent

Fe	Cr	Mo	Mn	Si	C	P	S
96.01	2.19	0.93	0.49	0.26	0.095	0.014	0.01

Experimental

0,1mg/cm² KCl

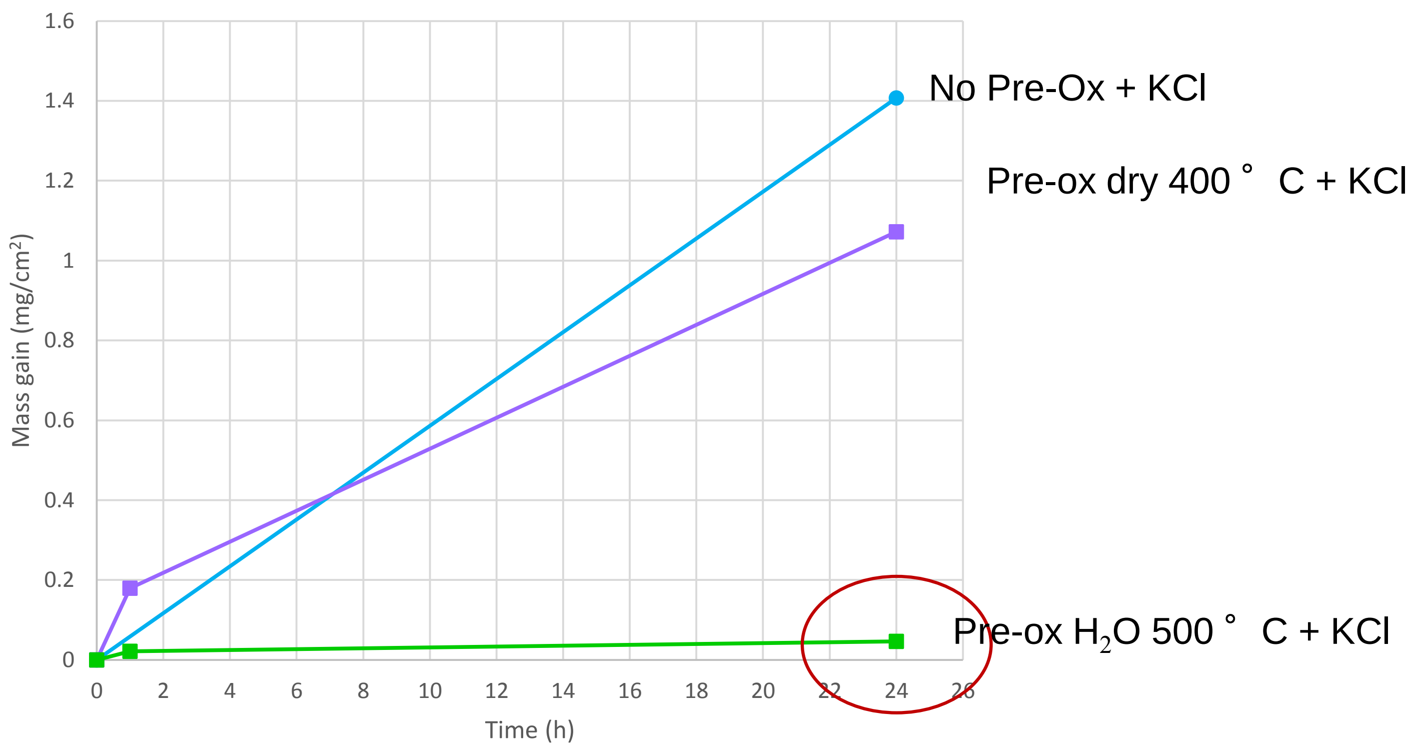


$5\%O_2+20\%H_2O+N_2$

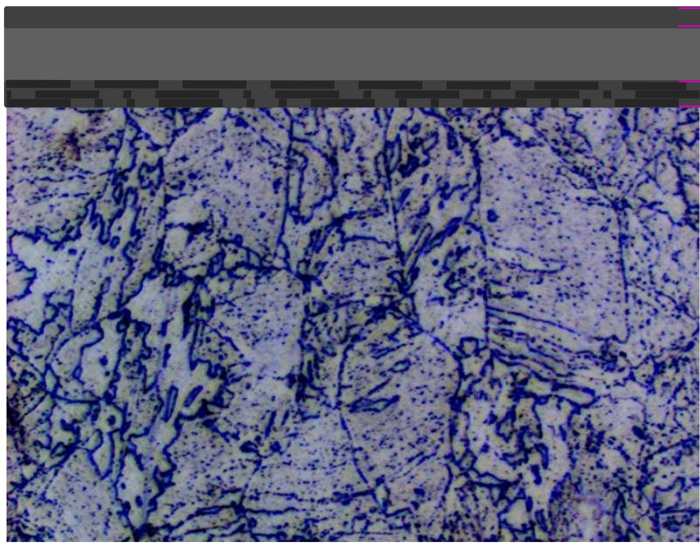
400 ° C

Pre-Oxidation	
5%O_2+N_2	5%O_2+20%H_2O+N_2
400 °C	500 °C

T22 exposed to 5%O_2+20%H_2O+N_2 0,1mg/cm^2 KCl at 400 ° C



Experimental: Starting conditions



Pre-Oxidation		
$5\%O_2+N_2$	$5\%O_2+20\%H_2O+N_2$	
400 °C	500 °C	600 °C

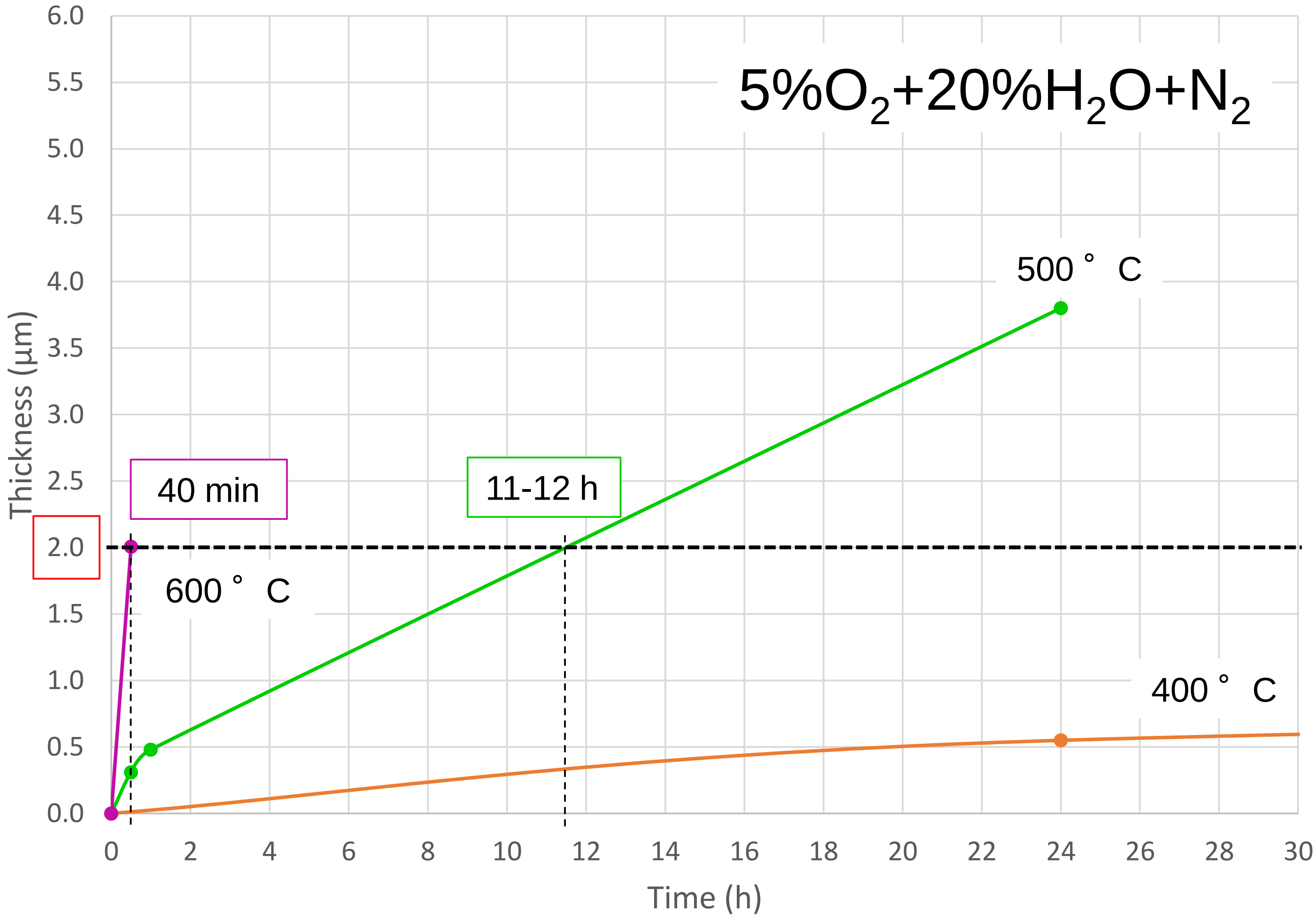
Tailor made oxides with similar thicknesses

Low alloyed steel T22
Elemental composition in mass percent

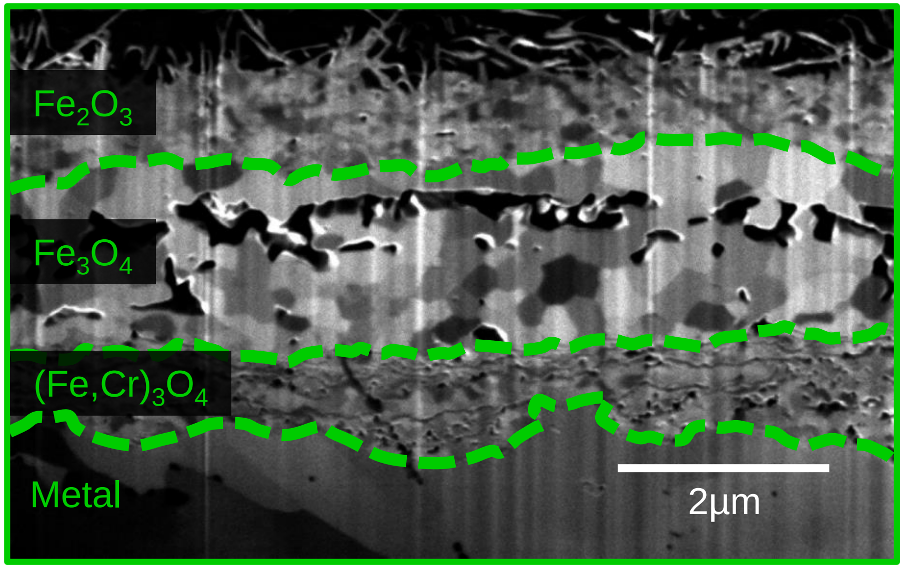
Fe	Cr	Mo	Mn	Si	C	P	S
96.01	2.19	0.93	0.49	0.26	0.095	0.014	0.01

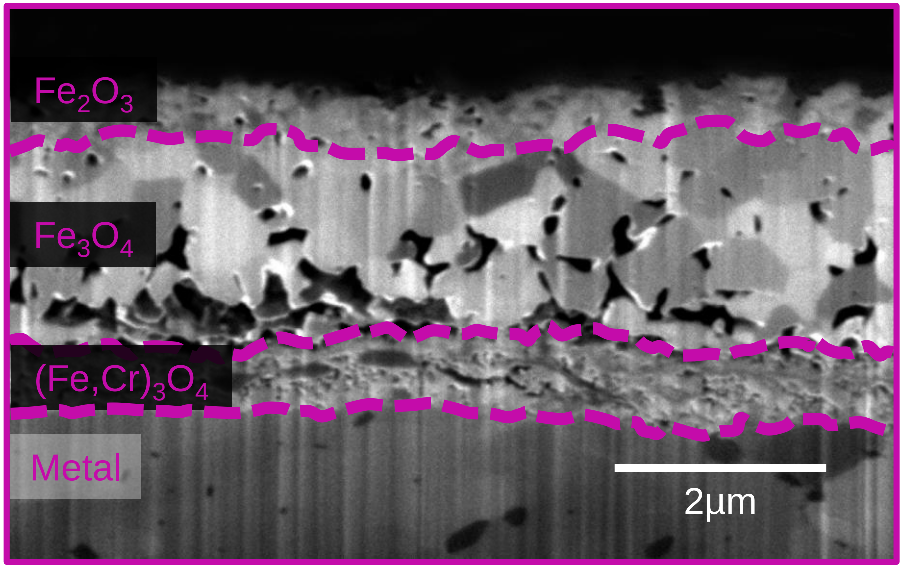
Pre-Oxidation Procedure – Tailor made oxides

Oxidation curve: Thickness vs Time



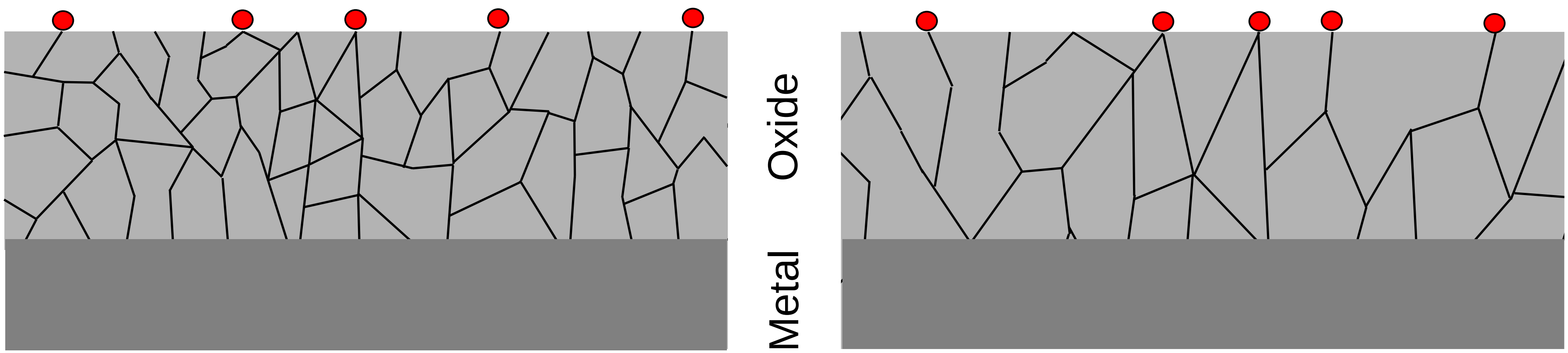
Pre-Oxidation	
$5\%O_2+20\%H_2O+N_2$	
500 °C 12 h	600 °C 40 min





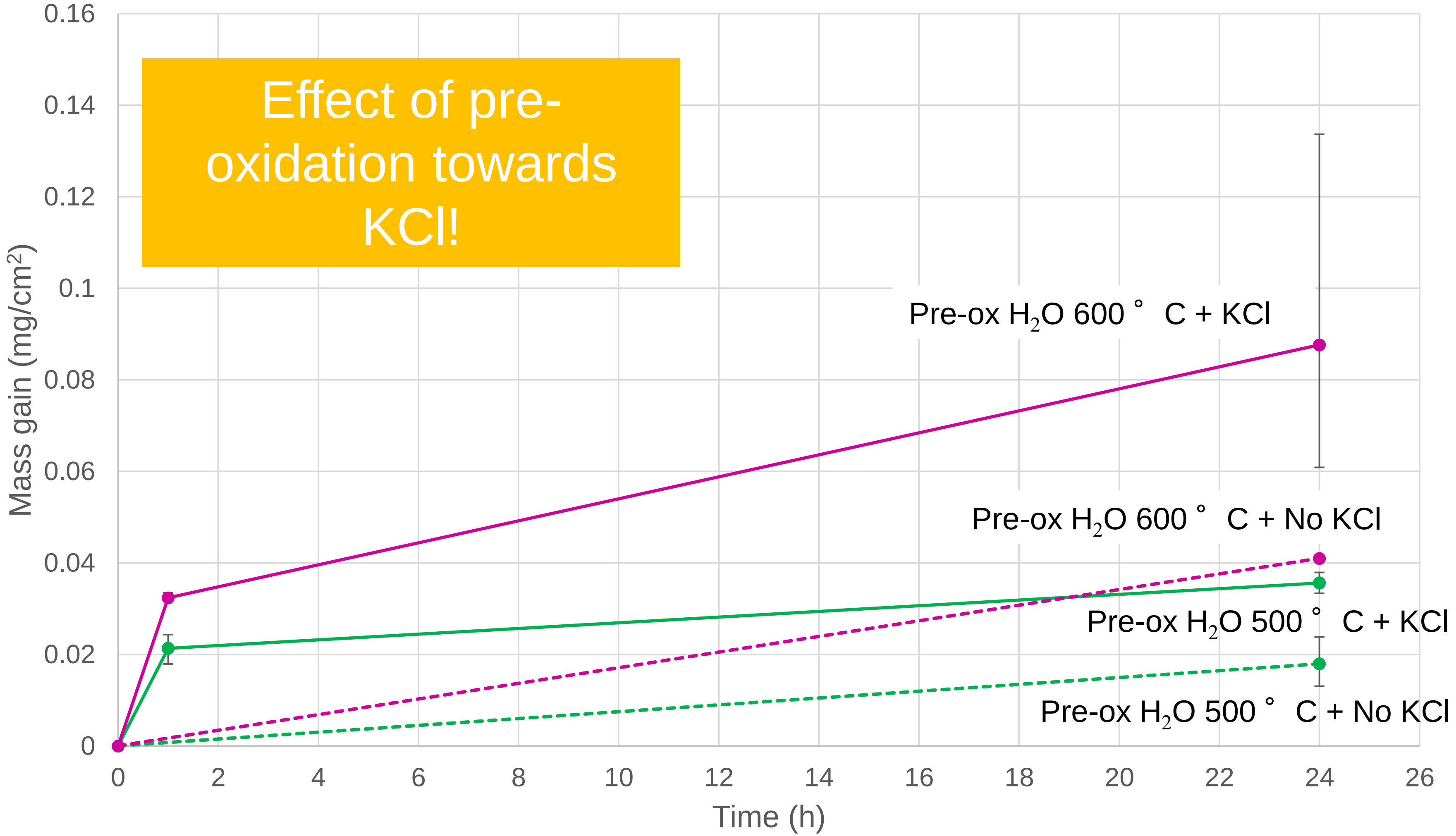
Oxides with different microstructures → Different effect of Cl?

Pre-Oxidation	
$5\%O_2+20\%H_2O+N_2$	
T1	T2

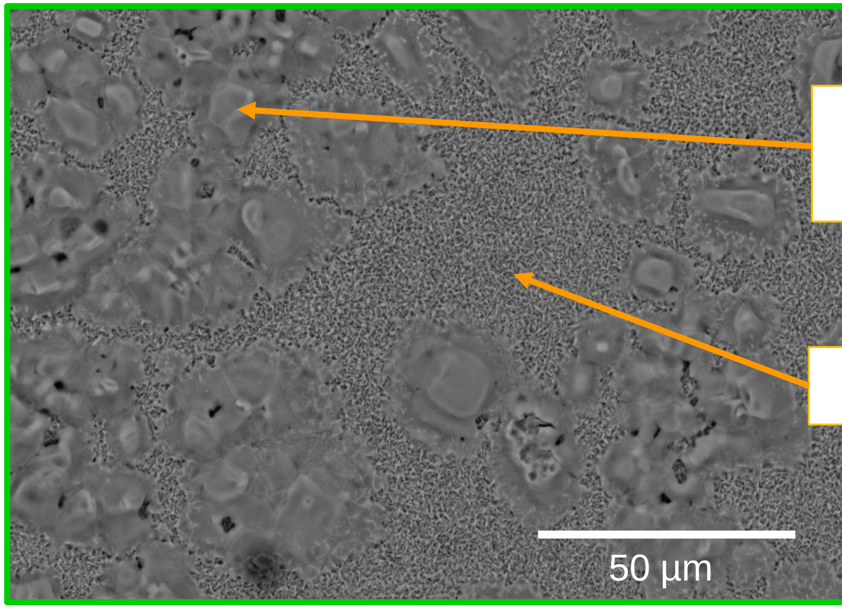


Oxides with different microstructures → Different effect of Cl?

KCl exposure of Pre-Oxidized T22 at 400 ° C

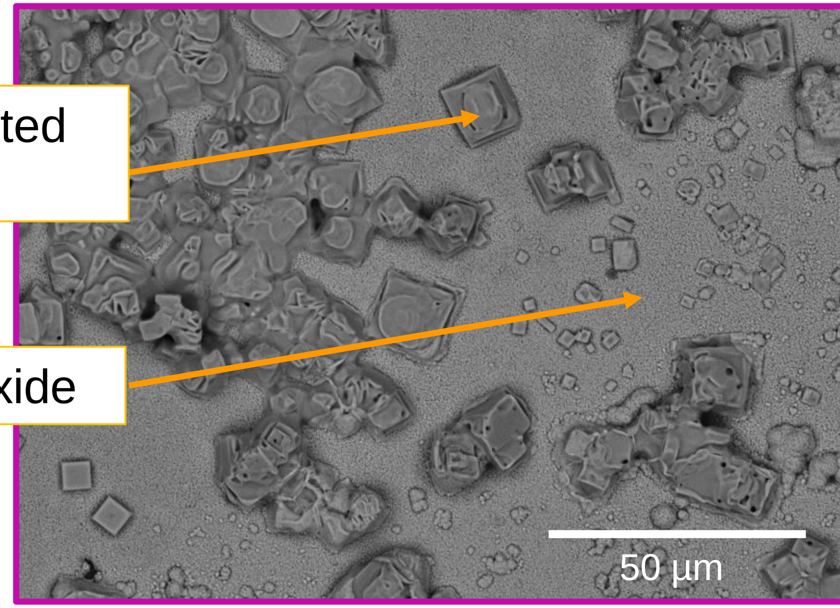


KCl exposure



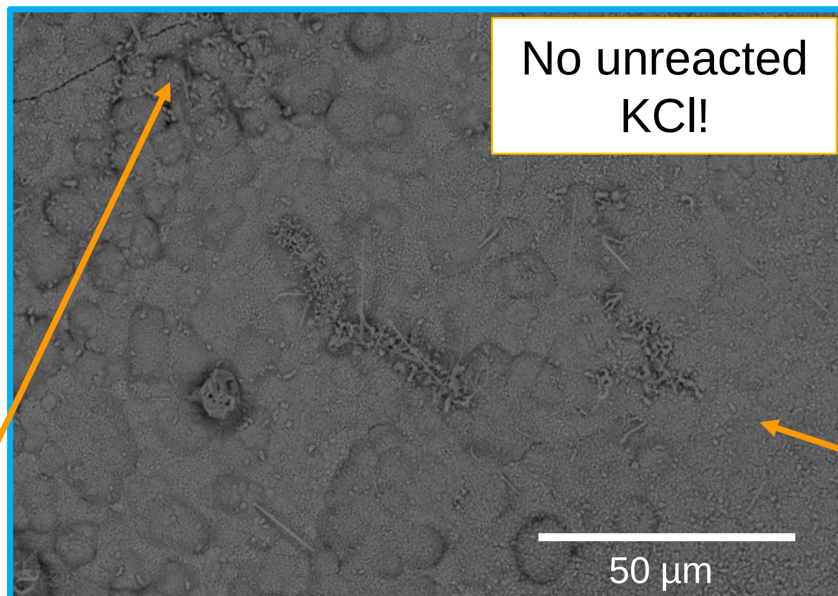
Unreacted KCl

Base Oxide



Pre-Oxidation
500 ° C

Pre-Oxidation
600 ° C



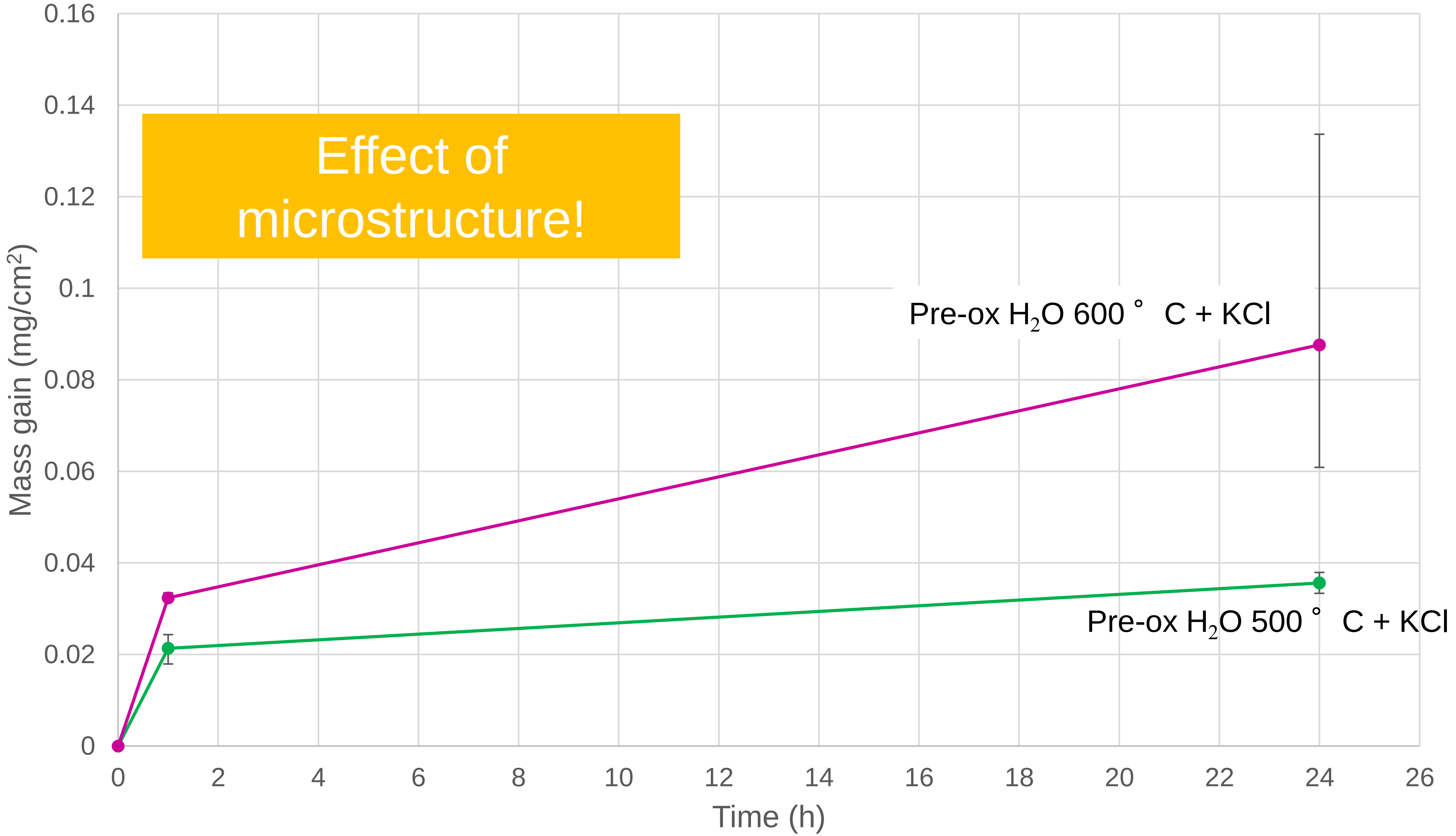
No unreacted KCl!

No Pre-Oxidation

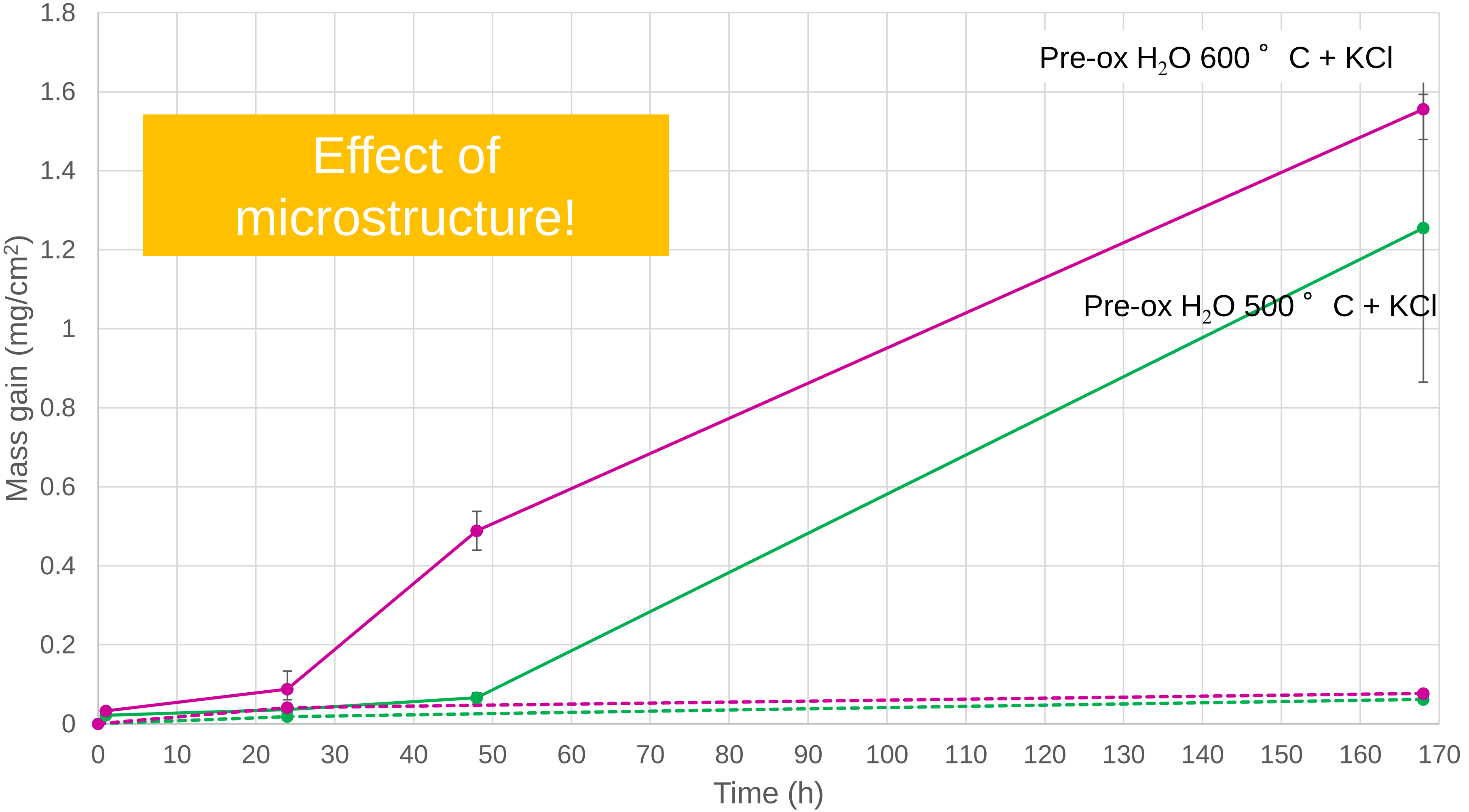
Rough Oxide

Smooth Oxide

KCl exposure of Pre-Oxidized T22 at 400 ° C



KCl exposure of Pre-Oxidized T22 at 400 ° C



Conclusions and Future Work

→ The presence of KCl accelerate the corrosion rate on already oxidized samples.

→ There is an effect of oxide microstructure on the propagation of corrosion attack.

→ Longer exposure times and higher temperatures are of great interest.

→ Exposures in presence of HCl.

→ More detailed microstructural study will be performed (TEM with EDS, EELS analysis).

Thank you for your attention

AVANCEZ

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