Institute of Combustion and Power Plant Technology

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Germany

ifk

Workshop on

Advanced USC coal-fired power plants

Vienna, Austria

Sept. 19 – 20th, 2012

Fireside Corrosion of Dedicated Austenitic Steels in Ultra-Supercritical Coal-Fired Power Plants

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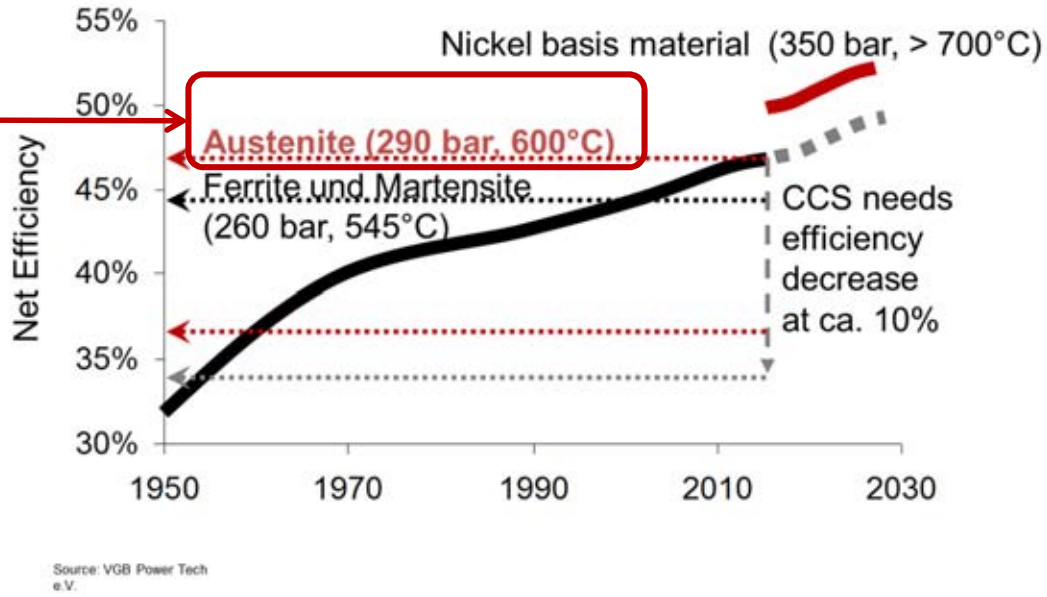
Motivation

(advanced) USC-PP*

*Ultra-Super-Critical Power Plant



Net efficiency considering different structural alloys due to courtesy of VGB powerTech e.V.

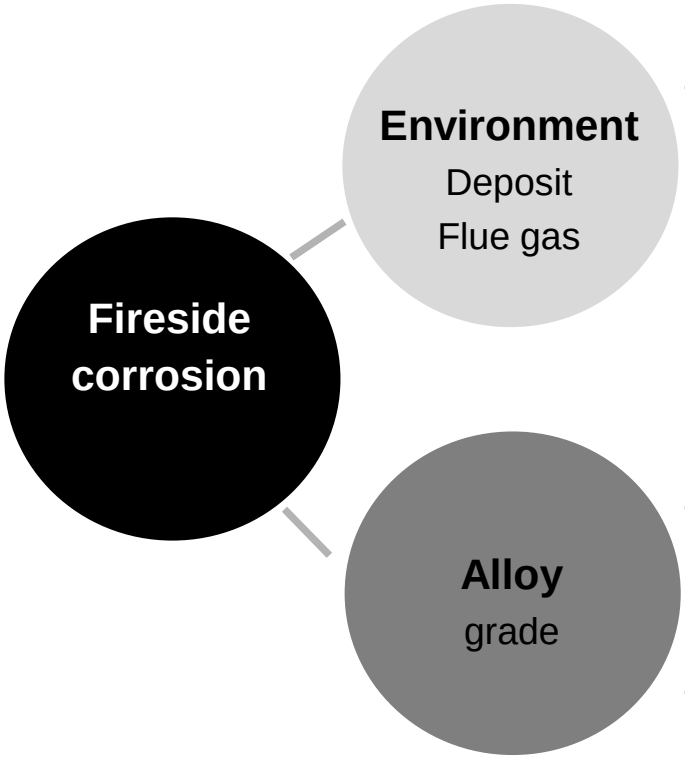
- Aimed higher total net efficiency of coal fired power plants
- Higher steam parameters
- New purposes of known materials

Corrosive behavior of modern super- and re-heater alloys?

Background > corrosion

corrosion

• "…irreversible interfacial reaction of a **material** with its **environment** (…) results, often but **not necessarily**, in detrimental effects to the usage of the material…" Dedinition of IUPAC

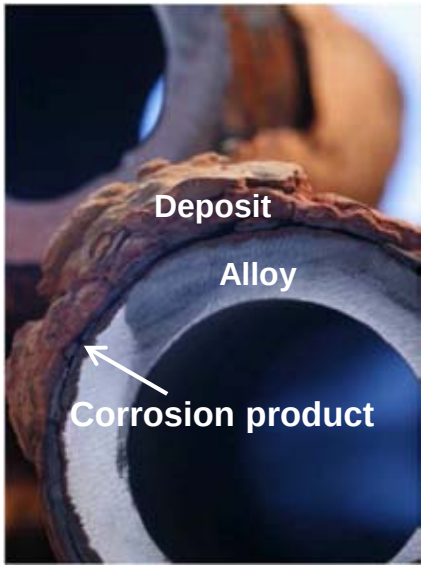


• Fuel:
→ Composition, Preparation

• Operation conditions
→ Firing system, Temperature, Residence time
→ Operation modus: continuous, cyclic
→ Cleaning systems, e.g. soot blowers

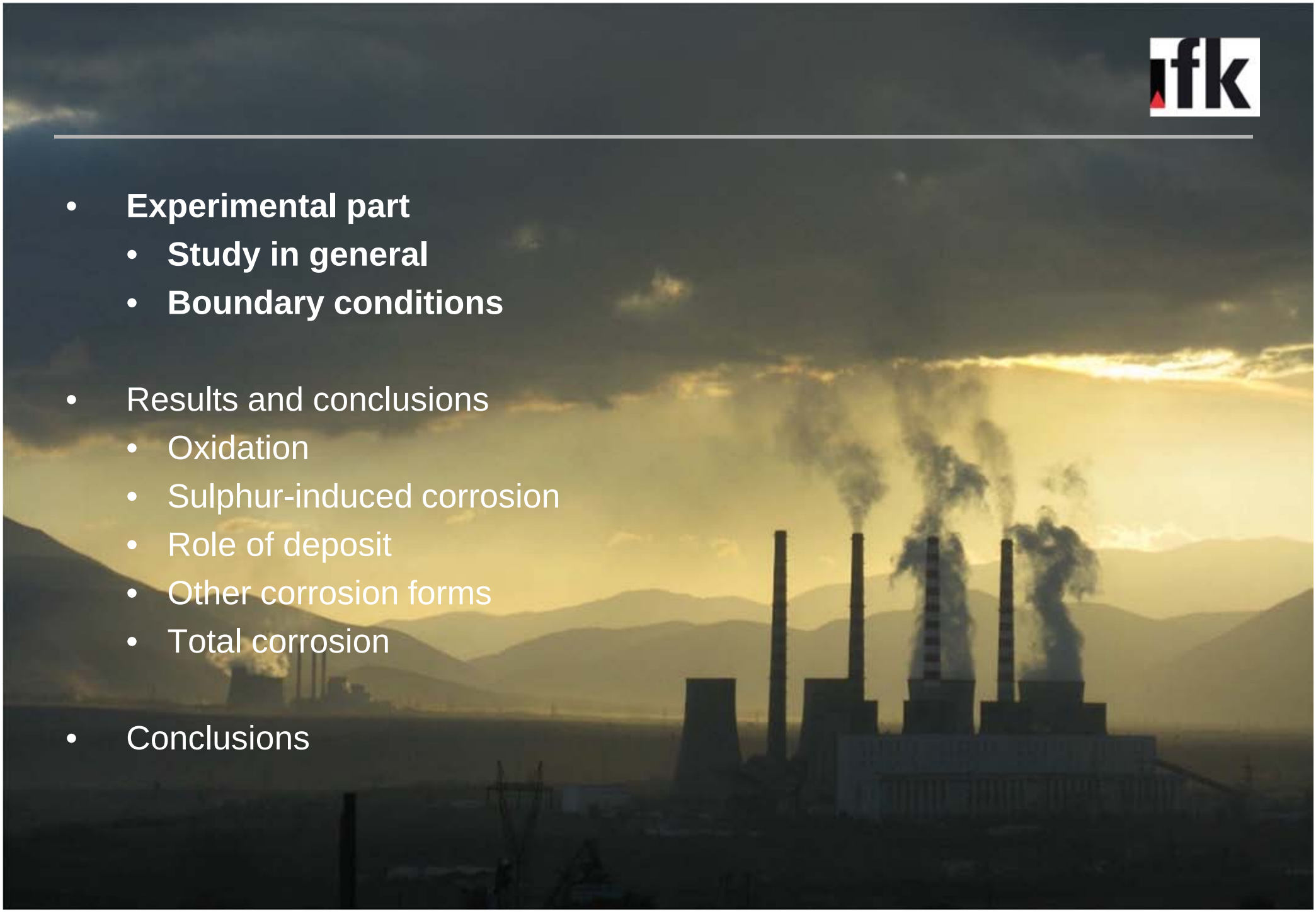
• Composition and preparation
→Cr, Fe, Ni, etc.

• Quality
→ Surface, Alloy homogeneity, etc.



Content

- Experimental part
  - Study in general
  - Boundary conditions
- Results and conclusions
  - Oxidation
  - Sulphur-induced corrosion
  - Role of deposit
  - Other corrosion forms
  - Total corrosion
- Conclusions



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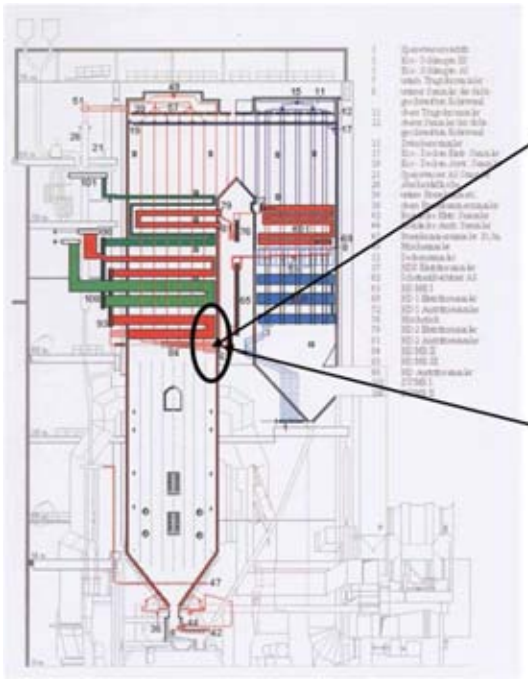
Experimental > Study in general

COORETEC – Corrosion, fouling and slagging in supercritical power plants with the new state-of-the-art materials

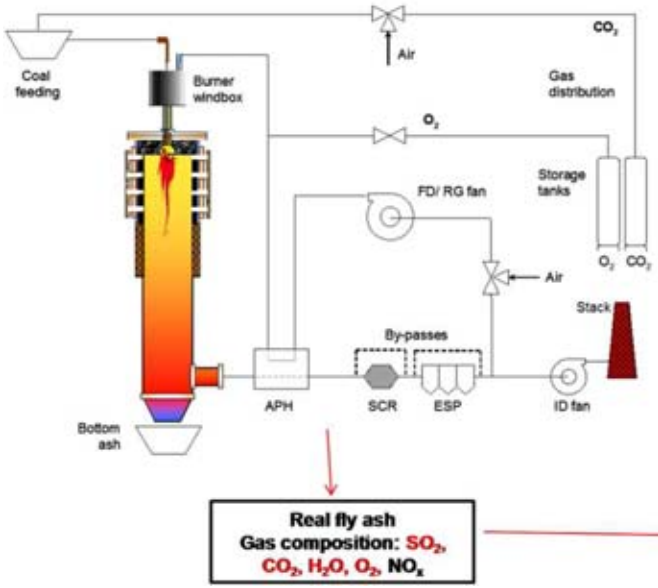
Tests up to > 600 h
3 power plants:
1 lignite, 2 bitumin. coal fired



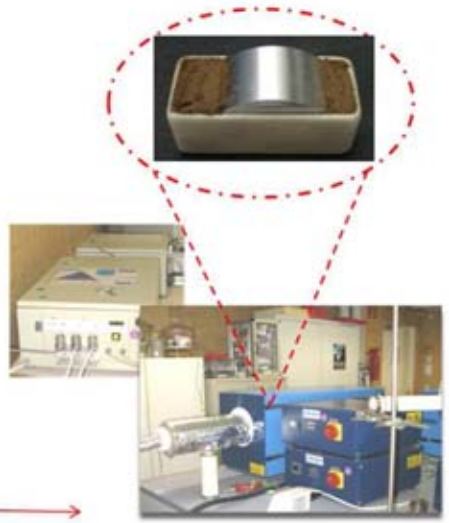
Probe 1 (650°C)
Austenitic materials
SH / RH materials
- I-18
- I-22
- I-25

Probe 2 (750°C)
Nickel-base superalloys
SH / RH materials
- N-20
- N-22
- N-25

Short-term tests
up to 100 h



Long-term tests
Up to 1000 h



This work and the specific COORETEC project is funded and supported by the **German Federal Ministry of Economics and Technology (BMWi)**, **EnBW Kraftwerke AG, E.ON Energie AG, RWE Power AG, Vattenfall Europe Generation AG, Steag GmbH, ALSTOM Boiler Deutschland GmbH, Hitachi Power Europe GmbH, ThyssenKrupp VDM GmbH, Salzgitter Mannesmann Stainless Tubes GmbH, Sandvik Materials Technology Deutschland GmbH, V & M DEUTSCHLAND GmbH** and **Allianz Risk Consulting GmbH** under **grant number 0327744A**.

Experimental > Boundary conditions > Alloys

Alloy	Unit	Cr	Ni	Fe	Other
I-18	**%-m.**	**18,3**	9,0	68,1	C, Si, Mn, P, S, Cu, Al, B, N, Nb
I-22	**%-m.**	**22,5**	25,1	43,0	C, Si, Mn, P, S, Co, Cu, Al, N, W, Nb
I-25	**%-m.**	**24,6**	21,2	51,9	C, Si, Mn, P, S, N, Nb

Experimental > Boundary conditions > Samples preparation

Tube material

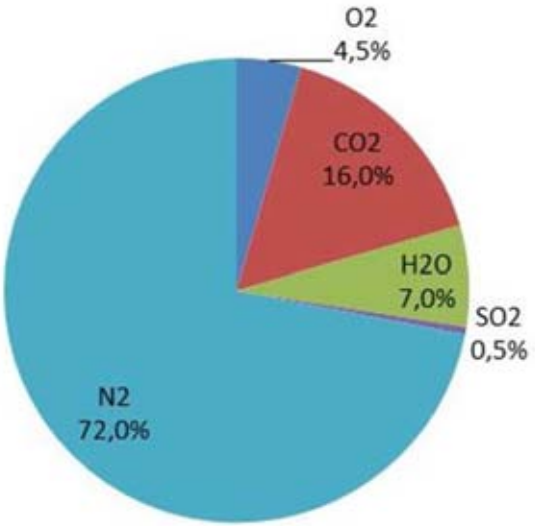
Ceramic cups

Deposit

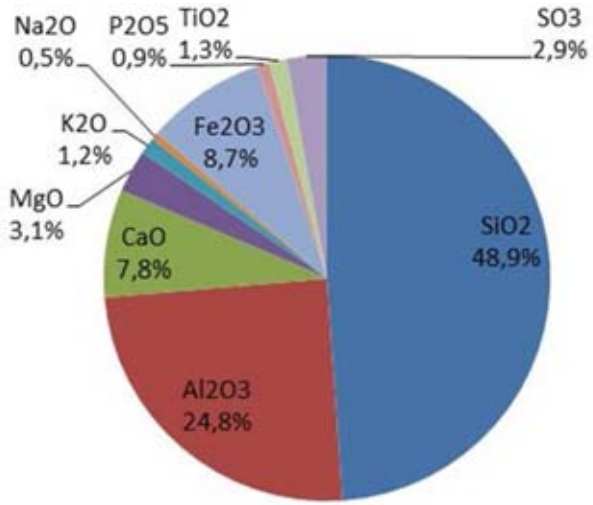
Sample

Time steps h:
24
350
1000

Gas composition
%-vol.



Deposit composition
%-wt.



650°C

Experimental > Boundary conditions > Exposures in power plants with IFK‘s corrosion probe

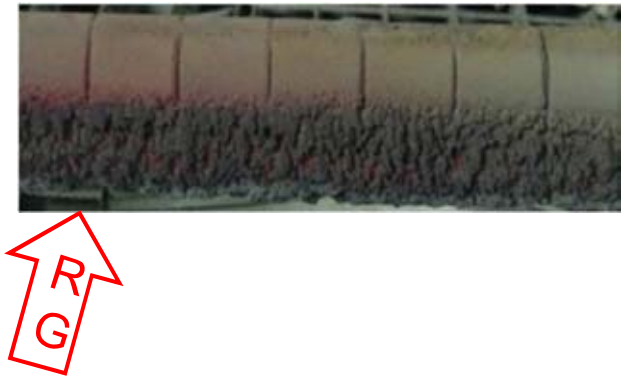
Lignite power plant

PP-JW

PP-JW, SO_2 up to 2400 ppm

SH 40m
Probe 1:
Alloy I-25
Alloy I-22
Alloy N-22
Alloy I-25
Alloy I-22
80 h

SH 40 m
Probe 1:
Alloy I-22
Alloy I-25
Alloy I-18
Alloy N-25
Alloy N-22
Alloy N-20
602 h



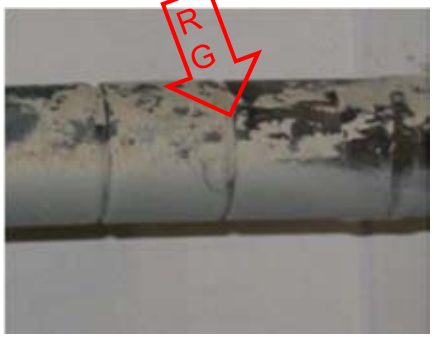
T_G ca. 1050°C

Hard coal power plants

PP-SV and PP-AB

PP-SV, SO_2 ~ 500 ppm

SH 73 m
Probe 1:
Alloy I-25
Alloy I-22
Alloy N-22
Alloy I-22
Alloy I-25
193 h



T_G ca. 1015°C

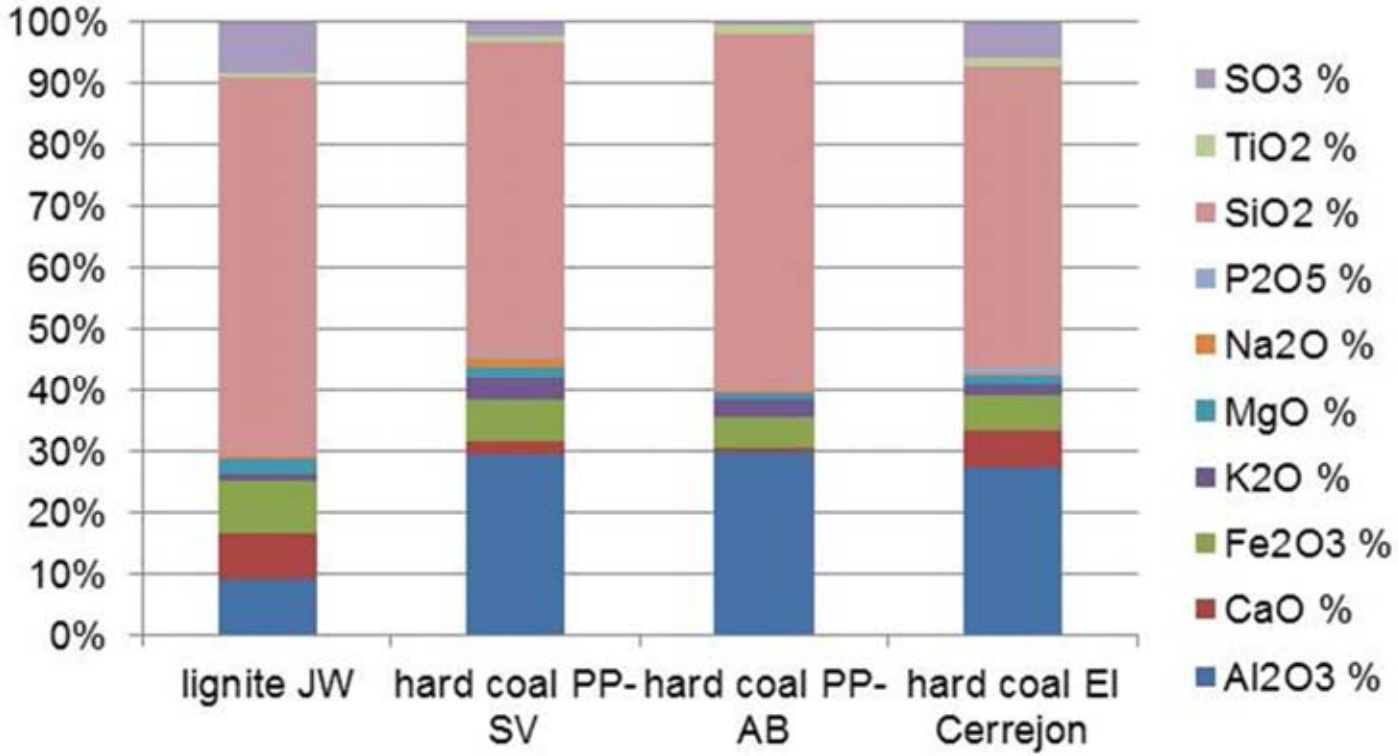
PP-AB, SO_2 ~ 600 ppm

SH 34m
Probe 2:
Alloy I-22
Alloy I-25
Alloy I-18
Alloy N-25
Alloy N-22
Alloy N-20
231 h

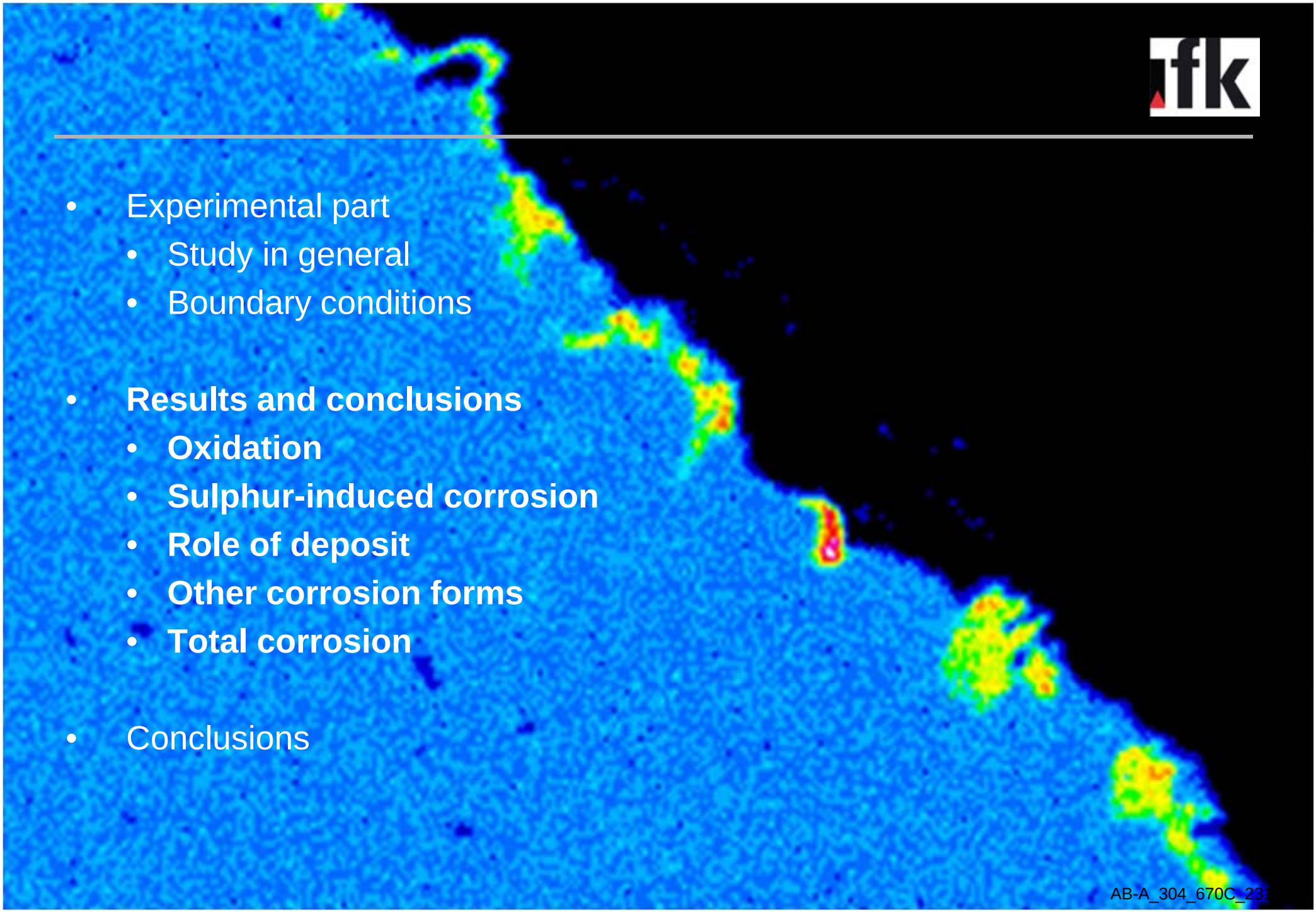
T_G ca. 1070°C

Experimental > Boundary conditions > Coals

S_{waf}	2,05	0,85	1,14	0,87 [%-wt]



- Mostly alumino-silicatic coals
- Little content of basic oxides → sulphur retention



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Results > Laboratory exposures > Corrosion progress

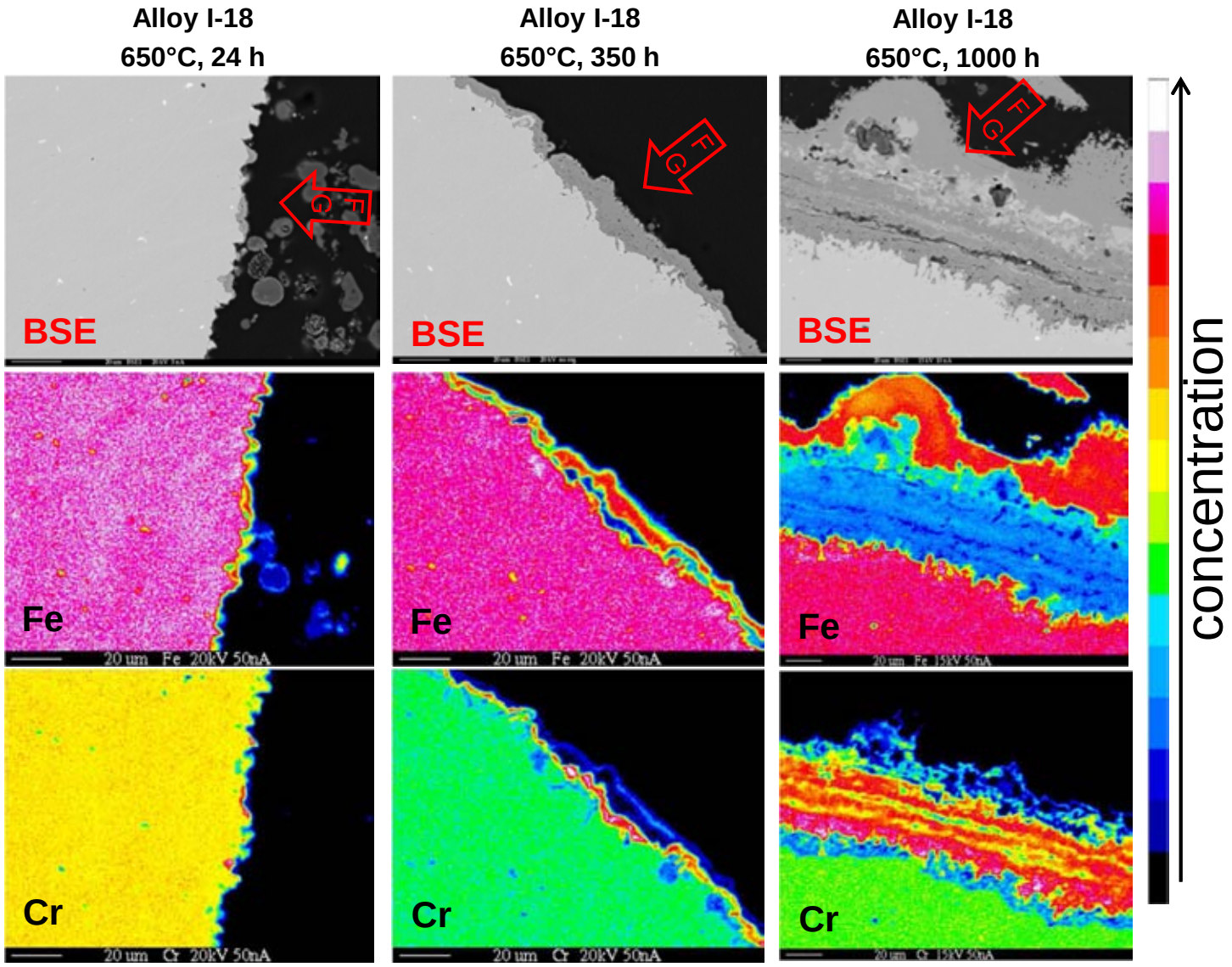
Development of oxide scale

•dependant on Cr-content

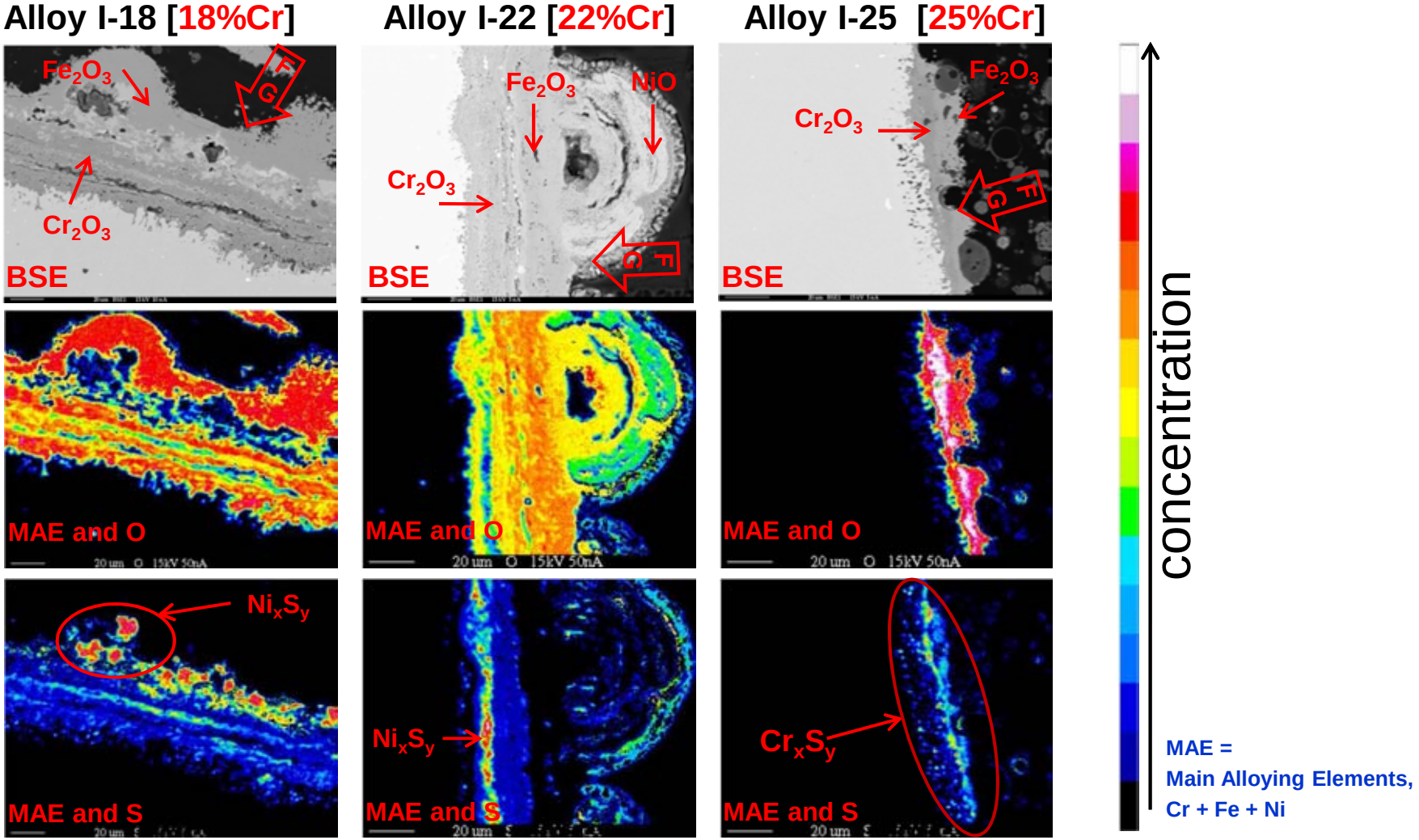
•not always continuous especially within first 350 h
•more homogene under absence of deposit

•double oxide layer:
→ outer: Fe-rich
→ inner: Cr-rich

After 1000 h sulphides in the oxide scale (here: Ni-S, Cu-S)



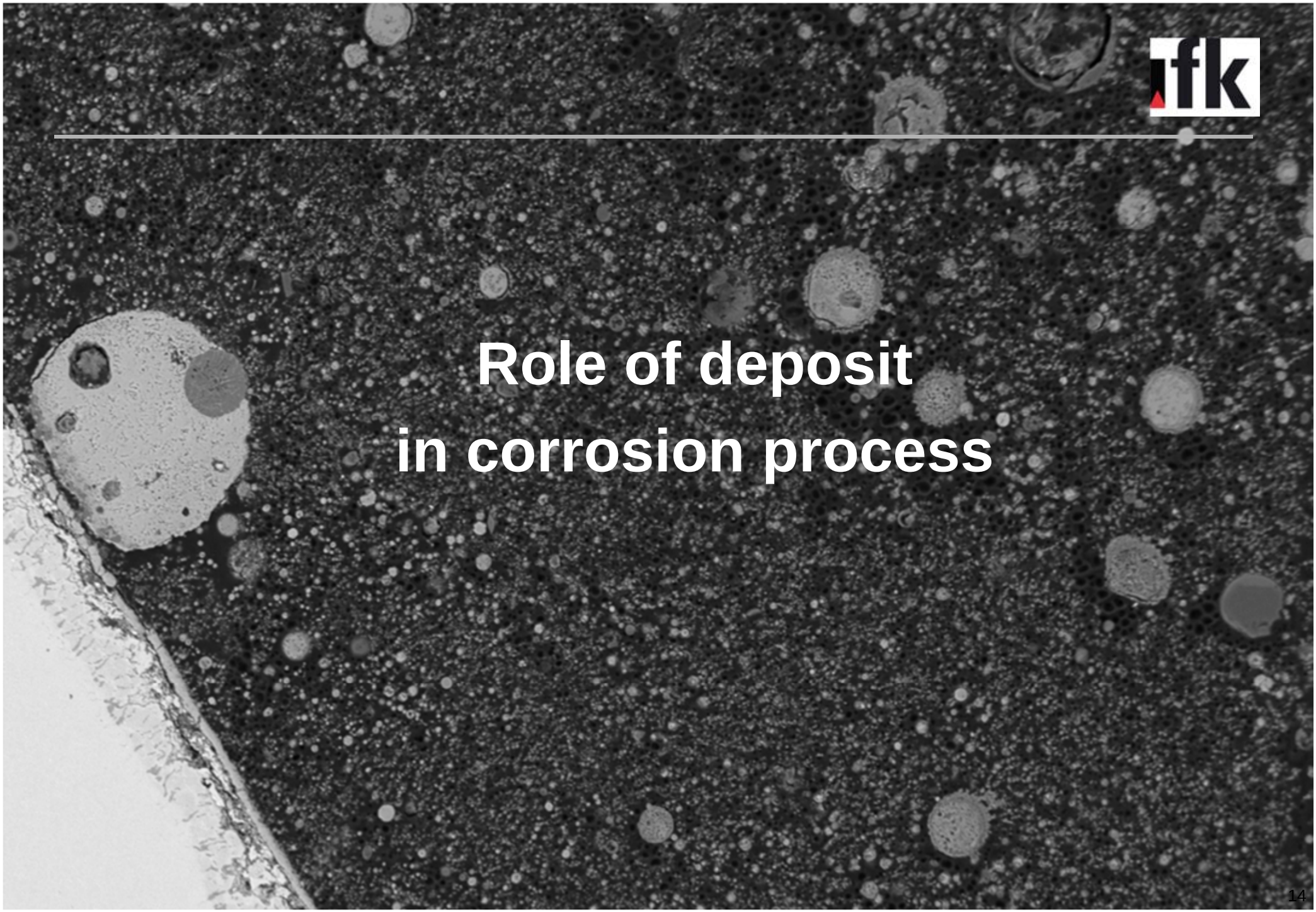
Results > Laboratory exposures > Sulphur induced corrosion



Sulphides present after 1000 h at all samples

however in different „positions“ and of different elements

With increasing Cr-content better performance of the alloy



Role of deposit in corrosion process

Results > Sulphur and sulphur induced corrosion

•Sulphur detected in deposits of all power plants

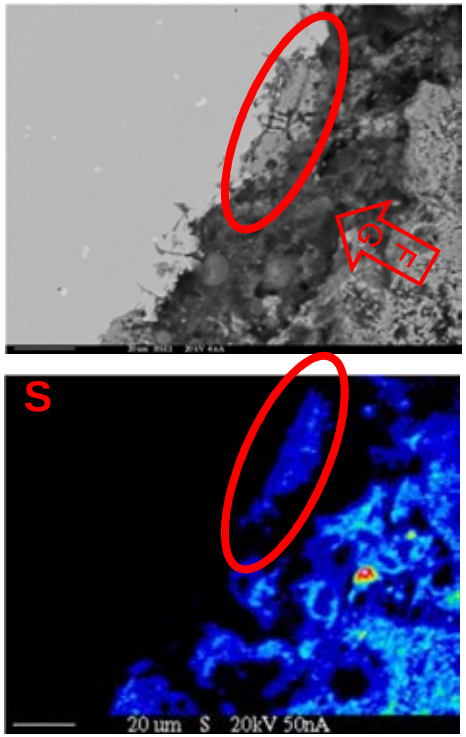
•Corrosion attack different in character

Spread

In lignite fired power plant

SO_2-rich atmosphere (> 2000 ppm)

Deposit dominated strongly by Fe_2O_3

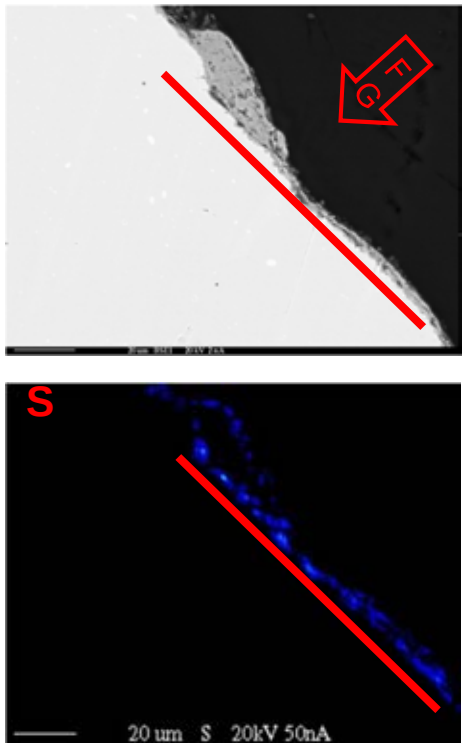


PP-SV Alloy I-25 600ºC 602h an.5

Spread locally

where very little deposit

In PP-SV SO_2-lean atmosphere (ca. 500 ppm)

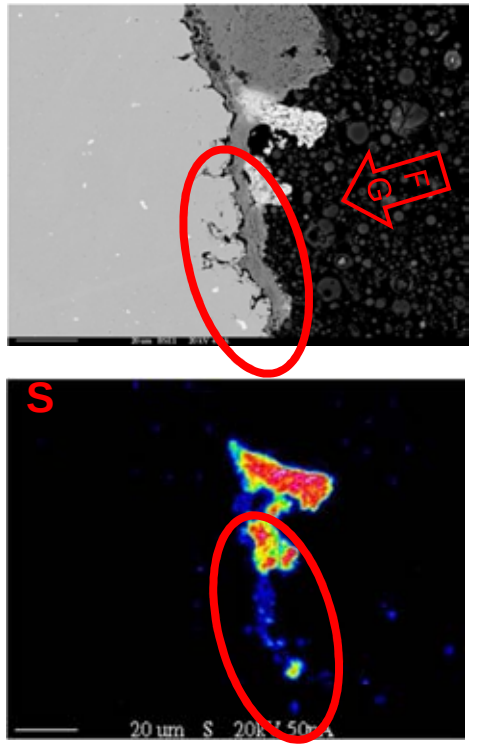


PP-SH Alloy I-22 600ºC 193h an.2

Local

Attack through single S-rich partly molten unstable particles

SO_2-lean atmosphere (ca. 600 ppm)

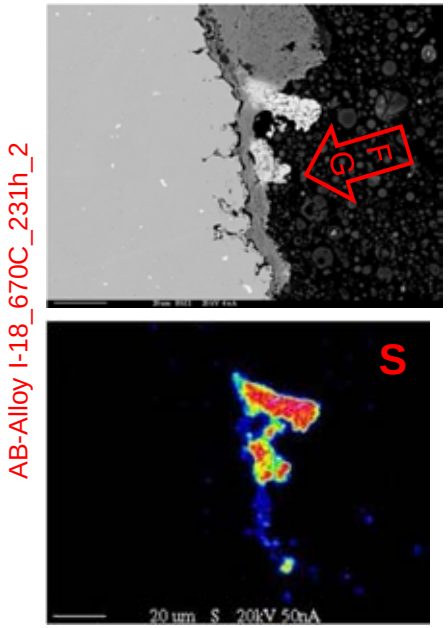


PP-AB Alloy I-18 670ºC 231h an.2

Results > role of fly ash in sulphur induced corrosion > PP-AB

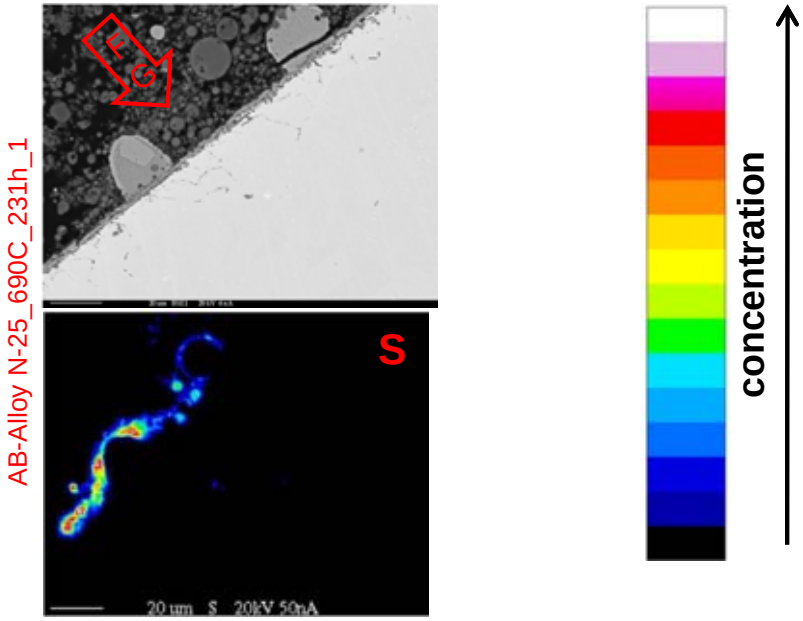
CORROSION! ☹

Direct contact between S-rich unstable particle and oxide scale



NO CORROSION! ☺

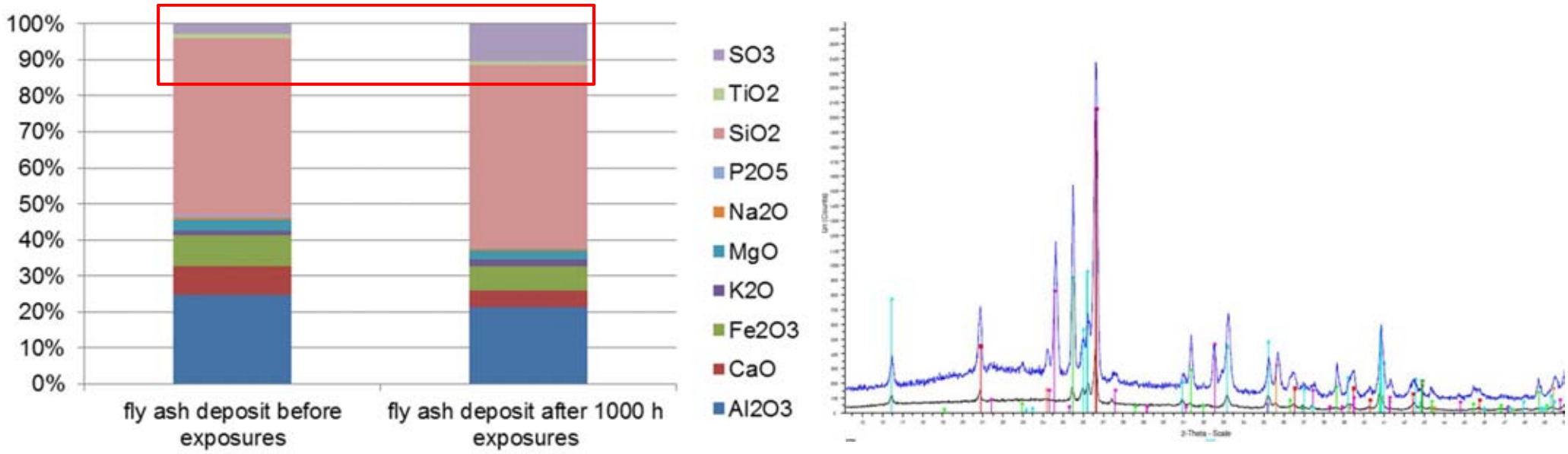
Particles acting as „S-sink“



low SO_2 ~ 590 ppm, $S_{coal,\ waf}$ = 1,14 %

sulphur induced corrosion **only locally**

Results > Deposit > Lab study

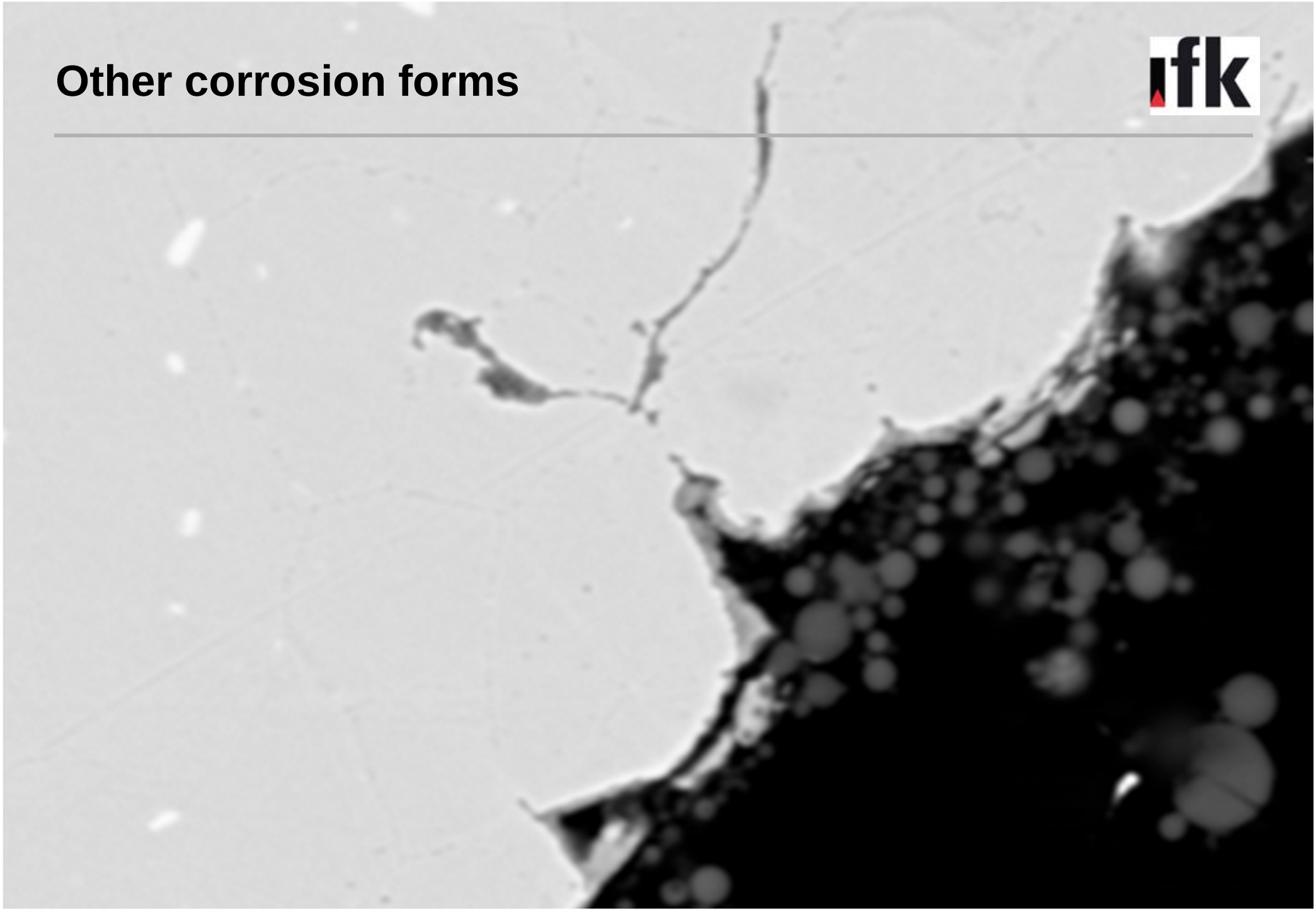


Deposit adsorbs sulphur

- higher anhydrite content
- after exposures: calcium magnesium sulphate

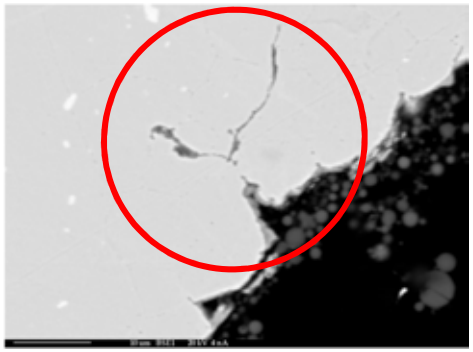
After fly ash saturated, no protective barrier against gaseous sulphurous species

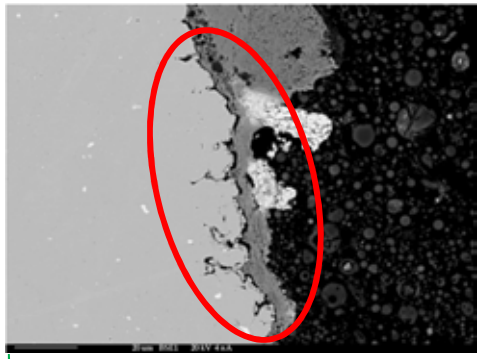
Other corrosion forms

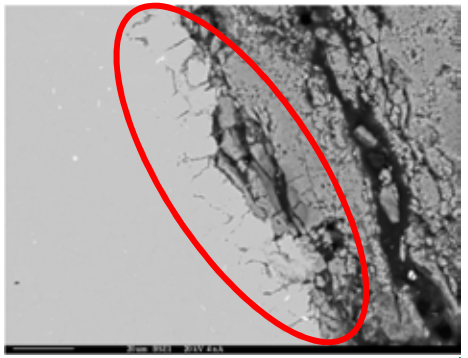


Results > intergranular and internal oxidation

The same exposure conditions







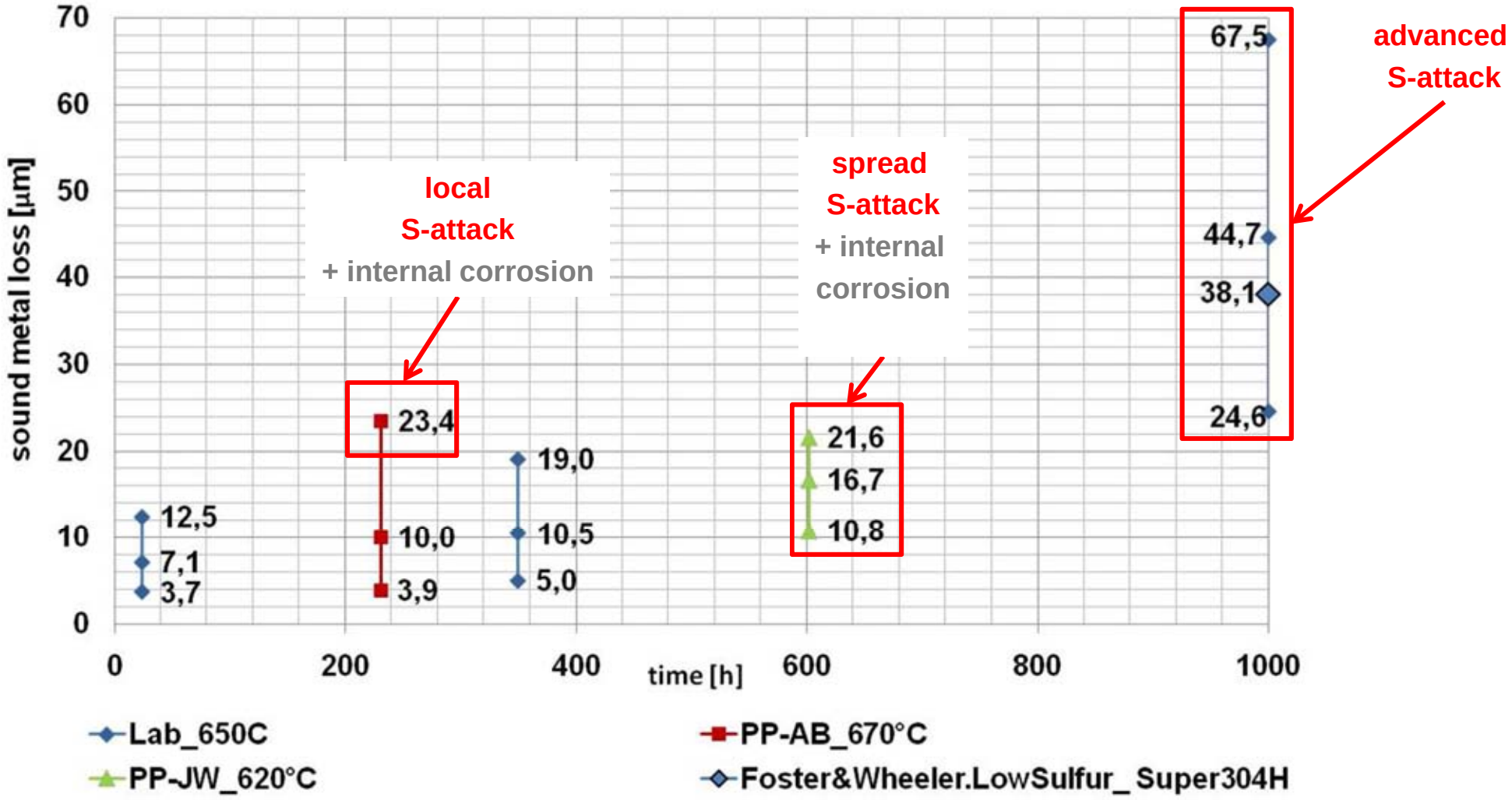
The same alloy

PP-AB-alloy I-25	PP-AB-alloy I-18	PP-AB-alloy I-18
650ºC	670ºC	620ºC
231h	231h	602h
Image 6	Image 2	Image 2

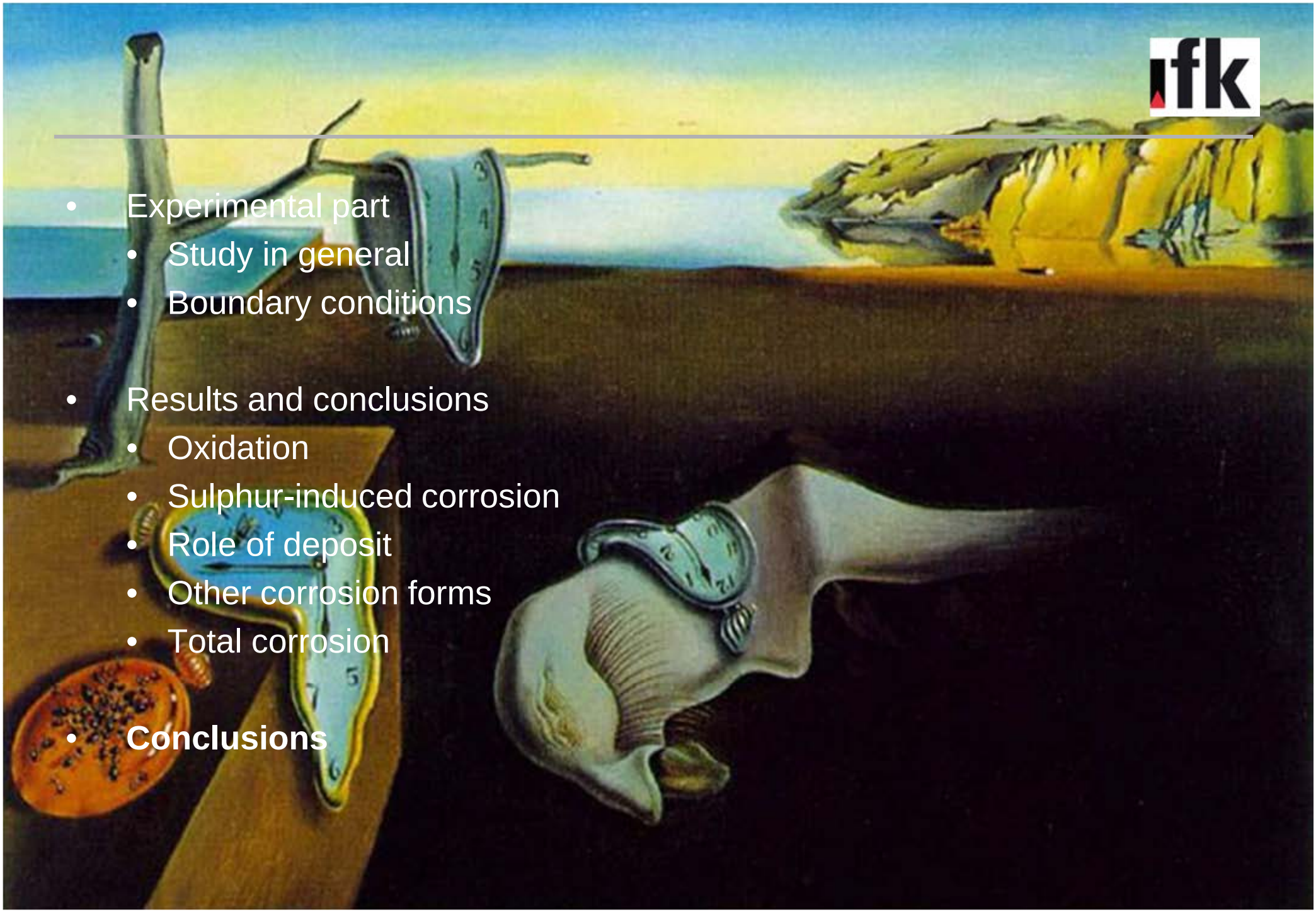
Intergranular and internal oxidation:

- Noticed in power plants
- Not witnessed in laboratory exposures
- Gas temperatures in all power plants similar

Results > Alloy I-18 (18% Cr)



The data was compared vs. data found in the literature and presented by Foster&Wheeler on a similar alloy; Very good agreement observed.



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Conclusions

Conc. oxidation

- With **increasing chromium content**:
  - better development of **protective oxide scale** up to 350 h
  - **smaller corrosion product** at up to 1000 h

  - **best performance of alloy I-25 (25 % Cr)**, confirms [Stanko and Hack]

- **Up to 350 h** partly only **oxide-rich isles** at the alloys surface

- **In power plants:** locally a uniform well developed oxide scale; often only oxide isles and partly oxidized intergranular corrosion pits

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- **Double oxide** scale:
  - outer: iron rich
  - inner: chromium rich

Conclusions

Conc. sulphur-induced corrosion

- Corrosion strongly influenced by sulphur at samples **exposed at 1000 h**;
  → **deposits saturated** with sulphur (anhydrite ↑, calcium-magnesium sulphate) and **after 350 h** stop acting as „S-sink“

- **Sulphides** noticed in laboratory tests in all three materials after 1000 h, however varying in character (copper-, nickel-, chromium-sulphides)

- **Sulphur** in contact with oxide scale noticed in all power plants samples, however **varying in character** and depending on the exposure conditions

Overall corrosion

- Results from exposures in power plants **fit well** data from laboratory exposures, however partly **different corosion morphologies and forms** noticed in the laboratory and in power plants

- Alloy I-18 and I-25 witness some **intergranular oxidation**, however noticed only in power plants (two plausible reasons: temperature difference btw. both sides of the tube‘s wall: atmosphere vs. cooling medium AND/OR surface stresses caused by the pipes geometry)
  → **chromium depletion** along the grain boundaries

Special thanks

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Special thanks to my **co-authors,** especially to my boss **Jörg Maier** for all the discussions we've run.

Thank you for your attention

Questions?