

Sulfur recirculation and improved material selection for high temperature corrosion abatement

– Investigating different aspects of corrosion memory (KME 714)



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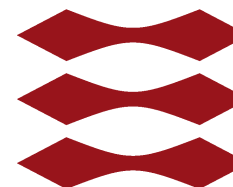
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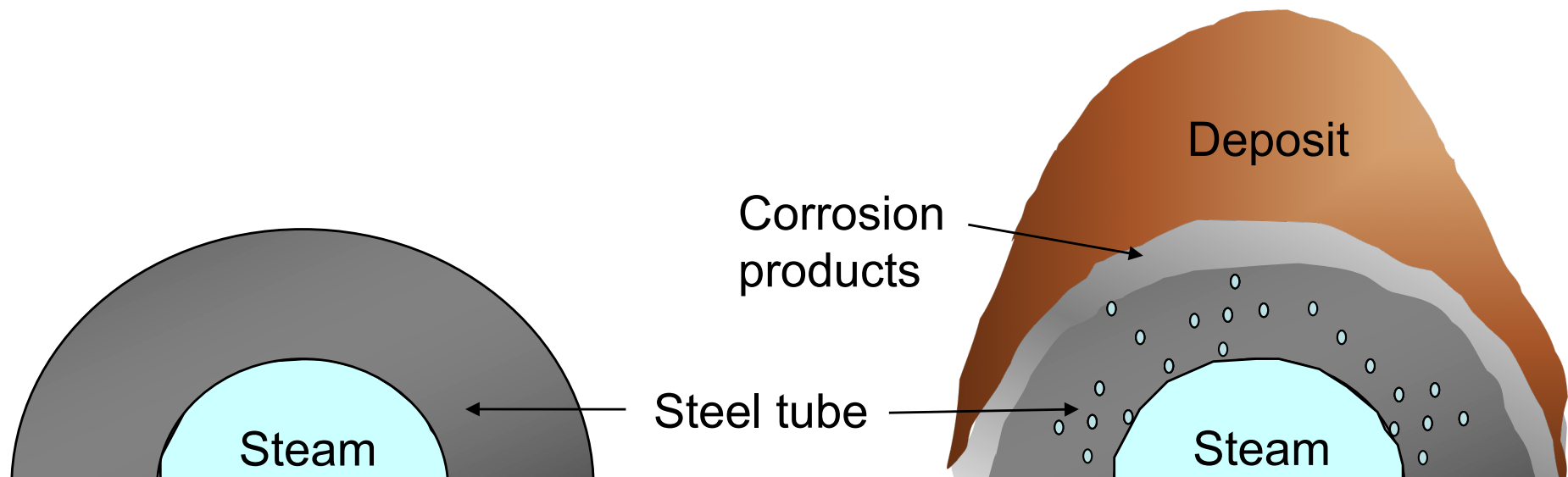
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Corrosion memory – Boiler operation history important

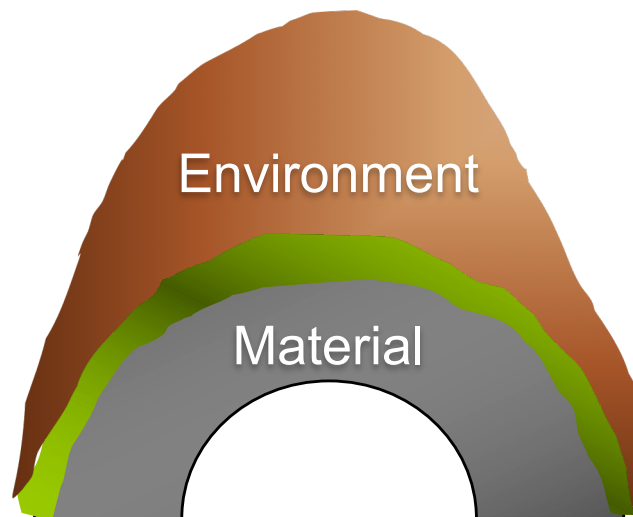
KCl/K₂SO₄



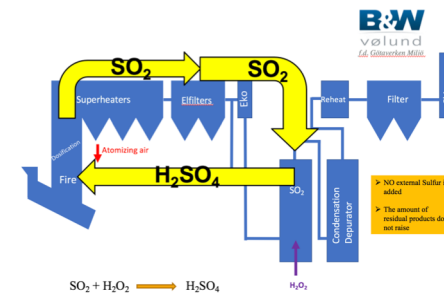
How will the corrosion attack be influenced by already formed deposit/microstructure/oxide scale...?

Research focus and correlation to KME goals

Corrosion memory



Sulfur recirculation

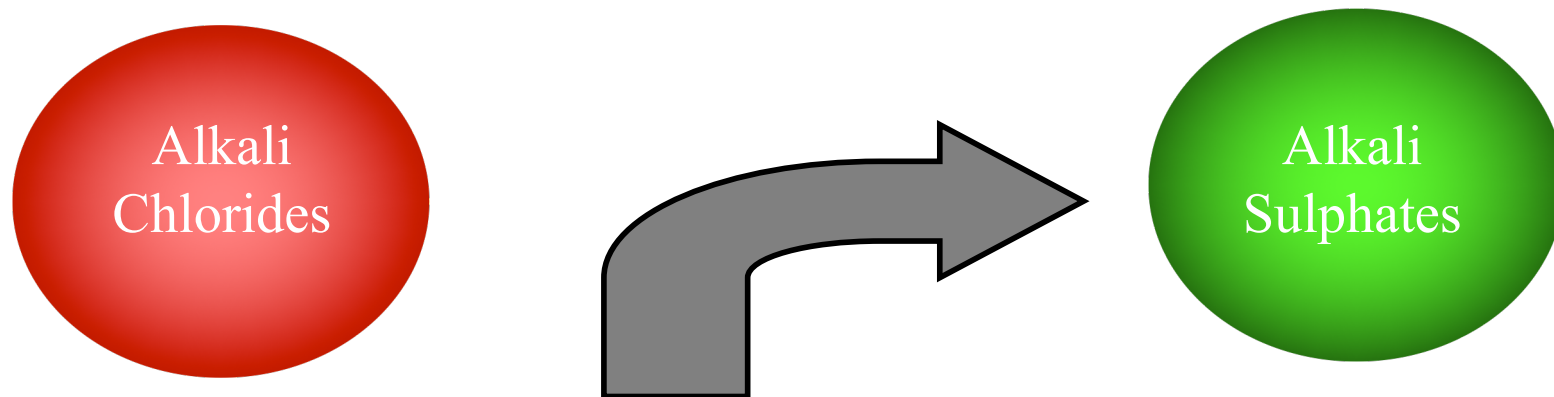


Full scale installation

KME goals:

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

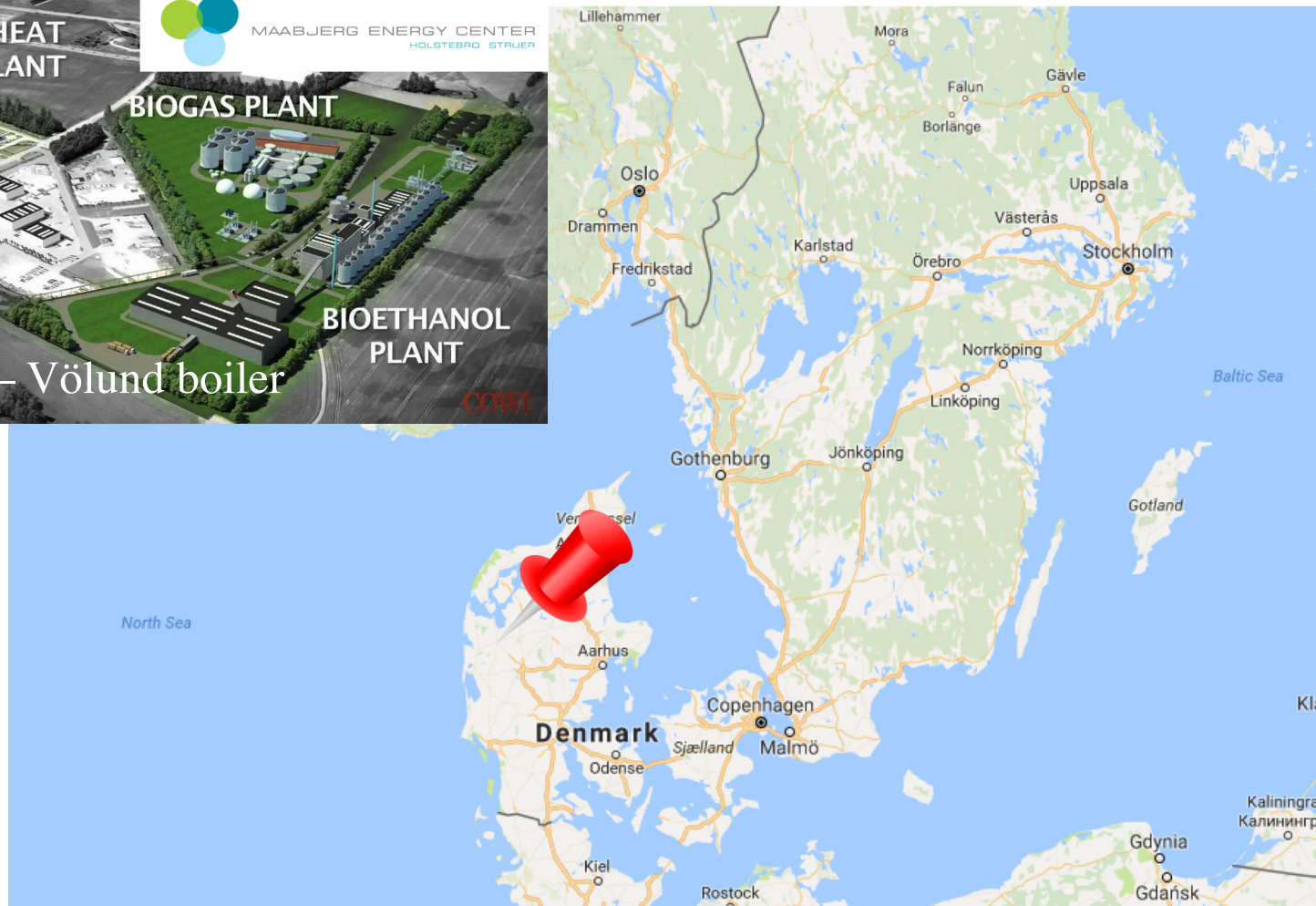
Mitigating alkali induced corrosion of high temperature steels - Change the fireside environment



Adding sulfur or sulfur-rich fuels

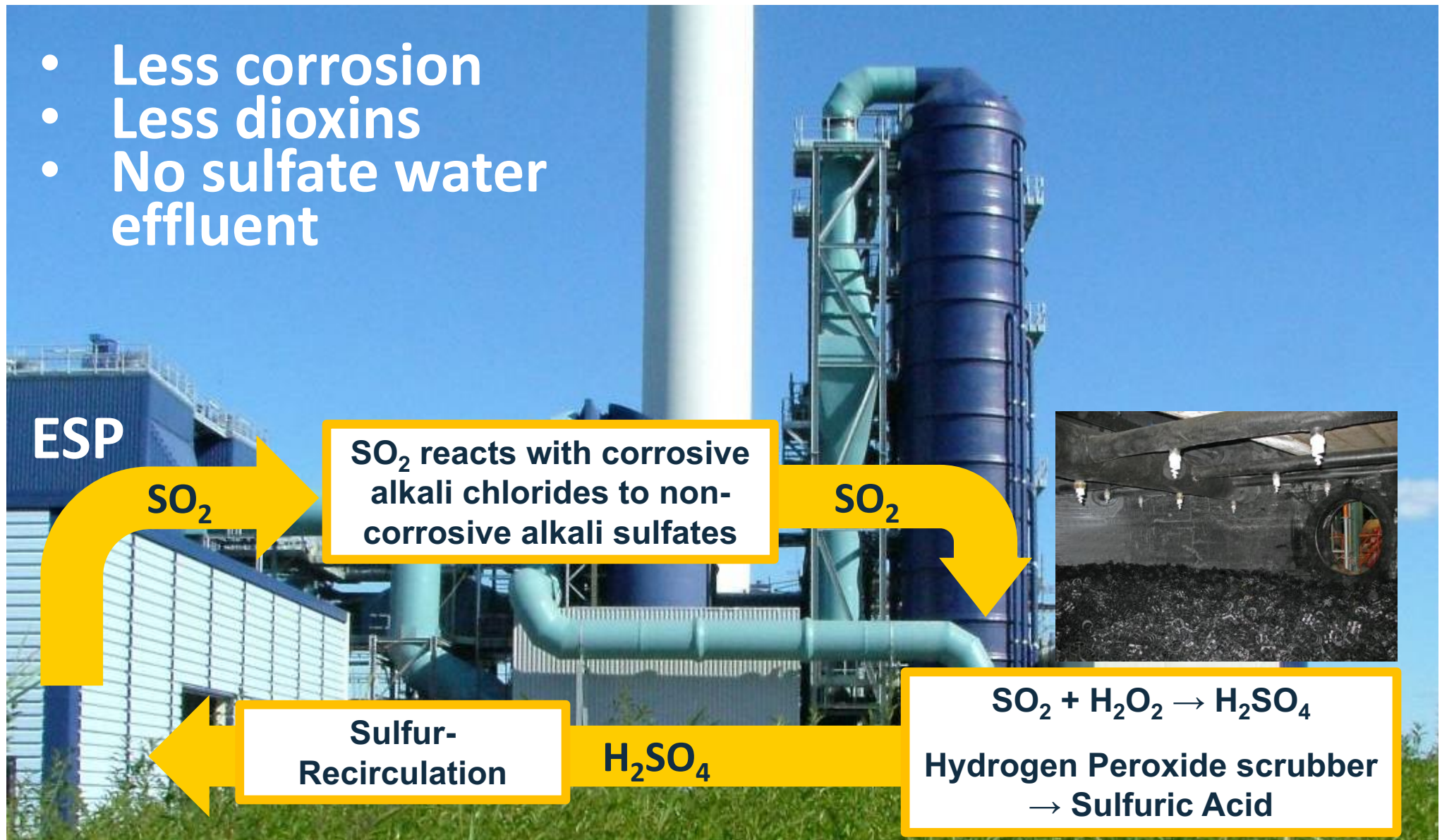
- Elemental sulfur
- Ammonium sulfate
- Full scale installation Sulfur Recirculation?
- Municipal sewage sludge

Sulfur recirculation – full scale installation



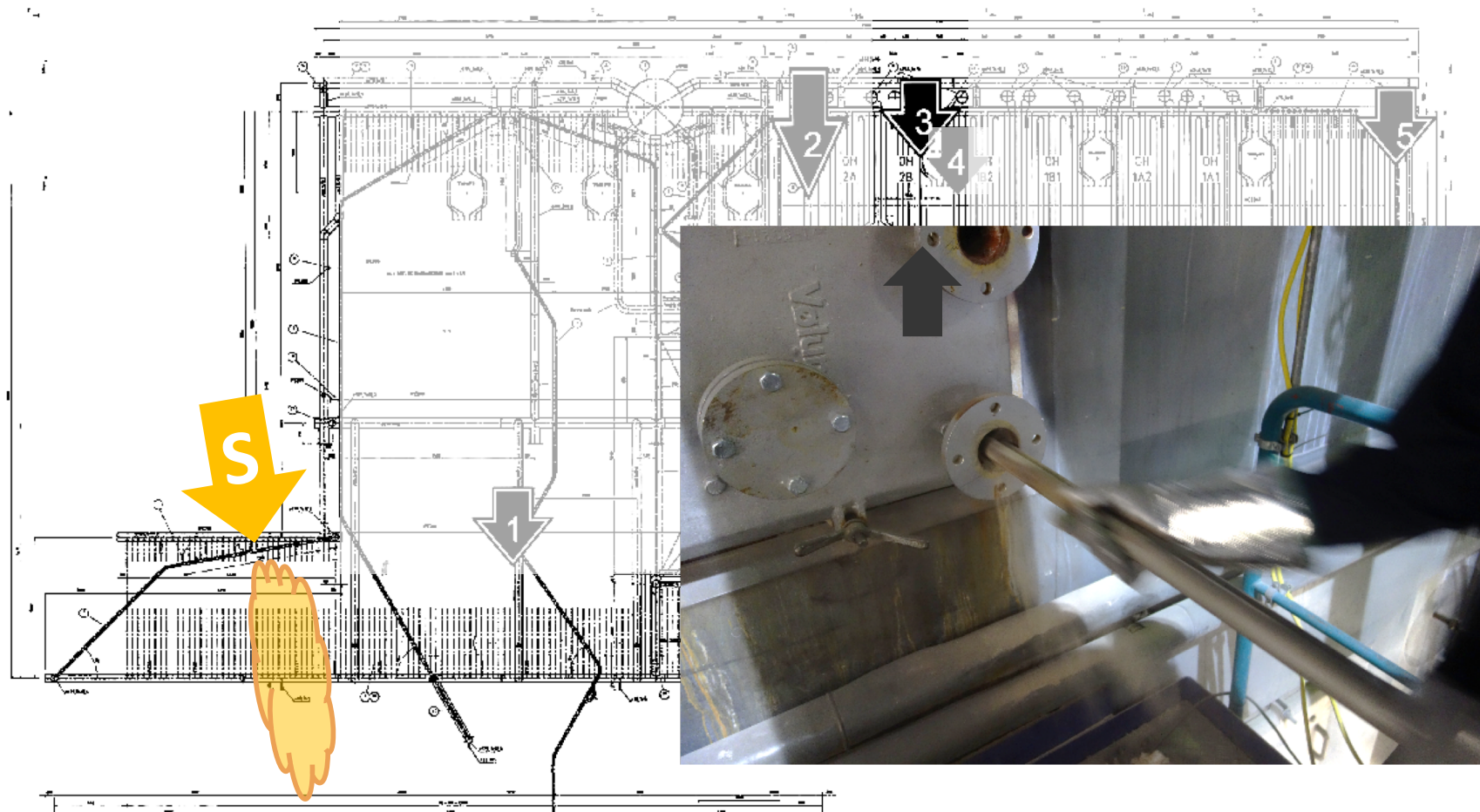
MEC: Sulfur Recirculation since October 2016

- Less corrosion
- Less dioxins
- No sulfate water effluent



Sulfur recirculation – deposit formation

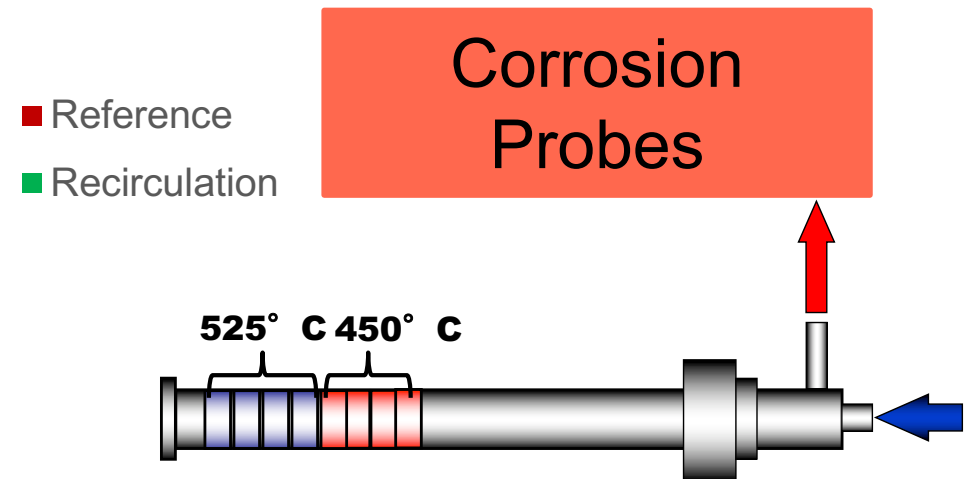
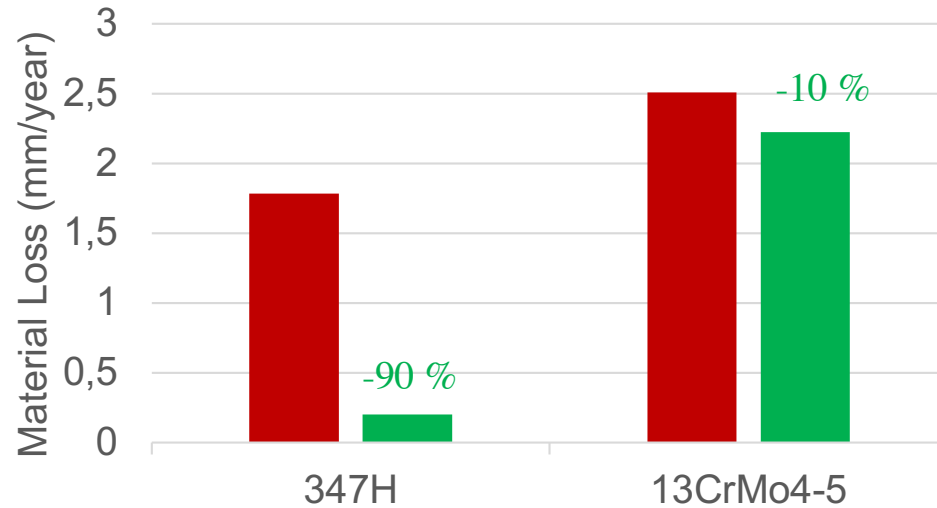
Reference line (waste)	Superheater deposits = 1,84%Cl	Probe deposit = 2,65wt%Cl
Recirculation line	Superheater deposits = 0,27%Cl	Probe deposit = 0,08wt%Cl



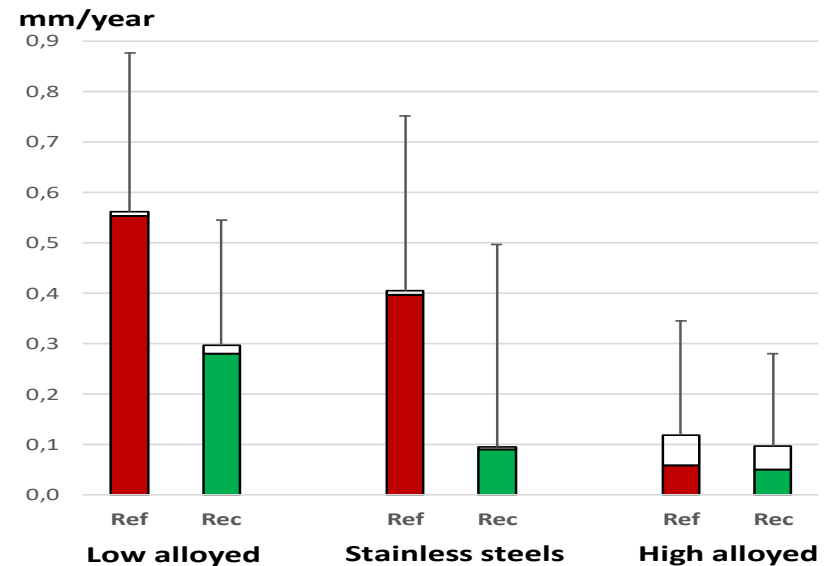
Less Cl = less corrosion? and dioxin formation

Sulfur recirculation – corrosion mitigation

Material loss



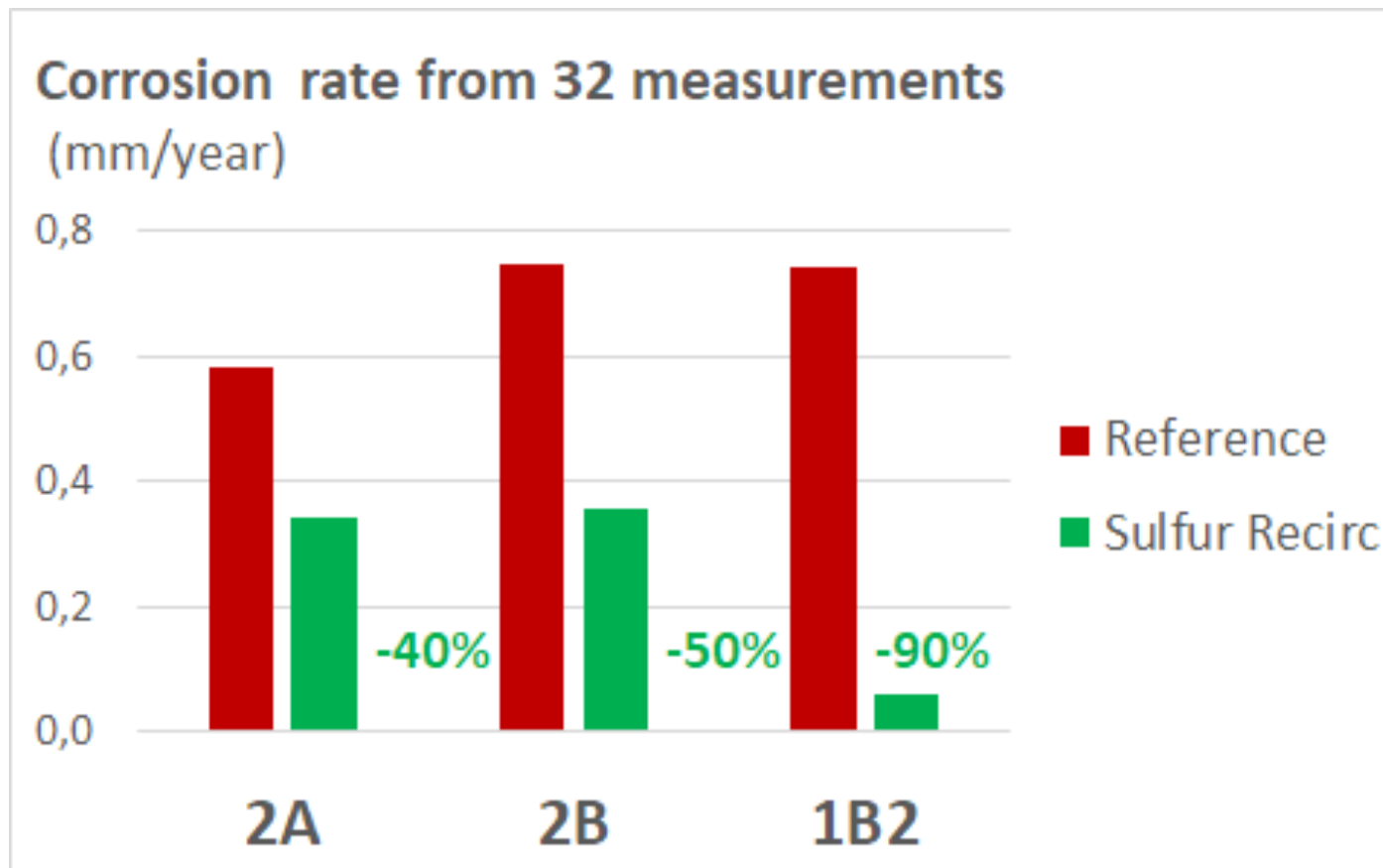
Superheaters



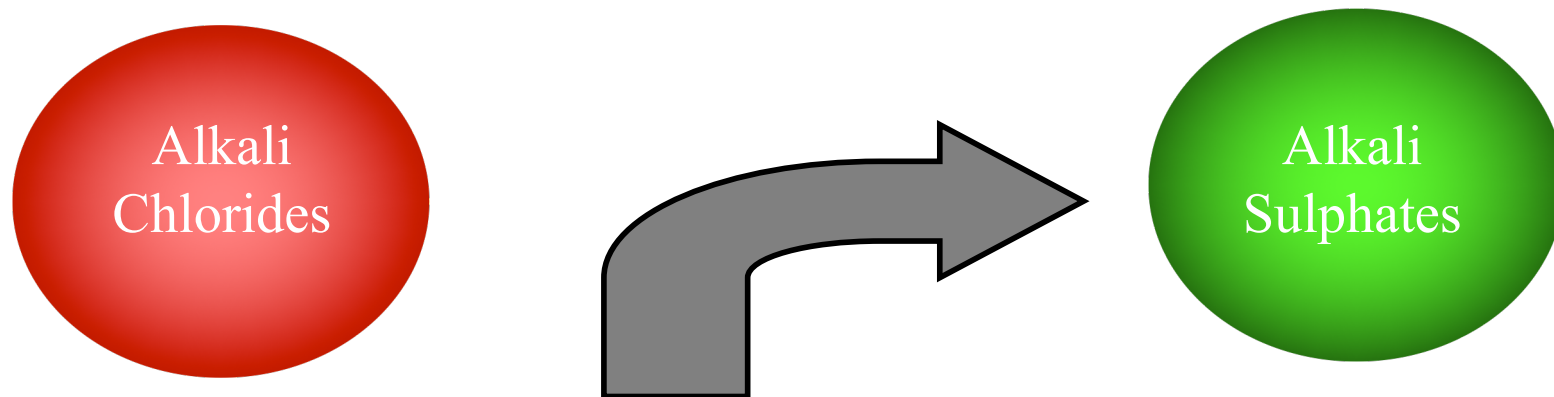
Sulfur recirculation – corrosion mitigation

Material loss

Superheaters – full scale measurements by MEC



Mitigating alkali induced corrosion of high temperature steels - Change the fireside environment

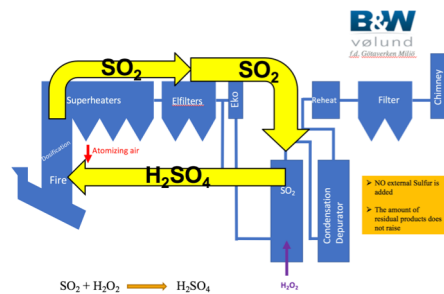


Adding sulphur or sulphur-rich fuels

- Elemental sulfur
- Ammonium sulfate
- ✓ • Full scale installation Sulfur recirculation!
- Municipal sewage sludge

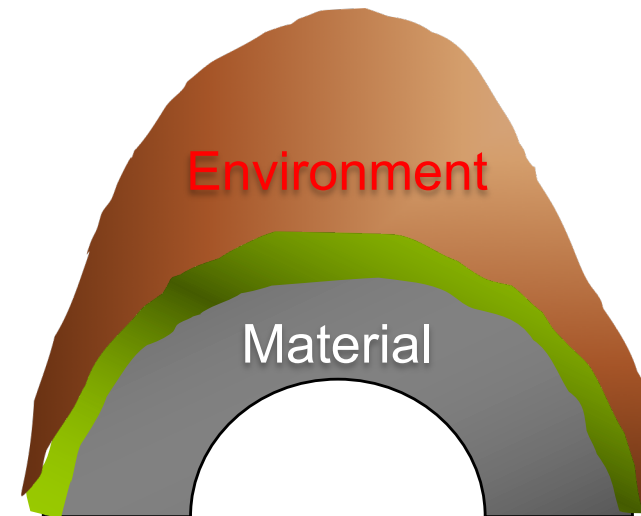
Research focus

Sulfur recirculation



Full scale installation

Corrosion memory

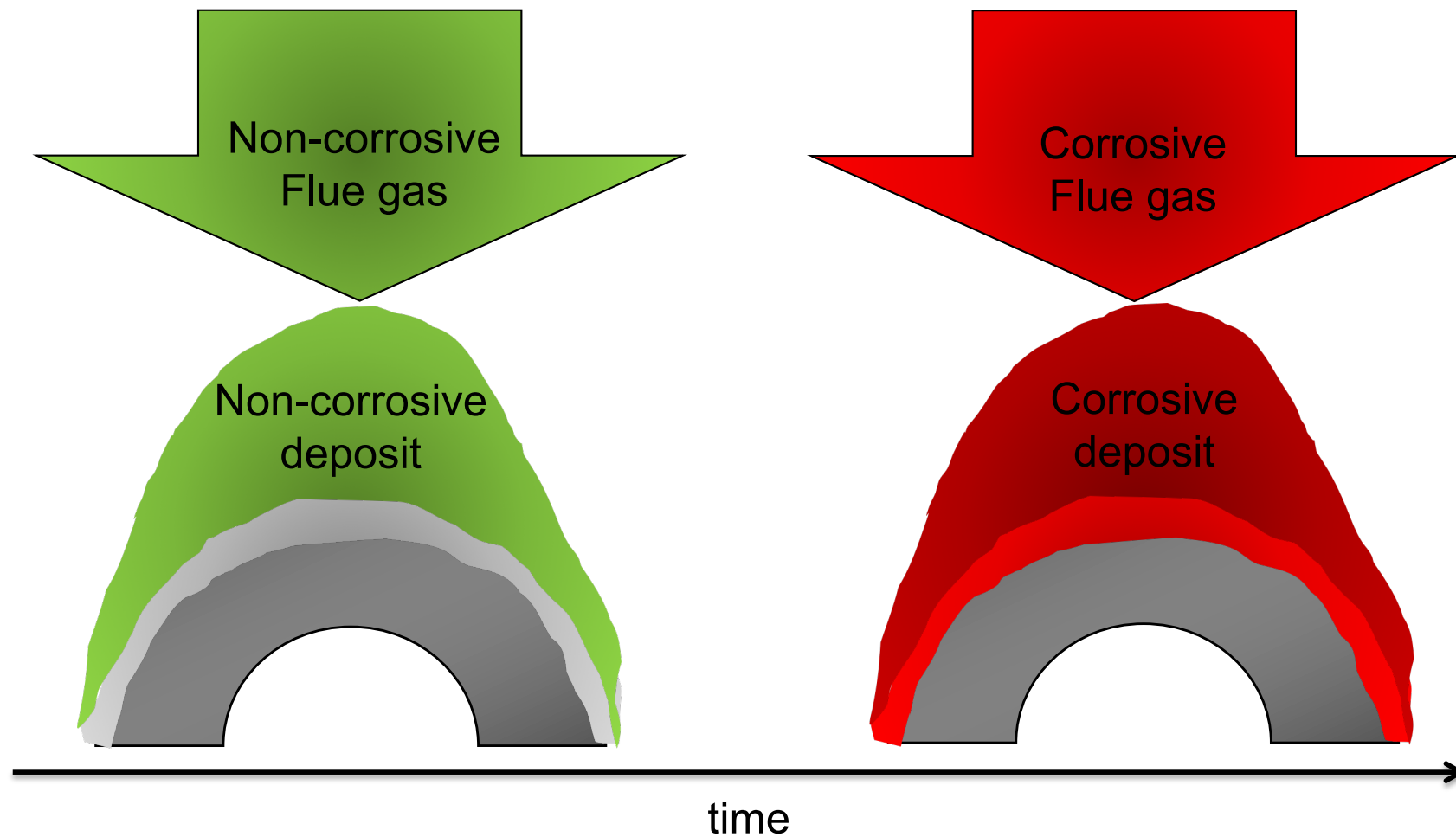


KME goals:

Increase green electricity production from combustion of biomass and waste
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Corrosion memory - Environment

Changing fuel – **more**/**less** corrosive flue gas – memory effect?

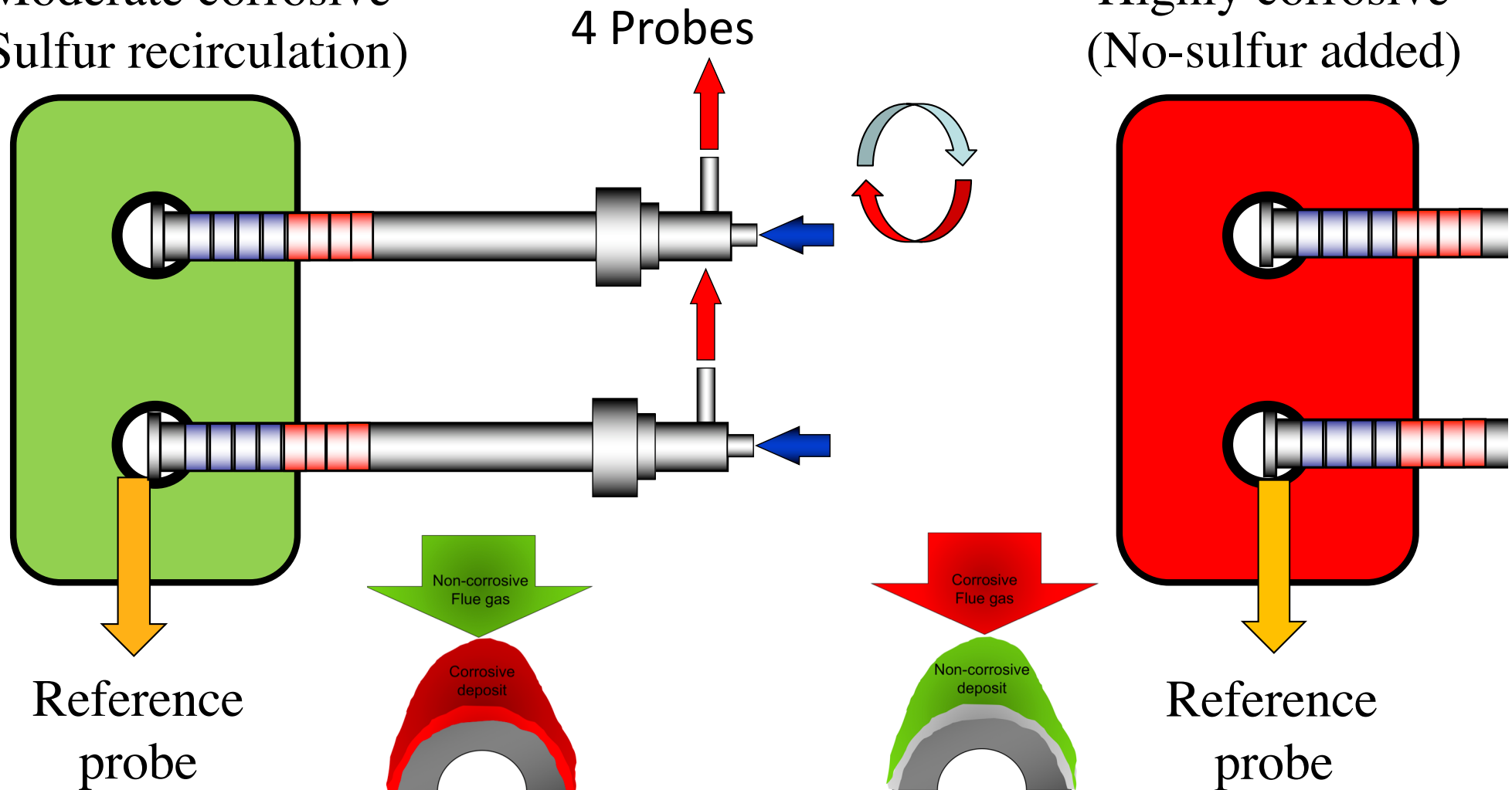


Simulating

Change in fuel – **more**/**less** corrosive flue gas – memory effect?

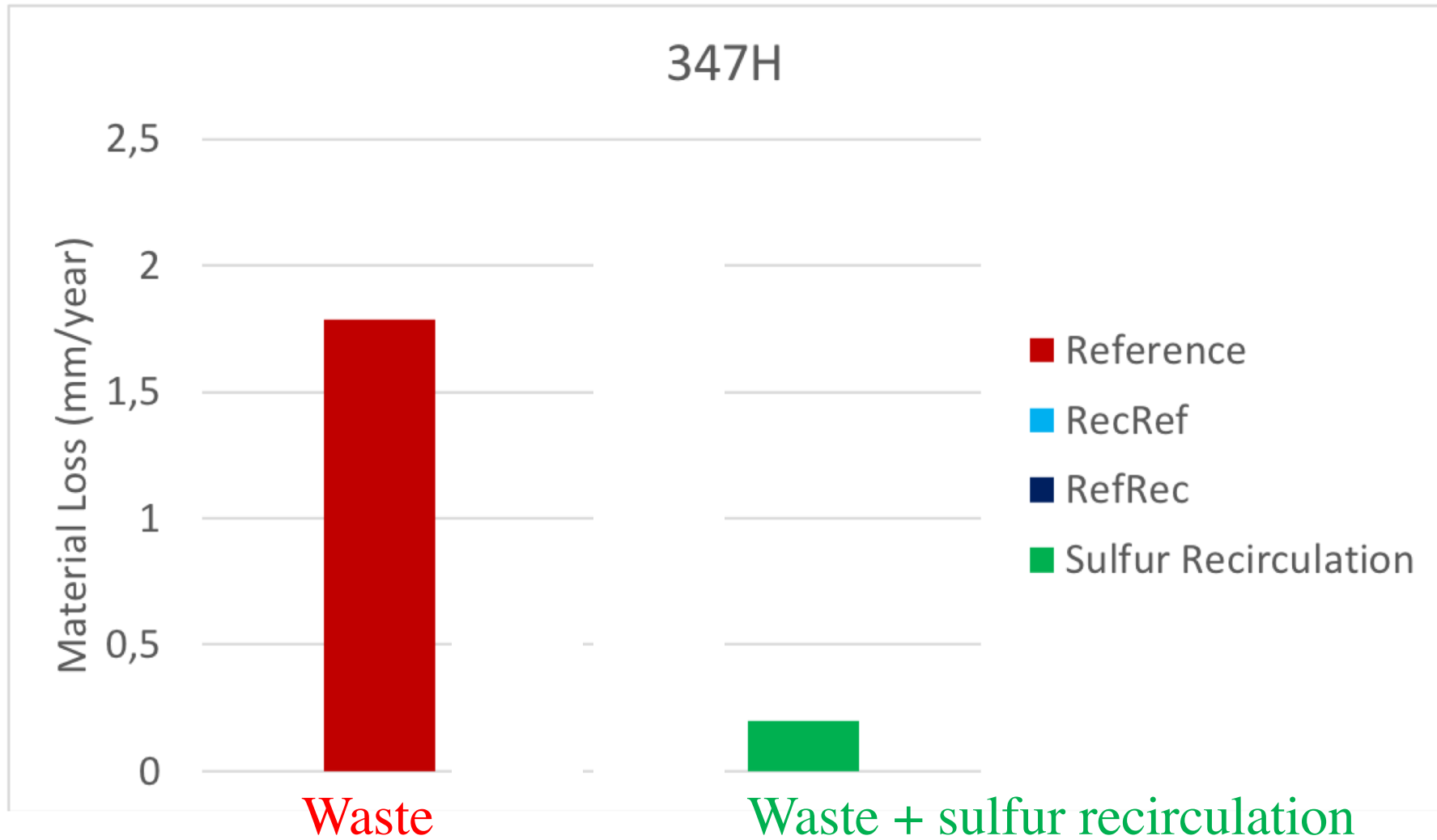
Moderate corrosive
(Sulfur recirculation)

Highly corrosive
(No-sulfur added)



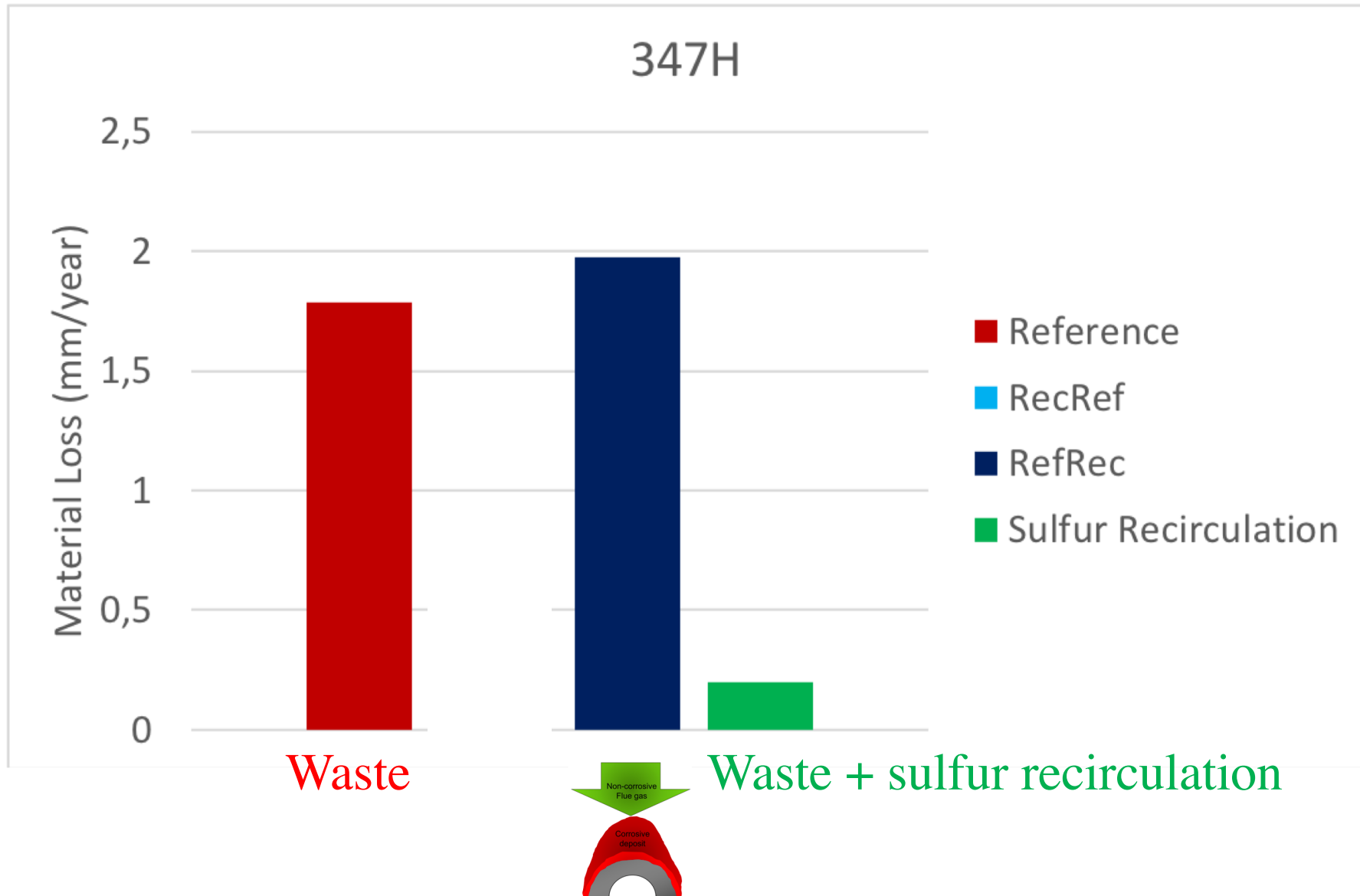
Corrosion memory - Environment

Stainless steel



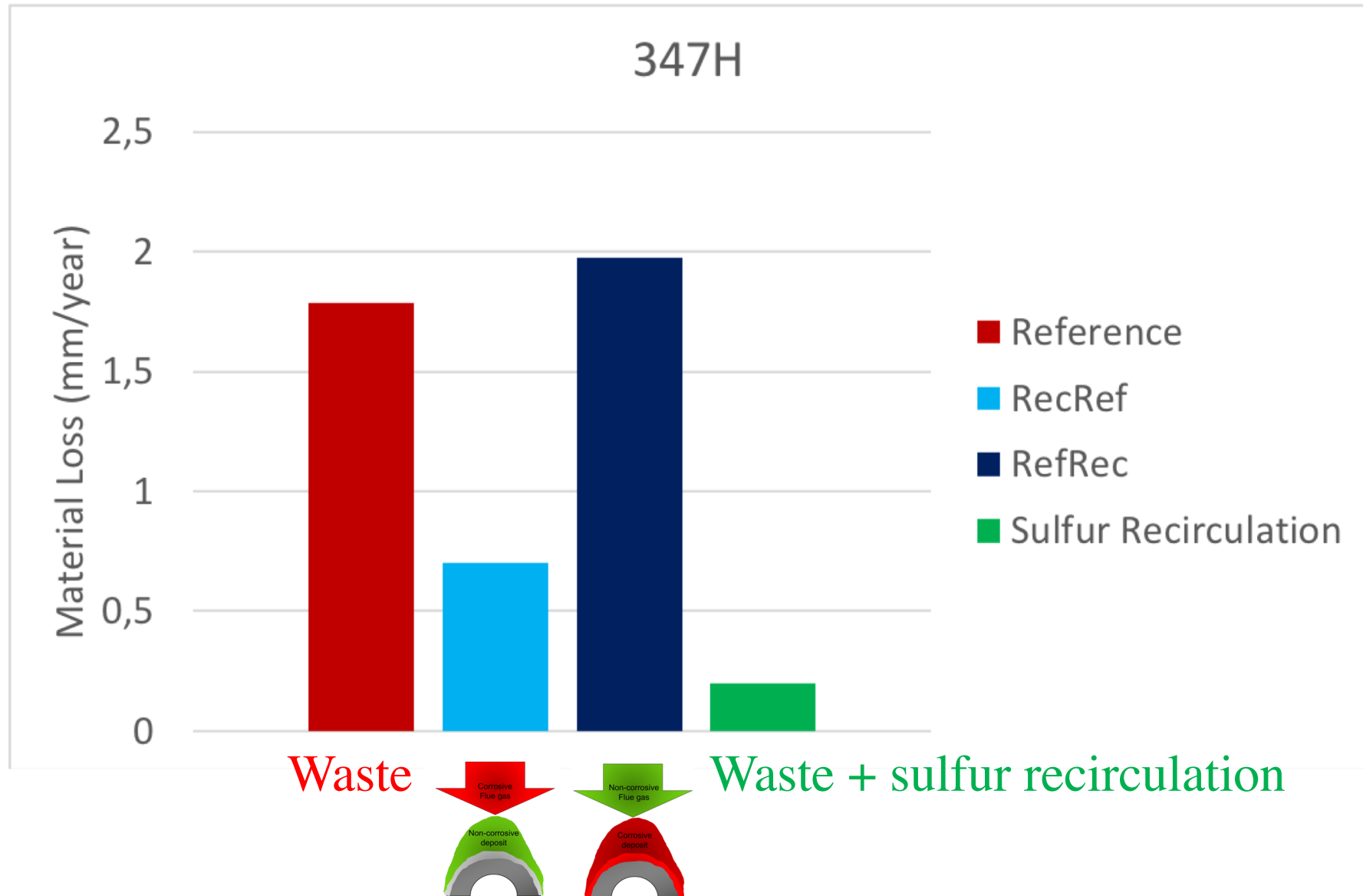
Corrosion memory - Environment

Stainless steel



Corrosion memory - Environment

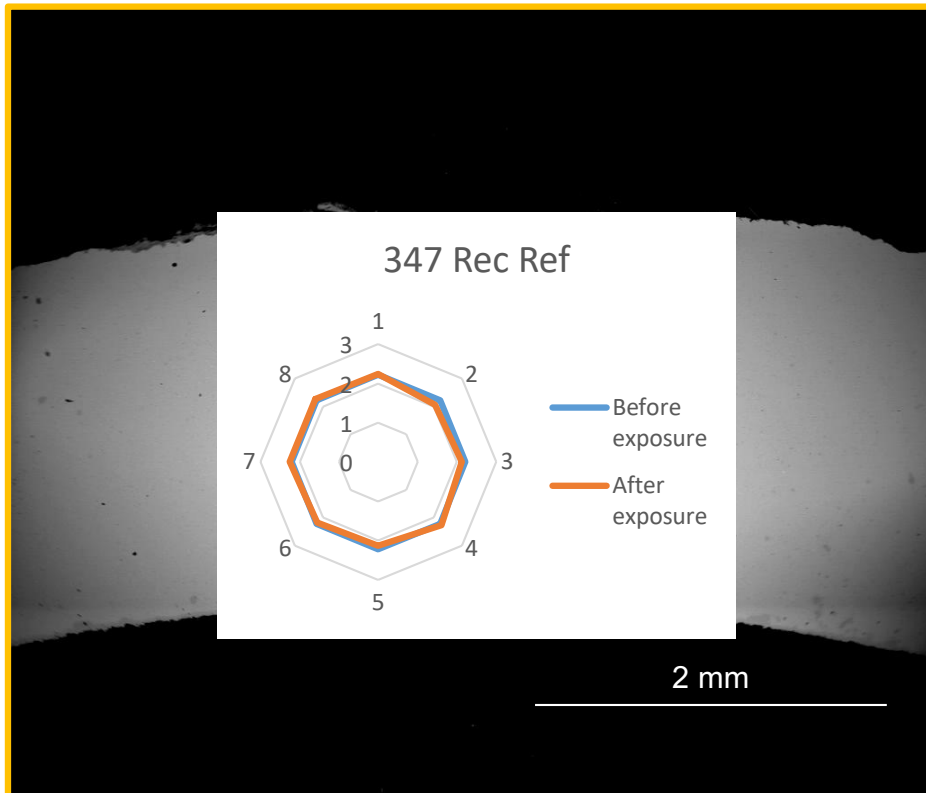
Stainless steel



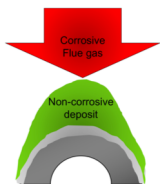
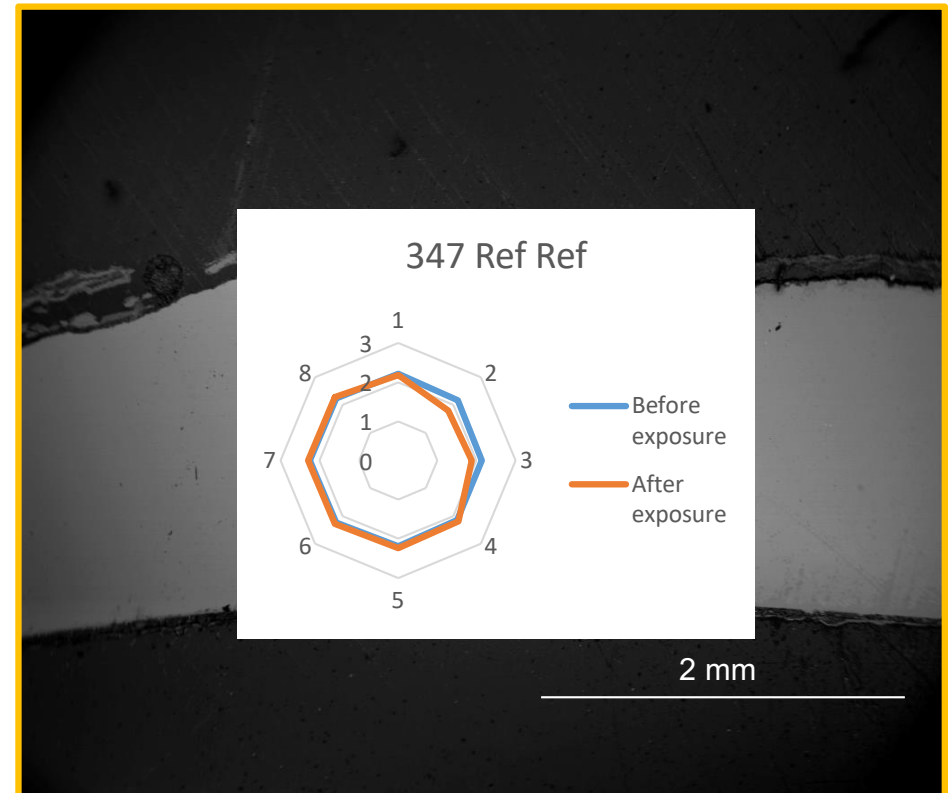
Corrosion memory – Environment

Example of analysis

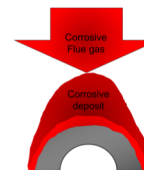
347H – Rec Ref



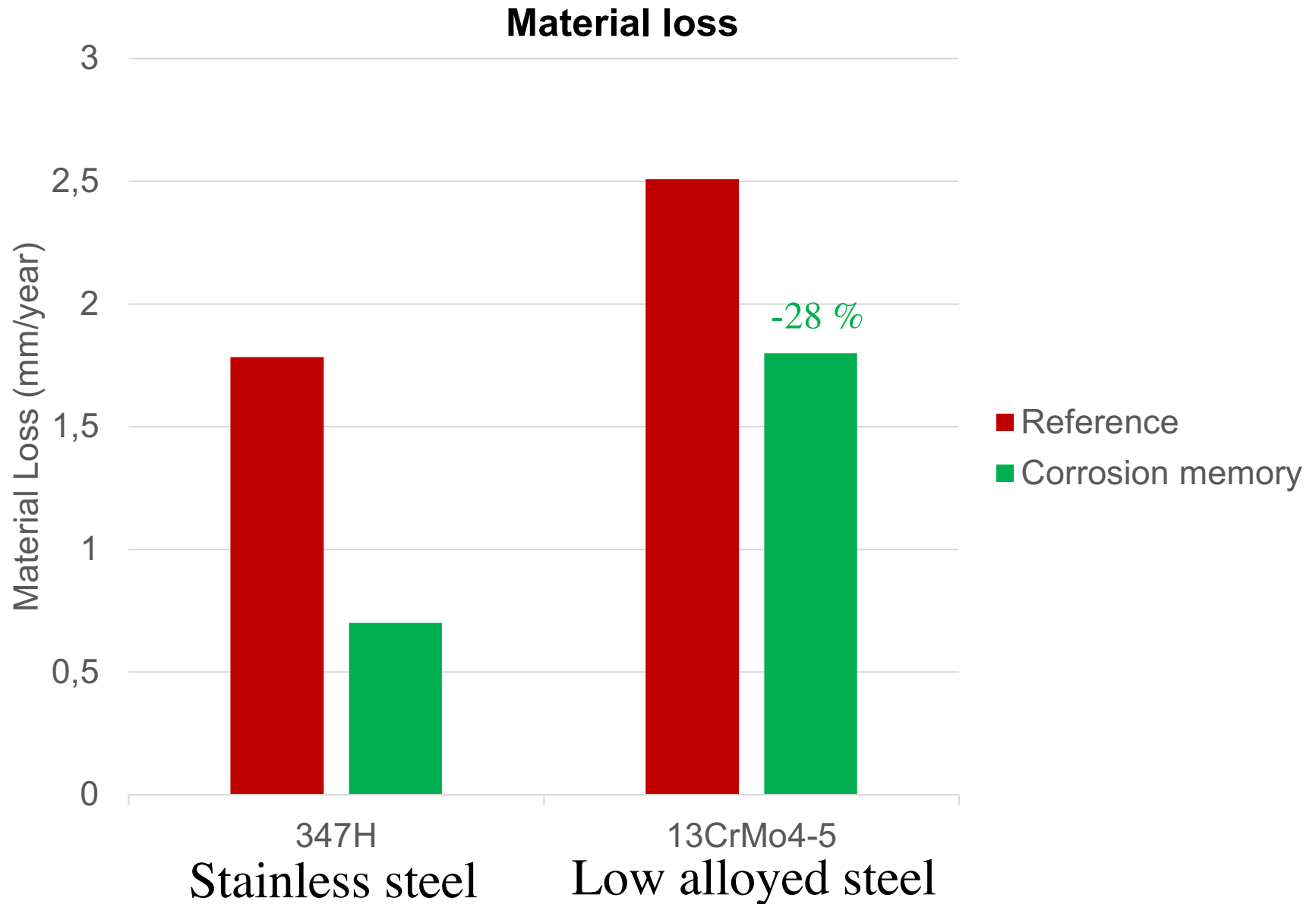
347H – Ref Ref



Positive memory effect!

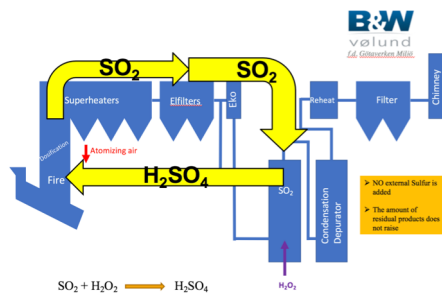


Corrosion memory – Environment



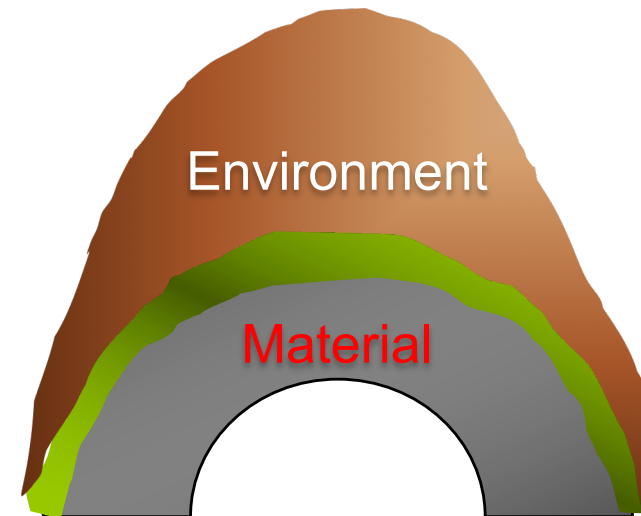
Research focus

Sulfur recirculation



Full scale installation

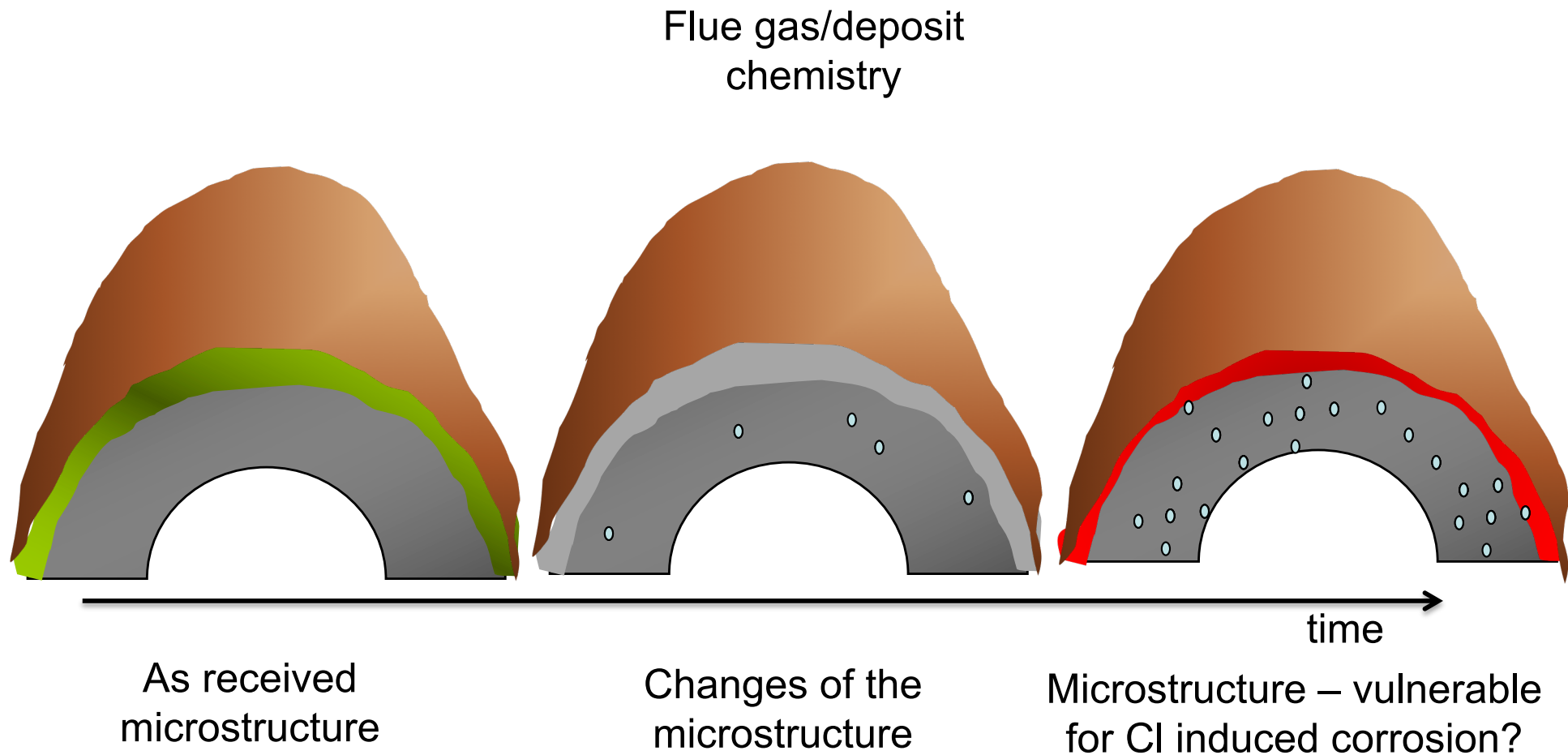
Corrosion memory



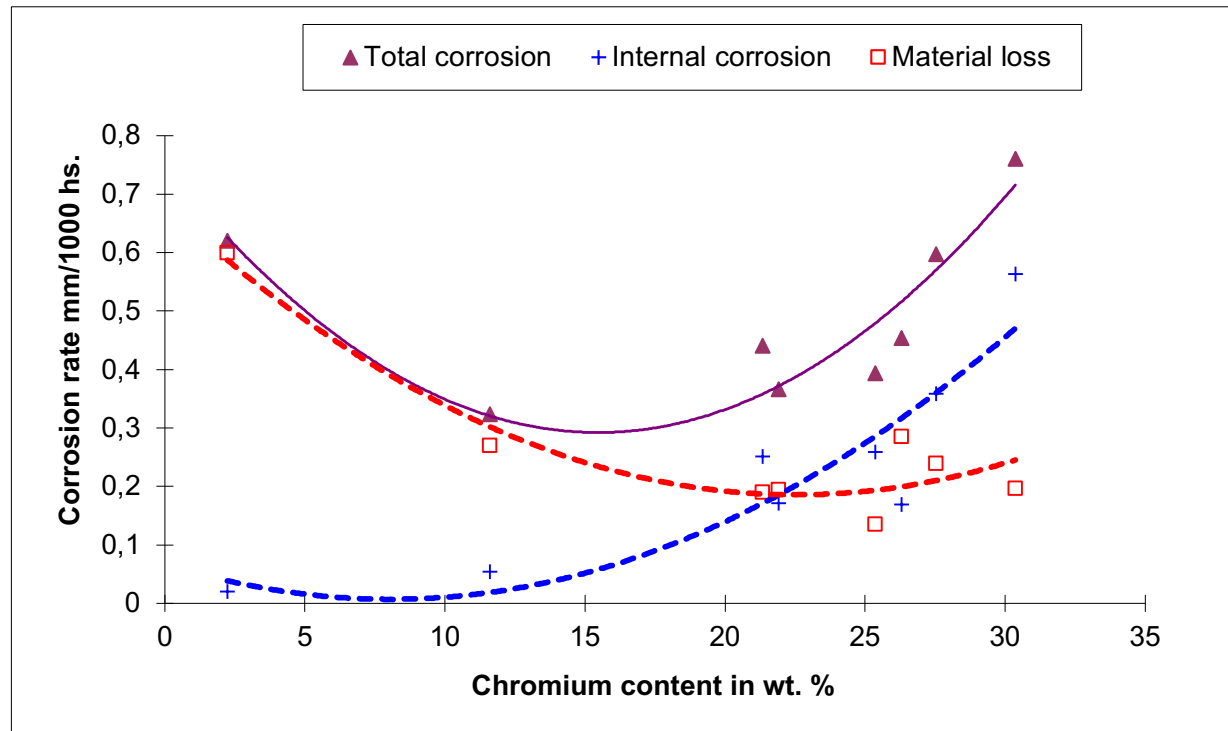
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Corrosion memory - Material

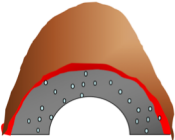
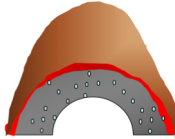


Background: Corrosion as function of chromium content



- High chromium content increases internal corrosion.
- High iron content gives high material loss.
- Chromium is good to form protective oxide but is also good at forming chlorides. Chromia is also broken down by formation of K_2CrO_4 .
- Increased temperatures results in evaporation of metal chlorides.

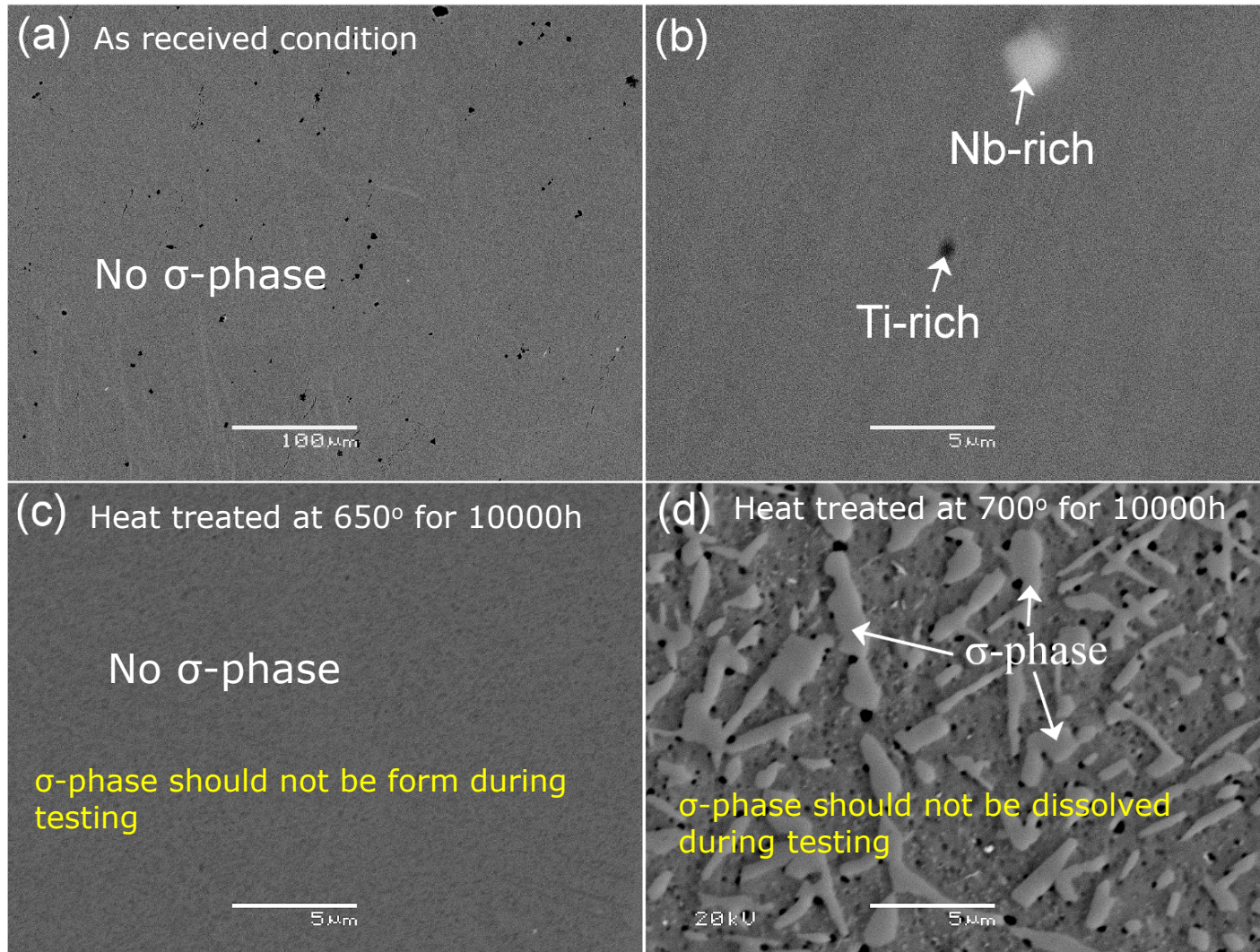
Laboratory exposures

Material	Condition	Time and Temperature	Exposure environment
Modified 310 	As-received 	168 h, at 600°C	5%O ₂ + 15% H ₂ O + N ₂
			5%O ₂ + 15% H ₂ O + N ₂ + KCl deposit
	Aged at 700°C for 10,000 hours		5%O ₂ + 15% H ₂ O + N ₂
			5%O ₂ + 15% H ₂ O + N ₂ + KCl deposit
TP347H FG 	As received 		5%O ₂ + 15% H ₂ O + N ₂
			5%O ₂ + 15% H ₂ O + N ₂ + KCl deposit
	Exposed for 100000 hours in coal fired plant with steam temperature 535°C		5%O ₂ + 15% H ₂ O + N ₂
			5%O ₂ + 15% H ₂ O + N ₂ + KCl deposit

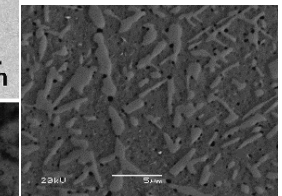
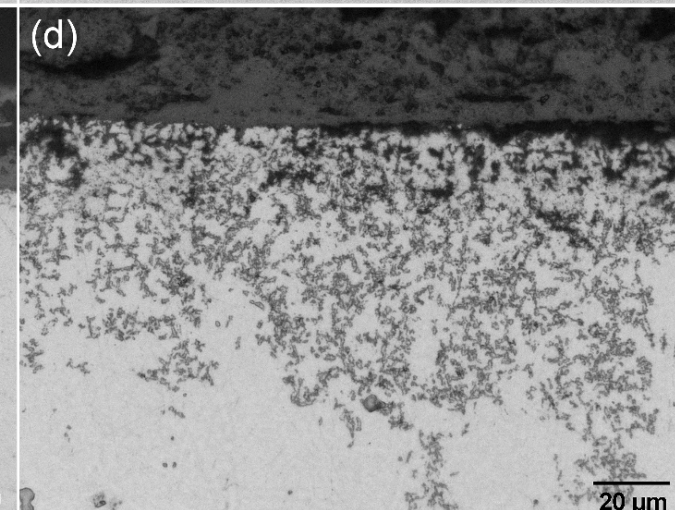
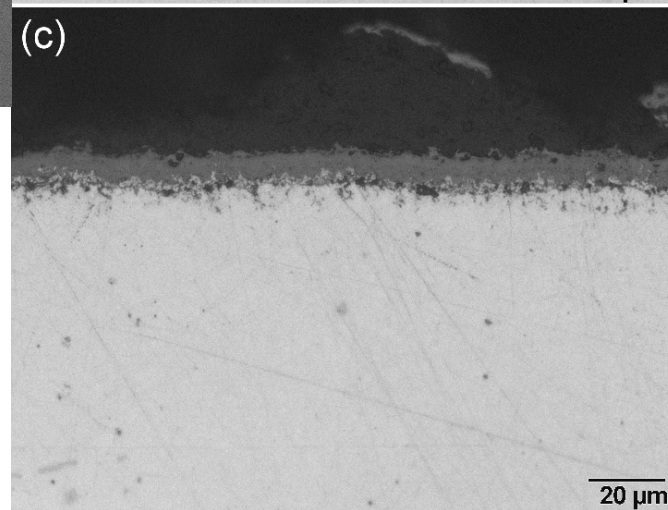
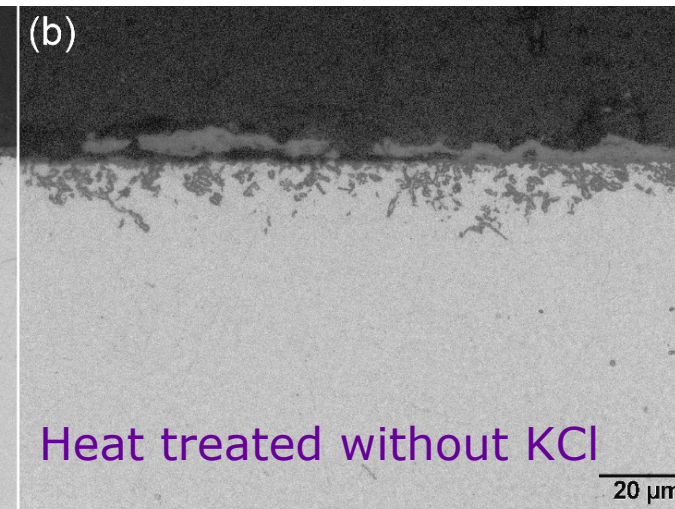
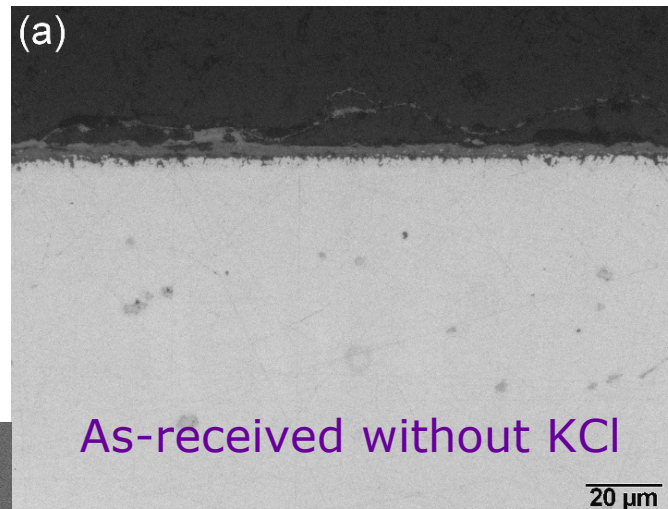
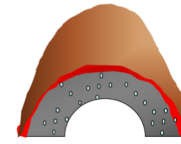
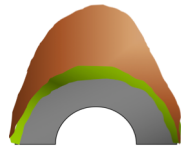
Microstructures of modified 310 before corrosion exposure

Why specifically this steel ?

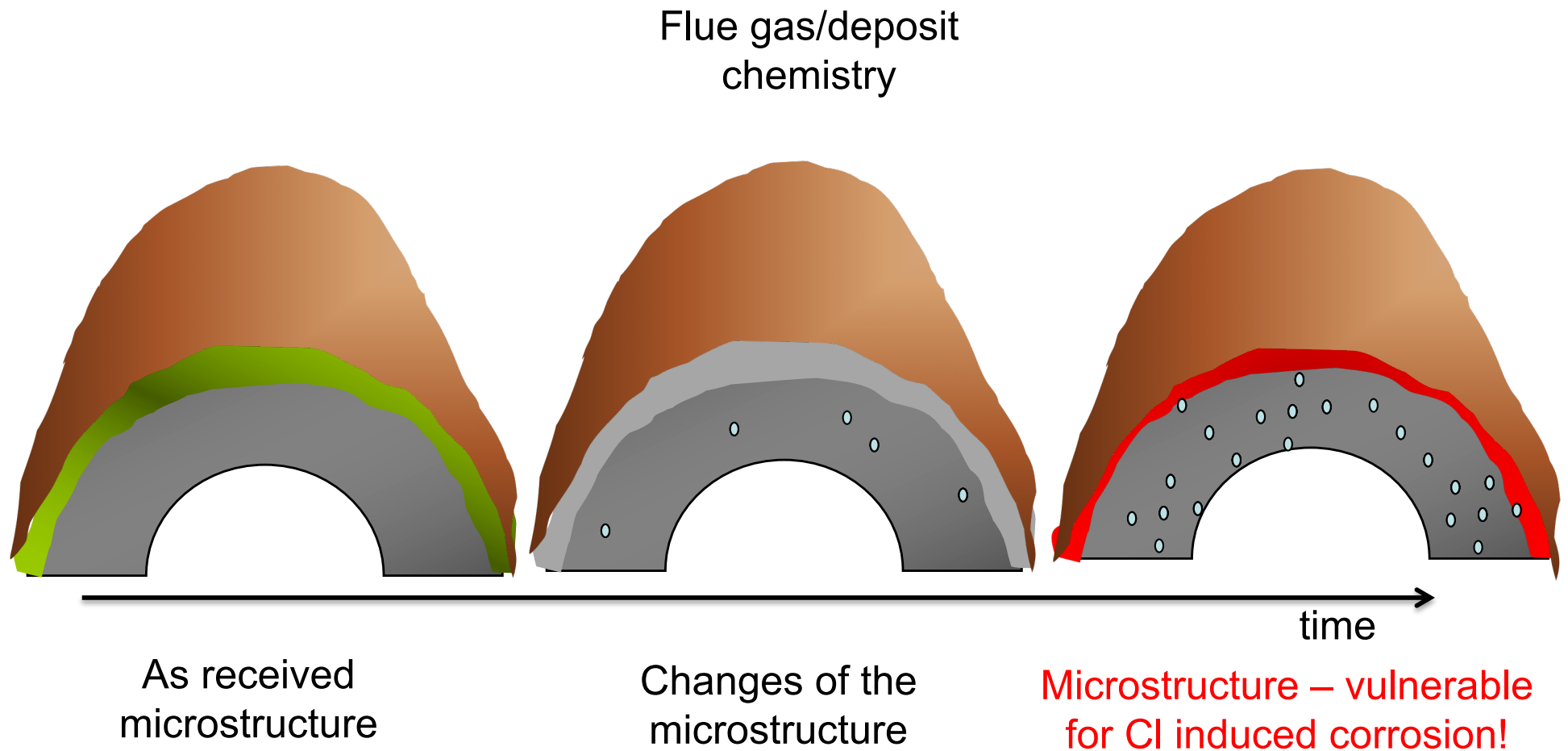
It allows testing the same material in to two widely different microstructure conditions



Deeper attack on heat treated modified 310



Corrosion memory - Material



Summary

- The Sulfur Recirculation technique - successful for decreasing corrosion of superheaters.
- Corrosion memory – environment:
 - Memory effects observed
 - Stronger effect on stainless steels
 - Less corrosion starting with good fuel/deposit
 - No/negative effect starting with a corrosive deposit?
- Corrosion memory - material:
 - Memory effect observed
 - Microstructure – vulnerable for Cl induced corrosion!

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COMBINED HEAT & POWER PLANT

BIOGAS PLANT



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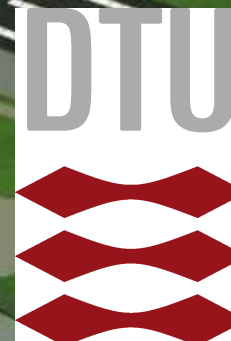


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