The Mechanisms of Corrosion – and how to avoid it them?

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1. Introduction

GKS = Coal-, Gas and WtE-CHP-Plant
Flow Chart of GKS GmbH

C-CHPP Steam Parameters:
115 bars; 535 °C

WtE-CHPP Steam Parameters:
65 bars; 435 °C
Availability = Economy

Deposits ↑

Corrosion →
Extended Corrosion Diagram - WtE

[Warnecke, 2003]
2. Understanding?
HTCl-Corrosion

Red Layer:
Mainly Cl and Fe (FeCl₂)
Thickness:
~ 100 – 250 μm

Green Layer:
Mainly S and Fe (FeS₂)
Thickness:
~ 100 – 200 μm

Blue Layer:
Mainly O und Fe (Fe₂O₃)
Thickness:
~ 800 – 1200 μm

Alkali- and Earth-alkali chlorides
Alkali- and Earth-alkali sulfates

H₂O- / Tubeside

Deposits/- Flue gas side
Examples for Coupling CFD and TEC

GKS-WtE-Boiler:

Used Programs:
CFX and FactSage
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Normal Operation: Particle Distribution

Average of 3 - 8 Measurements

Aerodynamic particle diameter [μm]

Mass concentration [g/m³]

Partikelgröße [μm]
Normal operation:
Chemical Composition of Particles – 3 Summed Fractions

**Fine fraction:**
Secondary particle (Na, K, Cl)
- Cl-high, decreasing
- S-low, partially increasing

**Coarse fraction:**
Primary particle (Ca, Si)
- Ca-high
- “Balance” increasing
Normal Operation: (De-)Sulphidation

Gas-phase:

- HCl
- SO₂

Particle-phase (<0.2 μm):

- Cl
- S

BE = Boiler End

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Corrosion Sensor

- Water cooled lance
- Air cooled sensor head
- Electrical contacts for measurement

Total Length ca. 3 m

Fittings for Thermocouples
Comparison: Plant Tubes vs. Sensor

Example:

3 months plant tubes:

- $\text{Fe}_a\text{Cl}_b$
- $\text{Fe}_c\text{S}_d$
- $\text{Fe}_e\text{O}_f$
- Alkali-Cl
- Alkali-S

3 months sensor rings:

- $\text{Fe}_a\text{Cl}_b$
- $\text{Fe}_c\text{S}_d$
- $\text{Fe}_e\text{O}_f$
- Alkali-Cl
- Alkali-S

Identical Structure of Tube and Sensor!
Thickness of Layers

![Graph showing thickness of layers over time for Iron Oxid, Tube Reduction, and Iron Chorine.](image)

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Correlation: Wall decline vs. Corr.-signal

(a) free corrosion potential
Ring 1: 15Mo3
Ring 2: Inconel
Ring 3: 15Mo3

(b) power-voltage-line
Ring 1: 15Mo3
Ring 2: Inconel
Ring 3: 15Mo3
Sensor data – systematic temperature variation

Corrosion conductance is depending exponentially on temperature
Reactions at boundary layers

1. $15\text{Mo}_3/\text{FeCl}_2$:
   \[2\text{FeCl}_3 + \text{Fe} \rightarrow 3\text{FeCl}_2\]

2. $\text{FeCl}_2/\text{Fe}_x\text{O}_y$:
   \[4\text{FeCl}_2 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Cl}_2\]
   \[2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3\]

3. $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$:
   \[4\text{FeCl}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 6\text{Cl}_2\]
   \[6\text{FeCl}_3 + 4\text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 9\text{Cl}_2\]

4. $2\text{NaCl}, 2\text{KCl}, \text{CaCl}_2 + 3\text{SO}_2 + 3\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4, \text{K}_2\text{SO}_4, \text{CaSO}_4 + 3\text{Cl}_2$

Metal chloride
Metal sulfate

(not complete until now!)
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How to avoid HT-Chlorine-Corrosion?

At superheater:

Chlorine Trap

HWS
Crossover 2./3. Pass: Chlorine Trap

Actual situation:
3 vaporiser tubes (distance: 400 mm)

Future condition:
T=180 (distance: 100 mm)
HWS – Effect of Cleaning
Adding Sulphur

- Direct sulphur and SO₂

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4. Summary / Perspective

- Boiler influences Gas/Aerosol within FG way
- Chlorine layered large particles depositing by impaction
- Interaction between flue gas and particles: sulphidation with release of chlor(ine) in the deposits
- Chlorine trap shall catch chlorides before SH
- Attack of chlorine should be modified by using process know-how or depositing protection layers

- Next step: Better understanding of chlorine formation in the combustion chamber (NGBW)