The Mechanisms of Corrosion – and how to avoid them?

Dr.-Ing. Ragnar Warnecke, GKS, Schweinfurt
Dr. rer. nat. Bernd Benker, CUTEC, Clausthal-Zellerfeld
Dipl. Phys. Christian Deuerling, GKS, Schweinfurt
Prof. Dr. Ferdinand Haider, Univ. Augsburg, Augsburg
Prof. Dr. Siegried Horn, Univ. Augsburg, Augsburg
Dr. Jürgen Maguhn, GSF, Neuherberg
Dipl.-Ing. Volker Müller, GKS, Schweinfurt
Dipl. Chem. Hermann Nordsieck, BIfA, Augsburg
Dipl. Phys. Barbara Waldmann, Univ. Augsburg, Augsburg
Prof. Dr. Ralf Zimmermann, GSF, Neuherberg

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Content

1. Introduction!
2. Understanding?
3. Solution?
4. Summary / Perspective!

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

1. Introduction

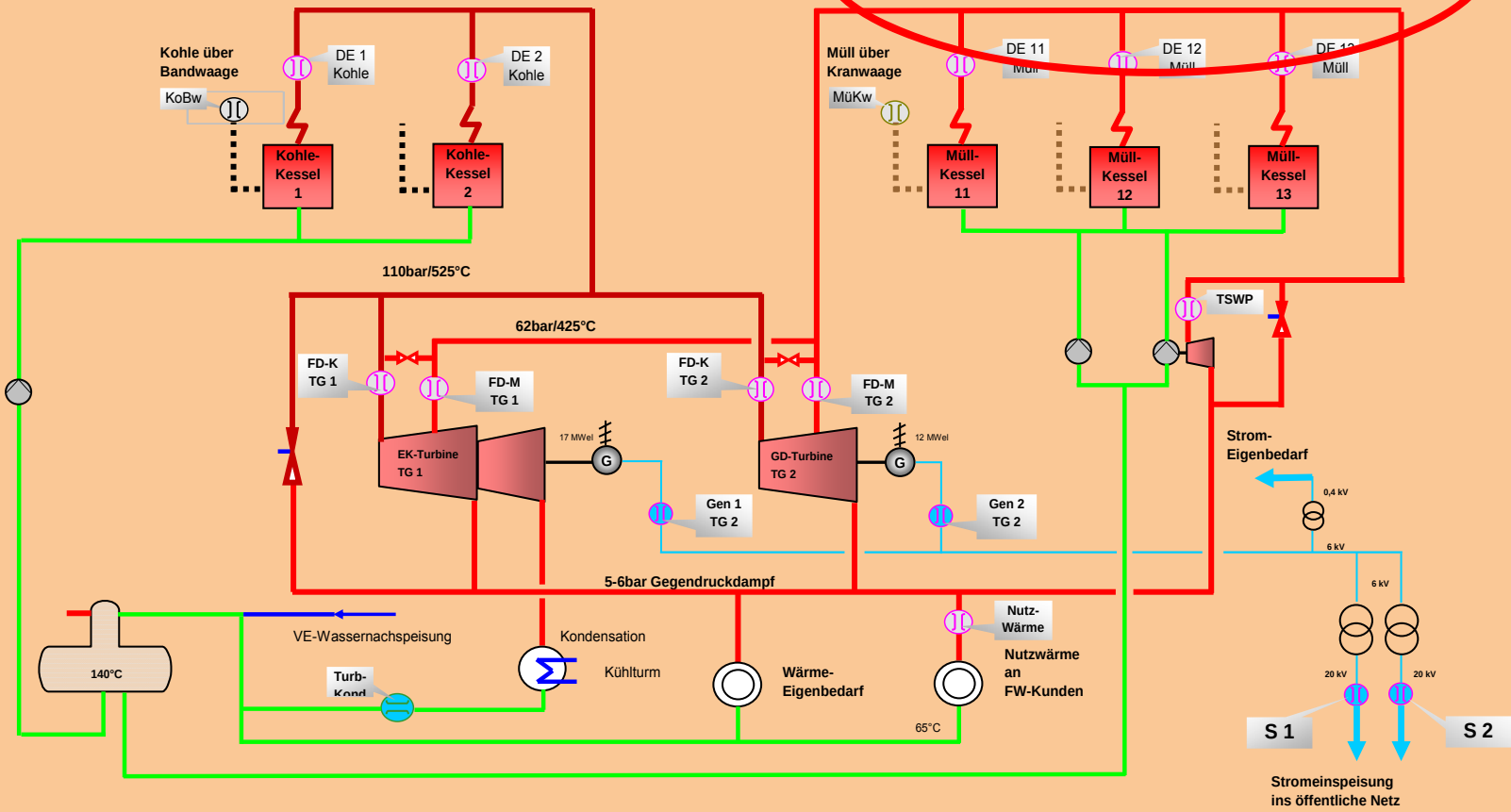
GKS = Coal-, Gas and WtE-CHP-Plant

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Flow Chart of GKS GmbH

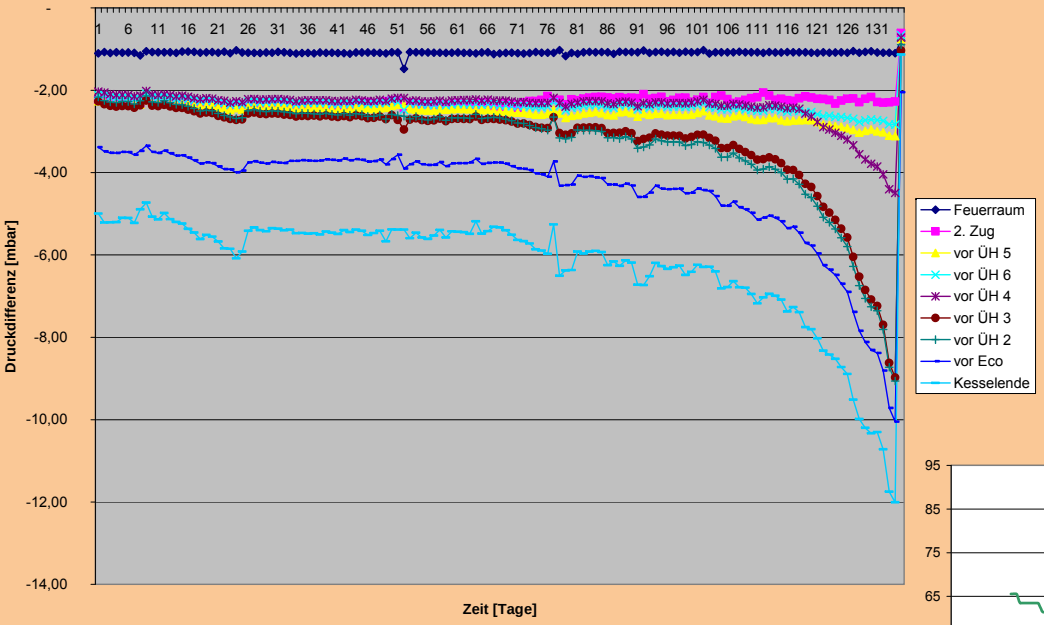
C-CHPP Steam Parameters:
115 bars; 535 °C

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



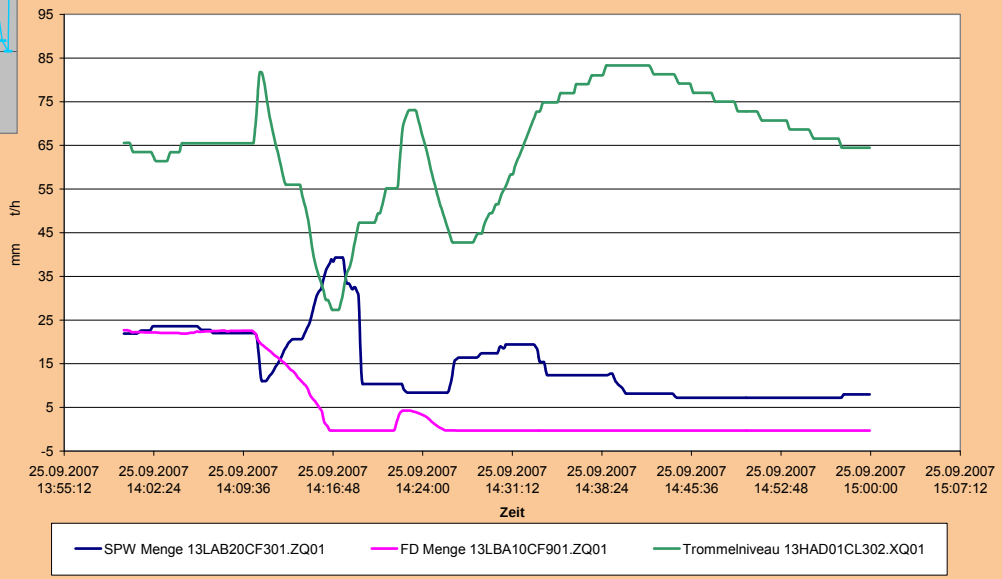
This Project was co-financed by the Baverian Ministry for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Availability = Economy



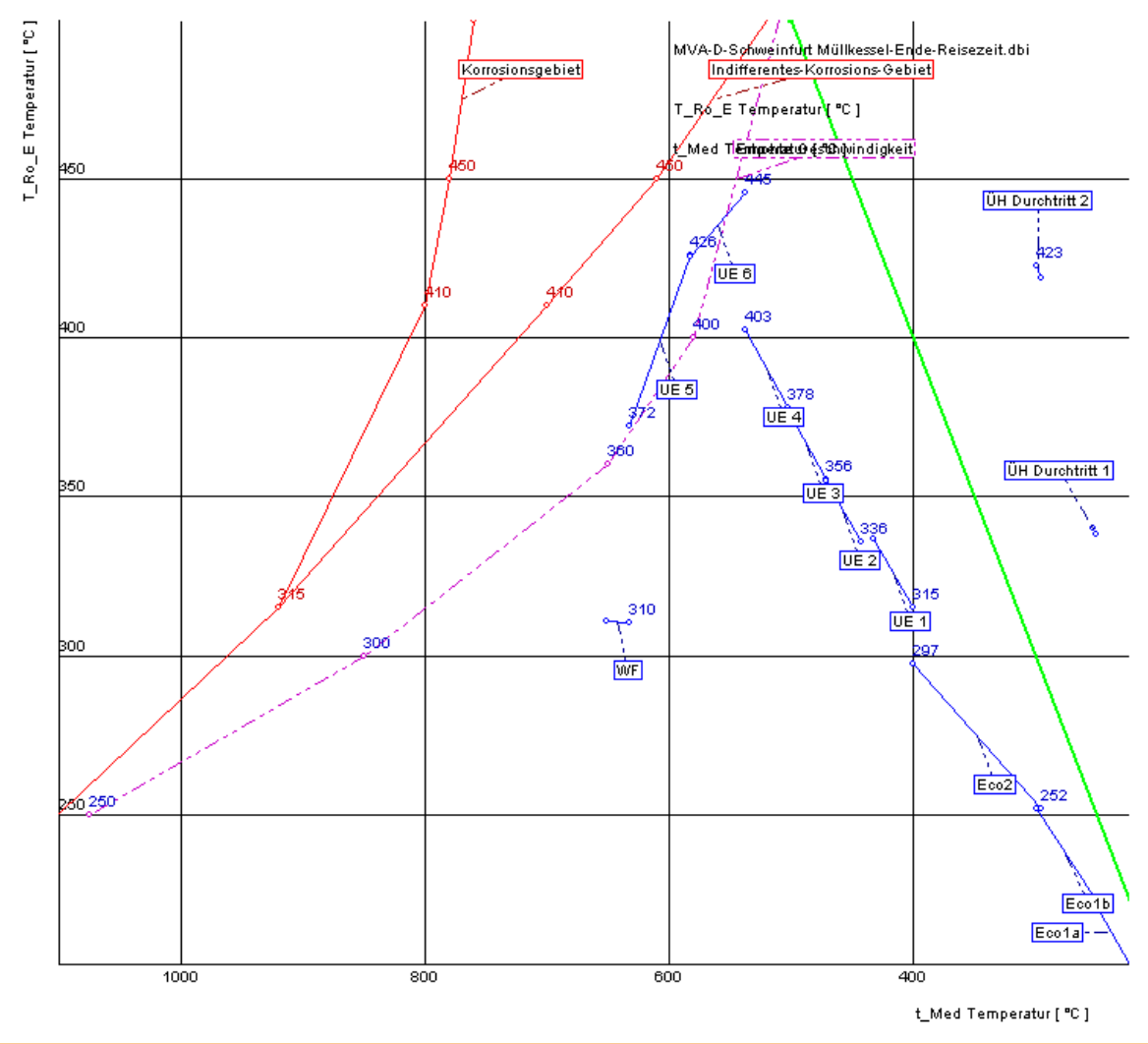
Deposits ↑

Corrosion →



This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

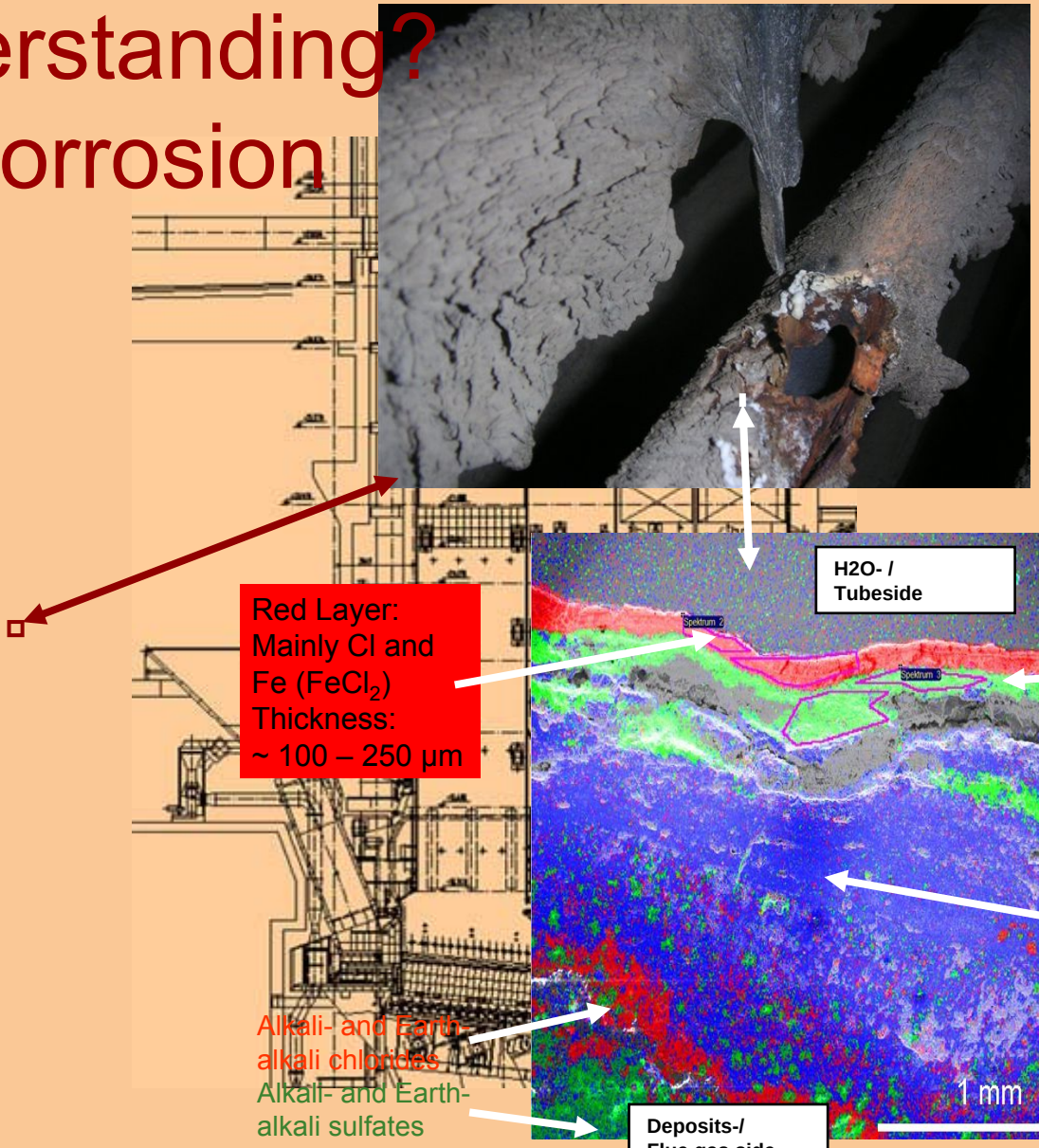
Extended Corrosion Diagram - WtE



Extended corrosion Diagram
[Warnecke, 2003]

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

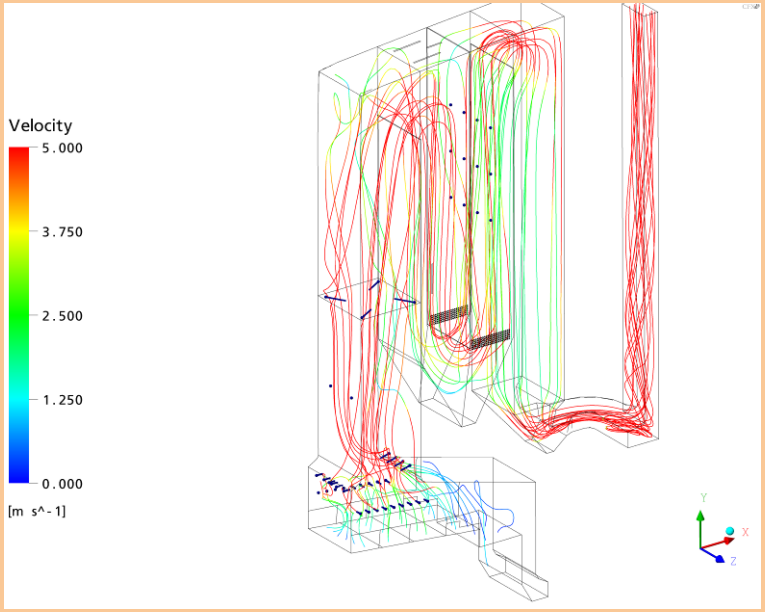
2. Understanding? HTCl-Corrosion

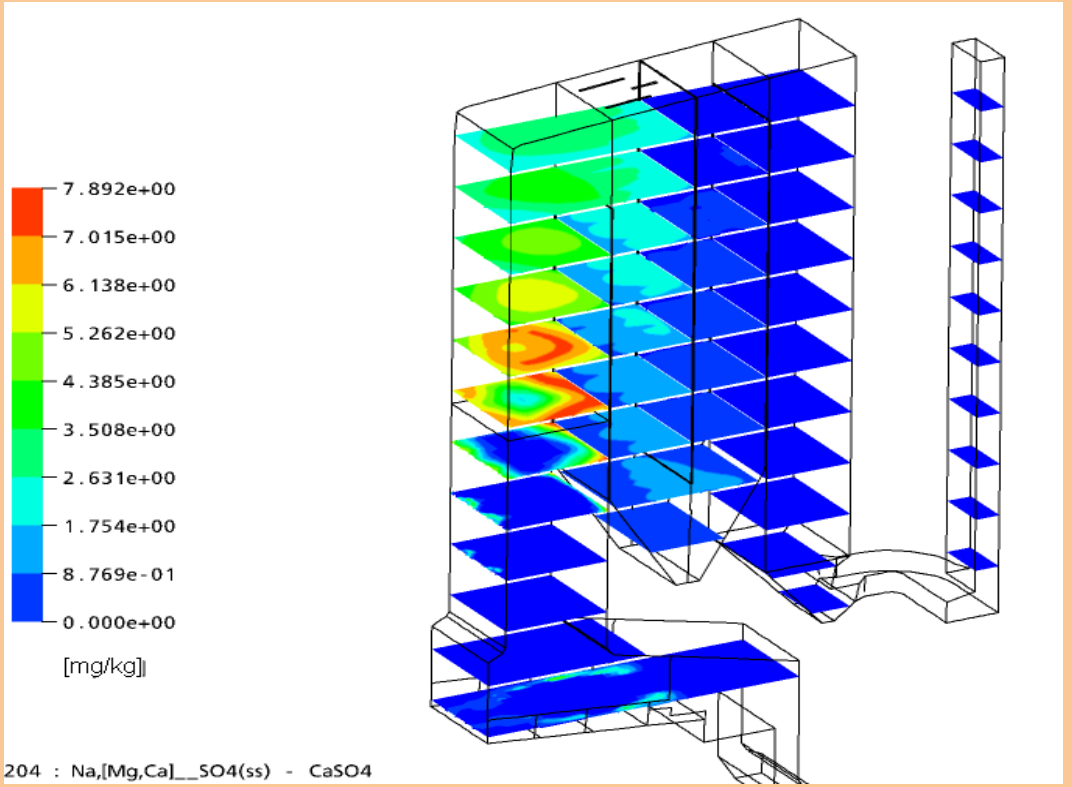


This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Examples for Coupling CFD and TEC

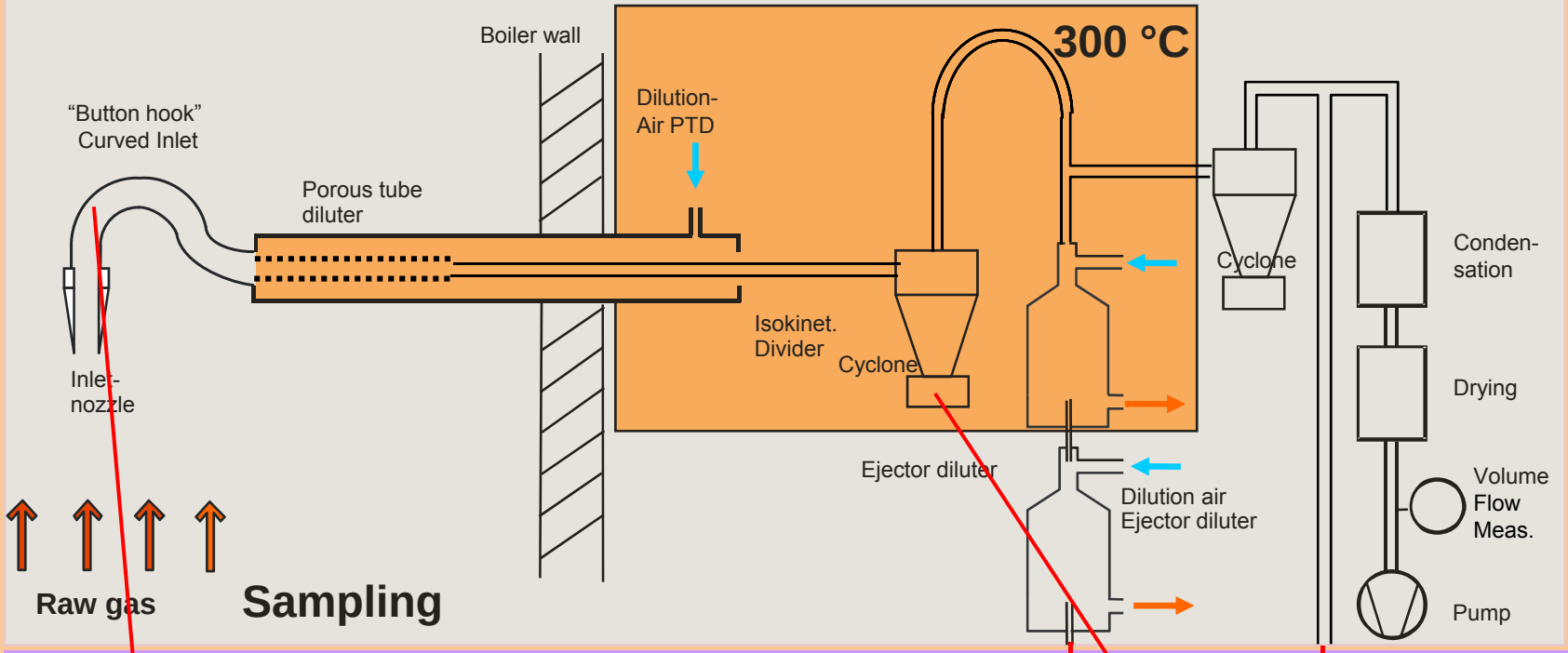
GKS-WtE-Boiler:

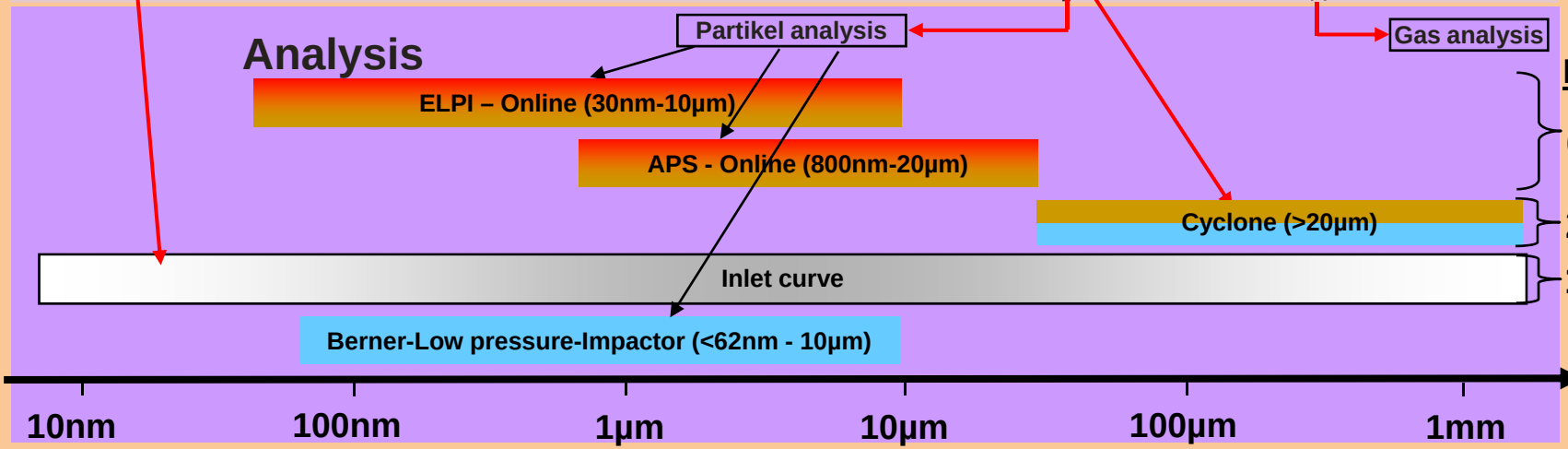




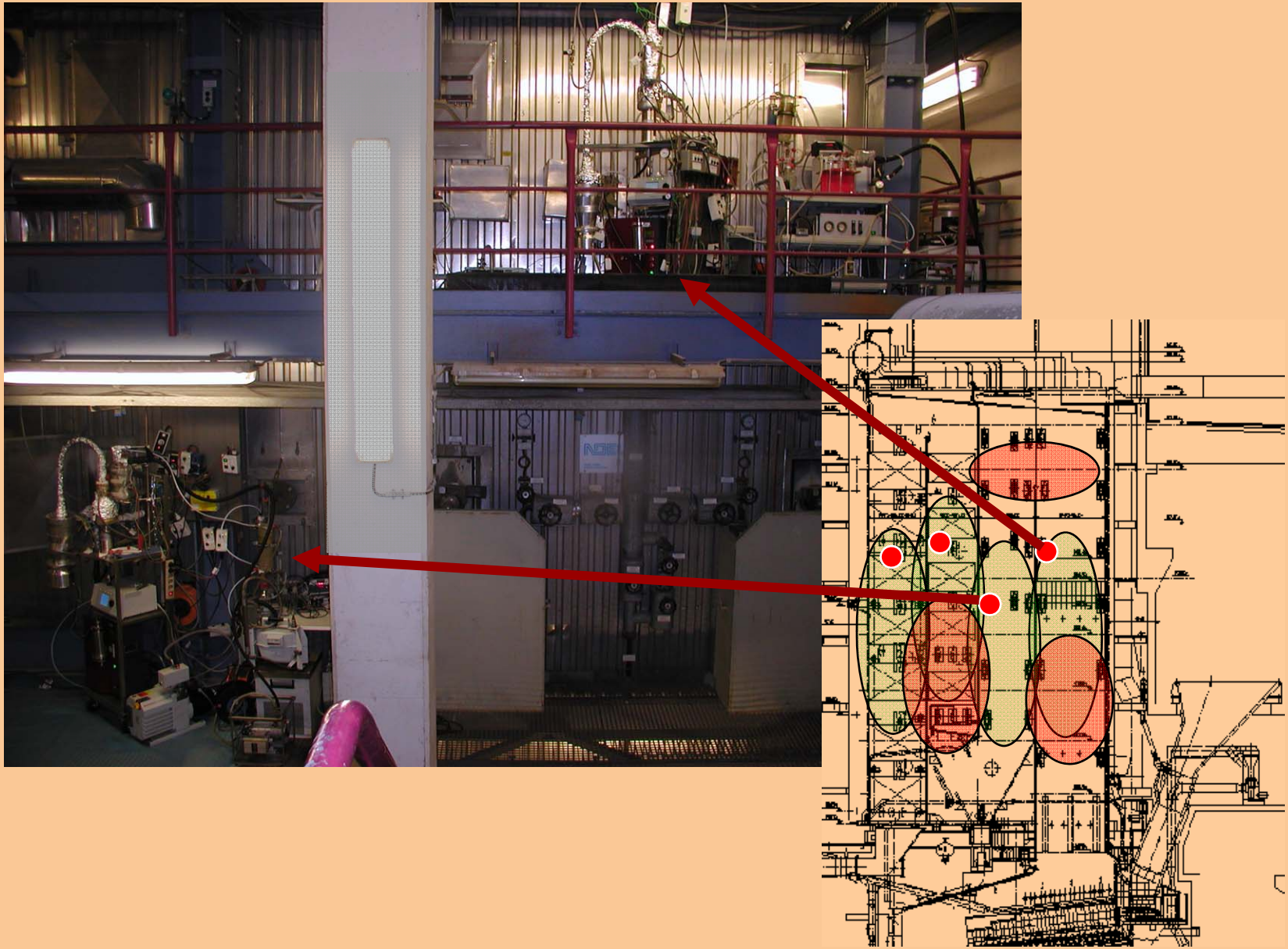
Used Programs:
CFX and FactSage

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)



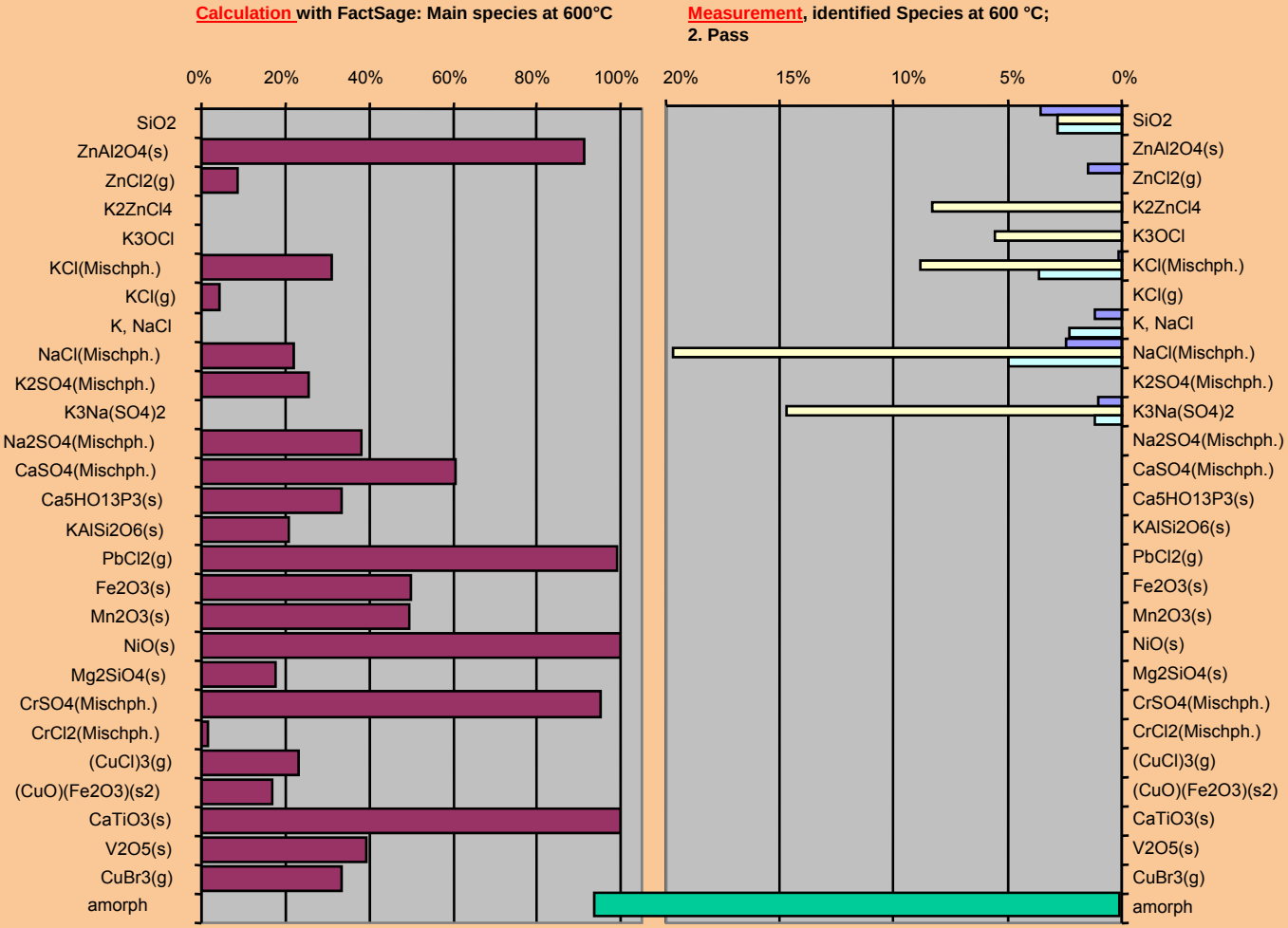


This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)



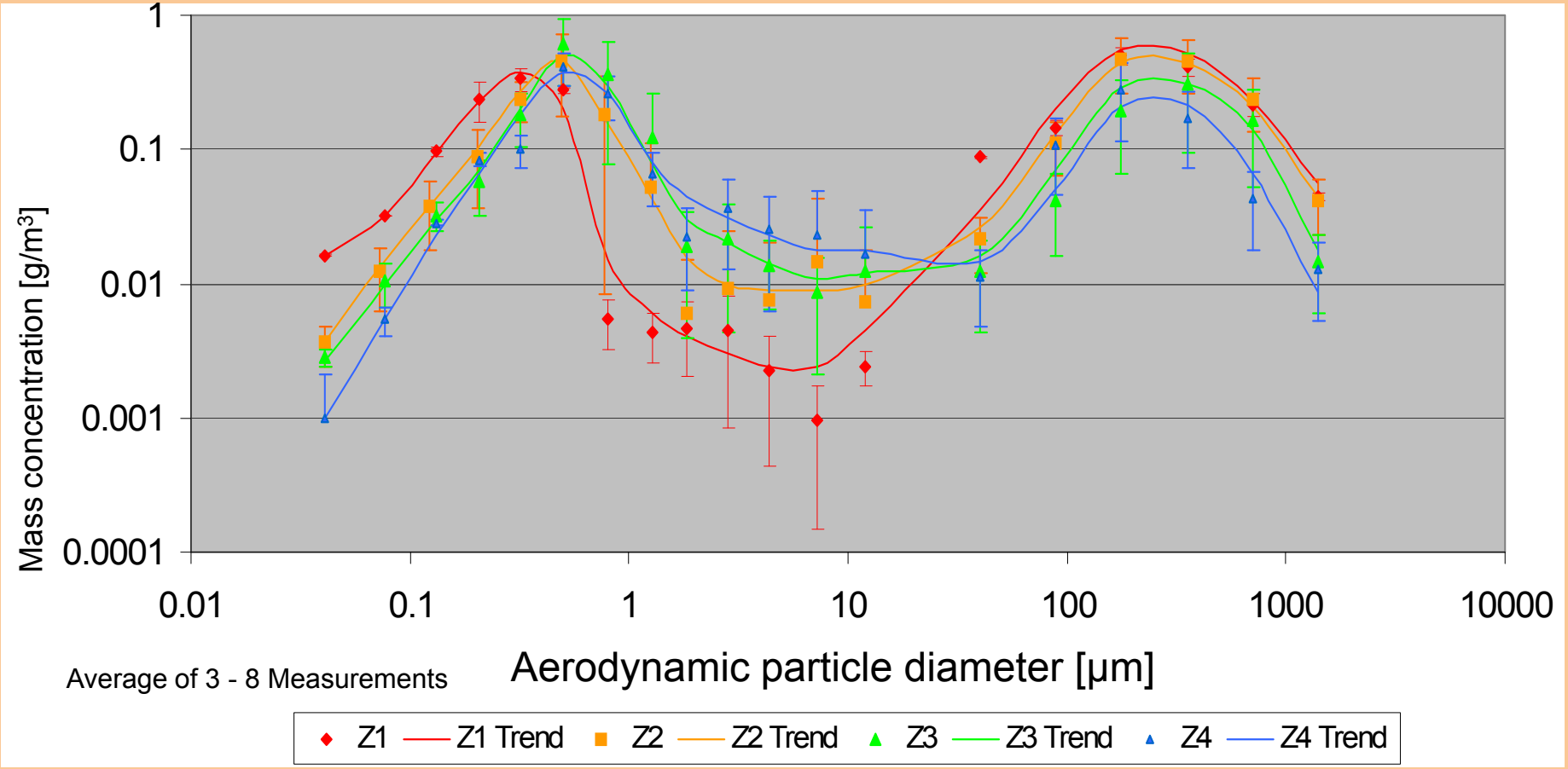
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Discrepancy: Calculation - Measurement



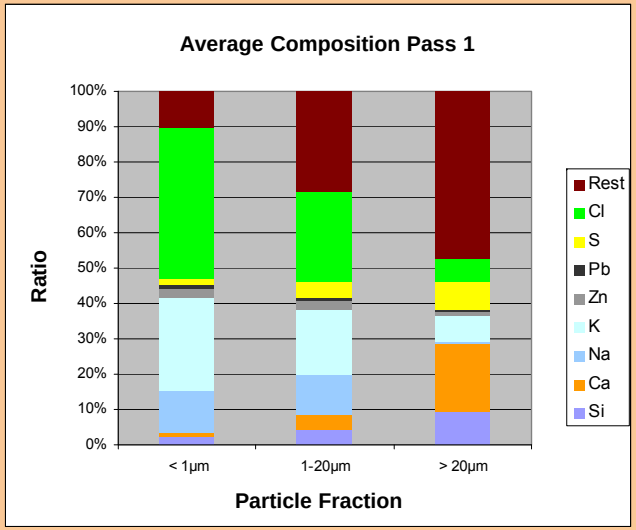
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

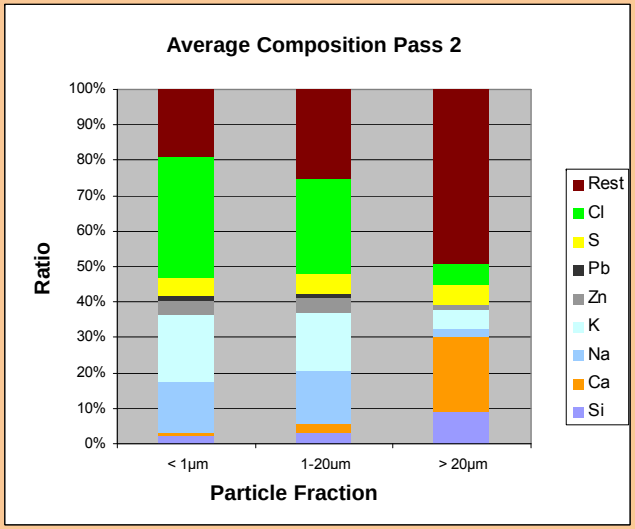
Normal Operation: Particle Distribution

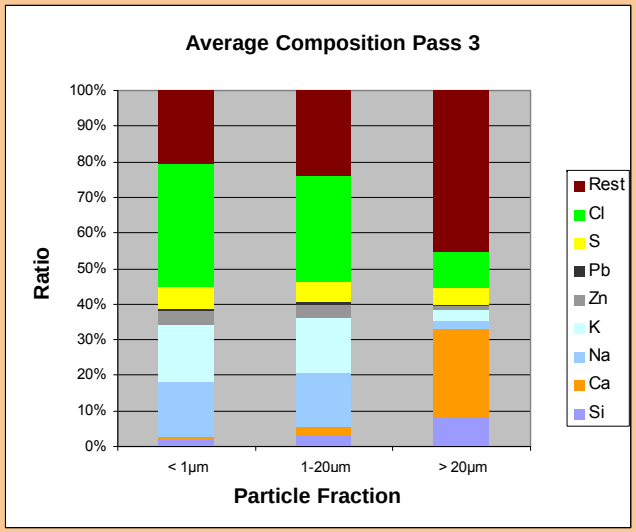


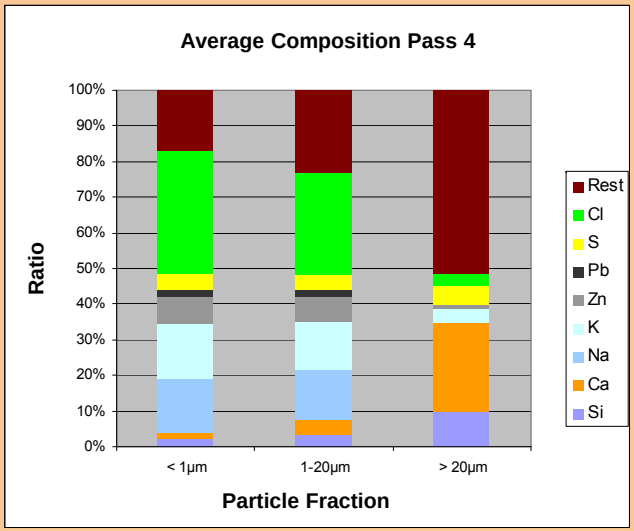
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Normal operation:
Chemical Composition of Particles – 3 Summed Fractions









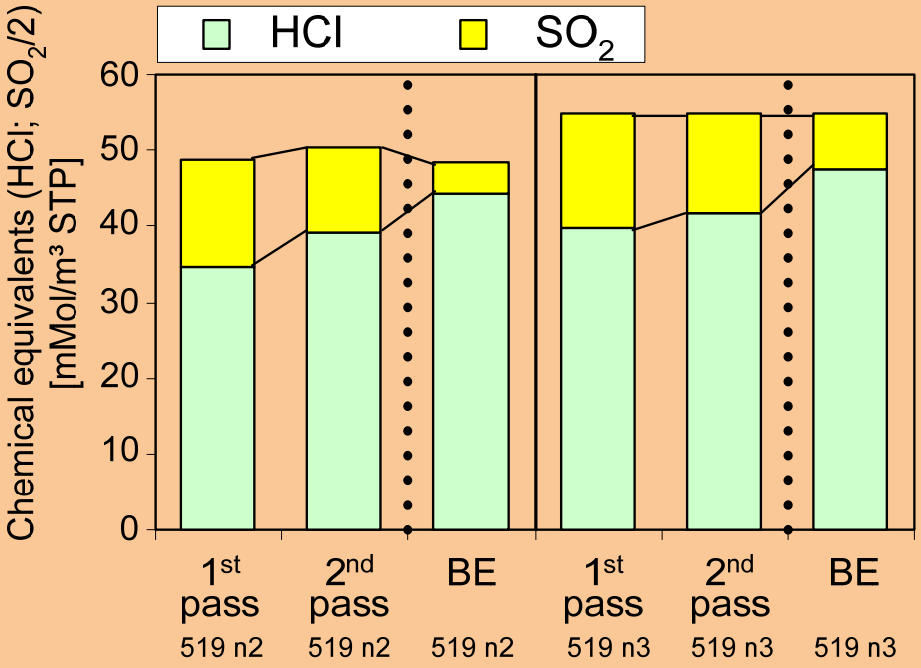
Fine fraction:
Secondary particle (Na, K, Cl)
- Cl-high, decreasing
- S-low, partially increasing

Coarse fraction:
Primary particle (Ca, Si)
- Ca-high
- "Balance" increasing

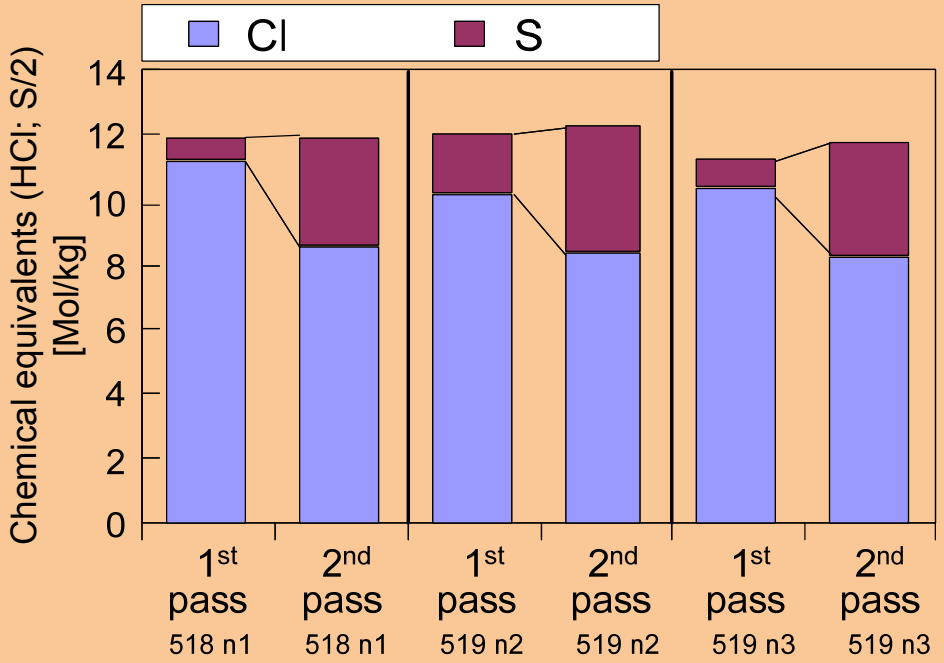
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Normal Operation: (De-)Sulphidation

Gas-phase:



Particle-phase (< 0,2 µm):

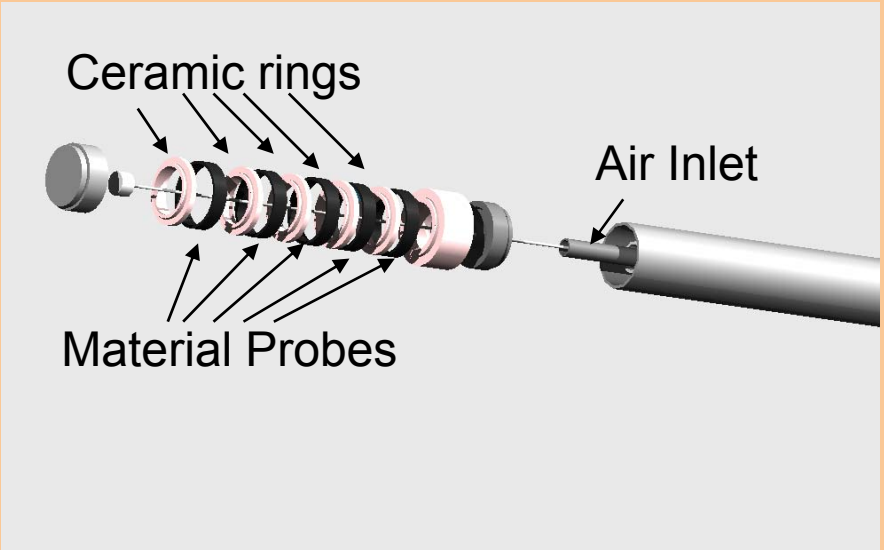


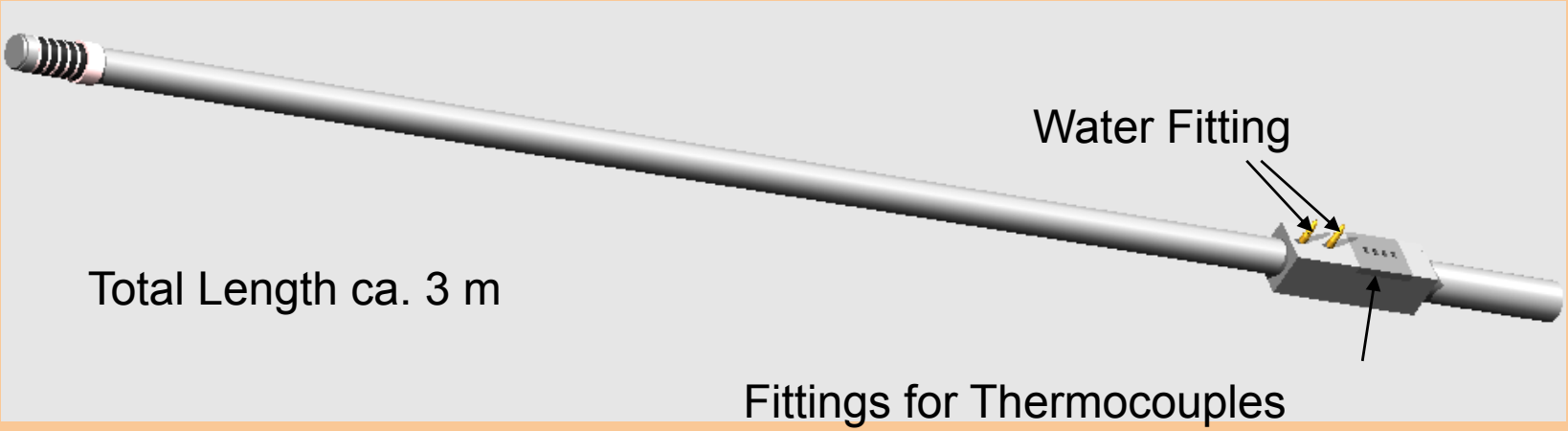
BE = Boiler End

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Corrosion Sensor

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



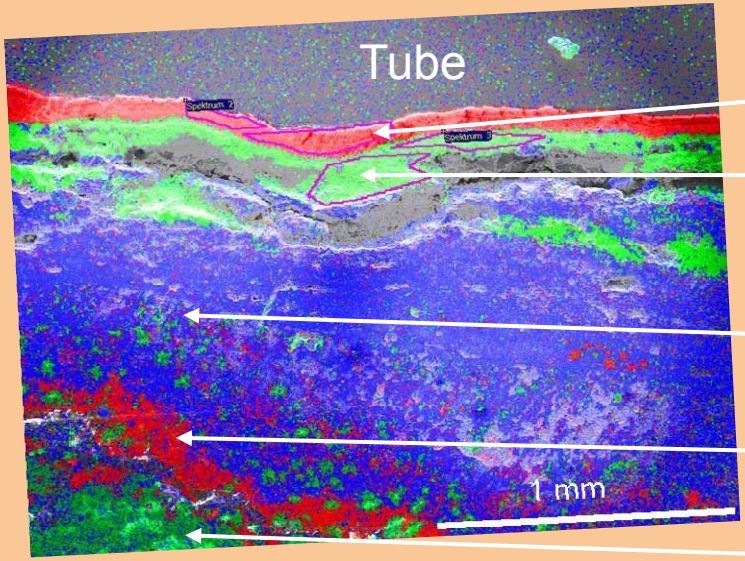


This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Comparison: Plant Tubes vs. Sensor

Example:

3 months plant tubes:



Fe_aCl_b

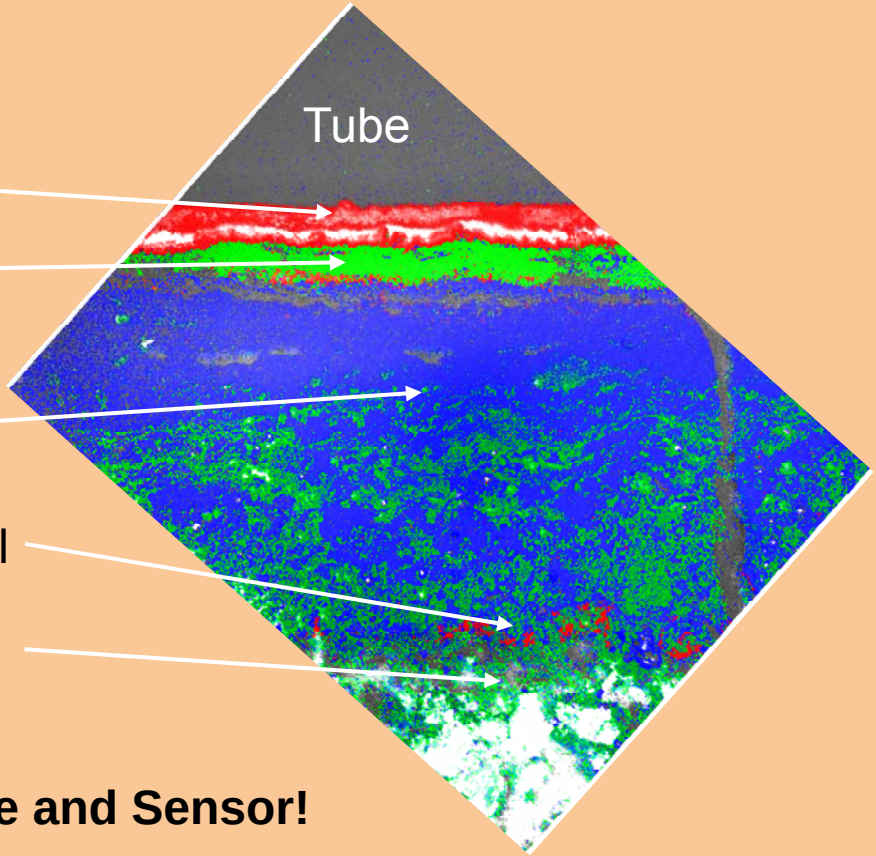
Fe_cS_d

Fe_eO_f

Alkali-Cl

Alkali-S

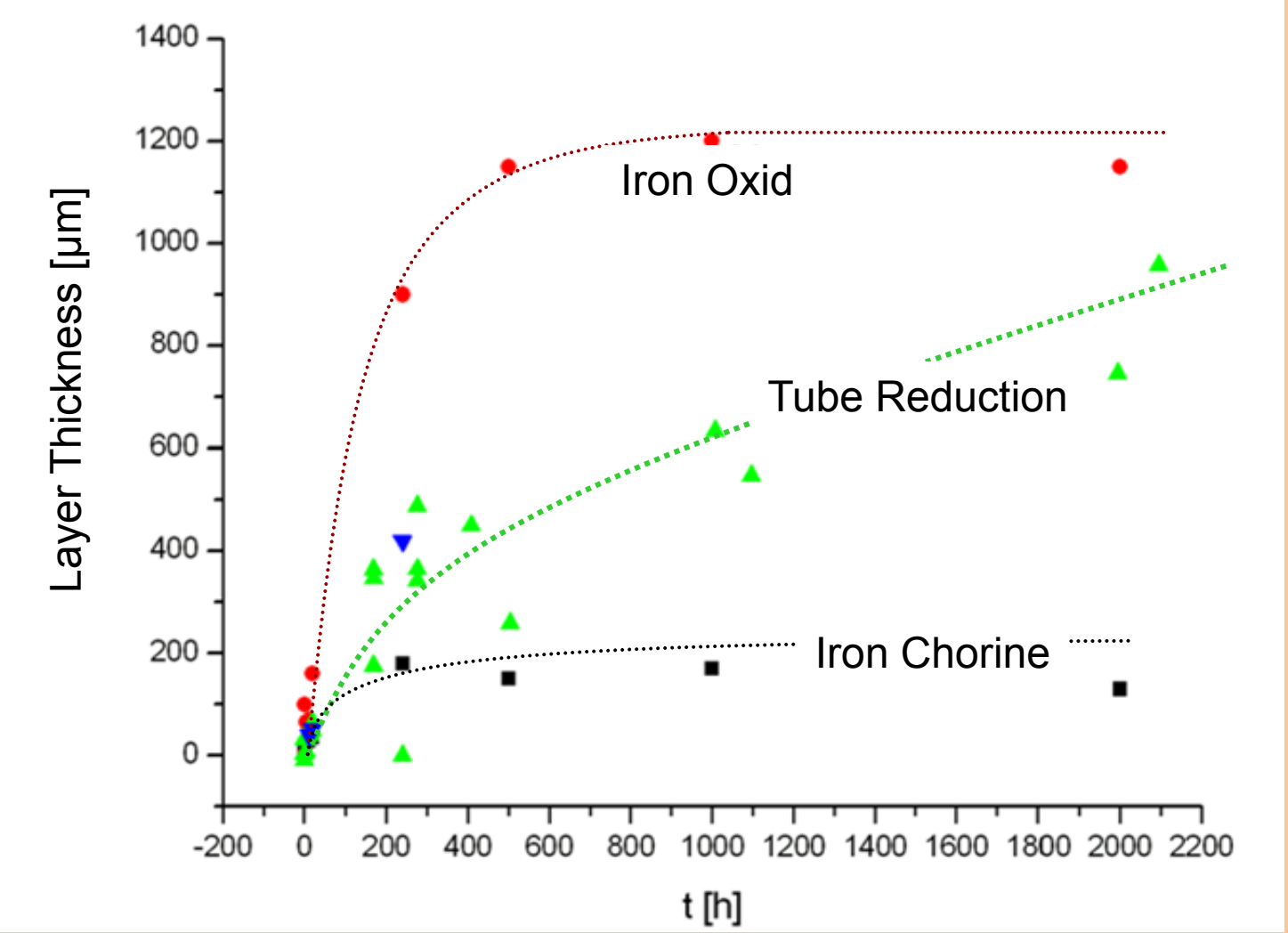
3 months sensor rings:



Identical Structure of Tube and Sensor!

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

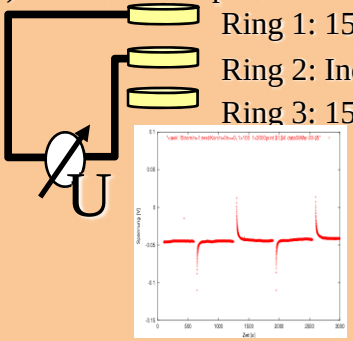
Thickness of Layers



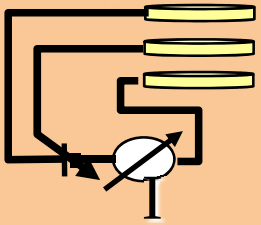
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

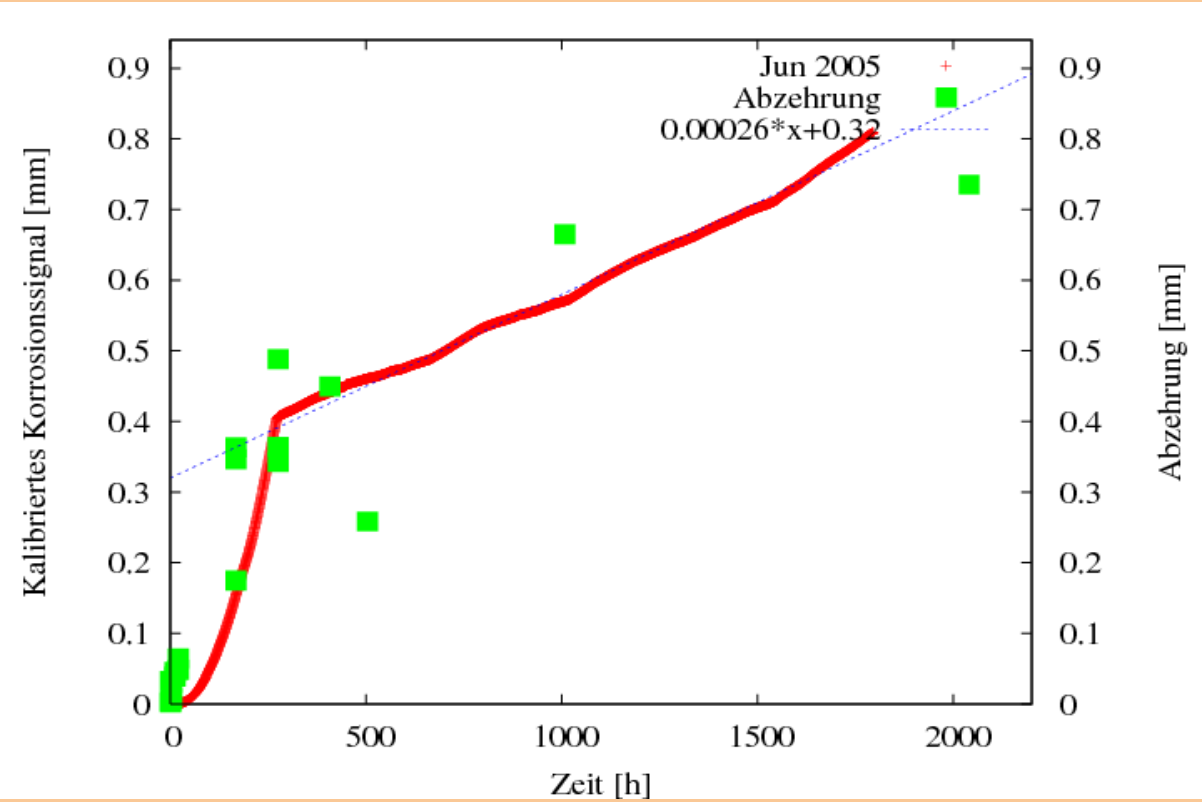
Correlation: Wall decline vs. Corr.-signal

(a) free corrosion potential



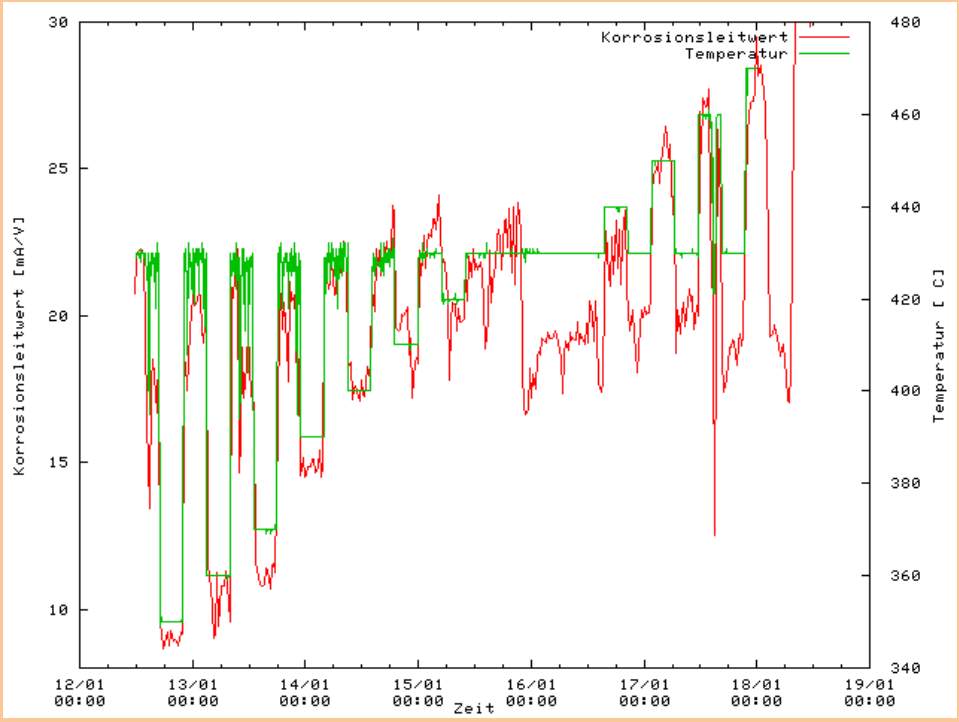
(b) power-voltage-line

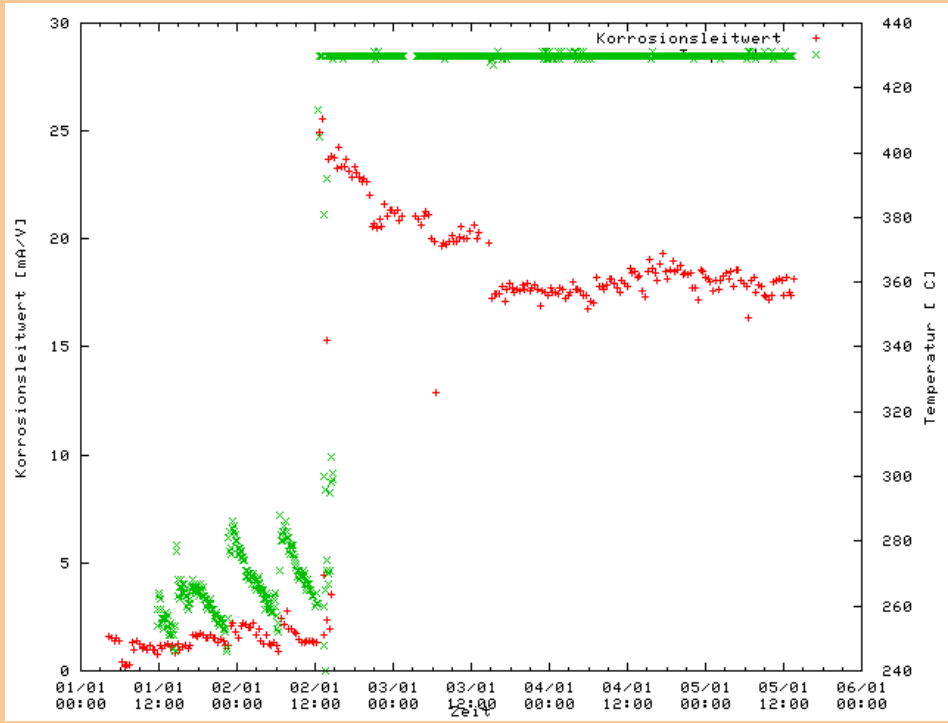




This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Sensor data – systematic temperature variation





Corrosion conductance is depending exponentially on temperature

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Reactions at boundary layers

- **15Mo3/$FeCl_2$:**

$$2FeCl_3 + Fe \rightarrow 3FeCl_2$$

•$FeCl_2$/Fe_xO_y:

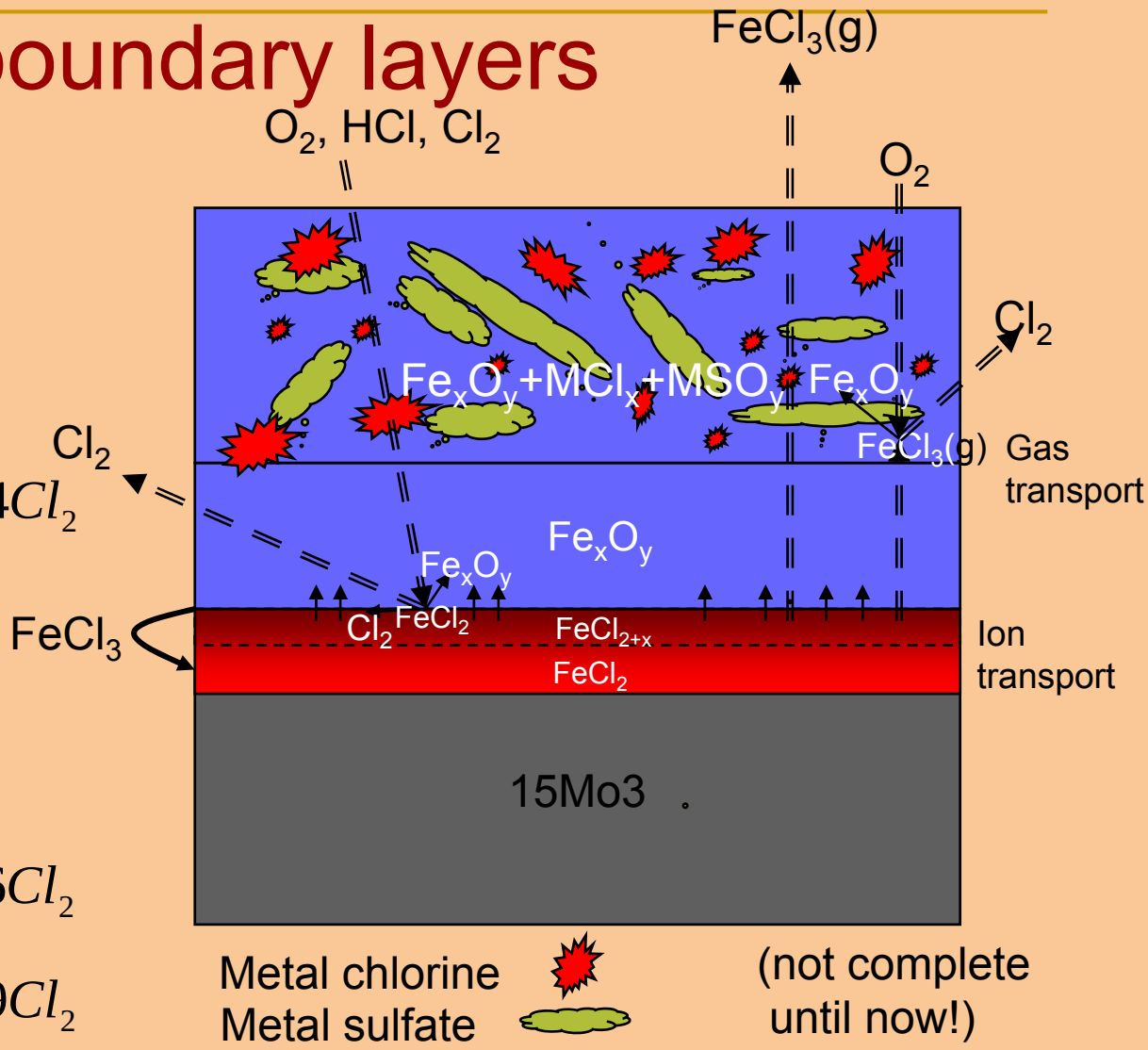
$$4FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4Cl_2$$

$$2FeCl_2 + Cl_2 \rightarrow 2Fe\,Cl_3$$

•Fe_2O_3/Fe_3O_4:

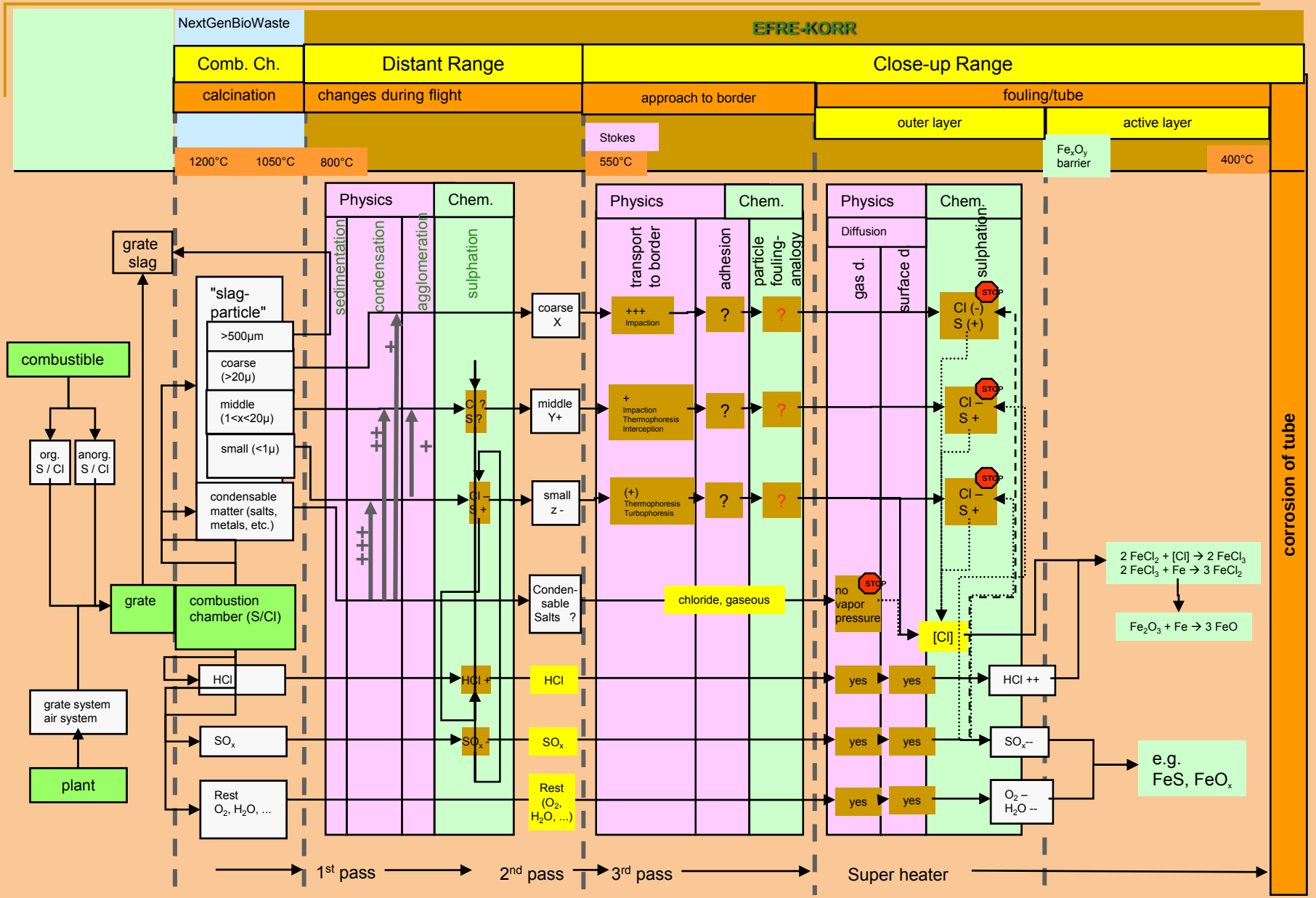
$$4FeCl_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6Cl_2$$

$$6FeCl_3 + 4O_2 \rightarrow 2Fe_3O_4 + 9Cl_2$$



$$2NaCl, 2KCl, CaCl_2 + 3SO_2 + 3O_2 \rightarrow Na_2SO_4, K_2SO_4, CaSO_4 + 3Cl_2$$

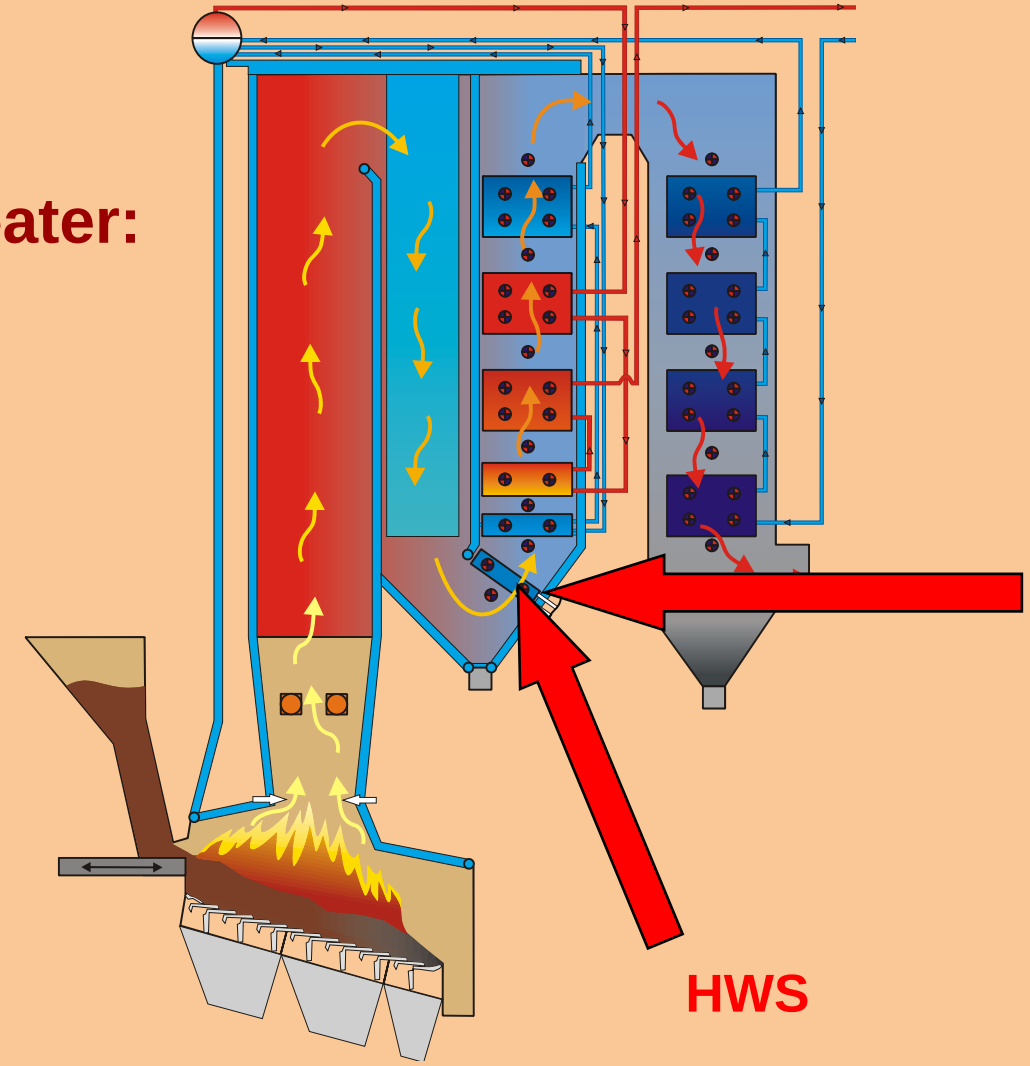
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)



This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

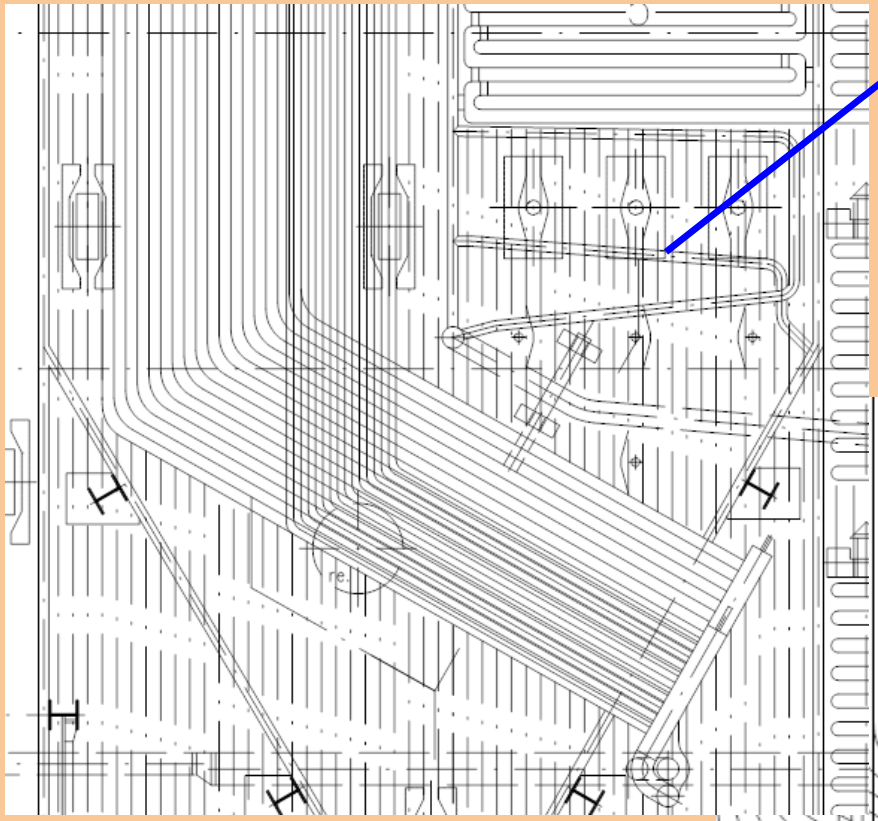
How to avoid HT-Chlorine-Corrosion?

At superheater:



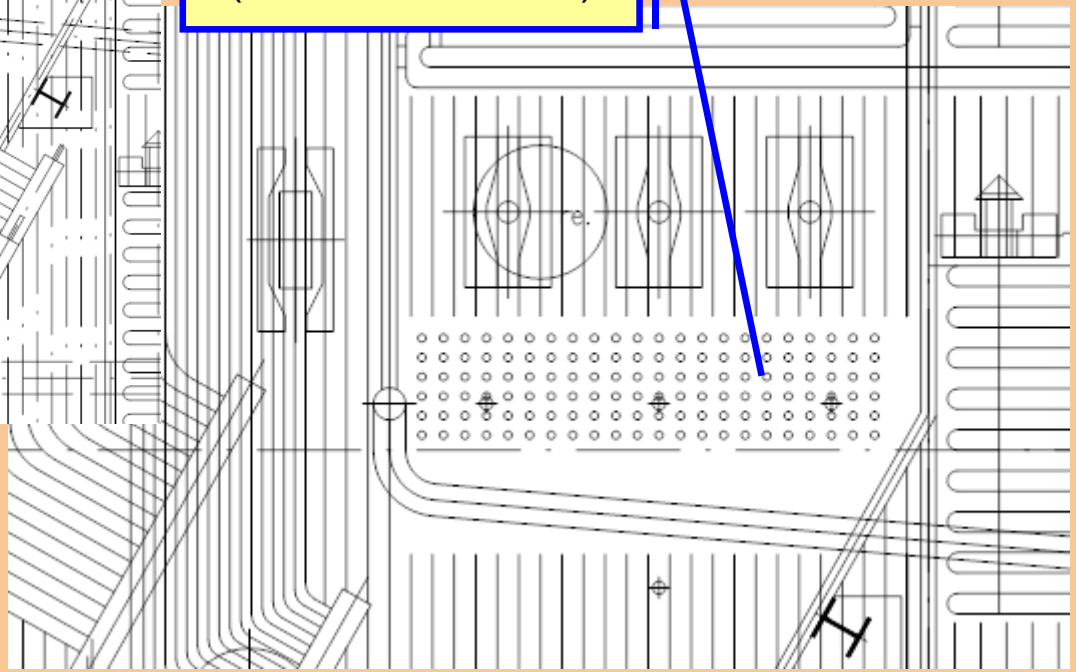
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Crossover 2./3. Pass: Chlorine Trap



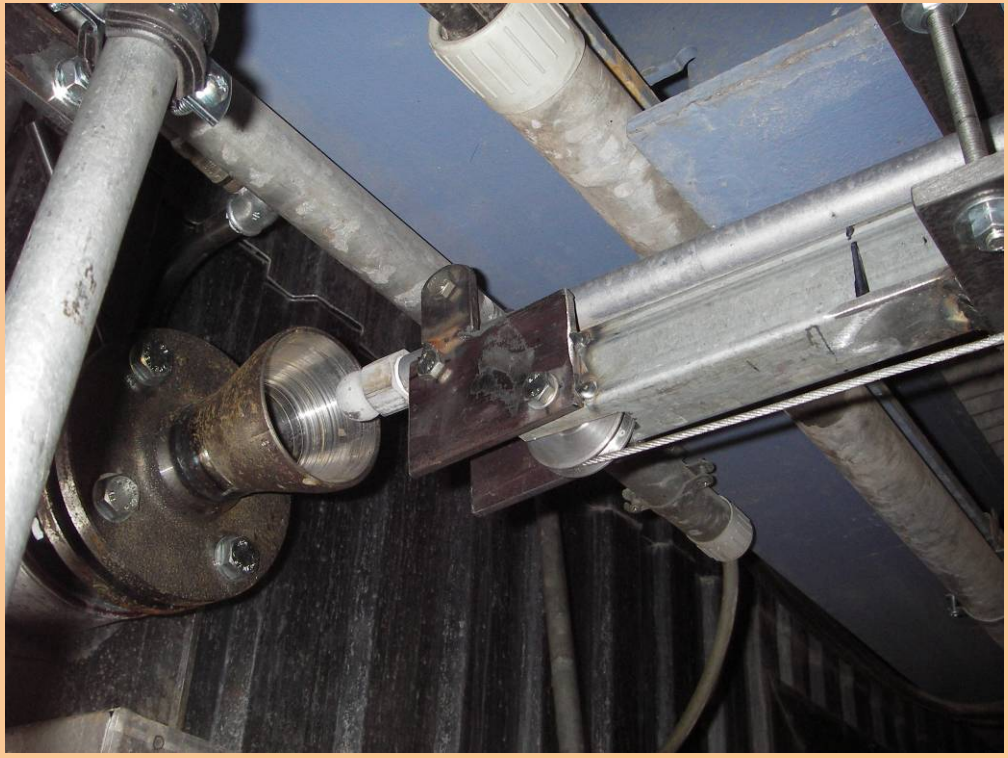
Actual situation:
3 vaporiser tubes
(distance: 400 mm)

Future condition:
T=180
(distance: 100 mm)



This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

HWS



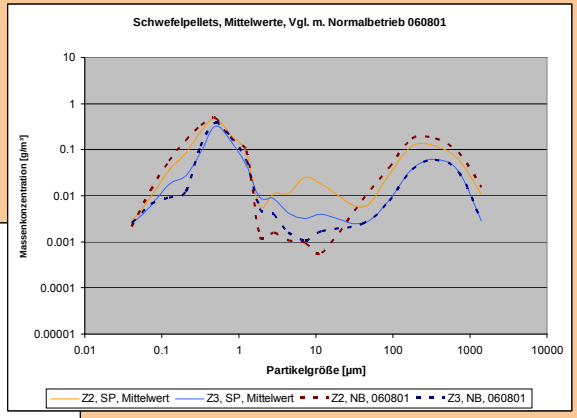
This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

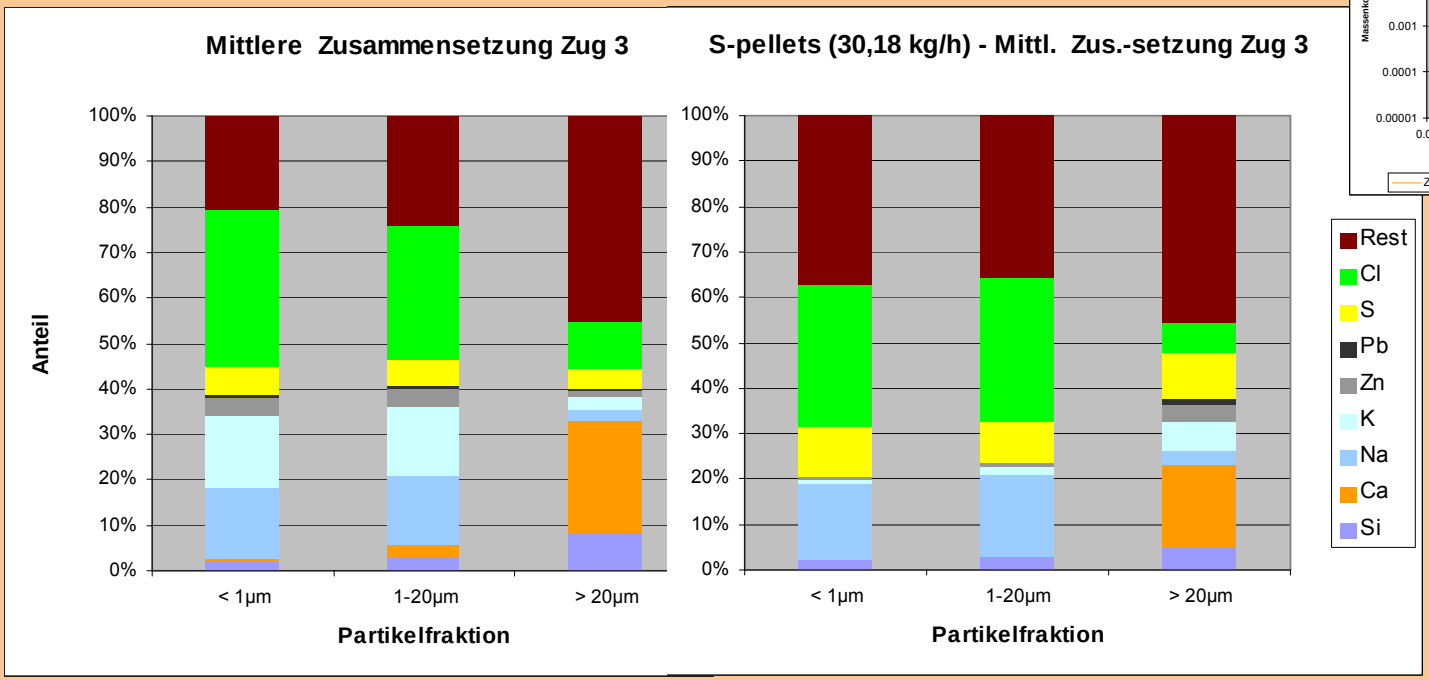
HWS – Effect of Cleaning

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

Adding Sulphur

- Direct sulphur and SO_2





→ Increasing of sulphur content, without reducing chlorine

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)

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)

This Project was co-financed by the Baverian Ministery for Environment, Health and Consumer Protection within the European Regional Development Fund (ERDF)