High Temperature Chlorine Corrosion as a Result of Incineration of Contaminated Fuel

- Reasons, Mechanisms and Solutions -

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1. Principles
2. Fuel, combustion chamber and boiler
3. Processes at the Corrosion Boundary Layer
4. Measurements against HTC-Corrosion
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1. Principles

GKS – Waste-to-Energy Plant

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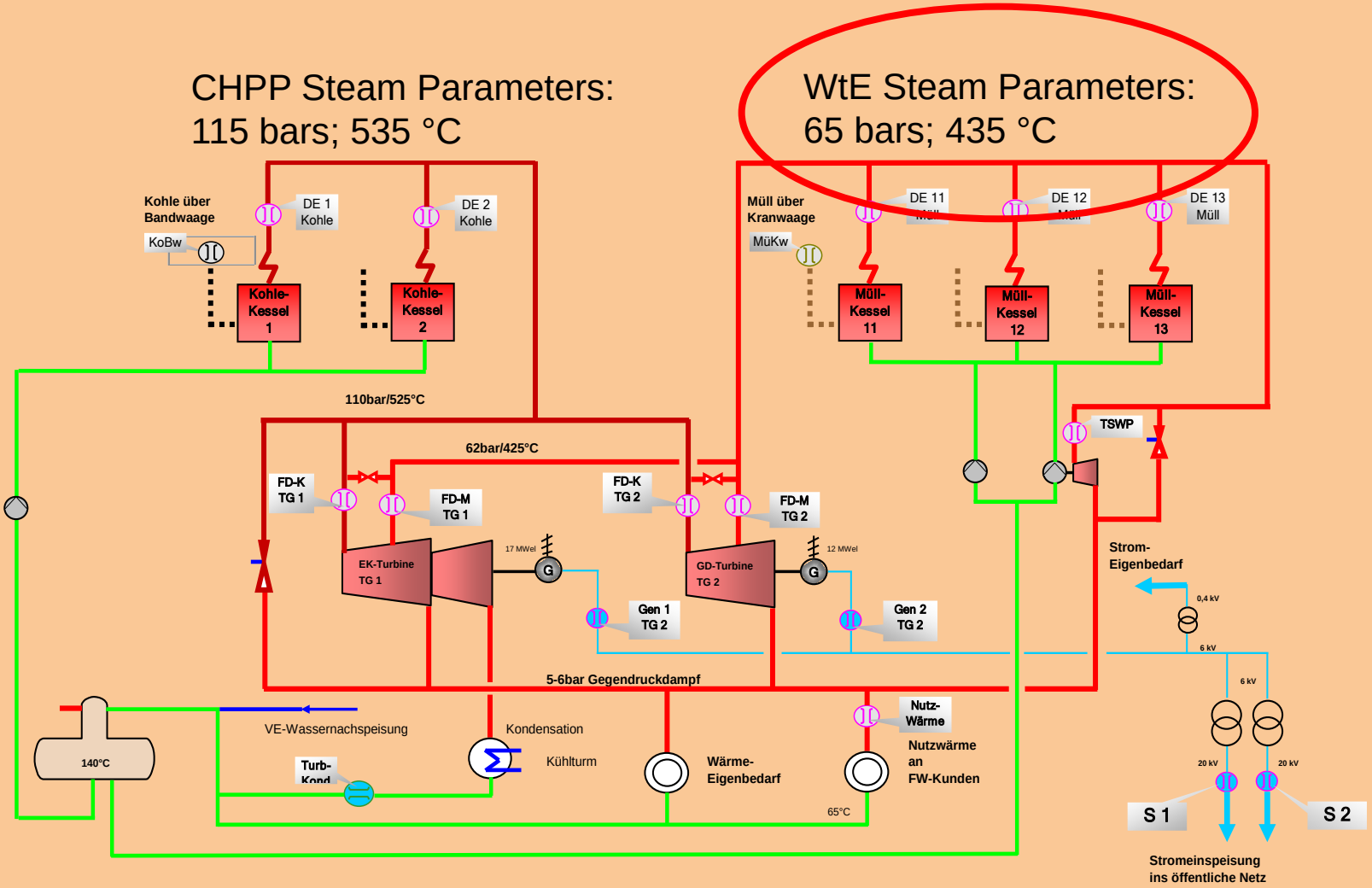
Flow Chart of GKS GmbH

CHPP Steam Parameters:
115 bars; 535 °C

WtE Steam Parameters:
65 bars; 435 °C



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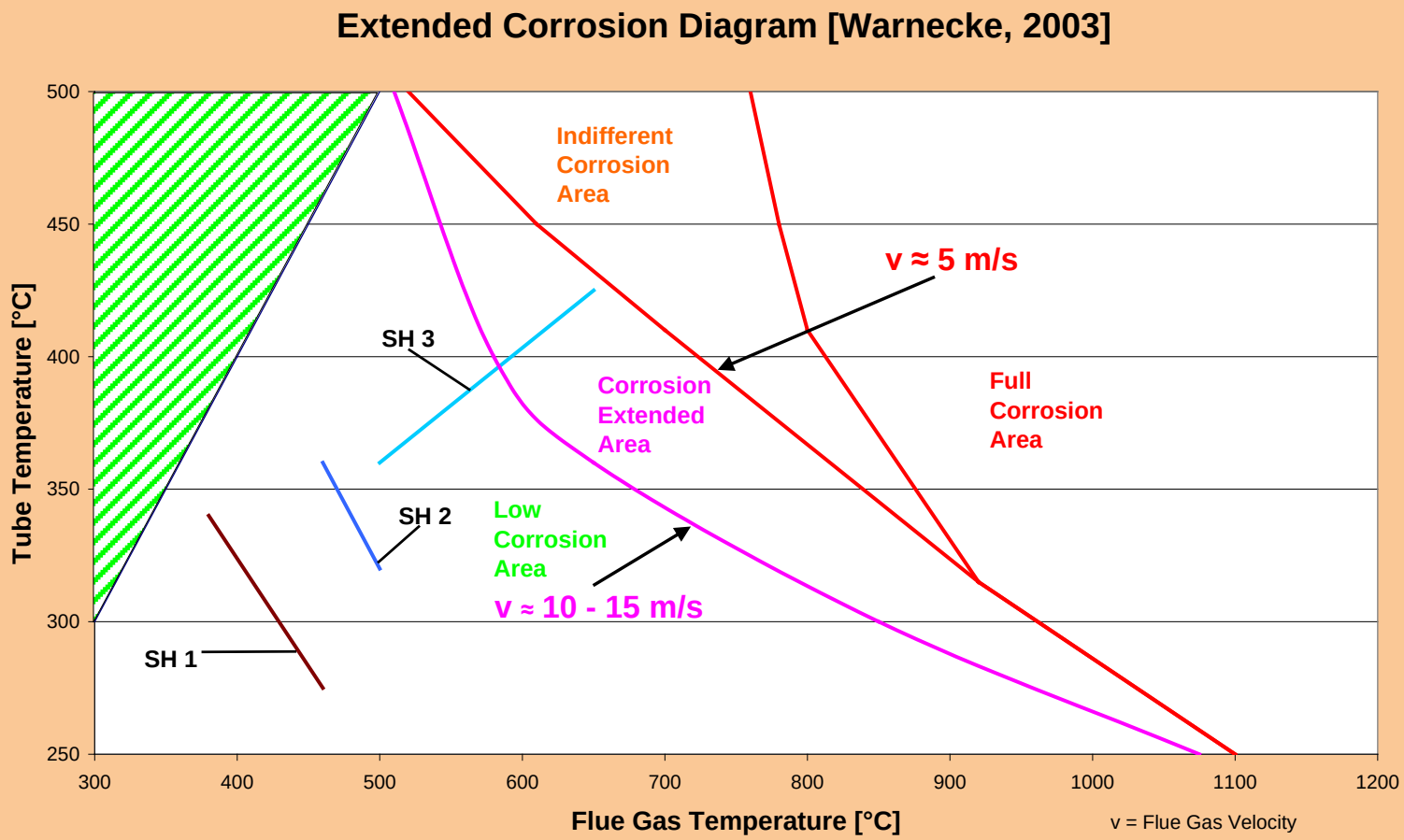
Extended Corrosion Diagram



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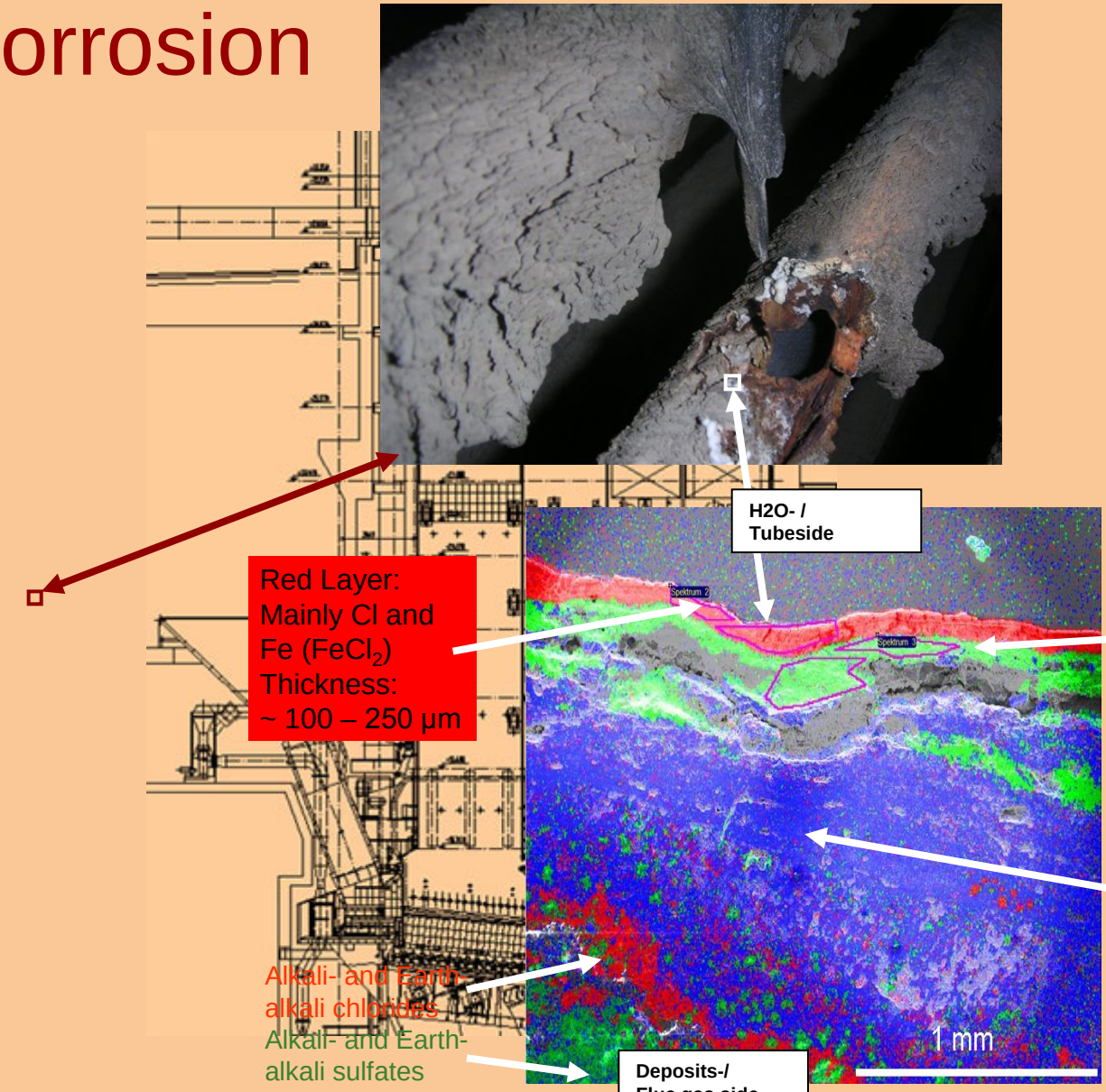
HTC-Corrosion



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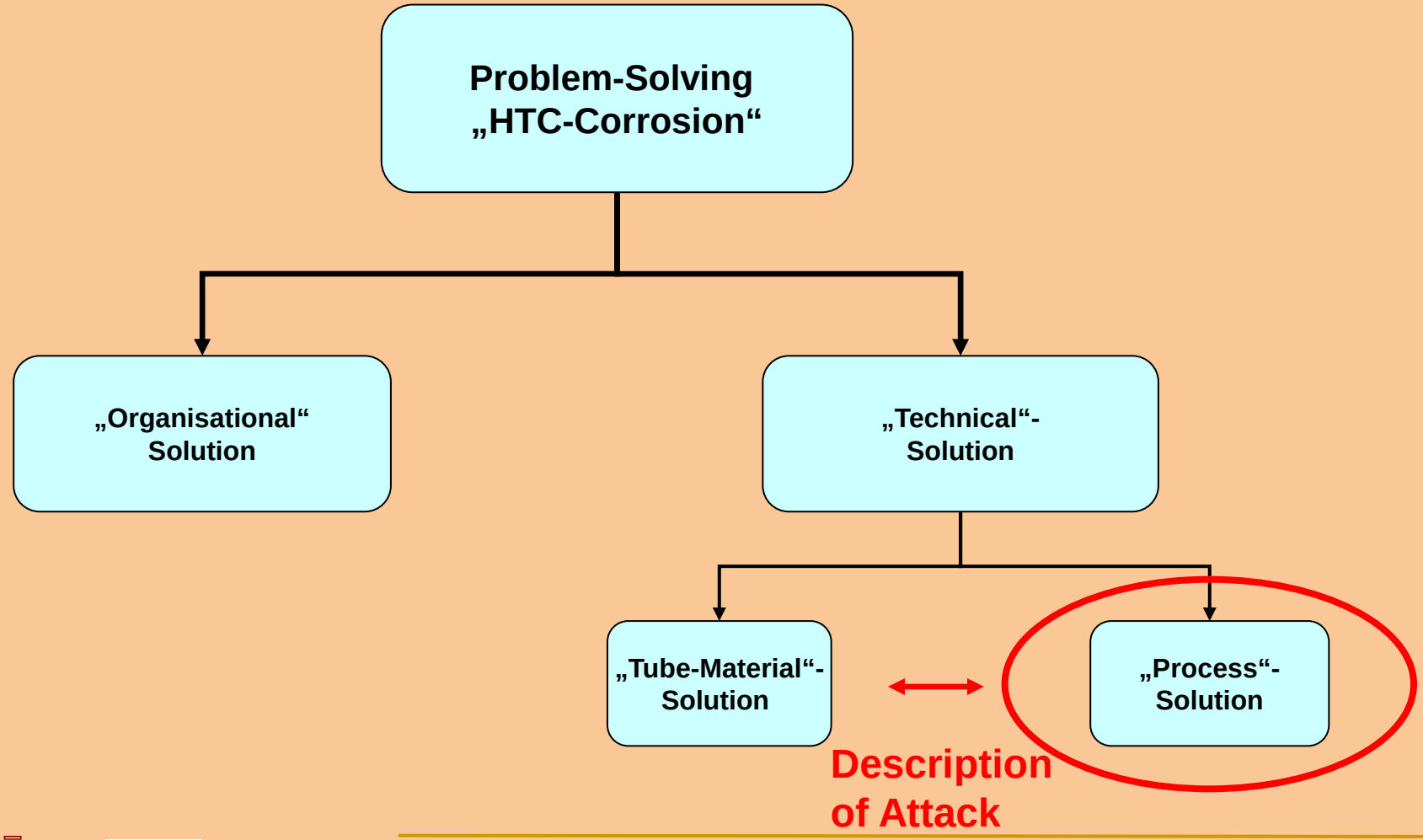
Problem Solving - Strategies



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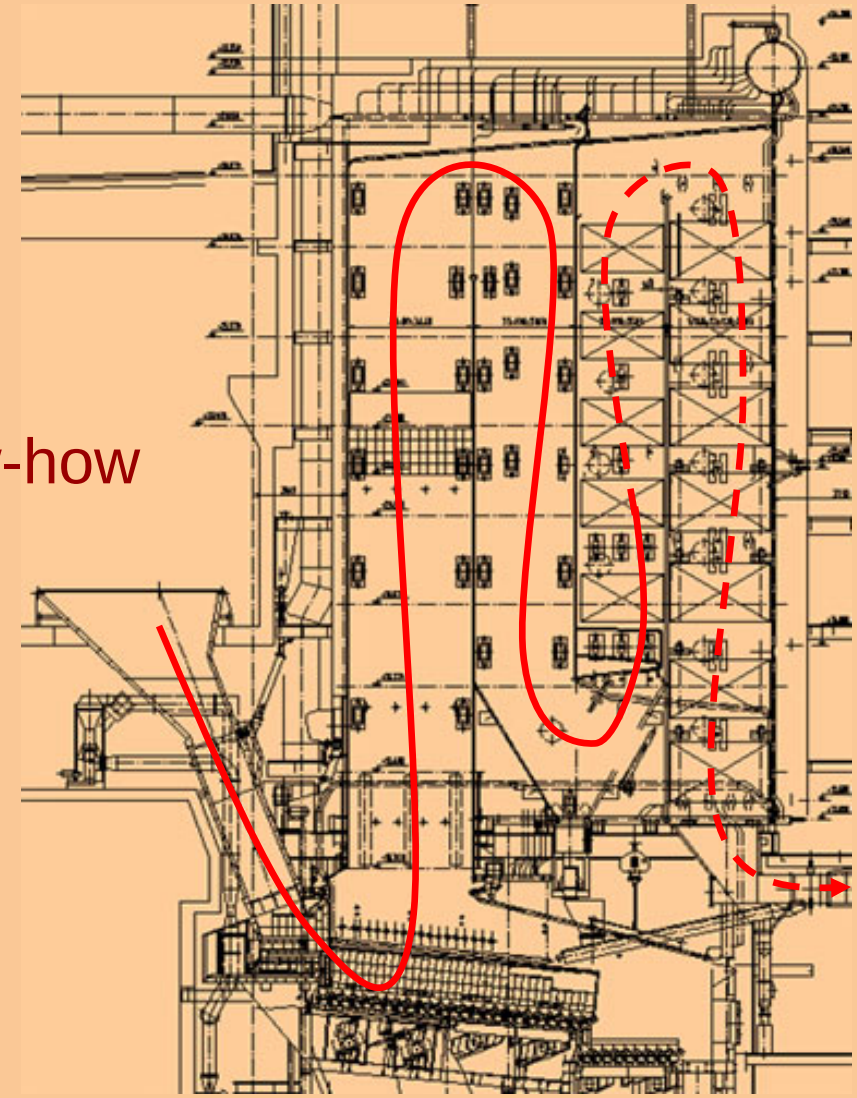
2. Fuel, combustion chamber and boiler

Process Know-how



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Global Release of Minor Components

	Waste		Bottom ash	Boiler ash	Fly ash	Scrub. Res.	Emissions
GKS [kg/Mg]	1.000,000		250,000	7,000	7,000	20,000	0,010
Vehlow [kg/Mg]	1.000,000		250,000	3,000	12,000	11,000	0,050
			transfer factor (to residue)				
Element	**Waste**		**Bottom ash**	**Boiler ash**	**Fly ash**	**Scrub. Res.**	**Emissions**
	Concentration [mg element / kg waste]	Concentration [kg element / kg element waste content]					
S	4000	1,000	0,350	0,020	0,250	0,350	0,030
Cl	**7000**	**1,000**	**0,100**	**0,003**	**0,100**	**0,800**	**0,005**
Pb	700	1,000	0,670	0,010	0,300	0,010	0,010
Zn	1300	1,000	0,615	0,017	0,392	0,000	0,000
K	5000	1,000	0,750	0,024	0,120	0,000	0,001
Na	8000	1,000	0,938	0,008	0,030	0,000	0,000
Ca	26000	1,000	0,942	0,011	0,044	0,000	0,000

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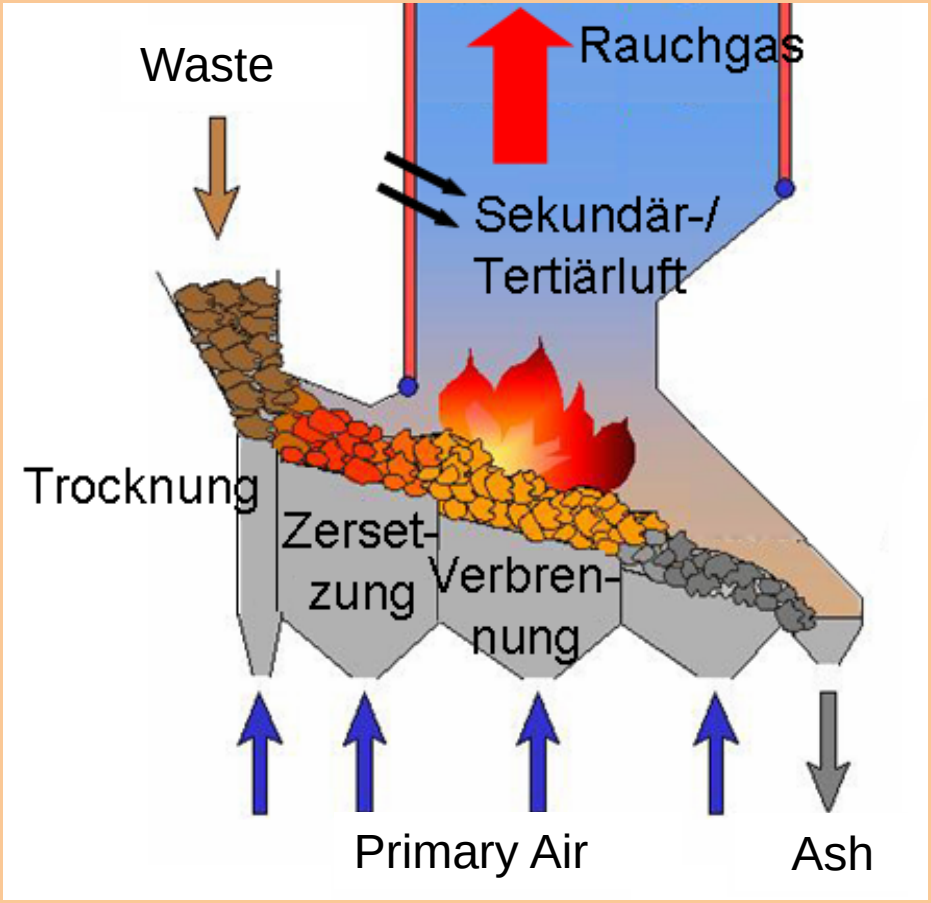
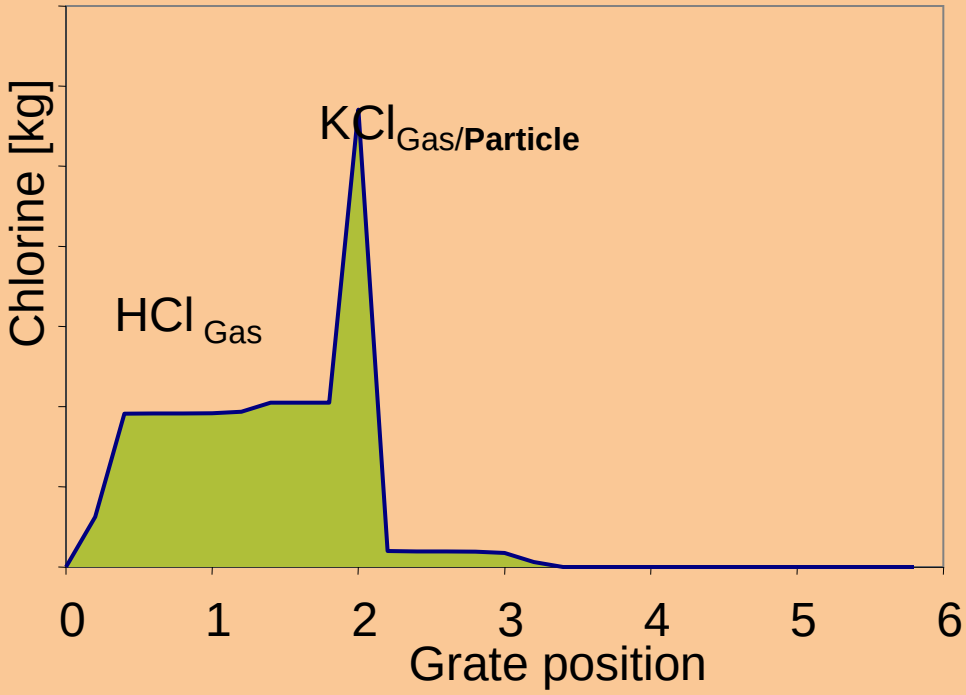
Release of Chlorines





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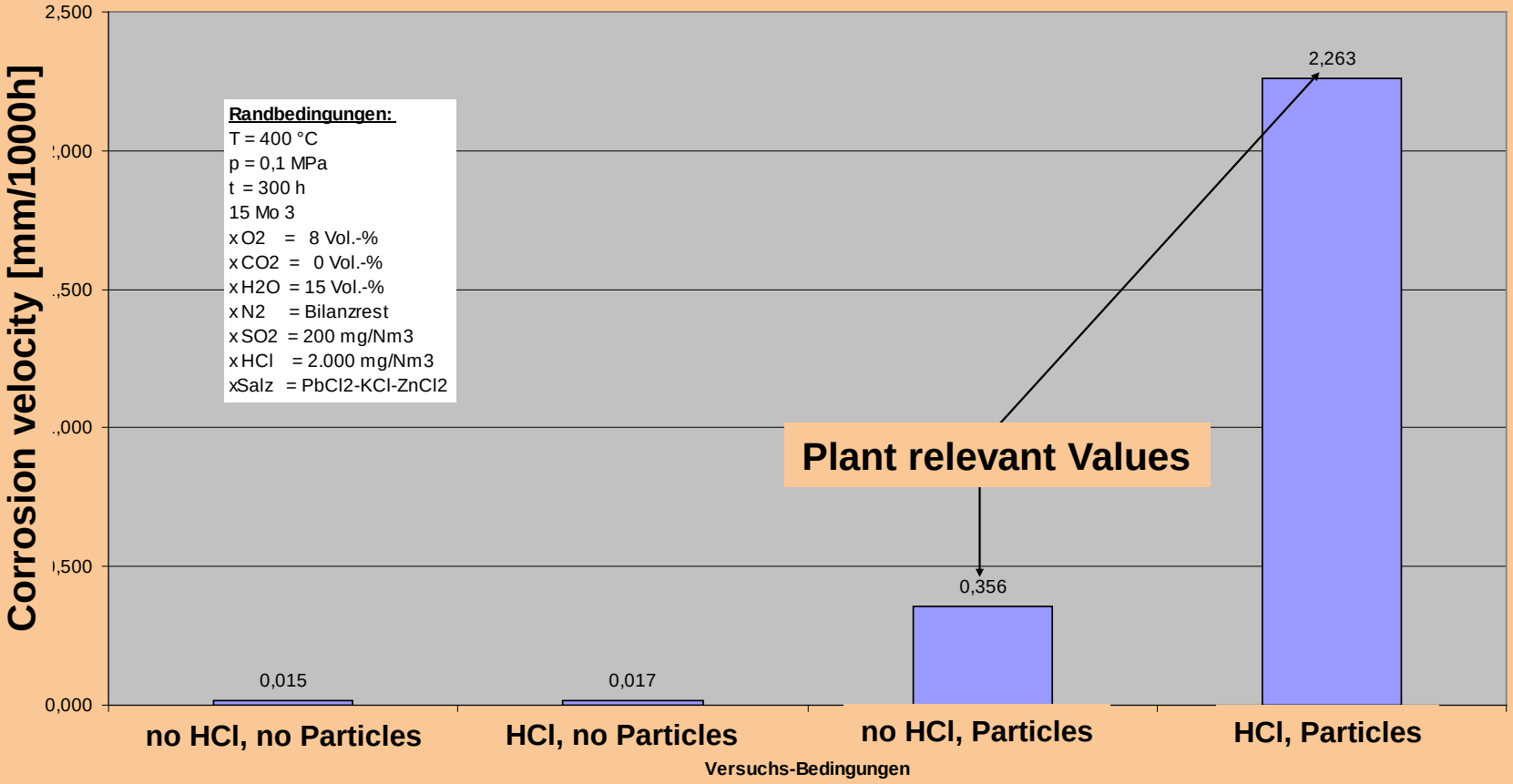
Relevance of Particles



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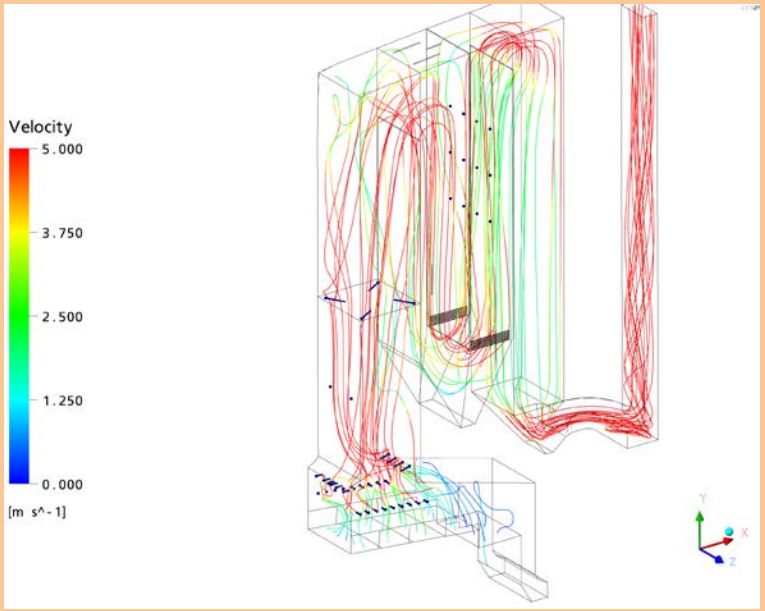
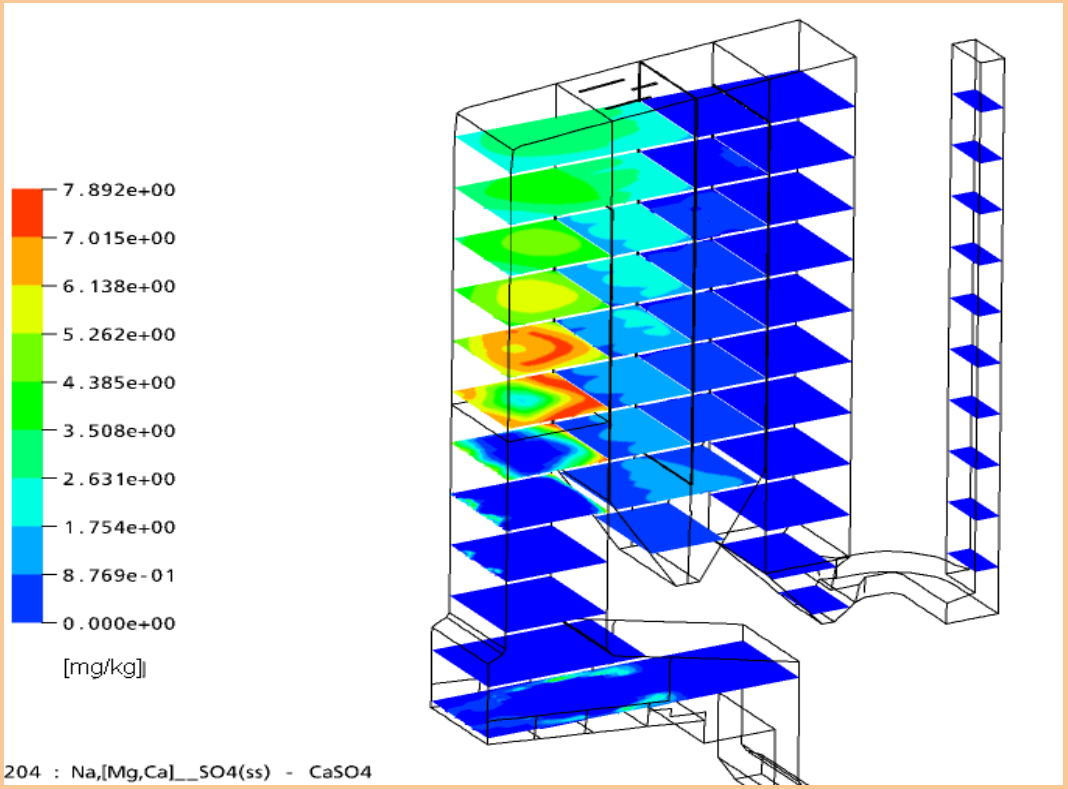
Examples for Coupling CFD and TEC





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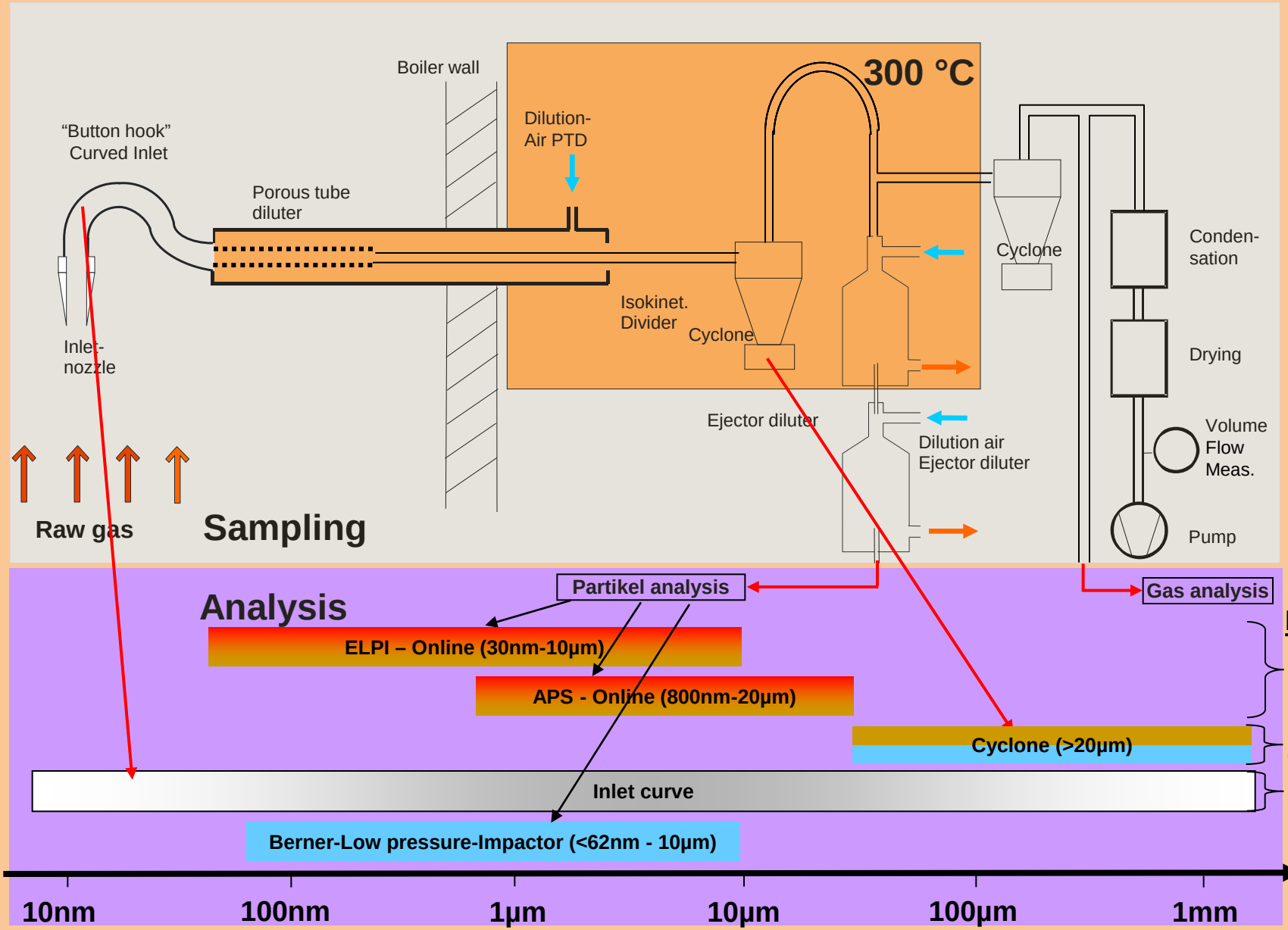

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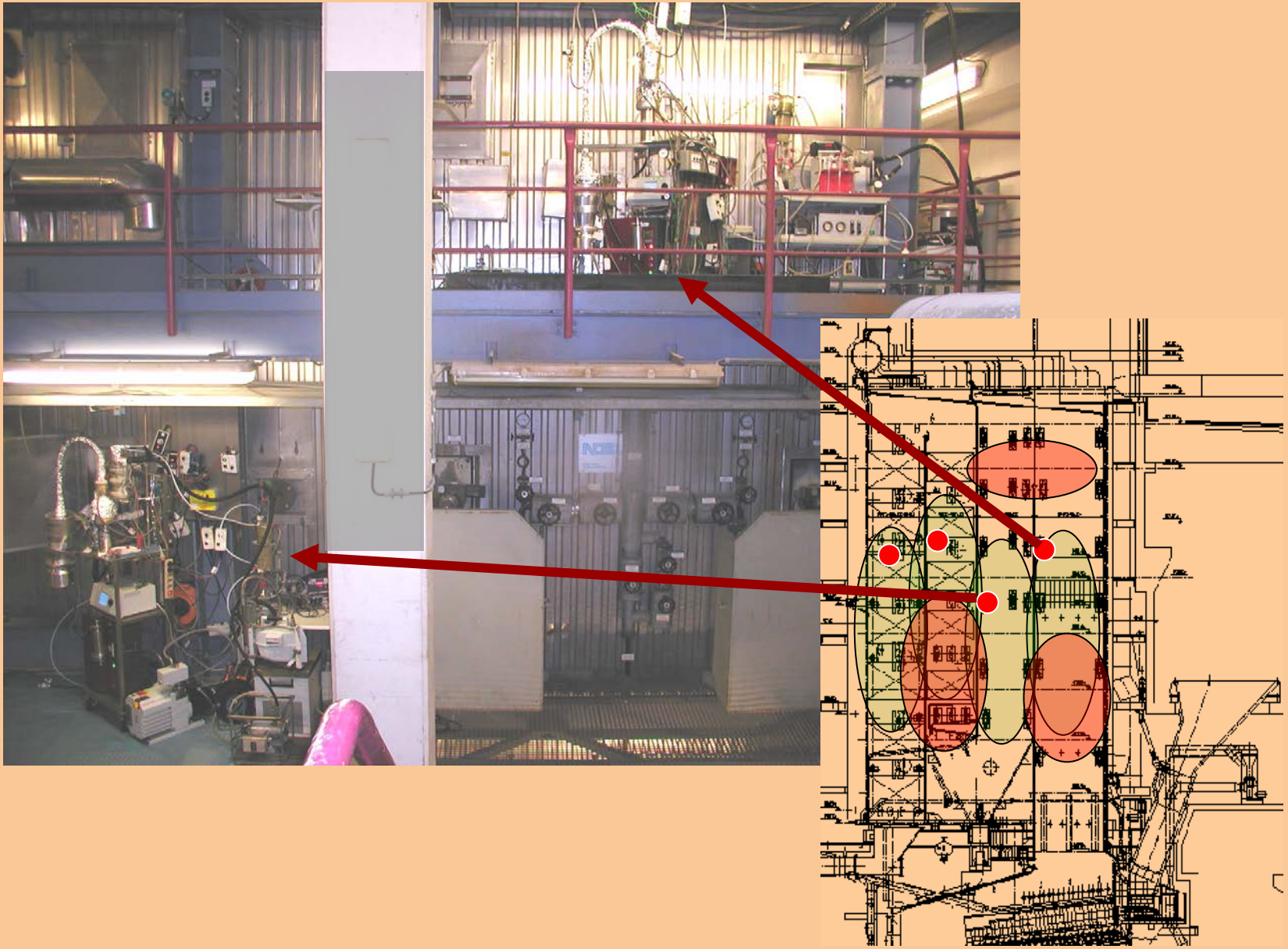

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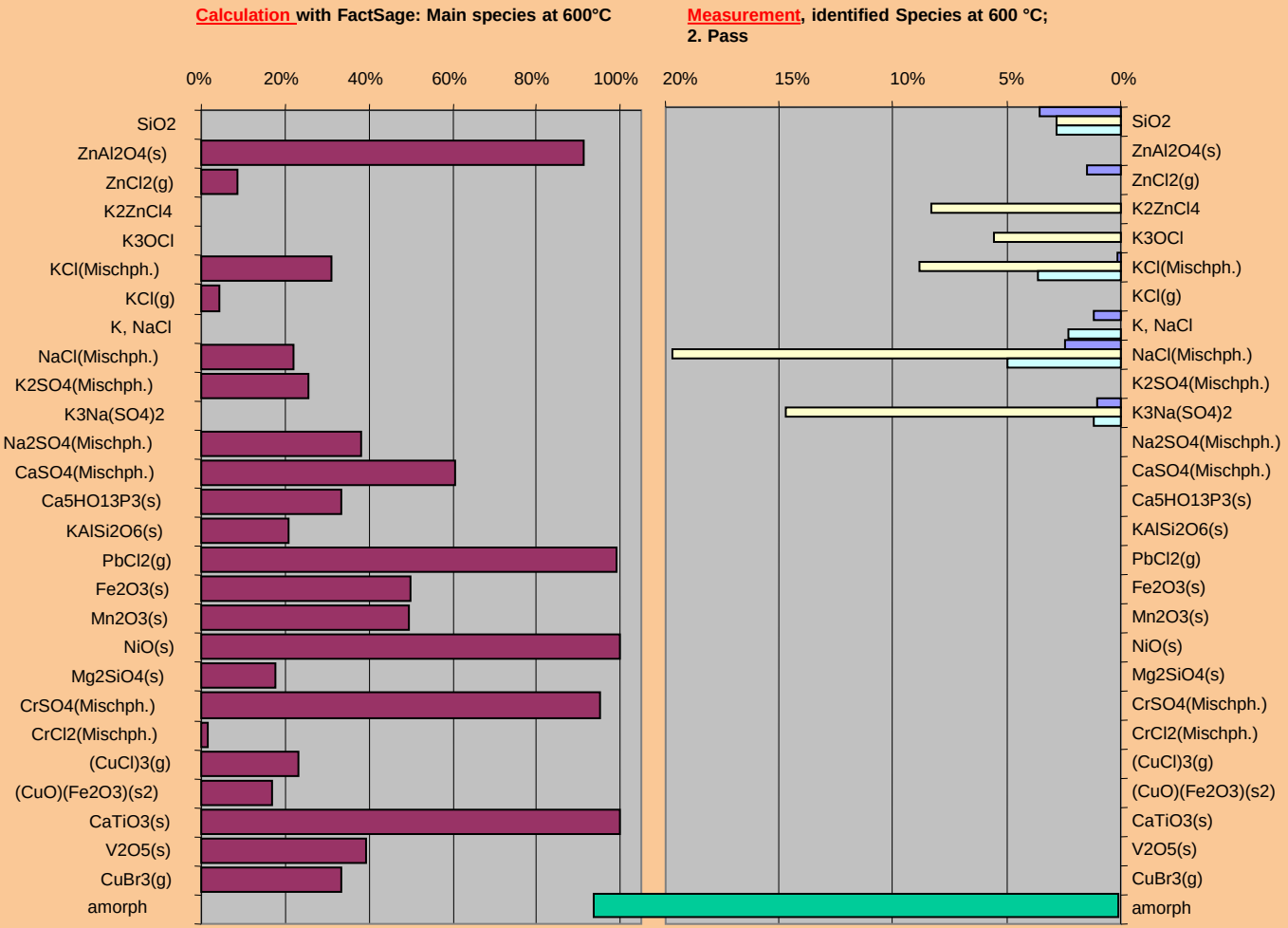
Discrepancy: Calculation - Measurement



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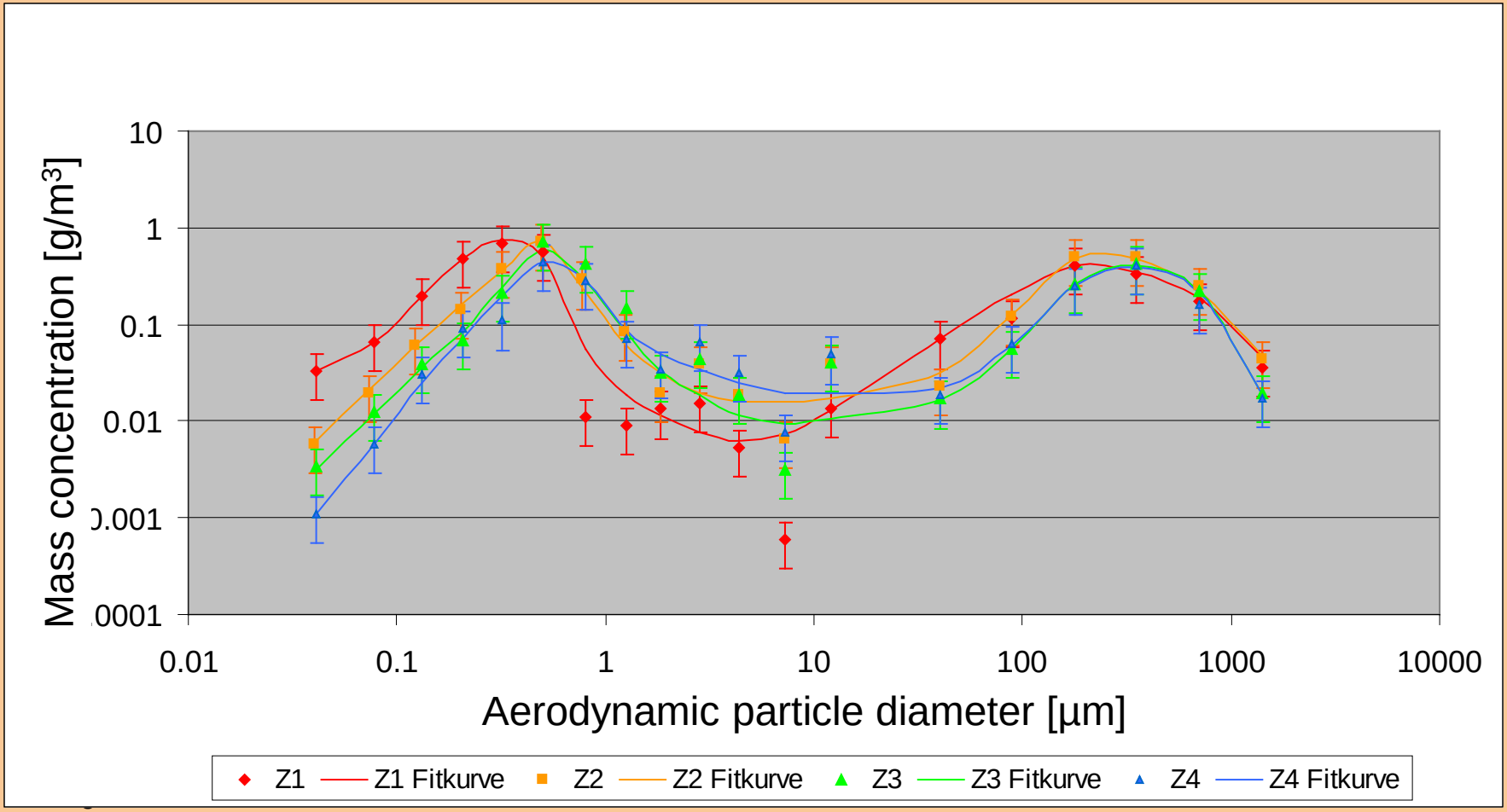
Normal Operation – Particle Distribution



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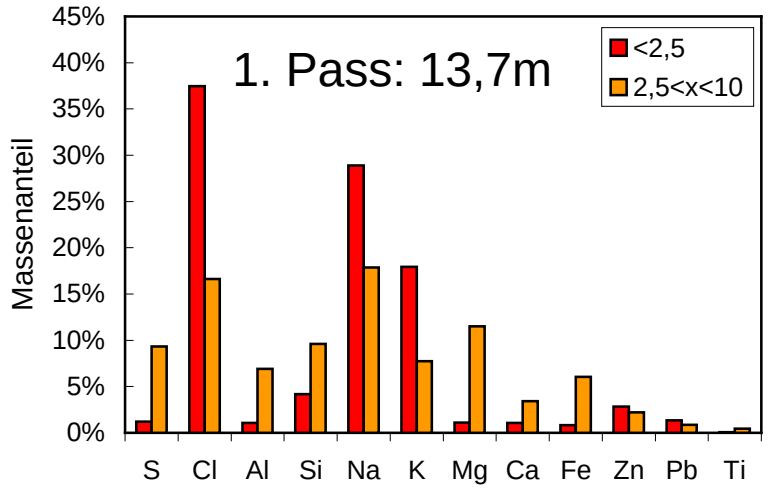
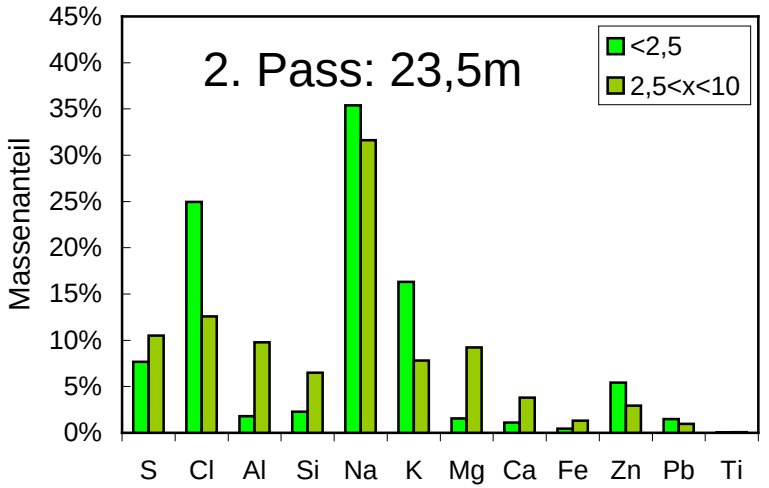
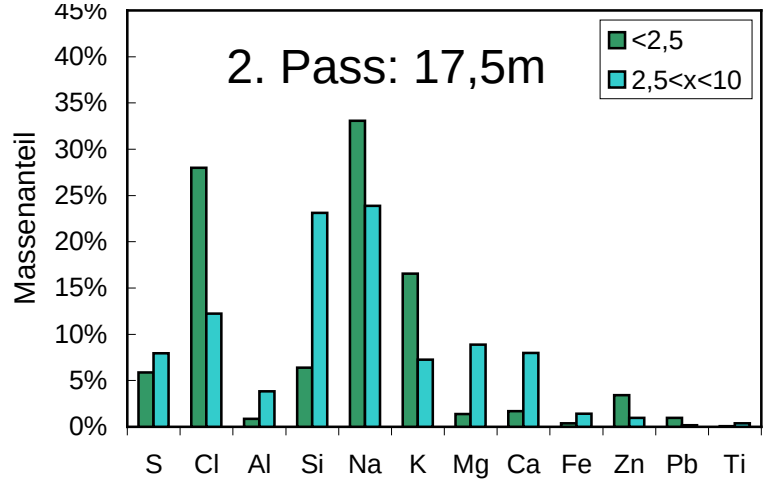
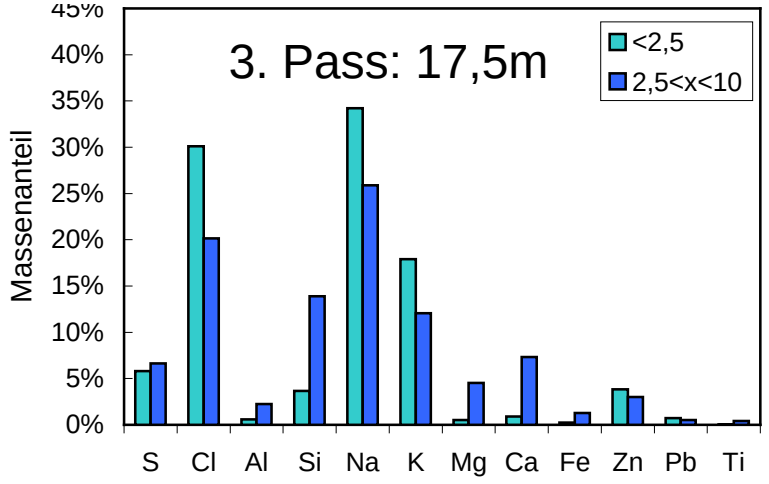
Normal operation:
Chemical Consistence of Particles <10µm









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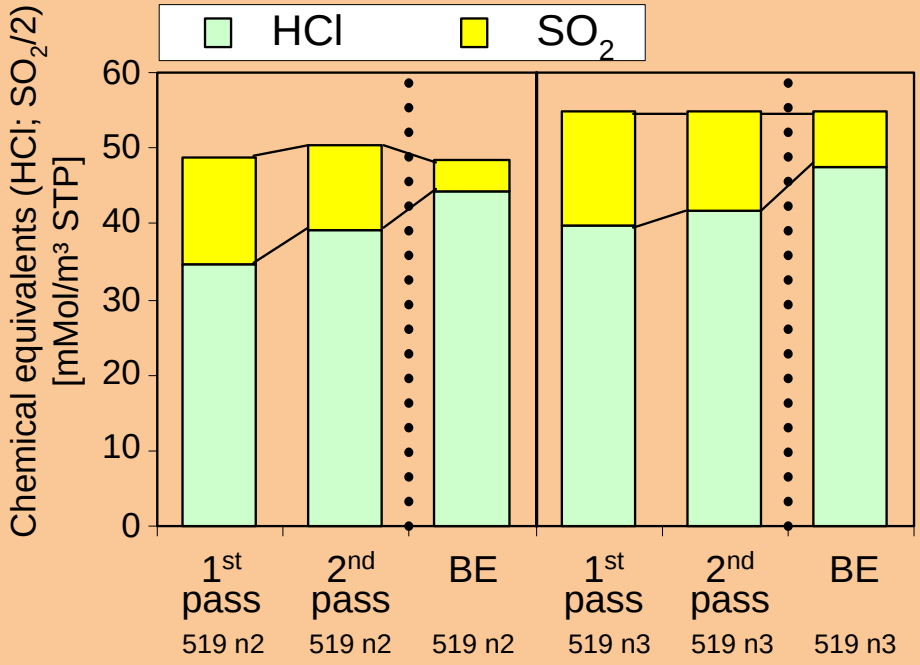
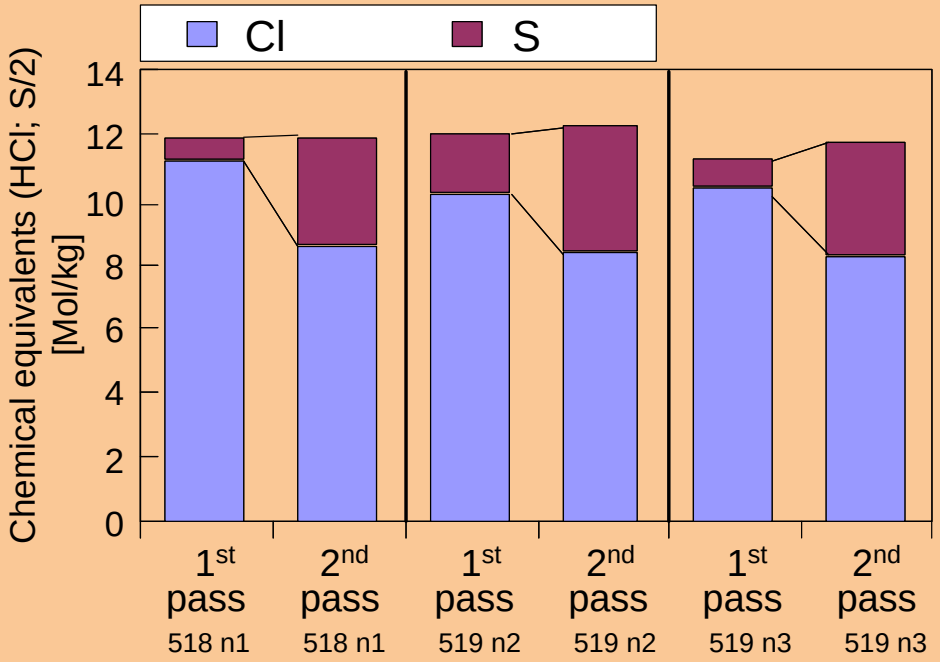
(De-)Sulphidation

gas-phase:



fine particles (< 0,2 µm):



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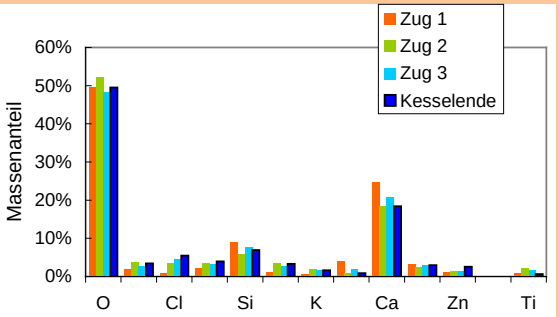
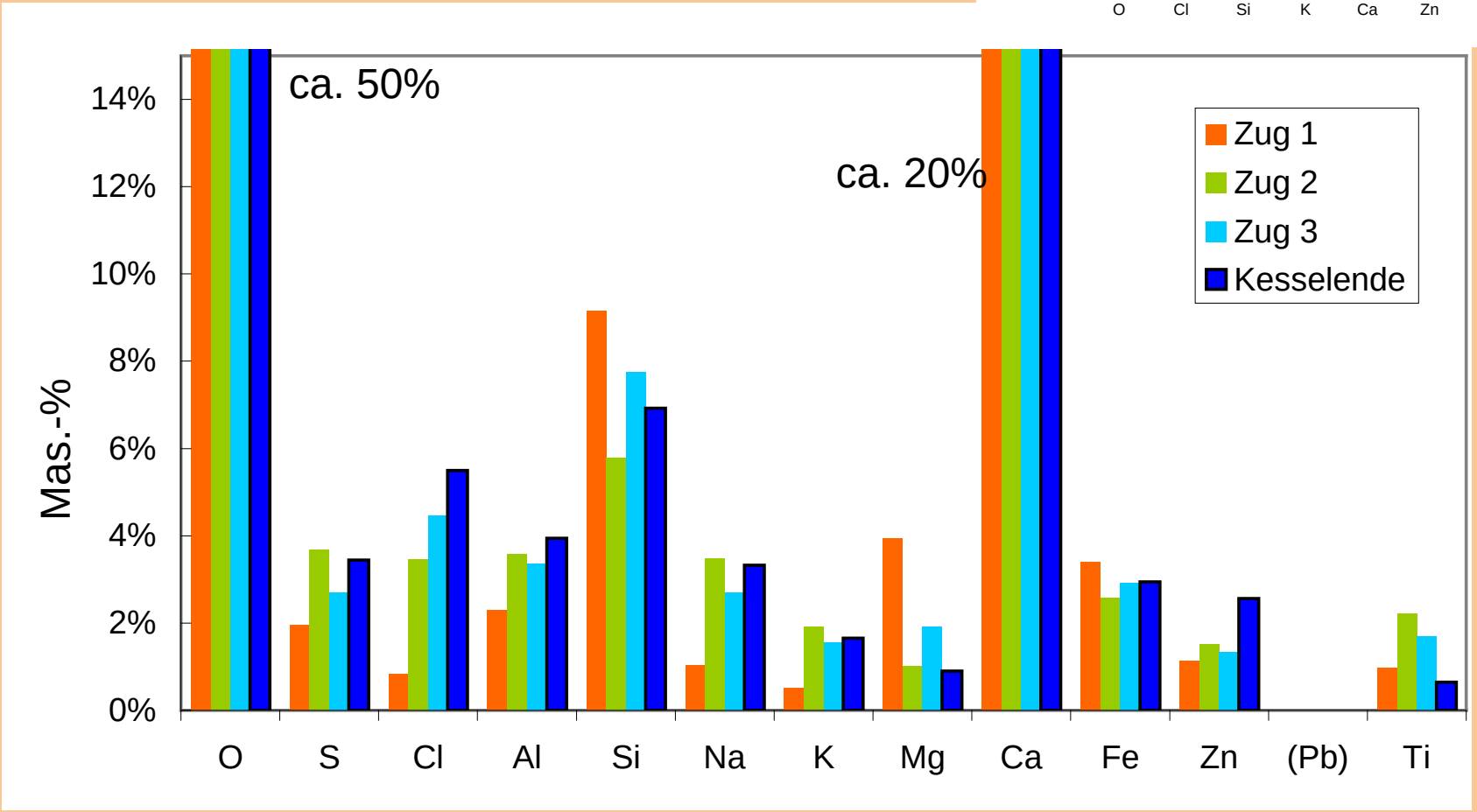
Normal operation: Chemical Consistence of Particles >10µm





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Deposit Content in Mass-%

	Combustion Chamber	1. Pass		2. Pass	Vertical Boiler		Horizontal Boiler		
					3. Pass	4. Pass	3. Pass	4. Pass	
	Right side wall; middle height	On refractory	Above refractory	Middle height	(Last-) Superheater	Eco	Middle height	(Last-) Superheater	Eco
SiO_2	30,4	18,6	12,2	8,2	6,9	8,7	9,4	6,4	7,9
TiO_2	2,7	2,5	1,6	1,2	1,2	1,3	1,1	0,8	0,6
Al_2O_3	9,6	7,2	5,1	3,5	3,2	3,7	3,2	2,5	2,3
Fe_2O_3	9,8	7,0	4,7	3,4	4,5	4,2	2,4	9,2	2,5
CaO	30,5	29,4	23,9	16,3	24,0	18,1	19,2	17,2	9,6
MgO	2,5	2,2	1,4	1,0	1,2	1,1	1,1	0,8	0,6
K_2O	1,2	3,8	6,0	9,9	7,1	9,6	9,4	8,3	14,8
Na_2O	1,9	3,4	3,6	6,2	4,7	6,3	6,4	6,1	9,8
SO_3	3,1	15,5	22,4	34,4	36,1	29,5	33,9	34,5	35,4
Cl	0,7	1,7	4,8	3,6	2,3	3,9	3,6	5,0	4,0
ZnO	1,4	3,3	3,9	5,8	4,3	6,6	5,4	5,0	6,9
PbO	0,2	0,2	5,8	3,9	1,3	3,0	2,2	2,5	3,5
P_2O_5	3,1	3,1	1,9	1,1	1,3	1,2	0,9	0,8	0,9

Large Particles:

Ca 20 %

K 2 %

Na 3 %

S 3 %

Cl 4 %

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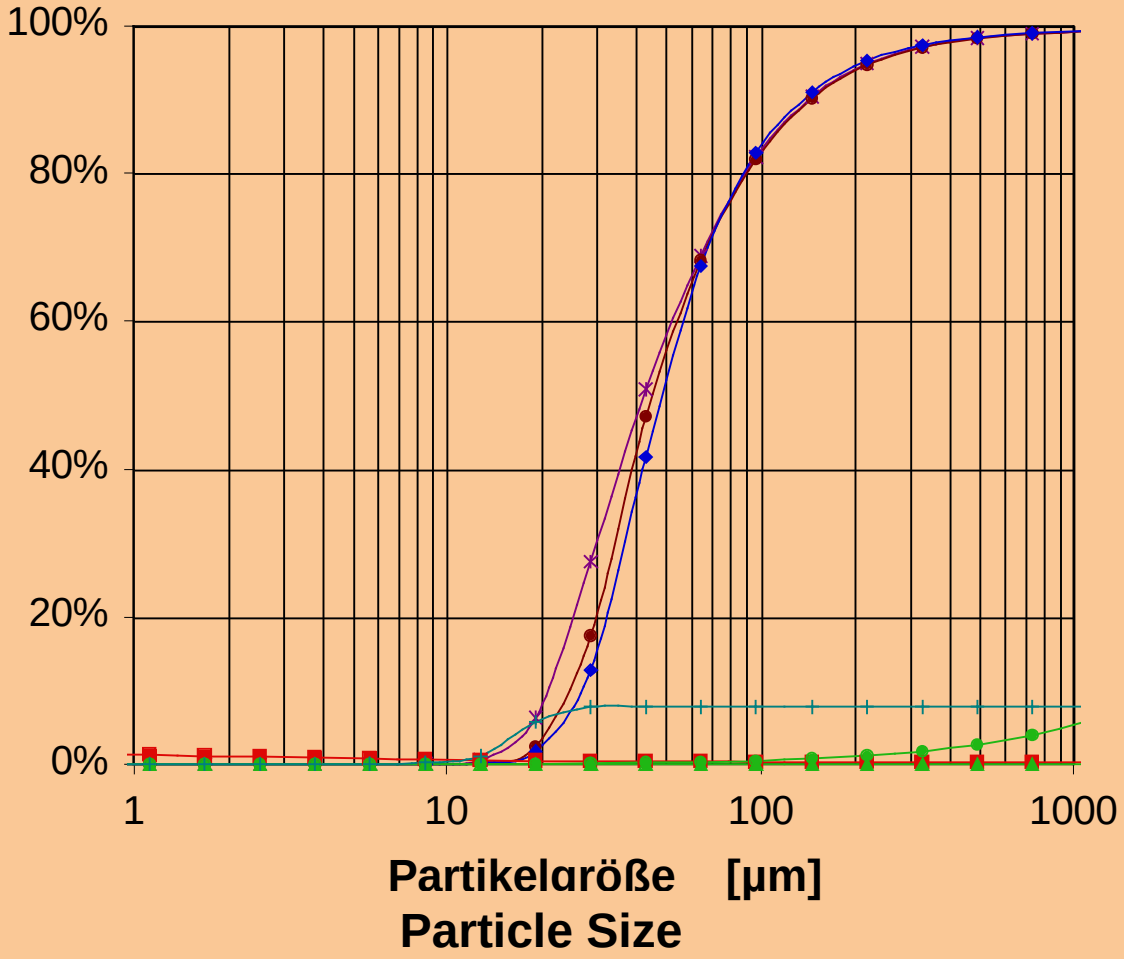
Deposition – Comparison of Mechanisms



d = 37 mm
u = 4,5 m/s

T = 600 °C
ΔT = 125 °C

η_{Haft} = 100 %

- Impaktion Muhr (Re=500)
- Impaktion Muhr (Re=50)
- Impaktion Landahl (Re=10)
- Thermophorese
- Interception Potential
- Interception viskos
- turb. Abscheidung

Impaction of large, chlorine layered particles

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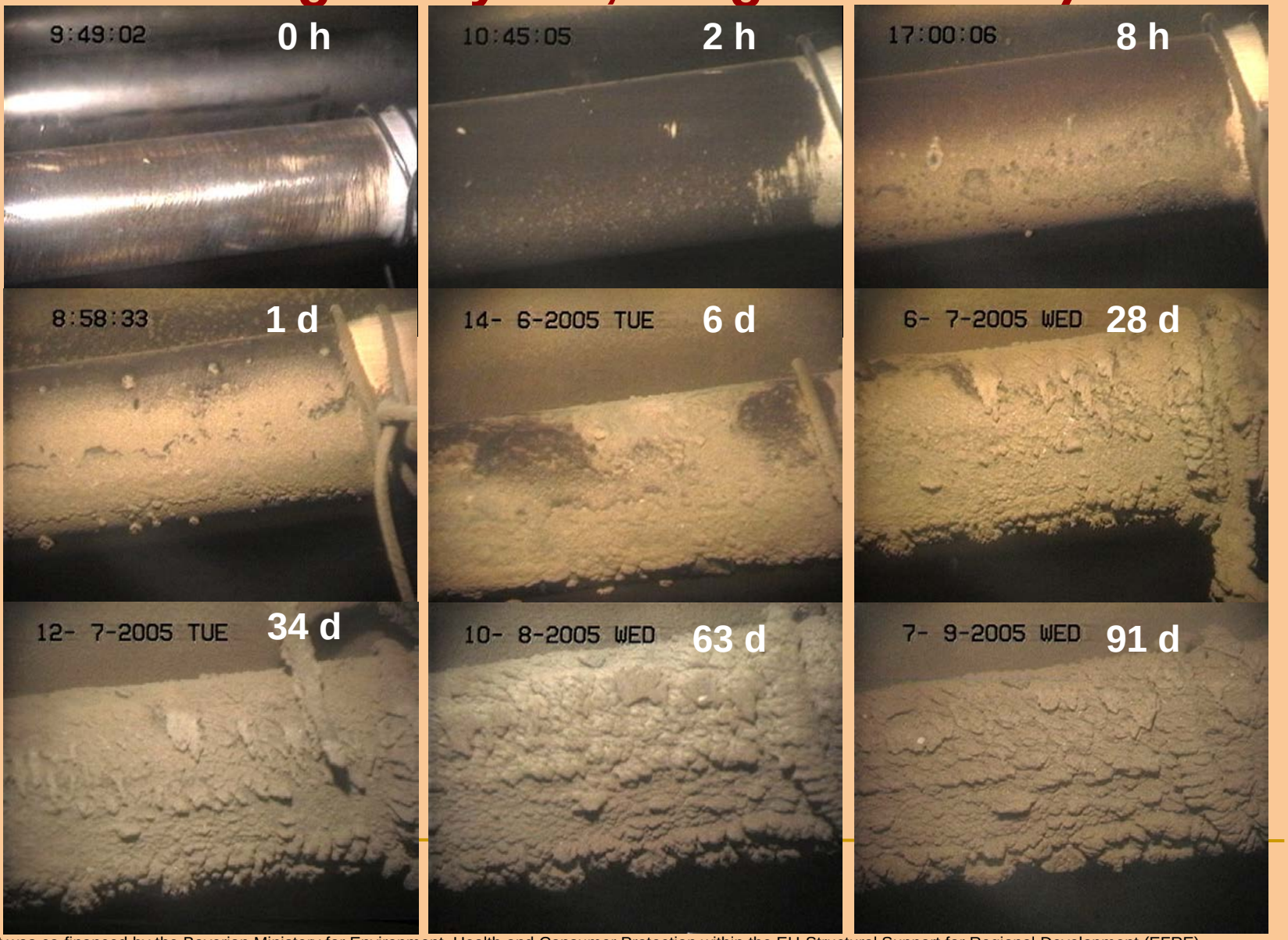
Continuous-Endoscopy of a Superheater (Soot blowing every 8 h; Single Pictures)



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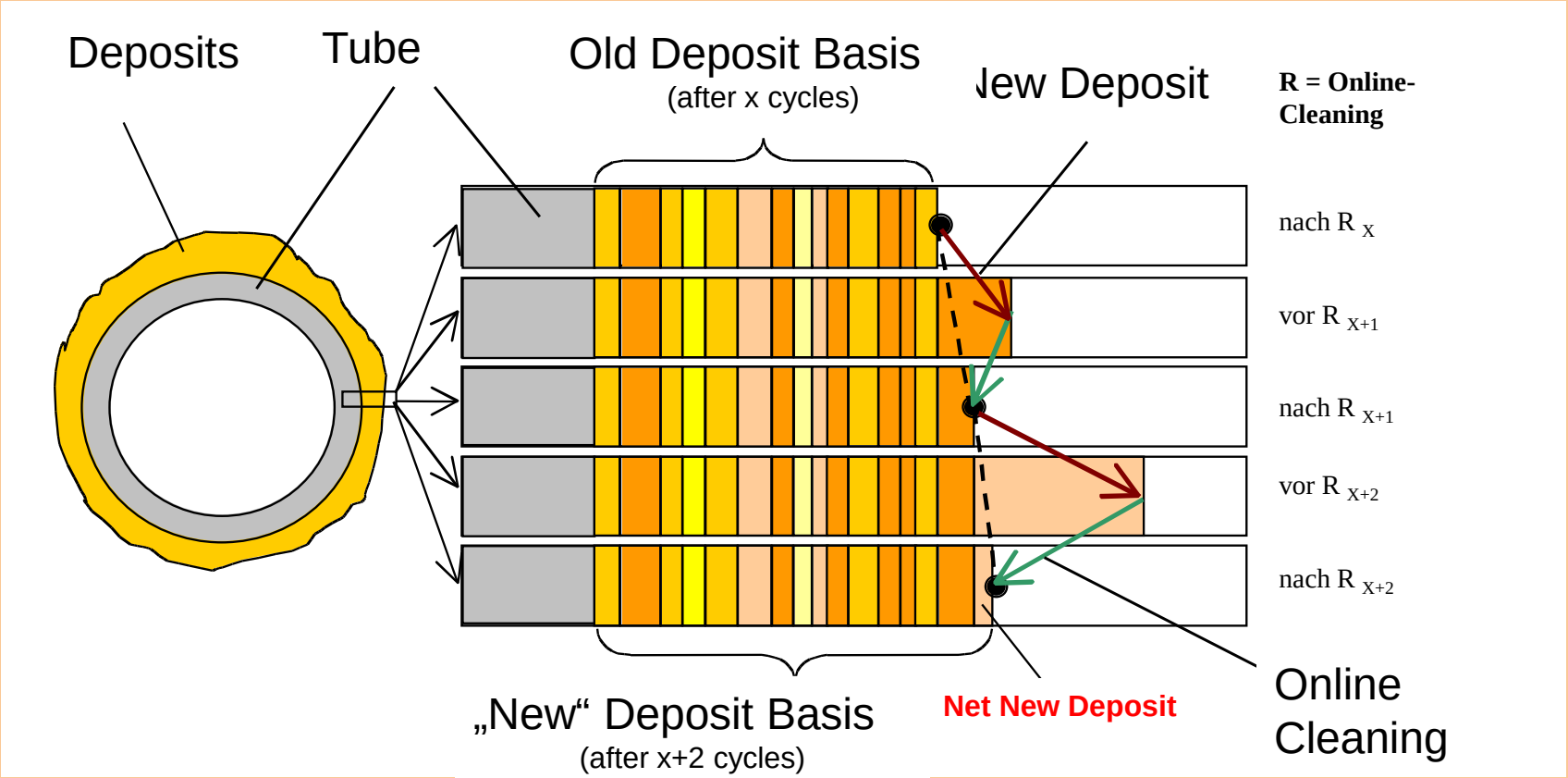
Net Deposits Formation



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Depositing at SH

		Deposit Mass	Deposit Thickness
Net		**7,5 kg/h**	**5 µm/h**
Tare	**Fly ash**	**10,5 kg/h**	**7 µm/h**
	Boiler ash 2./3. Pass	**10,5 kg/h**	**7 µm/h**
Gross		**28,5 kg/h**	**19 µm/h**

Heat impact on sulphidation:

- about 5 kW average heat transfer in the area of the last SH
- about 1 % increase of local heat transfer at last SH
- about 0,1 kW/m2 local heat transfer at last SH.

Main Boundary Conditions for Calculations:

- Average Porosity: 50 %
- Pure Density: 2 kg/dm^3
- Thickness of Deposits after 4.000 Oh: 20 mm
- Heating Surface: 150 m^2
- Availability: 7.600 h/a
- Cyclus of Soot Blowing: 1-times/8hA

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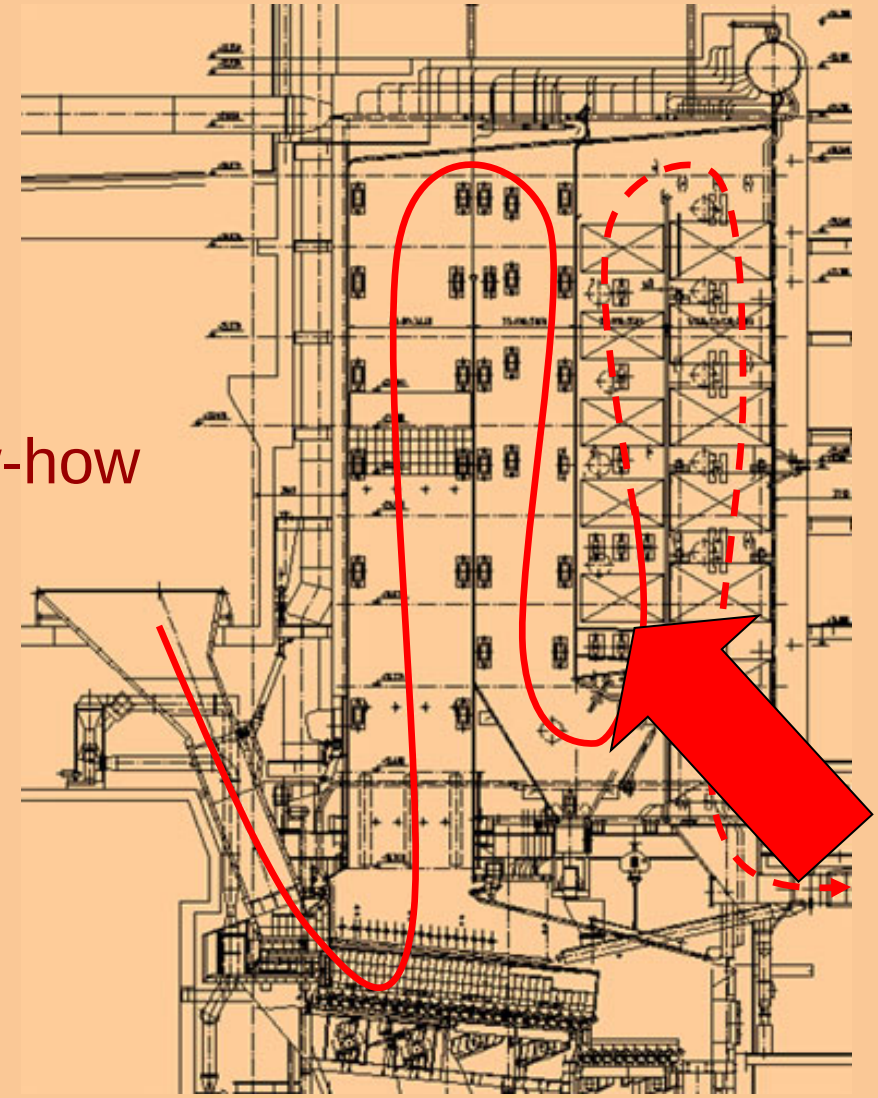
3. Processes at Corrosion Boundary Layer

Process Know-how



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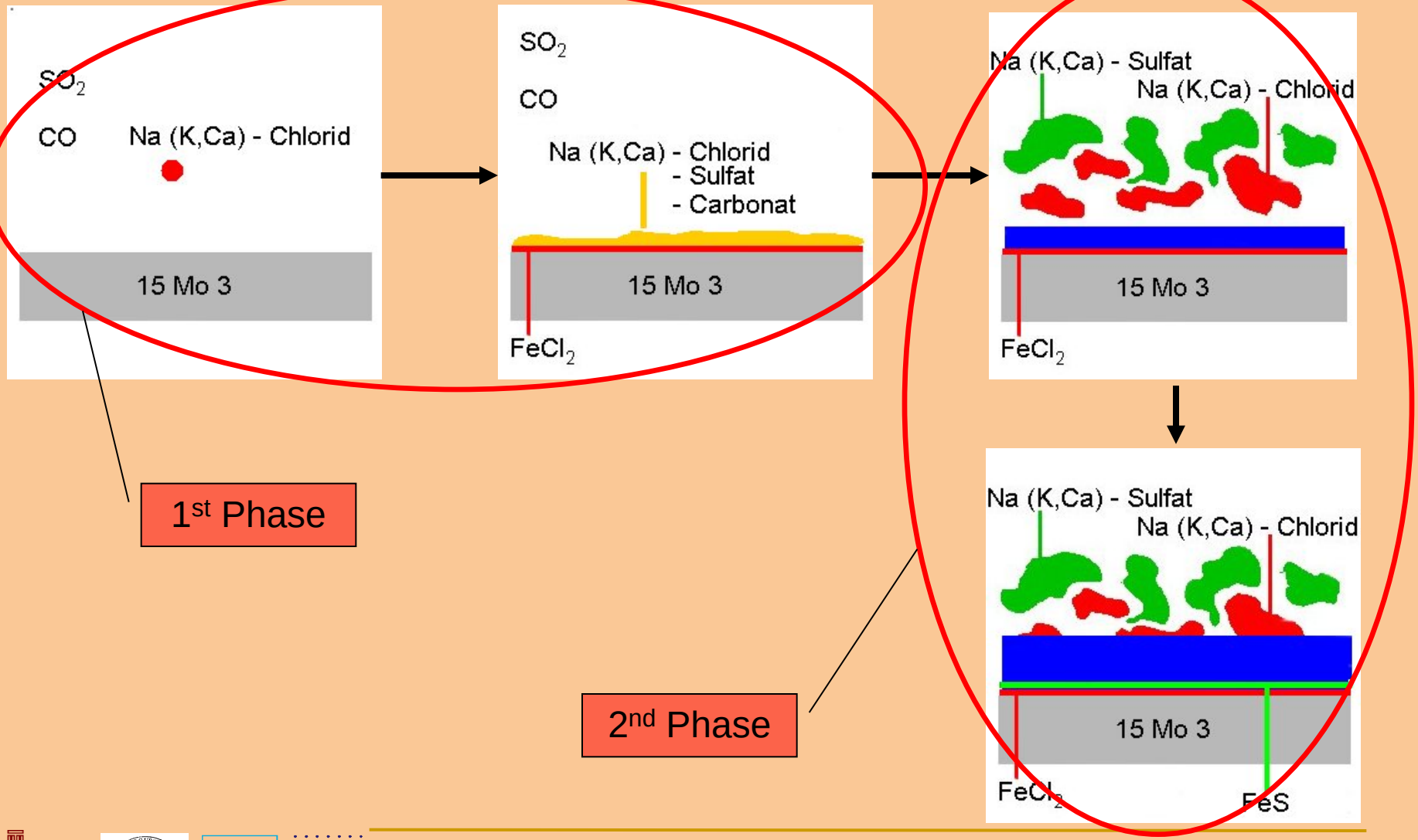
Corrosion Phases



1st Phase

2nd Phase

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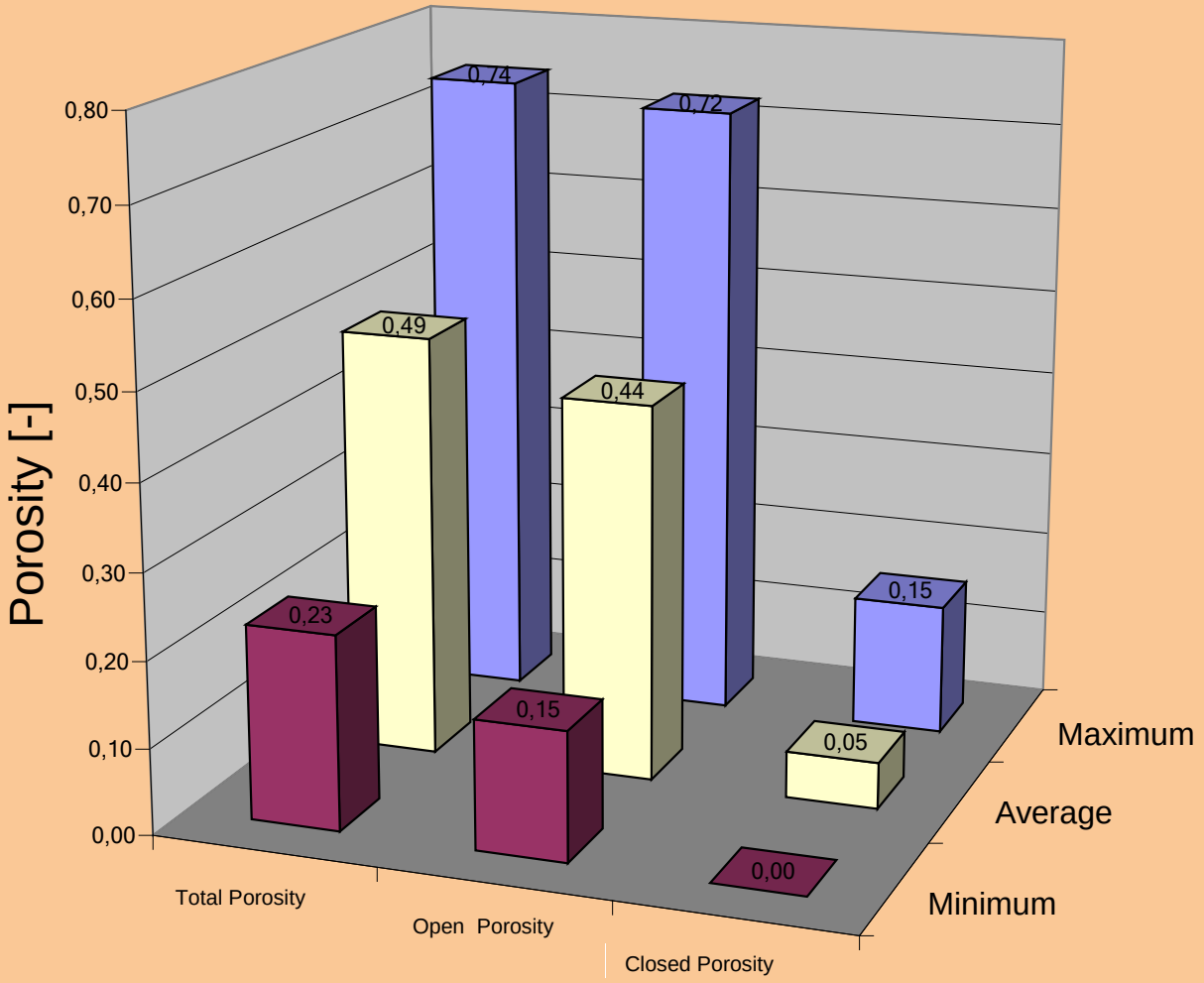
Porosity of outer Deposits



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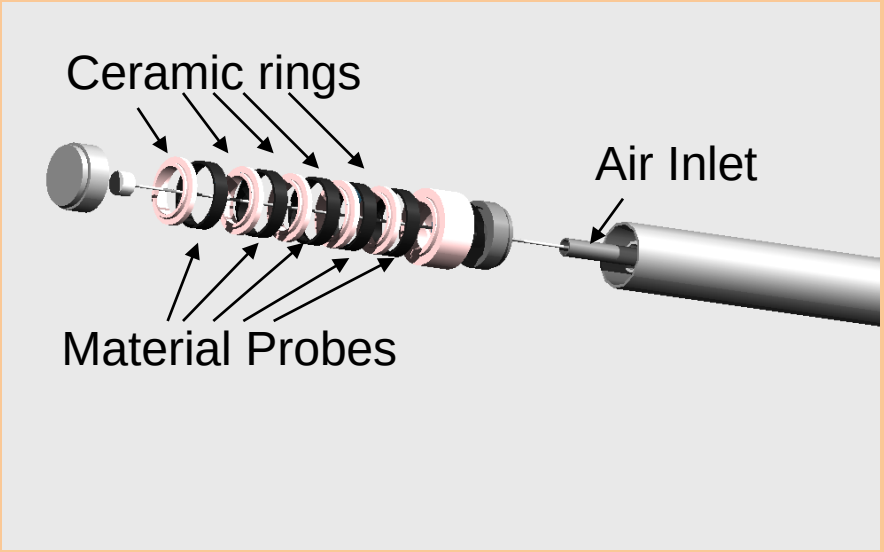
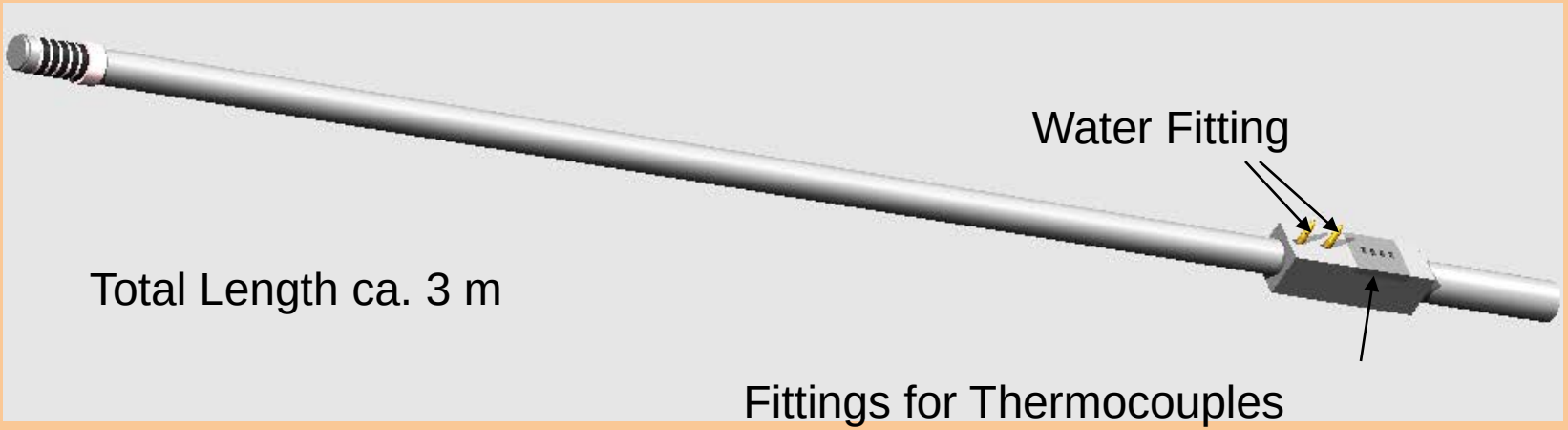
Corrosions Sensor

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





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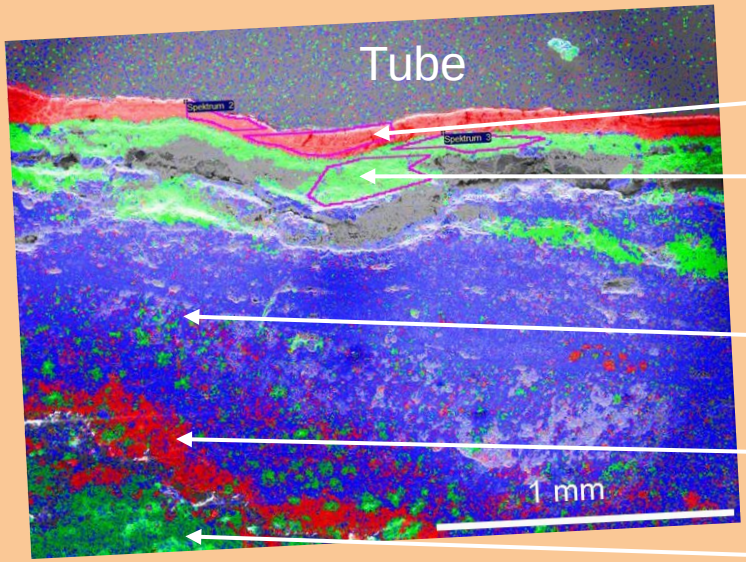
Comparison: Plant Tubes vs. Sensor

Example:

3 months plant tubes:

3 months sensor rings:



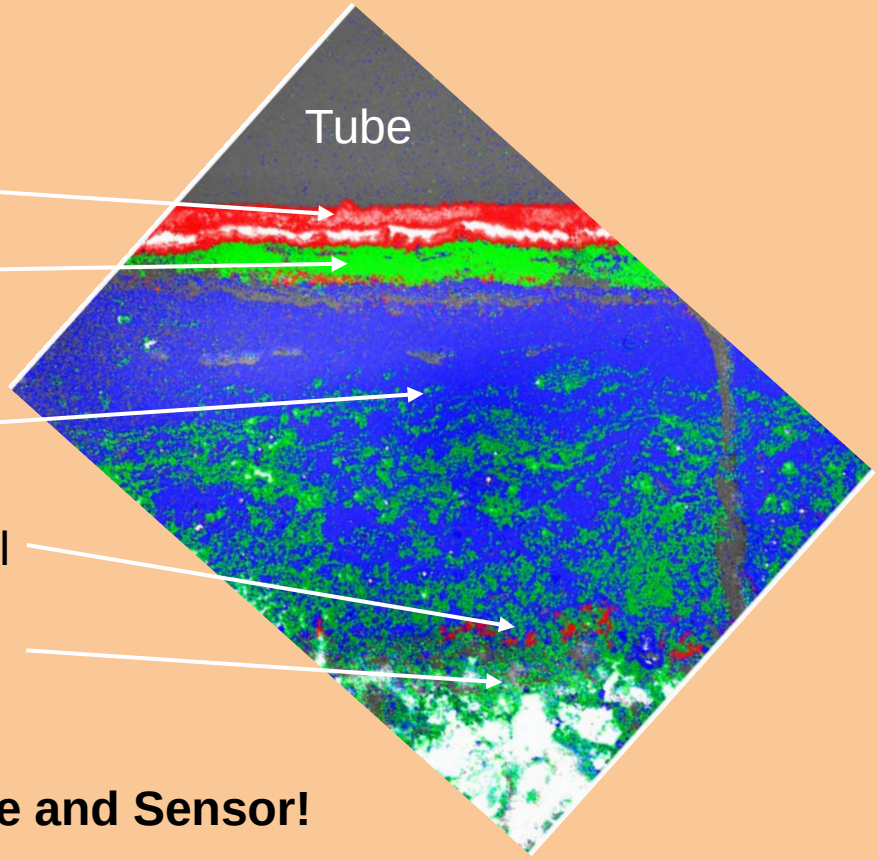
Fe_aCl_b

Fe_cS_d

Fe_eO_f

Alkali-Cl

Alkali-S



Identical Structure of Tube and Sensor!

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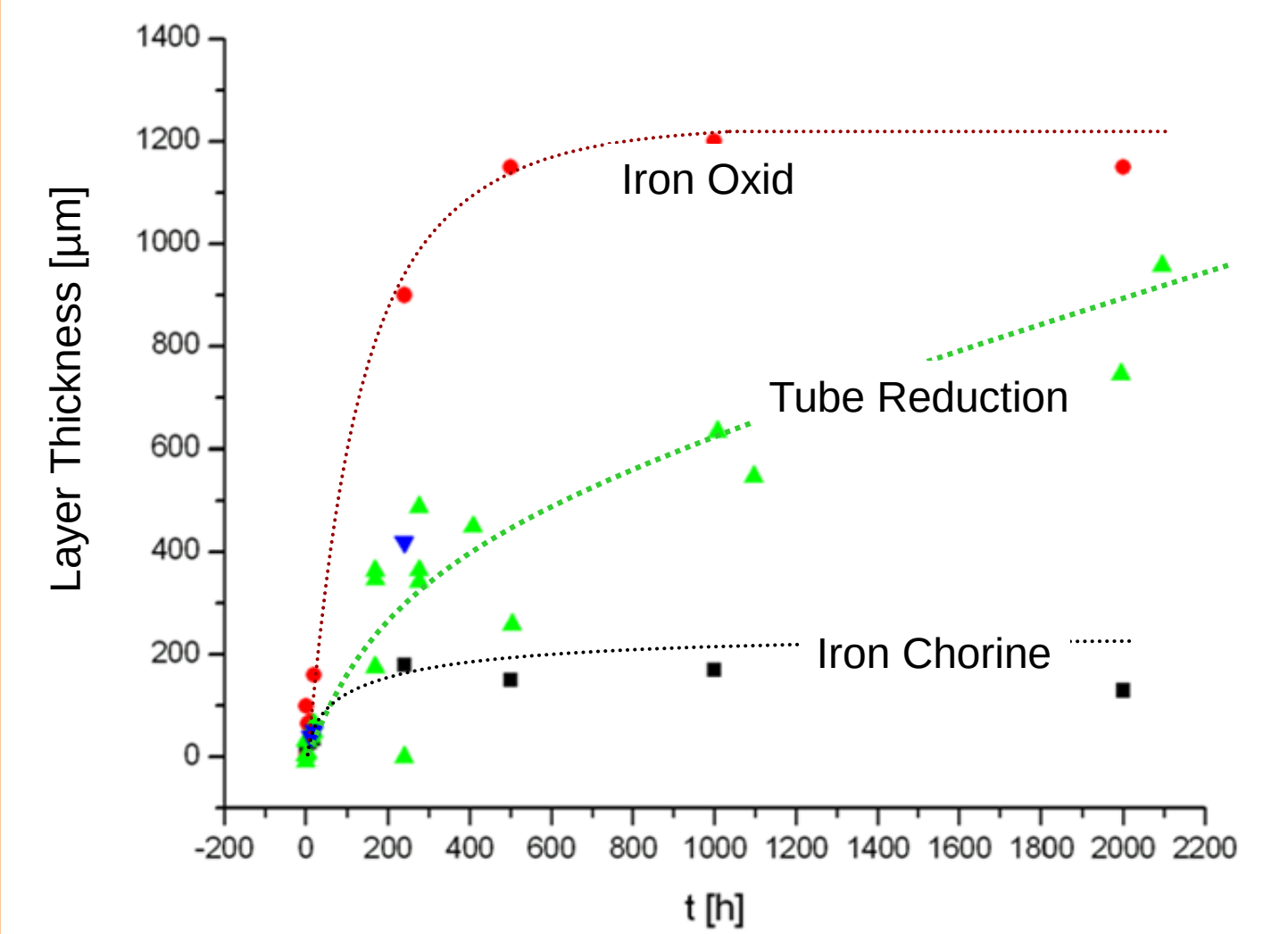
Thickness of Layers



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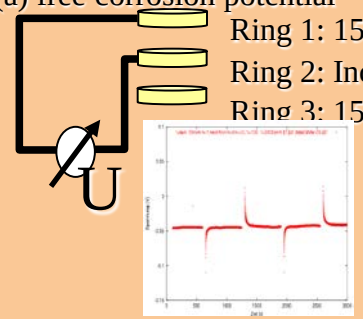
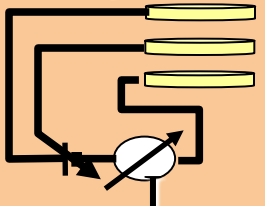
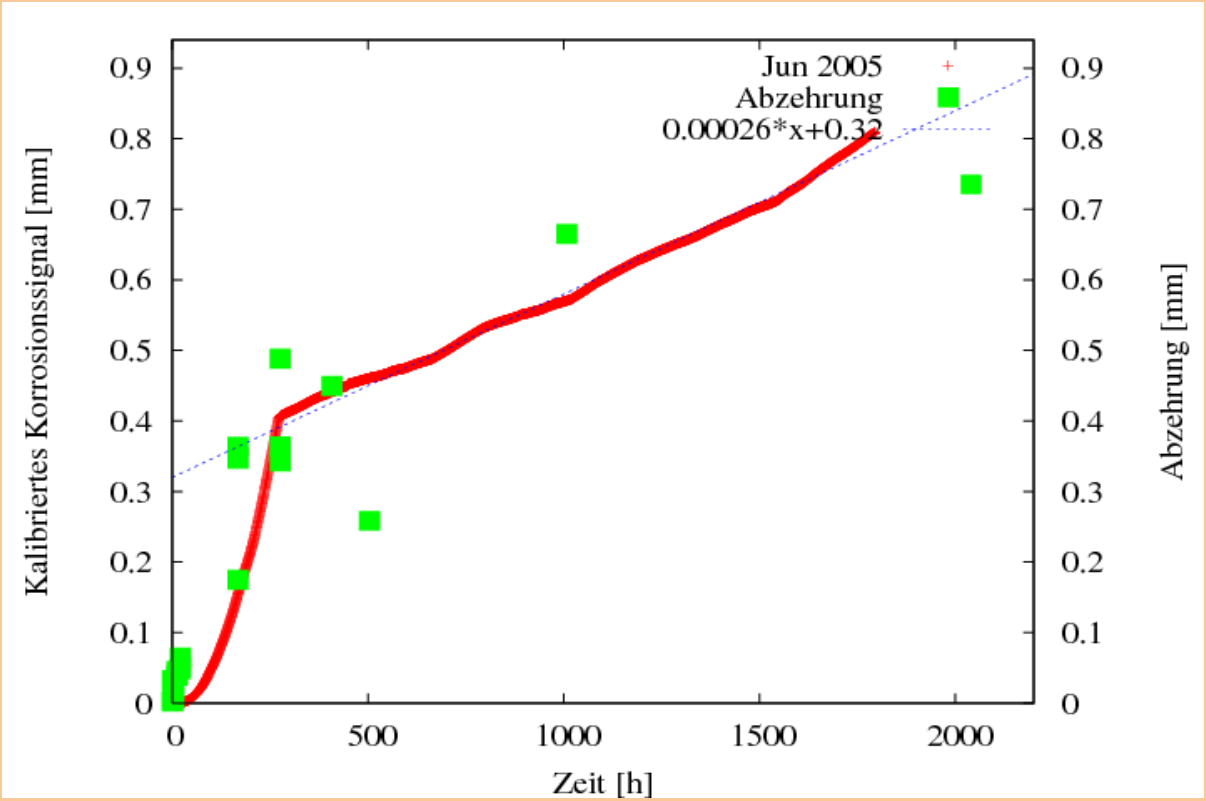
Correlation: Tube reduction vs. Corr.-signal

(a) free corrosion potential



(b) power-voltage-line





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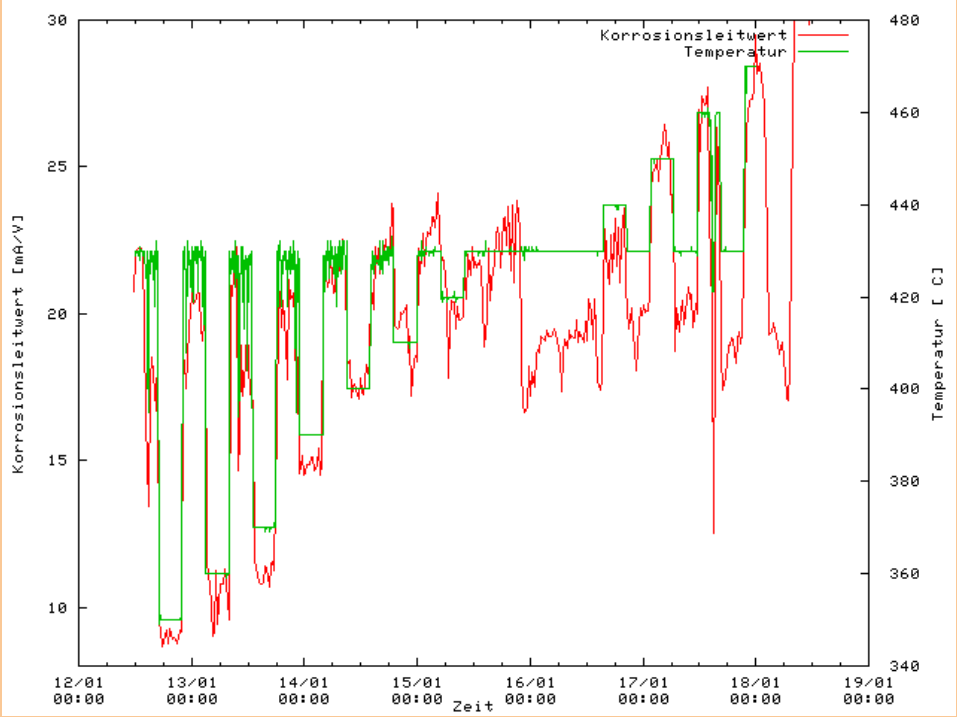
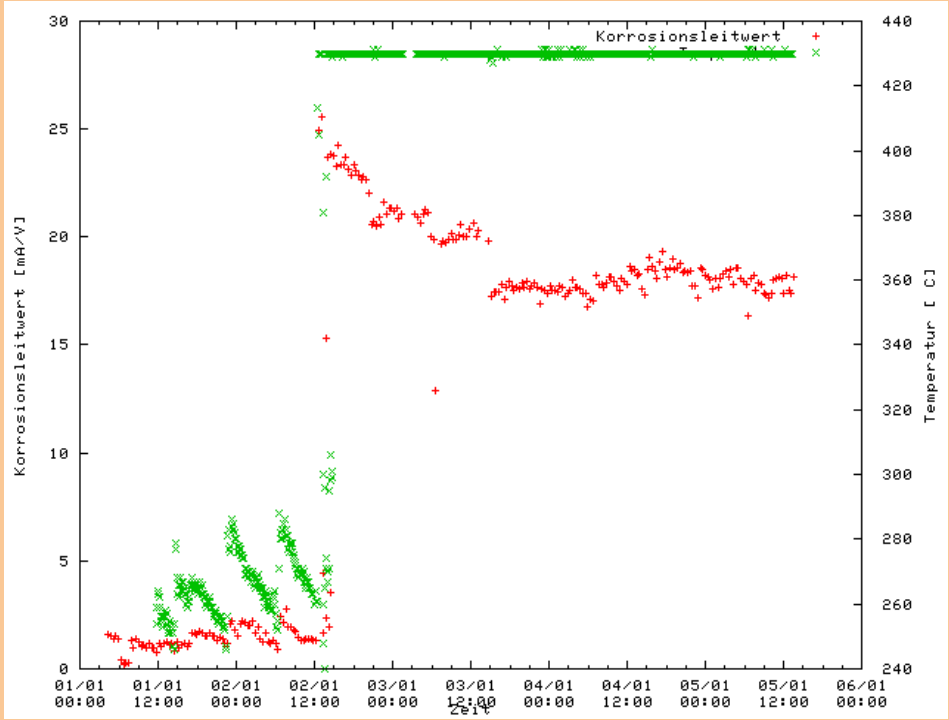
Sensor data – systematic temperature variation





Corrosion conductance is depending exponentially on temperature

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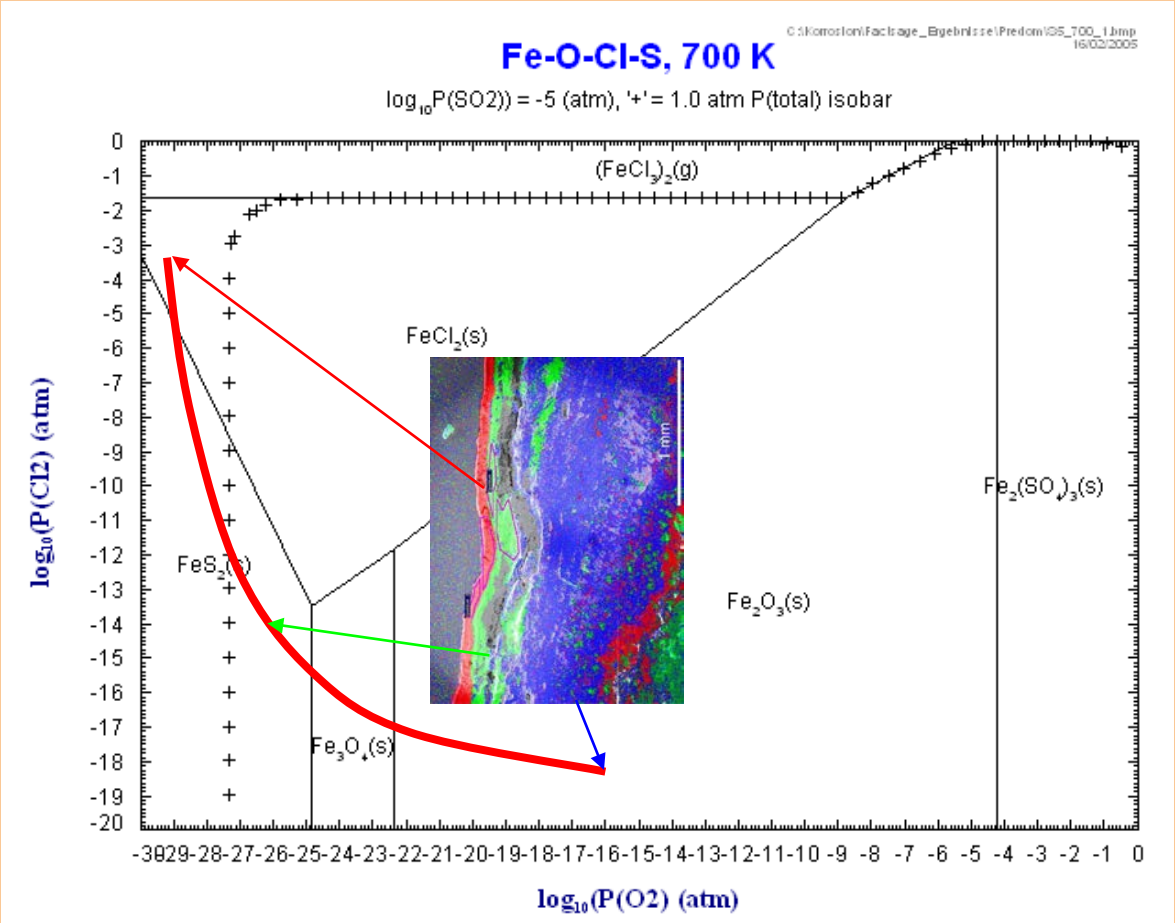
Thermodynamic Considerations about Layer Structure

Stability of phase depending on chlorine- and oxygen partial pressure

Assumption: Oxygen partial pressure increases with increasing distance to tube wall



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Reactions at boundary layers

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

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

- **$FeCl_2$/Fe_xO_y:**

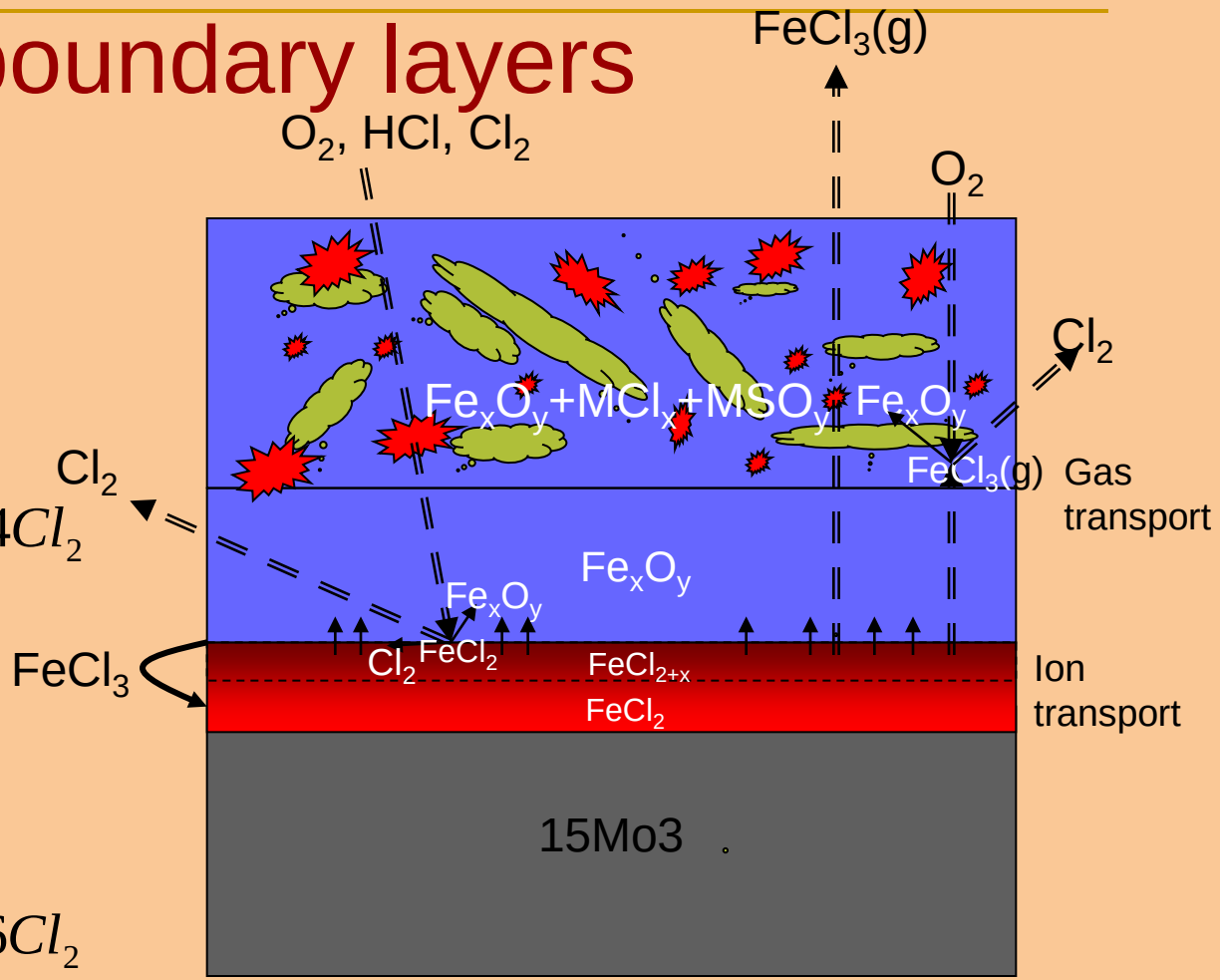
$$4FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4Cl_2$$

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

- **Fe_2O_3/Fe_3O_4:**

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

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



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

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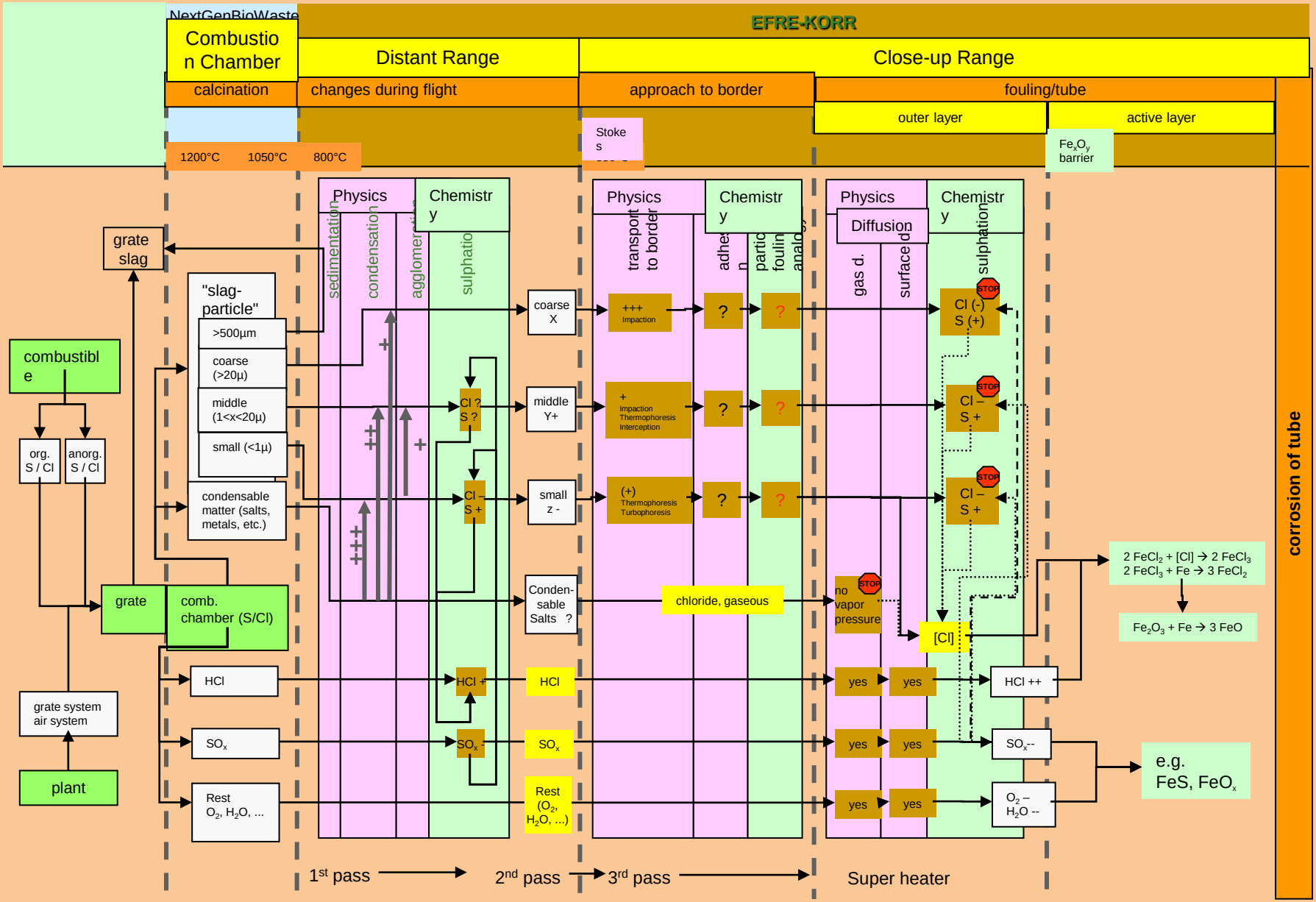

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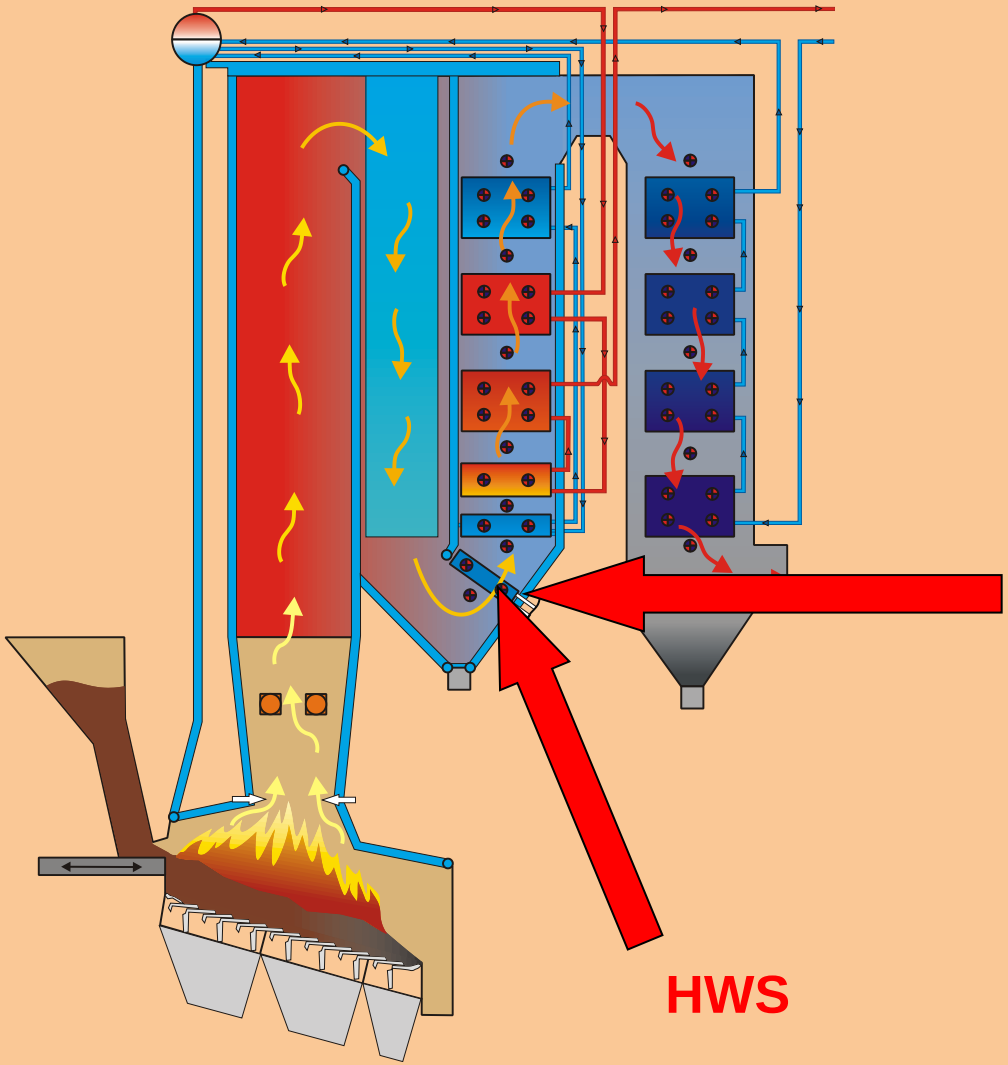
4. Measurements: Chlorine Trap



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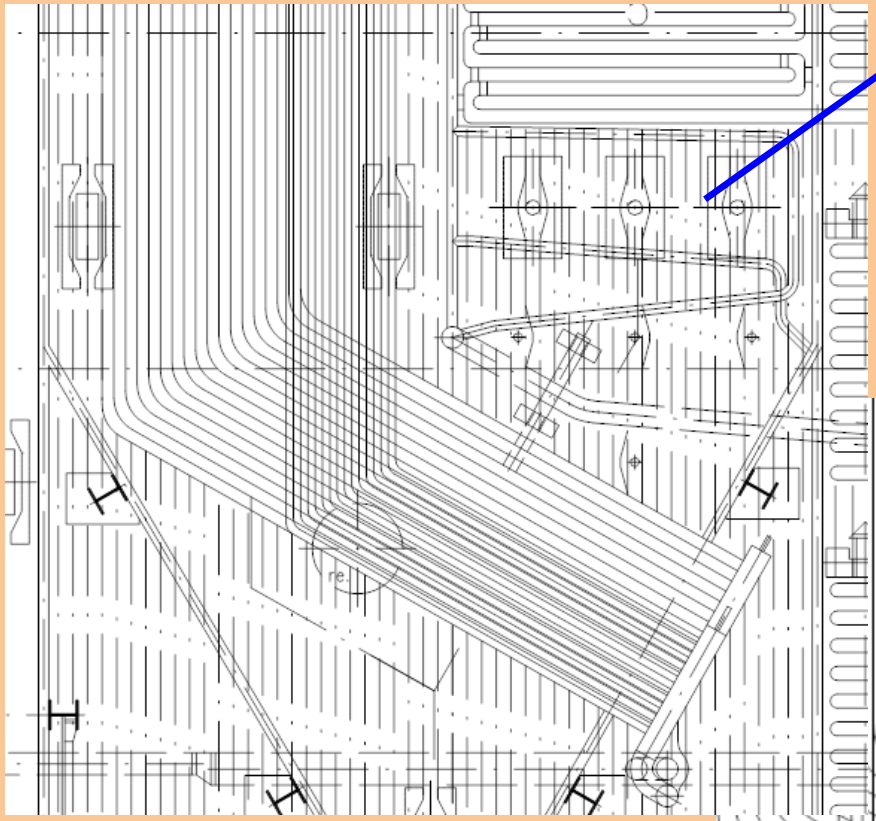
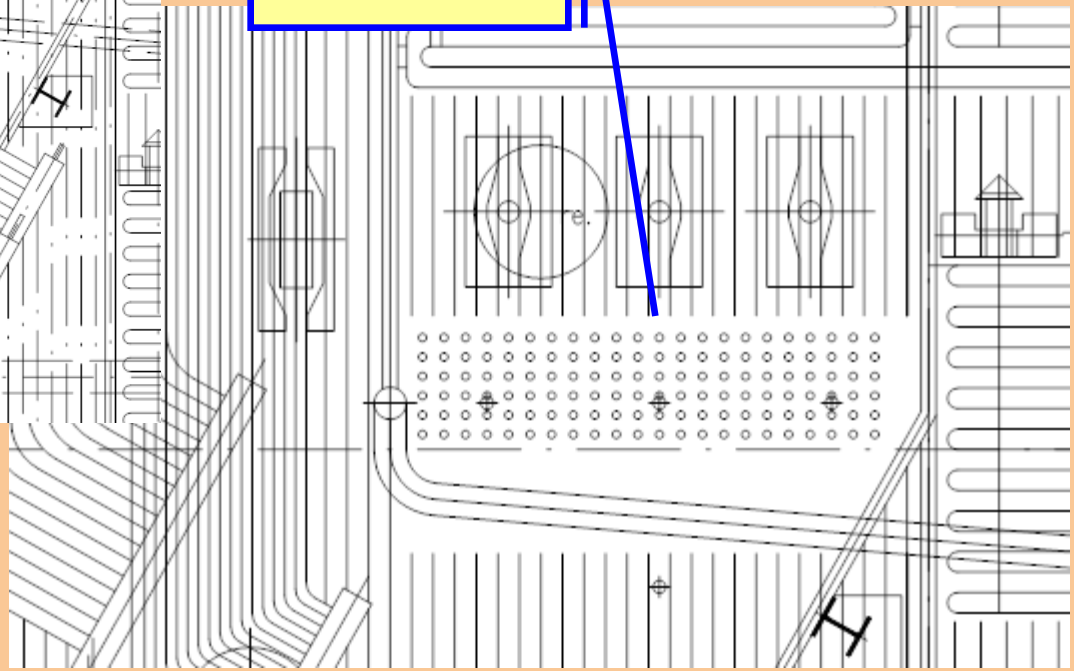
Crossover 2./3. Pass: Chlorine Trap



Actual situation: Evaporiser grid; T=400°C

Nominal condition: T=150



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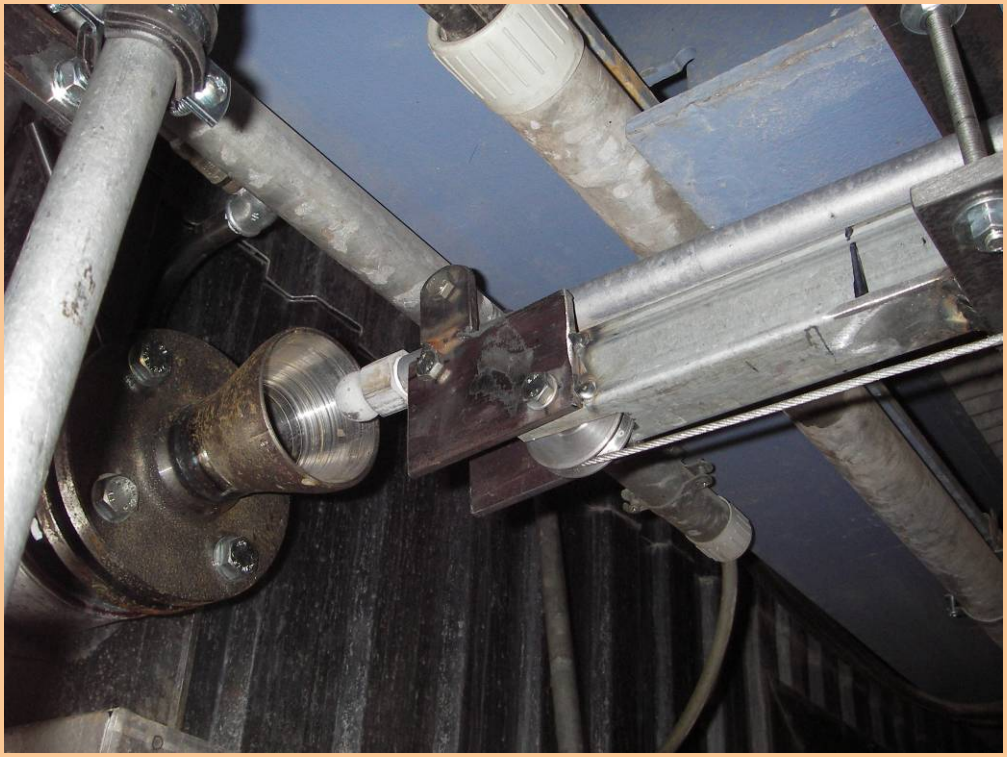
HWS



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HWS – Effect of Cleaning

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5. Summary

- Main source of „bad guys“: combustion chamber
- Boiler influences Gas/Aerosol within FG way
- Quasi-continuous depositing
- Chlorine layered large particles depositing by impaction
- Interaction between flue gas and particles: sulphidation with release chlorine 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

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