

Thermodynamic behaviour of particles in the flue gas of waste incineration plants

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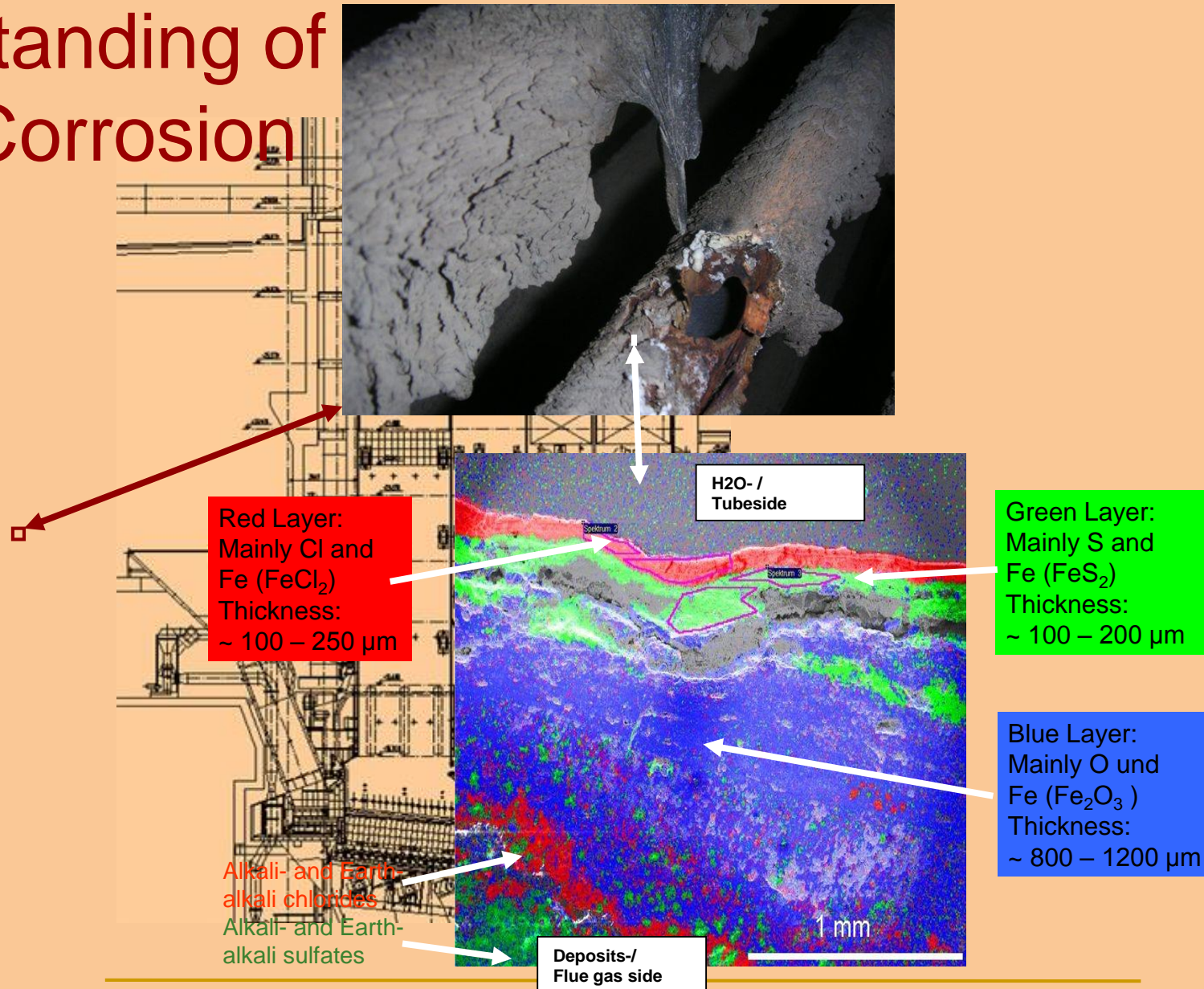
Daniel Ott, Univ. Augsburg

GKS-Waste-to-Energy Plant



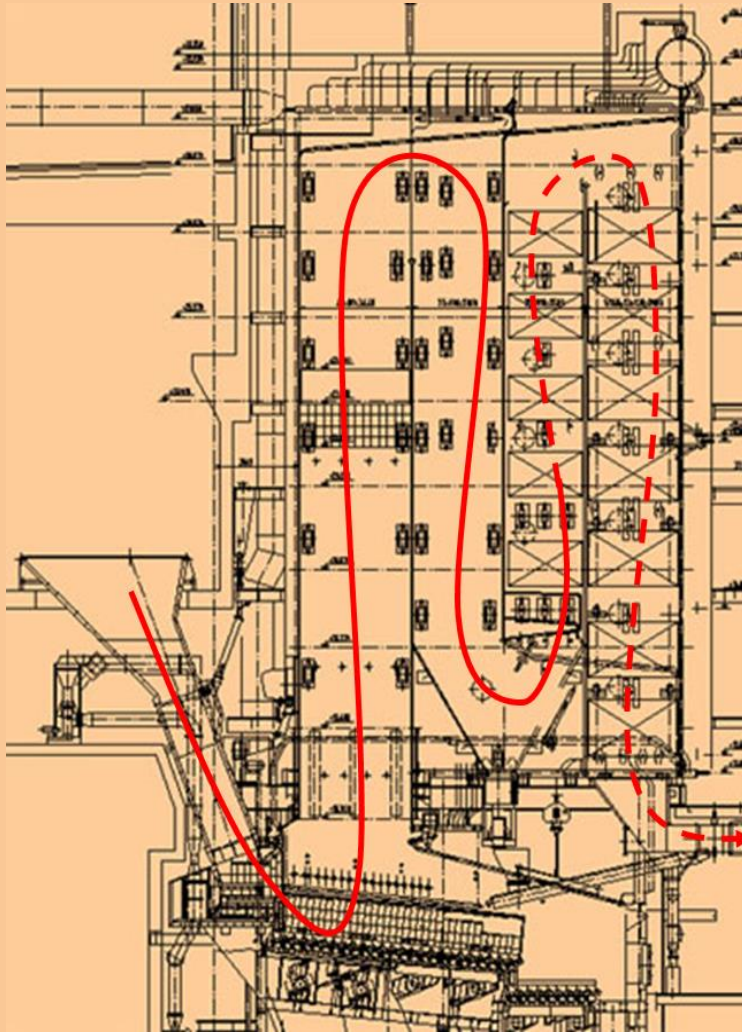
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At: GTT-User-Meeting, Herzogenrath, 2015

Understanding of HT-Cl-Corrosion



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Particles in Boiler

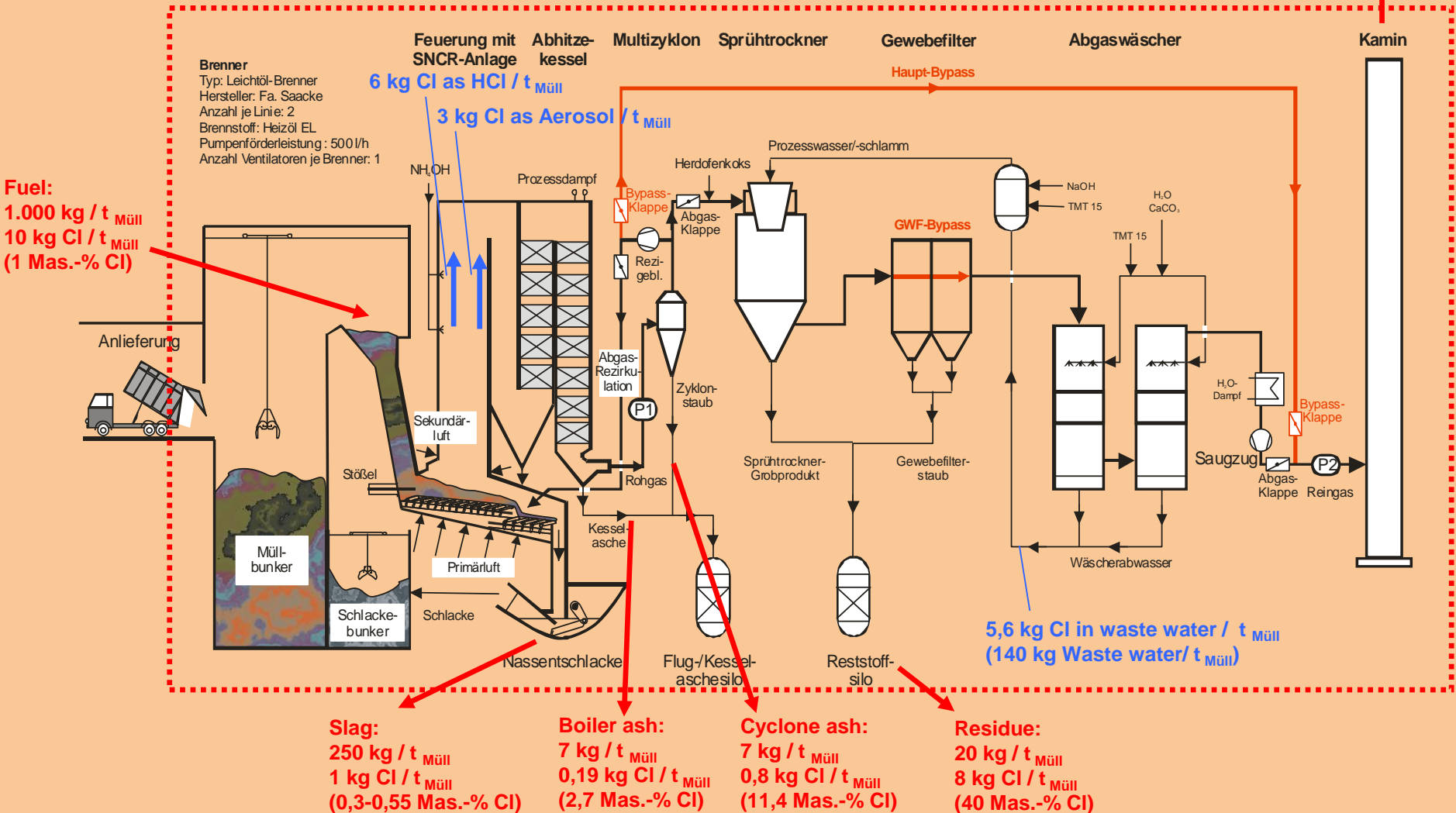


Superheater steam parameter:
Pressure: 65 bars
Temperature: 435 °C

Macro-Chlorine-Balance

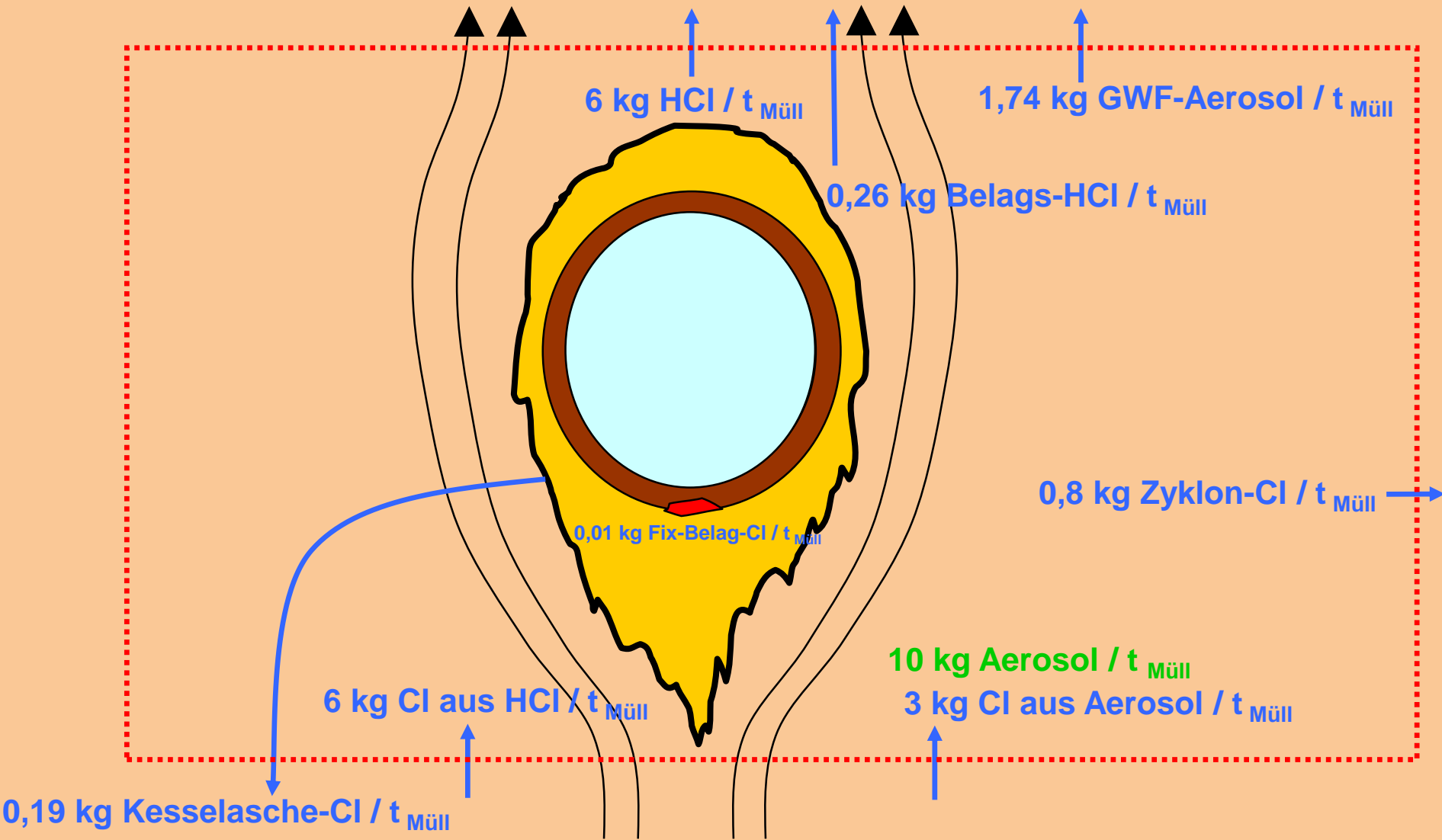
(Basedata: $5.000 \text{ m}_n^3 \text{ RG} / \text{t}_{\text{Müll}}$; $2 \text{ g Aerosole} / \text{m}_n^3$)

Clean gas:
 $6.000 \text{ kg} / \text{t}_{\text{Müll}}$
 $0,01 \text{ kg Cl} / \text{t}_{\text{Müll}}$
 (0,00017 Mas.-% Cl)



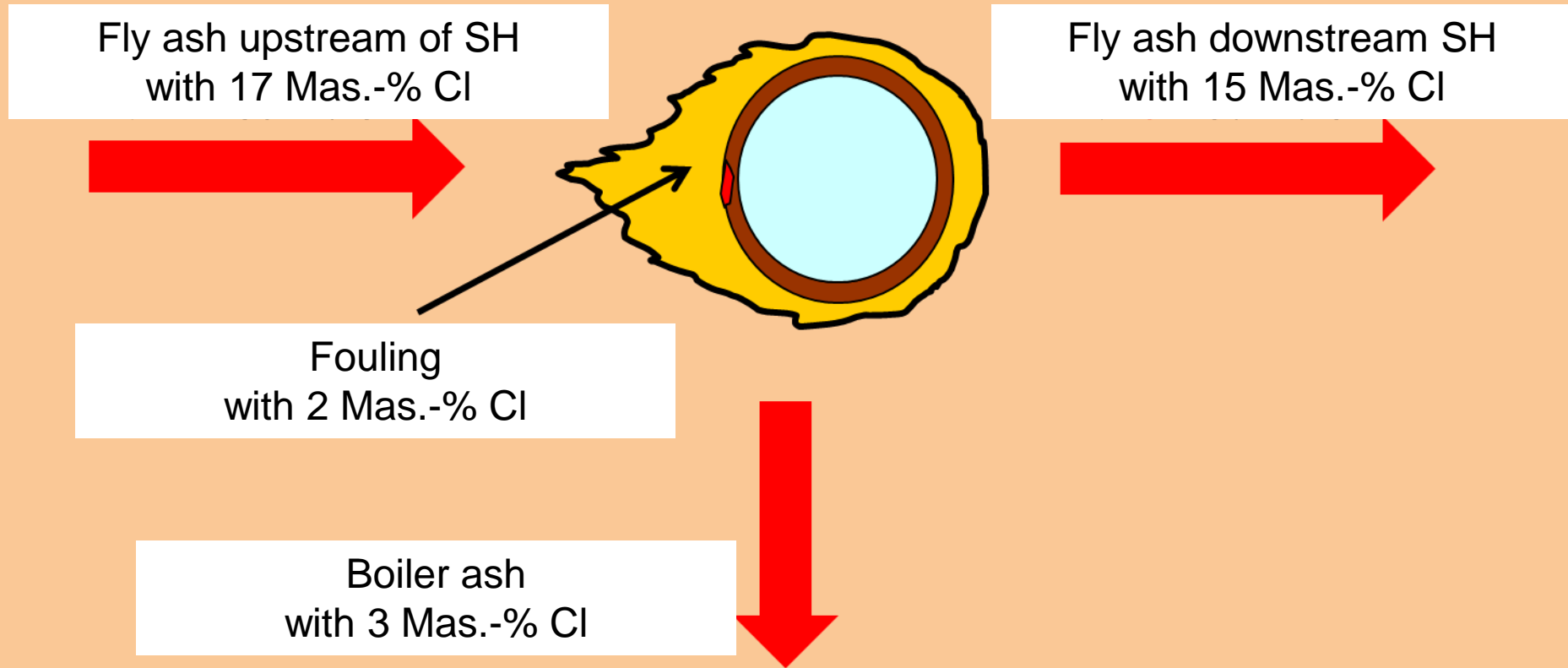
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Medio-Chlorine-Balance

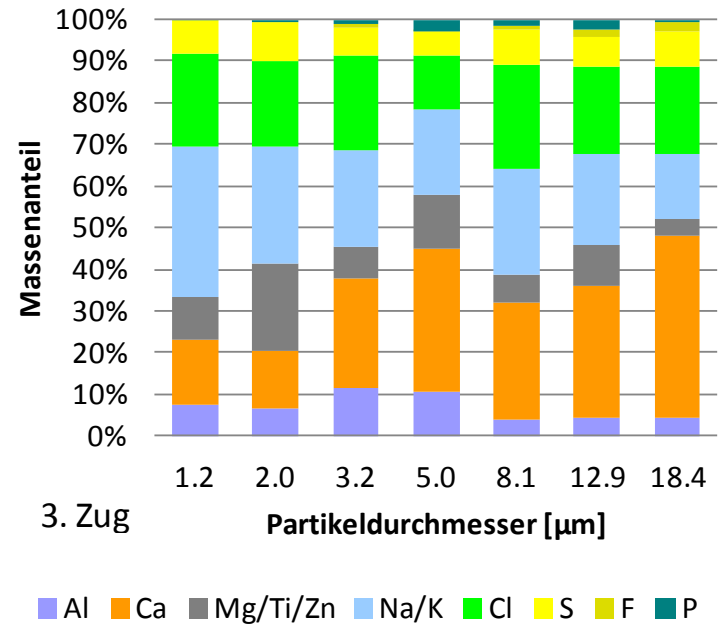
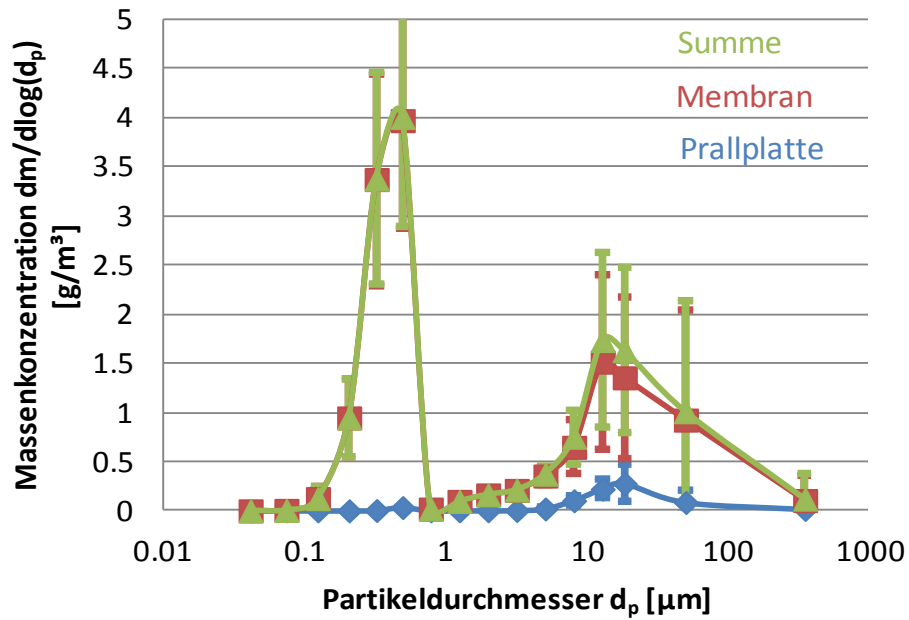


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Chlorine Turnover



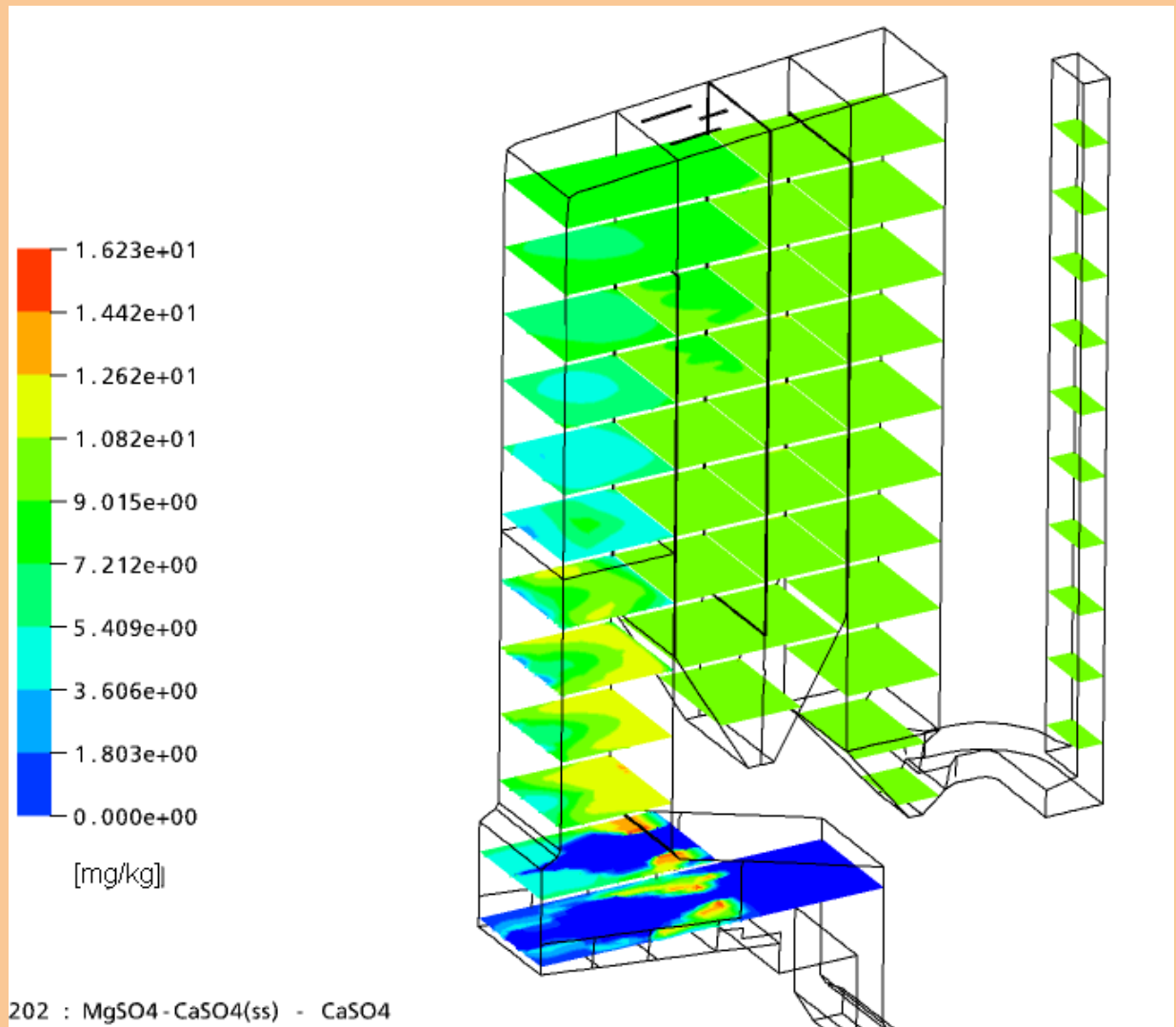
Particle size and consistence



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CFD-ChemApp-Coupling

1,500 Species



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Consistence of deposits

	Combustion Chamber (CC)	1st Pass		2nd Pass	Vertical-Boiler		Horizontal-Boiler		
		On Refractory	Above CC		Medium Height	3rd Pass	4th Pass	3rd Pass	4th Pass
	Mid of right Sidewall			(End-) Super-heater		Eco	Medium Height	(End-) Super-heater	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 ₂ O ₃	9,6	7,2	5,1	3,5	3,2	3,7	3,2	2,5	2,3
Fe ₂ O 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 ₂ O	1,2	3,8	6,0	9,9	7,1	9,6	9,4	8,3	14,8
Na ₂ O	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 ₂ O ₅	3,1	3,1	1,9	1,1	1,3	1,2	0,9	0,8	0,9

Parameters of Simulation

No. :	Educt-Species:	Amount:	Unit:
			(all in normal conditions)
1	O2	6 or 0	Vol.-%
2	H2O	15	Vol.-%
3	CO2	10	Vol.-%
4	C3H8	0 or 3	Vol.-%
5	N2	Rest	Vol.-%
6	SO2	0 or 400 or 4.000 or 40.000	mg/m ³
7	HCl	1.600	mg/m ³
8	Cl2	0 or 5.000 or 10.000	mg/m ³
9	Ca	4.000	mg/m ³
10	K	500	mg/m ³
11	Na	500	mg/m ³
12	Pb	250	mg/m ³
13	Zn	250	mg/m ³
Sum:	Sum:		

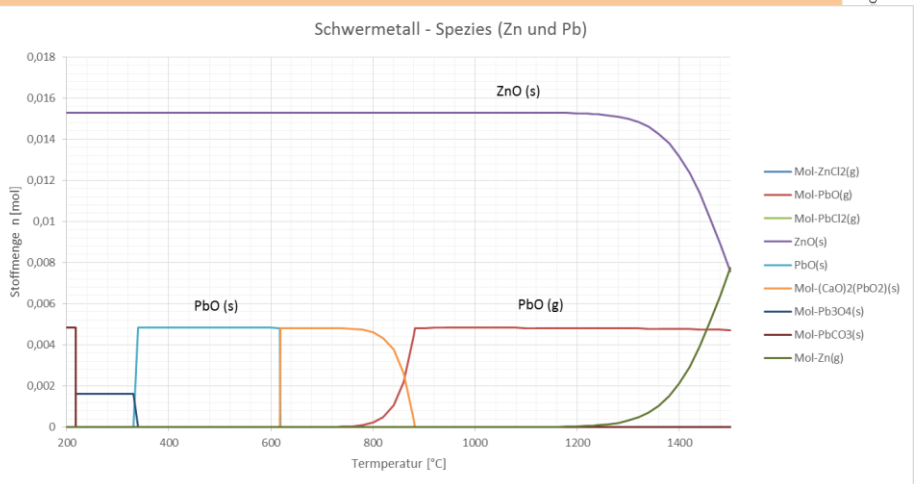
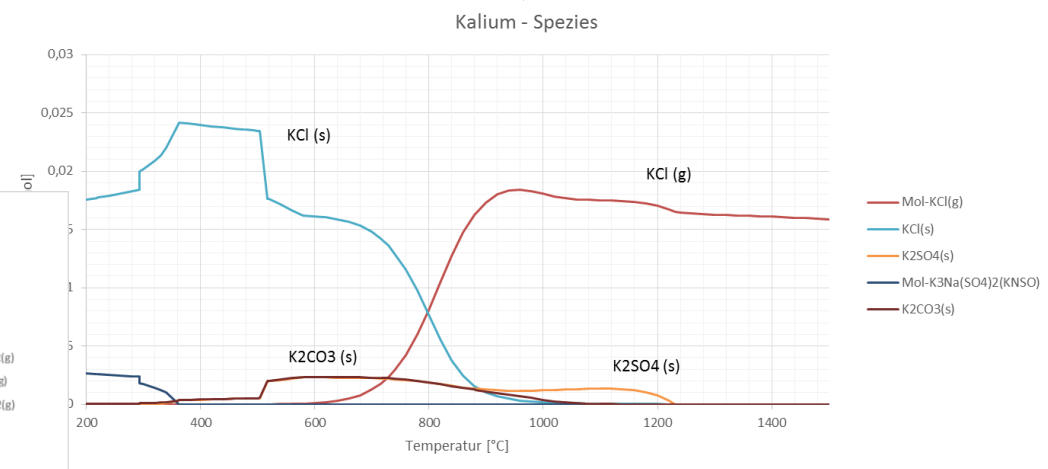
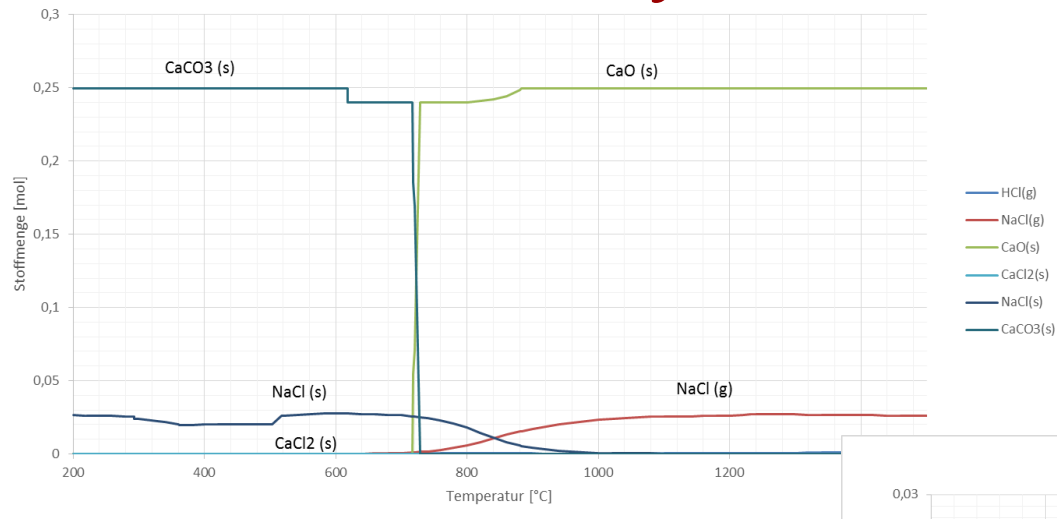
Investigated Cases

Case 1 = oxidising Atmosphere with less Chlor:	Case 1.1:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 400 mg/m ³ Cl2 = 0 mg/m ³	Case 5 = oxidising Atmosphere with high amount of Chlor:	Case 5.1:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 400 mg/m ³ Cl2 = 10.000 mg/m ³
	Case 1.2:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 0 mg/m ³ Cl2 = 0 mg/m ³		Case 5.2:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 0 mg/m ³ Cl2 = 10.000 mg/m ³
Case 2 = reducing Atmosphere with less Chlor:	Case 2.1:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 400 mg/m ³ Cl2 = 0 mg/m ³	Case 6 = reducing Atmosphere with high amount of Chlor:	Case 6.1:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 400 mg/m ³ Cl2 = 10.000 mg/m ³
	Case 2.2:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 0 mg/m ³ Cl2 = 0 mg/m ³		Case 6.2:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 0 mg/m ³ Cl2 = 10.000 mg/m ³
Case 3 = oxidising Atmosphere with medium amount of Chlor:	Case 3.1:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 400 mg/m ³ Cl2 = 5.000 mg/m ³	Case 7 = oxidising Atmosphere with medium amount of Chlor und high amount of Schwefel:	Case 7.1 (with high amount of SO2):	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 4.000 mg/m³ Cl2 = 5.000 mg/m³
	Case 3.2:	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 0 mg/m ³ Cl2 = 5.000 mg/m ³		Case 7.2 (with very high amount of SO2):	O2 = 6 Vol.-% C3H8 = 0 Vol.-% SO2 = 40.000 mg/m³ Cl2 = 5.000 mg/m³
Case 4 = reducing Atmosphere with medium amount of Chlor:	Case 4.1:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 400 mg/m ³ Cl2 = 5.000 mg/m ³	Case 8 = reducing Atmosphere with medium amount of Chlor and high amount of Schwefel:	Case 8.1 (with high amount of SO2):	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 4.000 mg/m³ Cl2 = 5.000 mg/m³
	Case 4.2:	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 0 mg/m ³ Cl2 = 5.000 mg/m ³		Case 8.2 (with very high amount of SO2):	O2 = 0 Vol.-% C3H8 = 3 Vol.-% SO2 = 40.000 mg/m³ Cl2 = 5.000 mg/m³

Oxi.: HCl only, no additional Cl (Case 1)

HCl "absorbed" by Na and K
 less by Ca
S "absorbed" by K at first

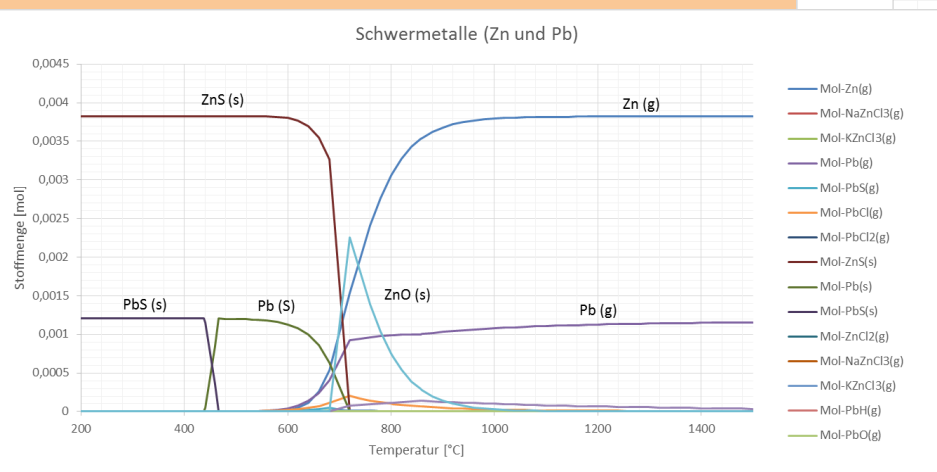
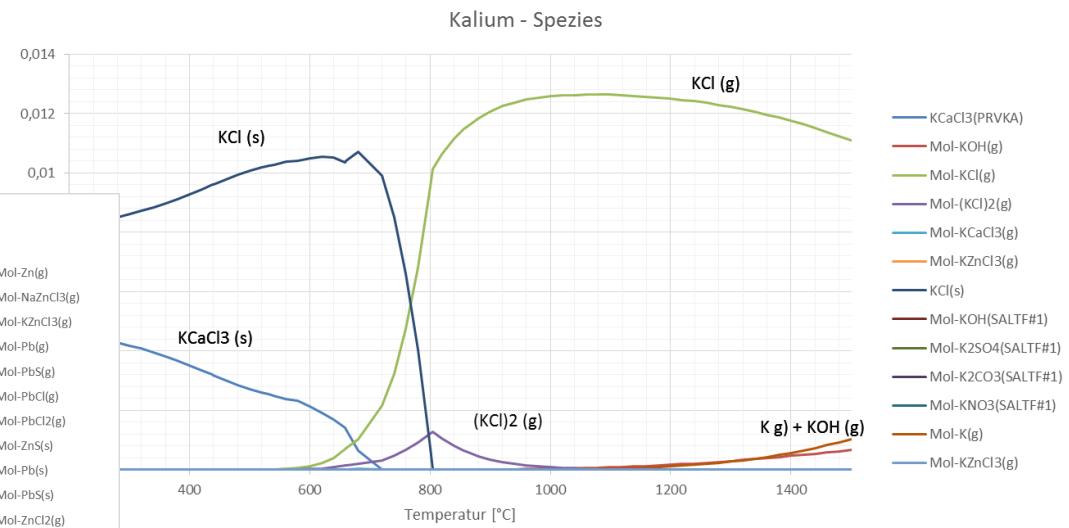
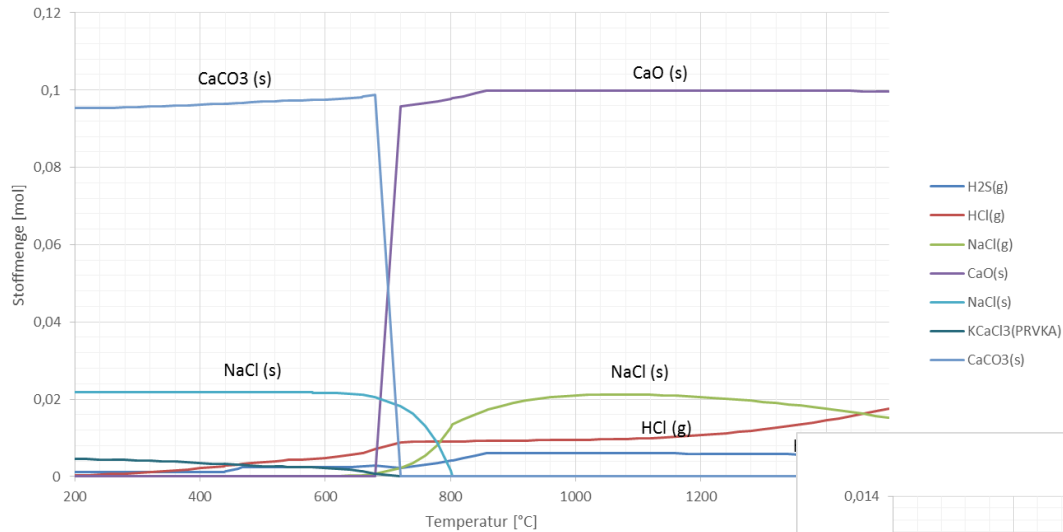
CaO formation at 700 °C
KCl^g ; **PbCl^g** at 850 °C



Red.: HCl only, no additional Cl (Case 2)

HCl “absorbed” mainly by Na, K
S “absorbed” mainly by Pb, Zn

CaO; KCl⁹ formation at 700 °C

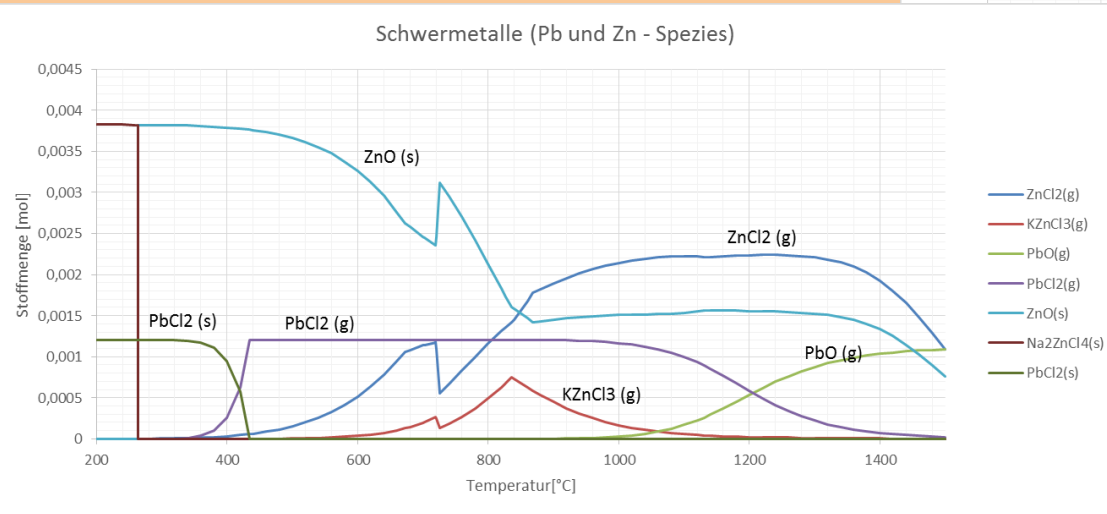
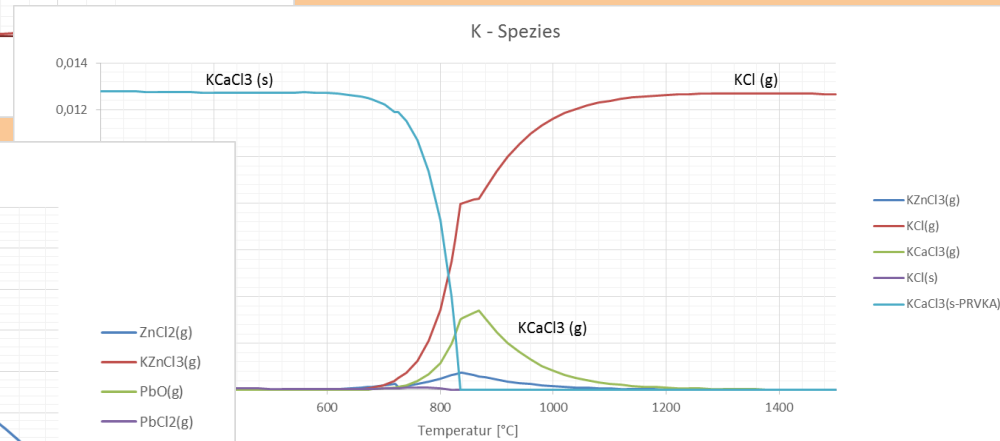
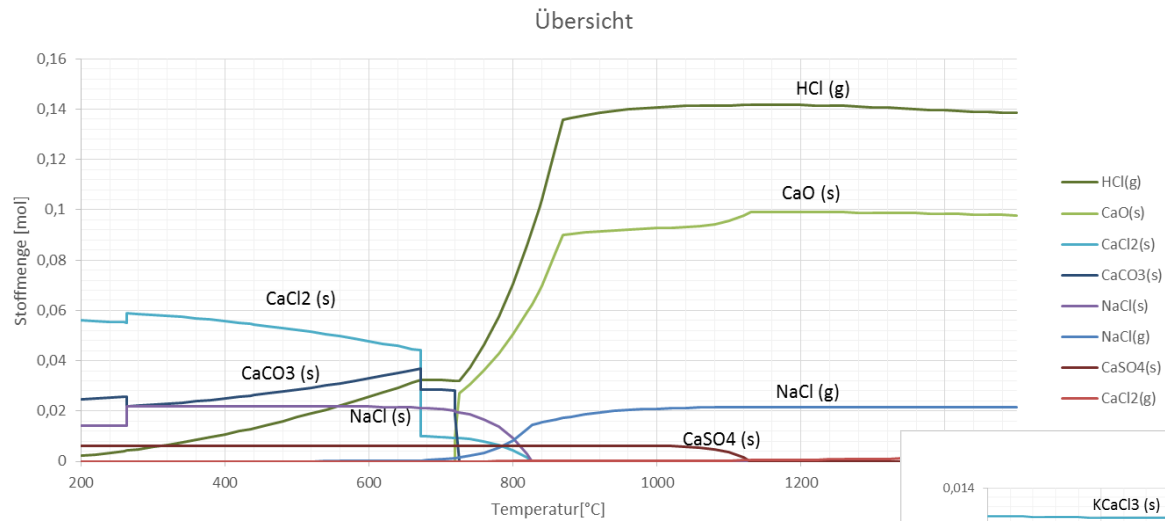


Oxi.: HCl, additional Cl (Case 3)

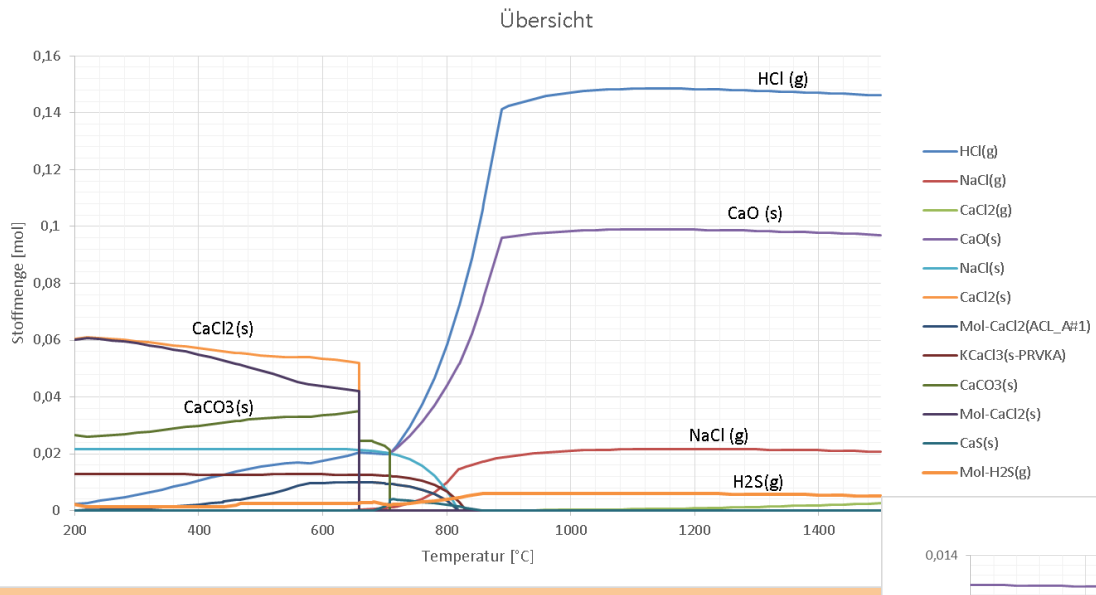
(low S)

Cl to HCl, Na, K, Ca
also to Pb, Zn
S "absorbed" by Ca at first

CaO; KCl^g formation at 800 °C

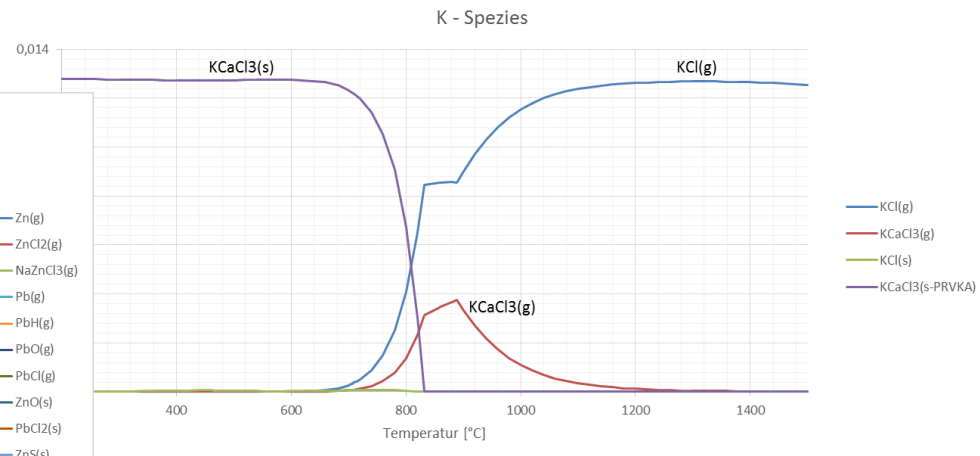
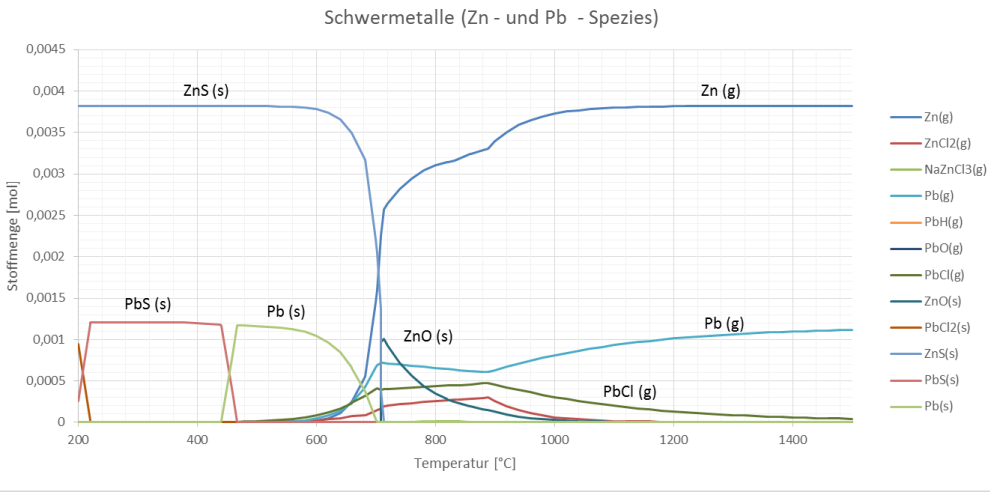


Red.: HCl, additional Cl (Case 4) (low S)



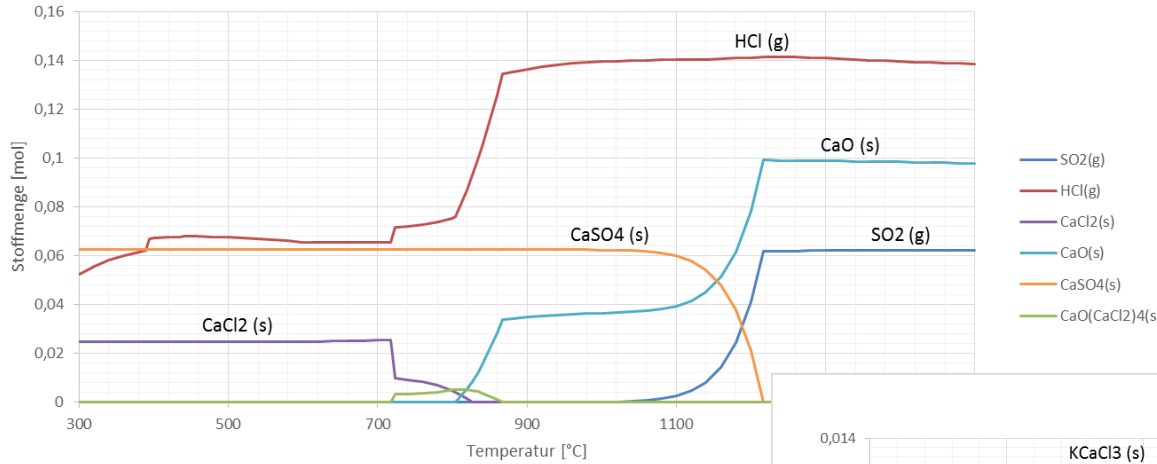
Cl to Na, K;
 HCl > 800 °C
 Ca < 700 °C, less Pb
S to Pb, Zn < 700 °C
 H₂S > 800 °C

CaO, KCl⁹ formation at 800 °C



Oxi.: A lot of Cl + S (Case 7)

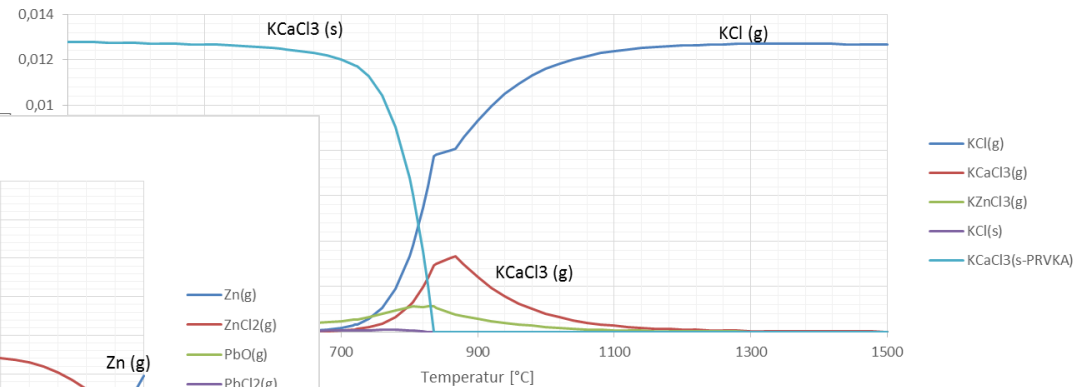
Übersicht



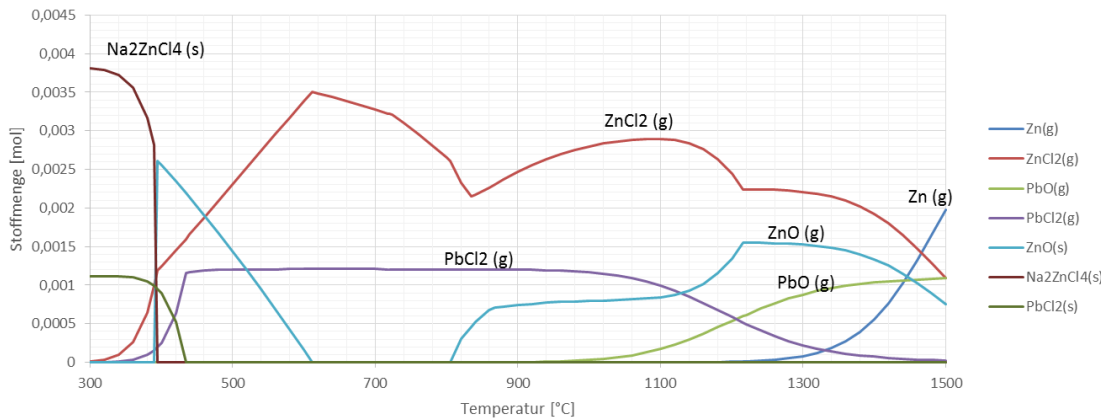
Cl to HCl, Na, K, Pb, Zn and Ca at low T
S to CaSO4 < 1200 °C,
 SO2 > 1200 °C

CaO, KCl⁹ formation at 800 °C

K - Spezies



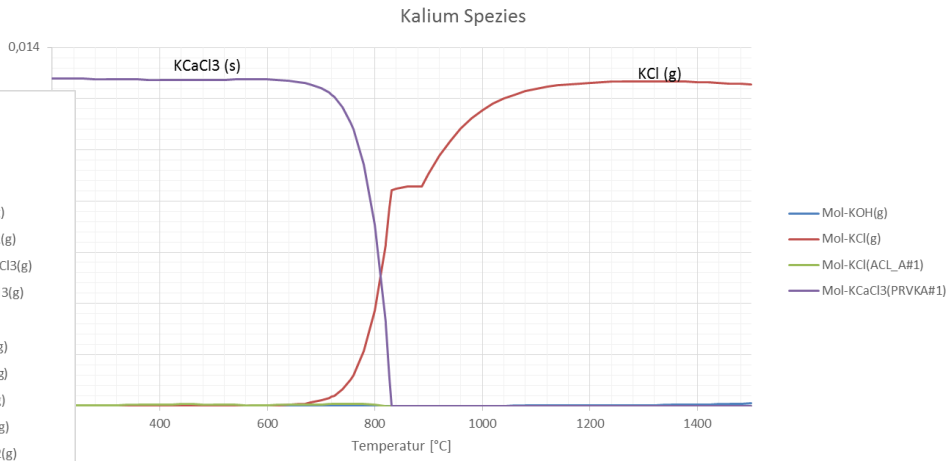
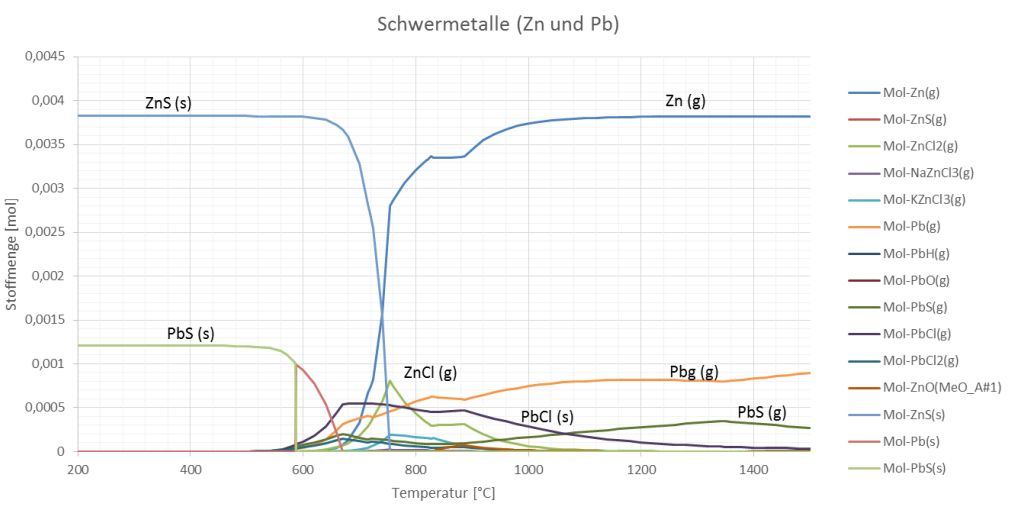
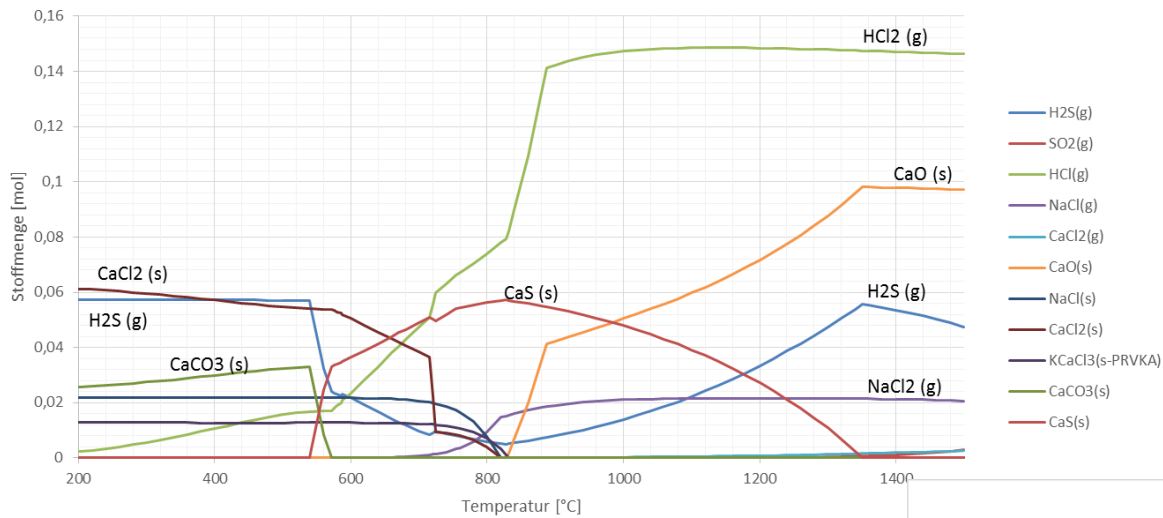
Schwermetalle (Pb und Zn - Spezies)



Red.: A lot of Cl + S (Case 8)

Cl to Na,K;
 HCl > 800°C;
 Ca < 600°C, less Pb
S to H₂S, CaS and
 ZnS, PbS at low T

CaO, KCl⁹ formation > 800 °C



Résumé

For the waste-to-energy system:

Chlorine: First built species: KCl and NaCl

Next step: $T < 800^{\circ}\text{C}$ to CaCl_2

$T > 800^{\circ}\text{C}$ to HCl

Similarity between oxidising and reducing

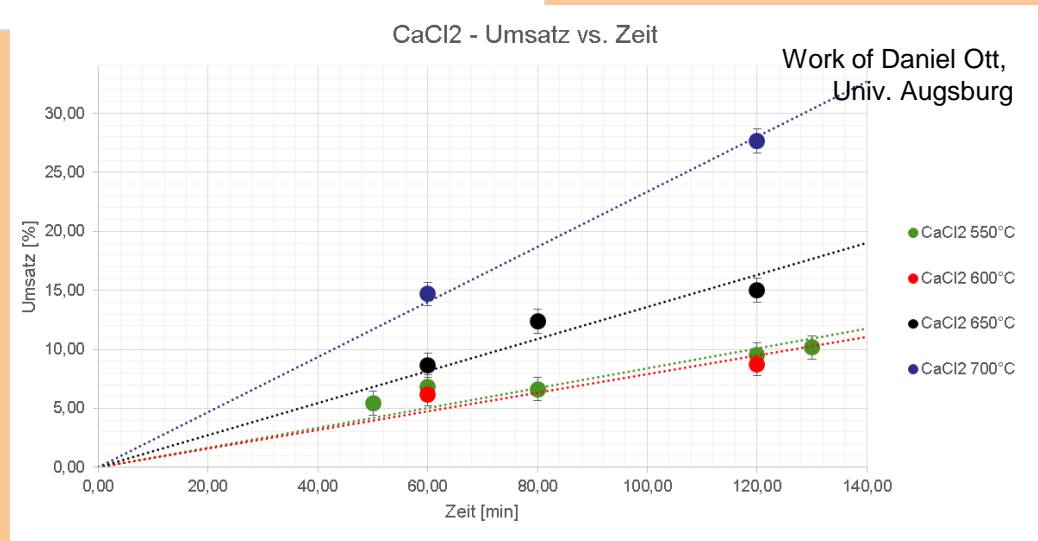
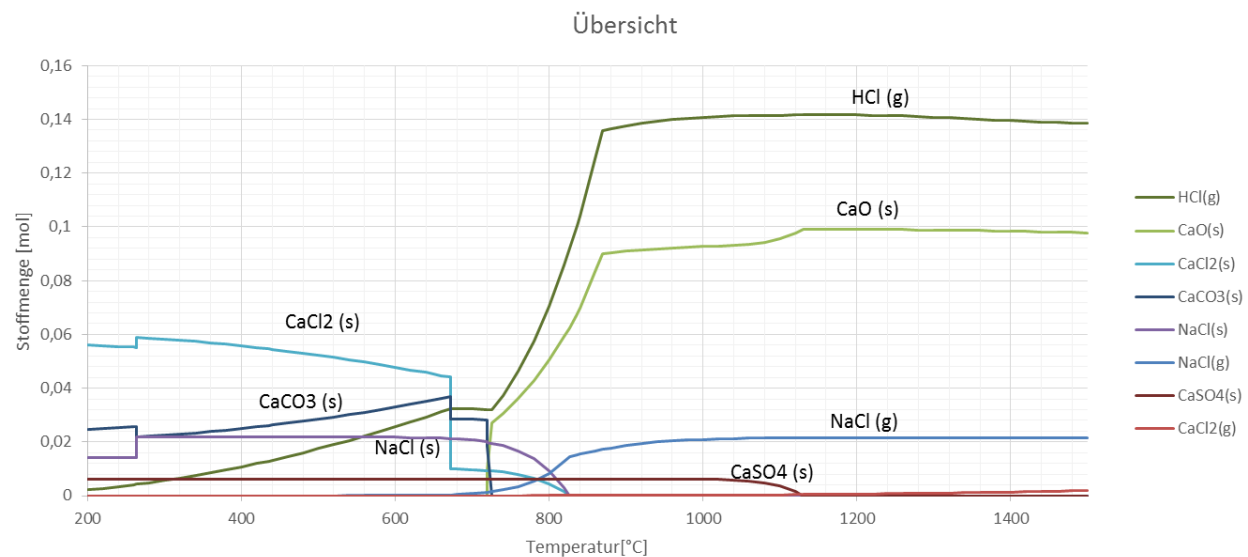
Sulphur: First built species: PbS and $\text{ZnS} < 700^{\circ}\text{C}$

Next step: $T < 600^{\circ}\text{C}$ and $> 1200^{\circ}\text{C}$ to H_2S

$T > 600^{\circ}\text{C}$ and $< 1200^{\circ}\text{C}$ to CaS

CaO formation is shifted from 800°C to 1100°C by adding S and/or O

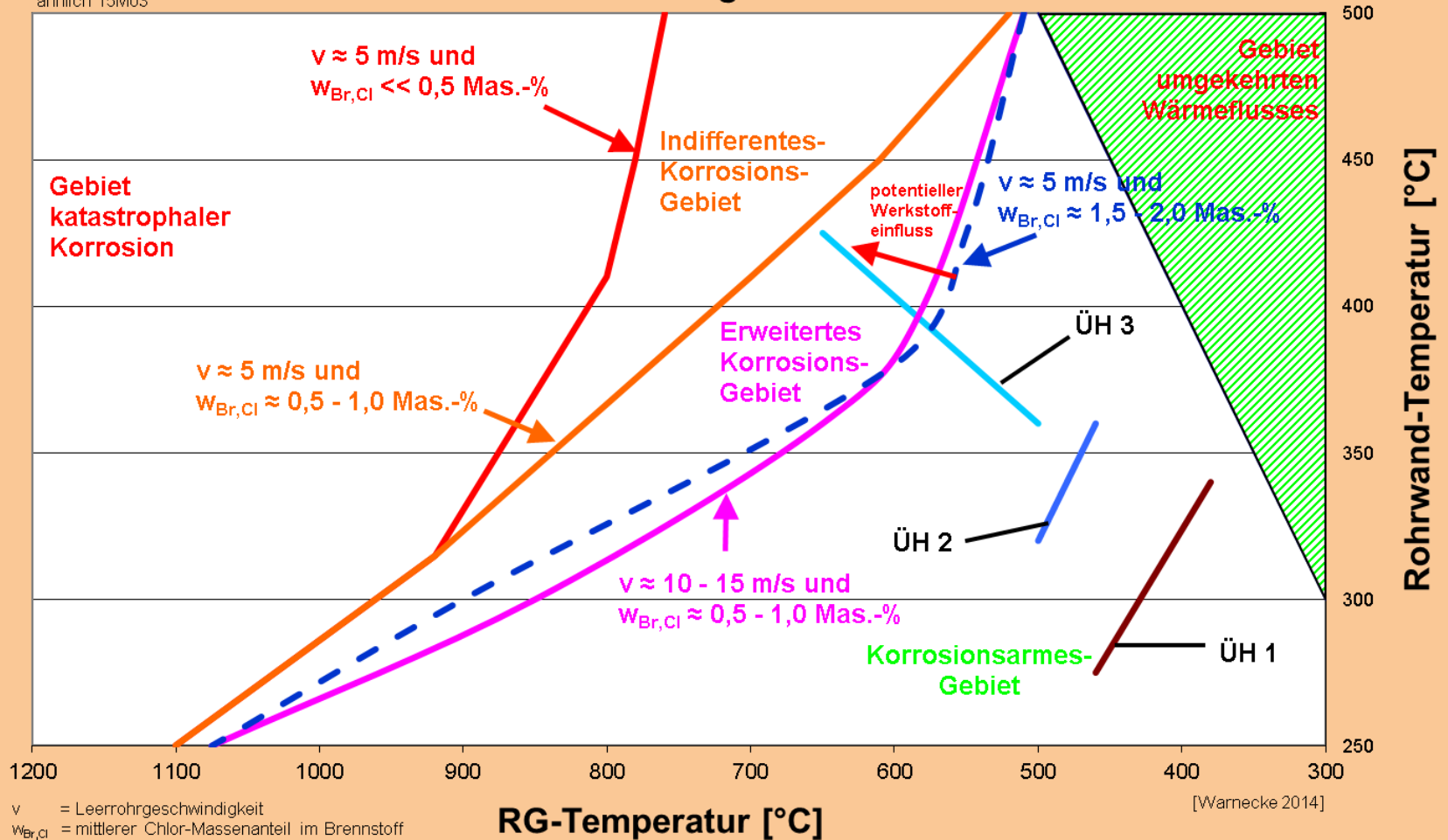
Kinetic Influences



Corrosion Diagram

Korrosionsdiagramm erweitert um Einfluss von RG-Geschwindigkeit und Brennstoff-Chlor

gültig für Werkstoffe
ähnlich 15Mo3



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4. Summary and Outlook

- Corrosion at superheaters is a severe problem in waste-to-energy plants. Chlorine content of particle causes this corrosion mainly
- Particle can probably be influenced on their way or react within the deposits
- FactSage delivers a better understanding of the relevant species
- Next step is to extend the species with Si, Al, Fe and investigate the particle consistence
- Kinetic investigations will be added to the thermodynamic calculations

Thank you for your attention and ...

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“VOKos”

as well as to PtJ for managing the whole
MatRessource measure!

