Lehrstuhl für Energiesysteme

Bundesministerium für Wirtschaft und Technologie

ALLIANZ INDUSTRIE FORSCHUNG

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EQUILIBRIUM CALCULATIONS FOR SULPHAT REACTIONS IN BIOMASS COMBUSTION

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Agenda.

1. Motivation.
2. State of the art.
3. The project aims.
4. Mechanisms of corrosion reduction.
5. Test facility.
6. Summary.
7. Forecast.

1. Motivation.

Pollution and chlorine corrosion are the main cause of the operation time limitation.

2. State of the art.

influence of corrosion.

combustion conditions.

fuel composition.

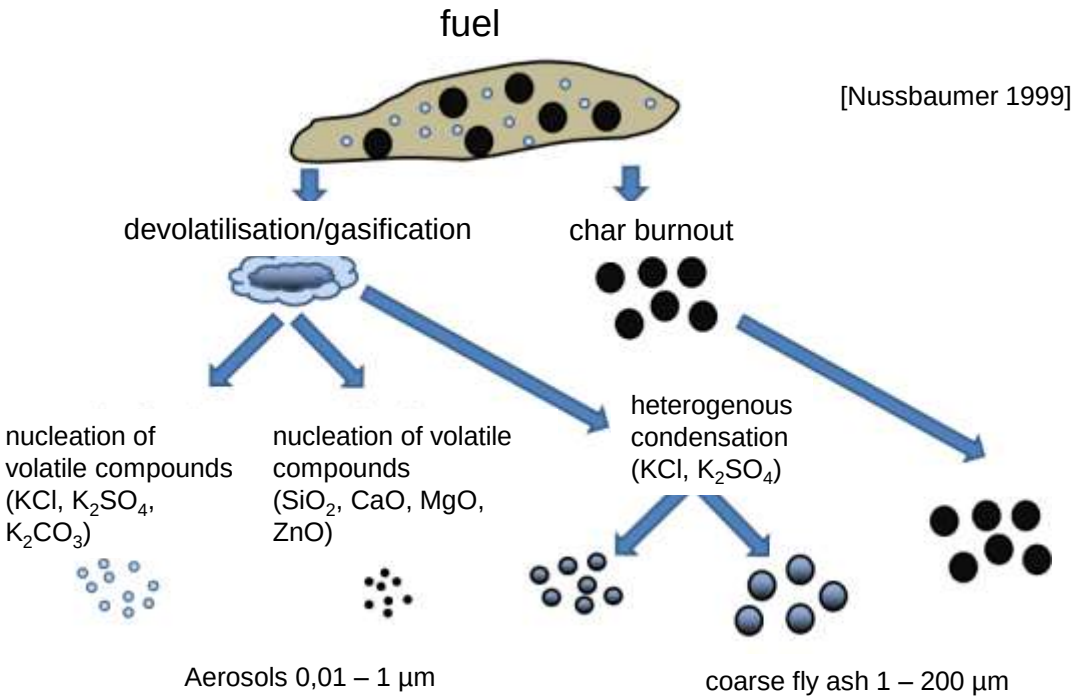
no correlation.

2. State of the art.

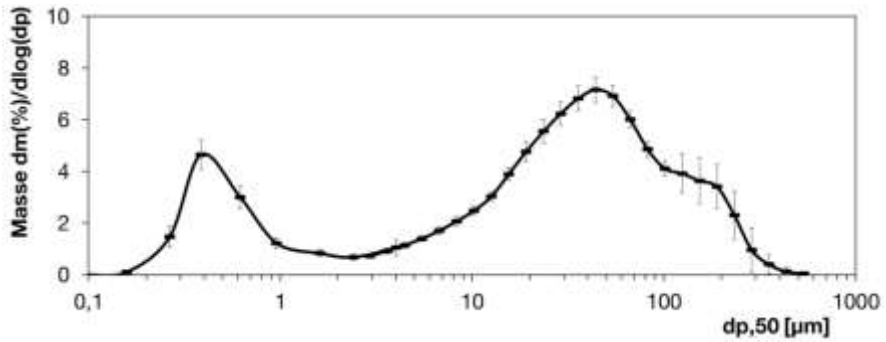
First step.

combustion.

aerosol and particle formation.



[Nussbaumer 1999]



[Balan 2013]

2. State of the art.

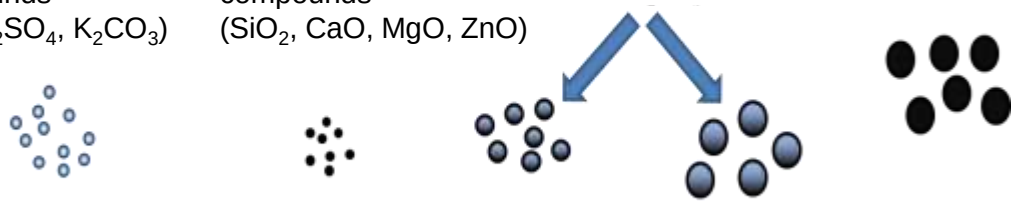
Second step.

deposition.

nucleation of volatile compounds (KCl, K_2SO_4, K_2CO_3)

nucleation of volatile compounds (SiO_2, CaO, MgO, ZnO)

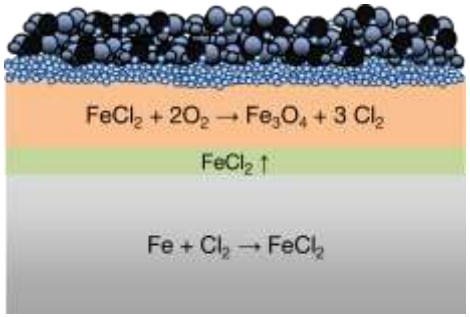
heterogenous condensation (KCl, K_2SO_4)



Aerosols 0,01 – 1 µm

coarse fly ash 1 – 200 µm

corrosion.



[Balan 2013]

2. State of the art.

Reduction options - Reaction with alkali metals M

(1) Sulfation:

$$2MCl + SO_2 + \frac{1}{2}O_2 + H_2O \longrightarrow M_2SO_4 + 2HCl$$

(2) Aluminum silicates:

$$2MCl + Al_2O_3 \cdot SiO_2 + H_2O \longrightarrow M_2O \cdot Al_2O_3 \cdot 2SiO_2 + 2HCl$$

CAUTION: competing reactions with Ca can inhibit the reactions!

3. The project aims.

Increasing energy and material efficiency.

Development of a corrosion reduction concept.

Innovation.

– Innovative insights by combination of established and proven measurement techniques.

– Online measurements in corrosion testing facility under controlled condition.

3. The project aims. Overview.

Fuel analysis.

natural and doped fuels.

- Elemental analysis
- Brief analysis
- Ash analysis
- Ash melting analysis
- Heat value analysis

Measurement in testing facility

- Variation of fuel compostion
- Constant operation conditions

- Particle sampling
- Flue gas analysis
- Deposition analysis
- Online & Offline corrosion measurement

Validation

FactSage

Measurement in power plant

Biomass plant Schkölen

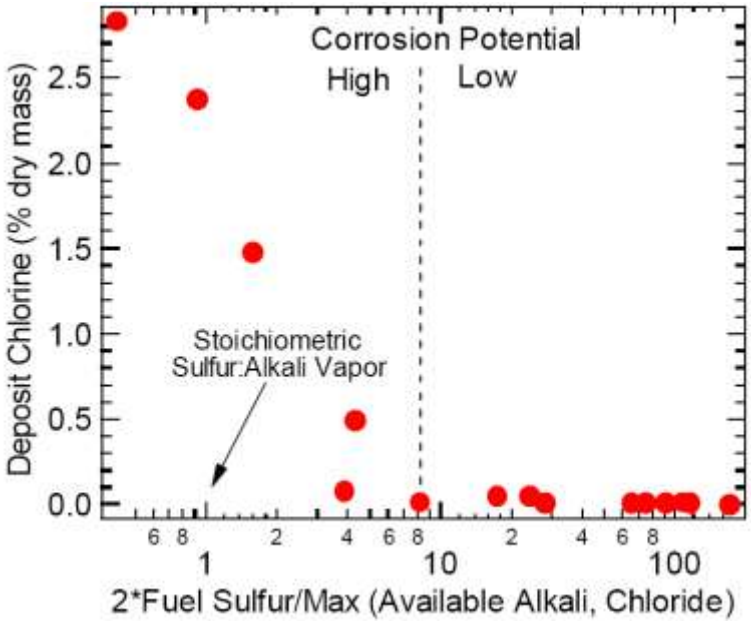
Corrosion reduction concept

4. Mechanisms of corrosion reduction. Sulfation.

$$2MCl + SO_3 + H_2O \longrightarrow M_2SO_4 + 2HCl$$

Dependencies:

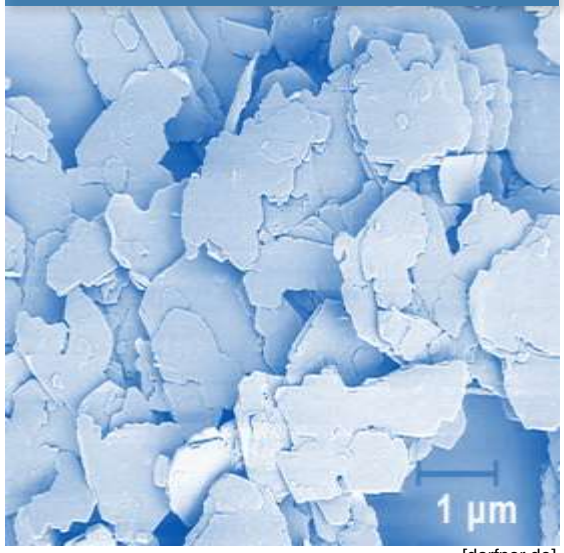
- Sulfur supply
- Vapor content
- Oxygen content (SO_3 formation)
- Temperature
- Residence time
- Competing reactions (Ca, Mg)
- Catalysts (iron oxides)



[Baxter 1997]

4. Mechanisms of corrosion reduction. Sulfation.

Additives:



[dorfner.de]

- Elemental sulfur,
- Sulfates: gypsum, $(NH_4)_2SO_4$ (Chlorout / patent: SE 0100220-3), $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$
- Sulfides (pyrite)
- SO_3, SO_2, sulfur carriers from flue gas cleaning, sulfur recirculation
- Sulfuric acid

4. Mechanisms of corrosion reduction. Sulfation.

Effects on emmision:

↑ SO_2

Effects on aerosols and particles:

Aerosols d_p< 1 µm:	↑ Particle size & ↑ particle number ↓ Cl- content
Coarse fly ash d_p > 1 µm:	Number of particles does not change ↑ Ca- and Si- content

4. Mechanisms of corrosion reduction. Sulfation.

Effects on depostion:

↑ Depostition rates

Stronger correlation between S and K content recognazible

↓ Cl- content

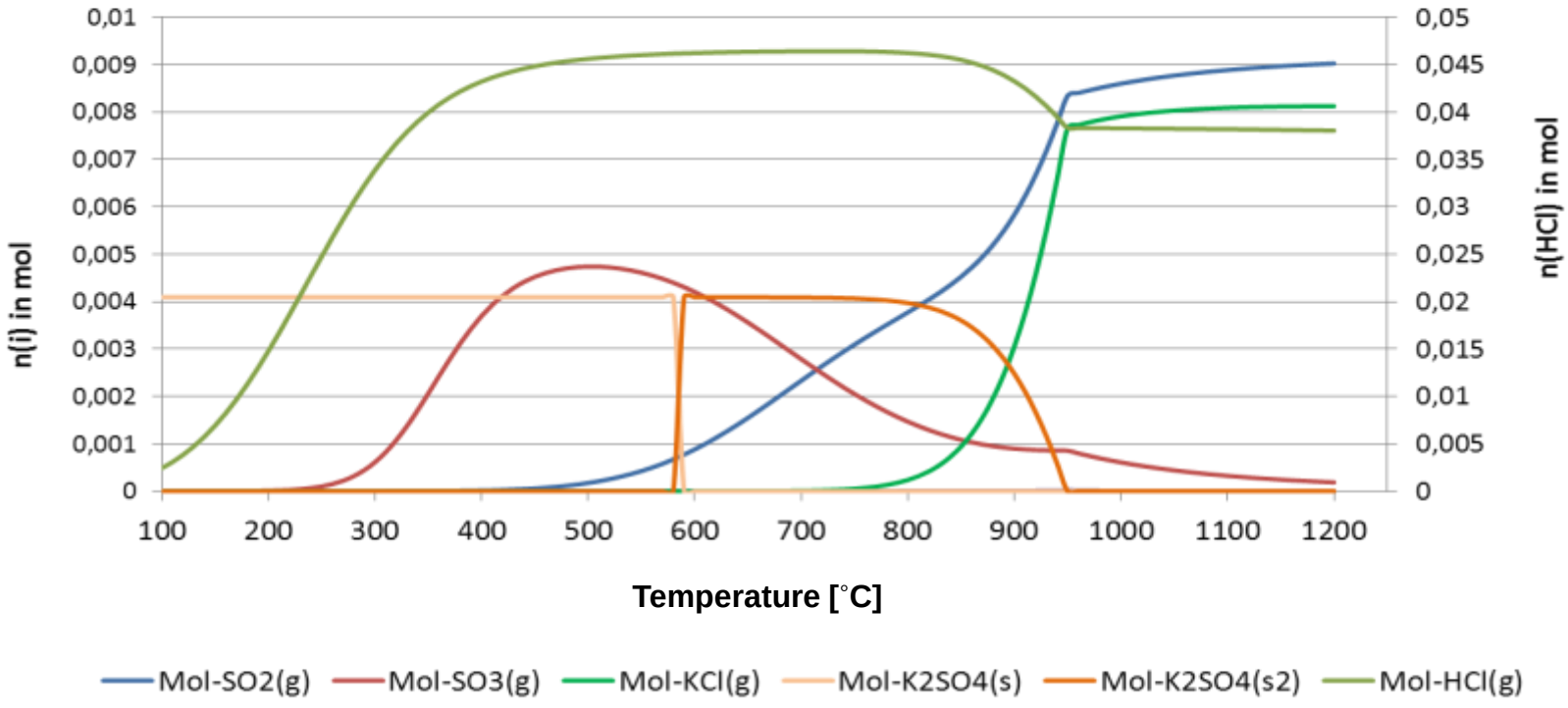
Effects on corrosion:

Sulfation in flight phase	positive
Sulfation of tube surface	negative

4. Mechanisms of corrosion reduction. Sulfation.

Equilibrium of sulfation

equilibrium position of sulfation (FactSage)



[Balan 2013]

4. Mechanisms of corrosion reduction. Embedding reactions.

$$2MCl + Al_2O_3 \cdot xSiO_2 + H_2O \longrightarrow M_2O \cdot Al_2O_3 \cdot xSiO_2 + 2HCl$$

Dependencies:

- Temperature / pressure
- Al / Si ratio and the reactivity
- Water content
- Residence time
- Getter (Specific surface area and particle size, etc.)
- Competing reactions (Ca, Mg)
- Type of co-combustion

4. Mechanisms of corrosion reduction. Embedding reactions.

Additives:

- Ash, glass, sand, vessel dust, clay minerals, limestone, burnt lime, dolomite, ophit,
- Zeolite, kaolin (Patent 250568), halloysite,
- Acid-activated bentonite and oxidic melts (Patent WO 98/03616)
- Sewage sludge, paper sludge, coal combustion mixed with biomass and peat

4. Mechanisms of corrosion reduction. Sulfation.

Effects on emmision:

↑ HCl

Effects on aerosols and particles:

Aerosols d_p< 1 µm:	↓ Number of particles (particle size remains the same) Cl and K dominant
Coarse fly ash d_p > 1 µm:	↑ Particle number ↑ Al content ↓ K and Cl

4. Mechanisms of corrosion reduction. Sulfation.

Effects on depostion:

↑ Deposition rates
↑ Al content
↓ Cl content
↑ Ash melting temperature (no sticky particles & depostions)

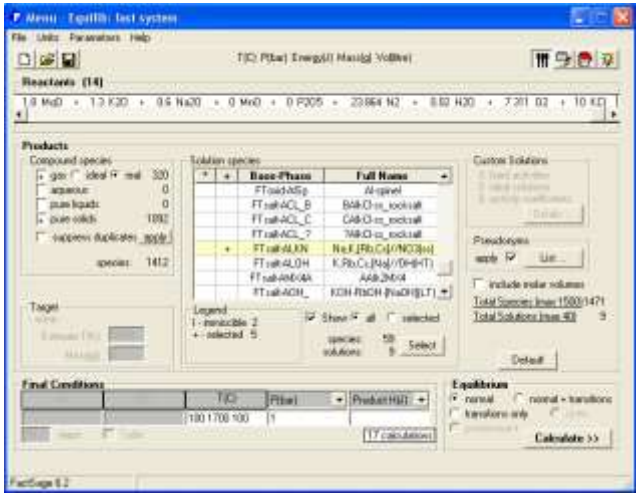
Effects on corrosion:

Tendency decline (?)

4. Mechanisms of corrosion reduction. Embedding reactions.

Input FactSage (ICP analysis & TGA settings)

Input in %	Kaolin (SM)	Sand (SS)	E-Glas	Ash (SWM)
SiO_2	59,84	93,31	59,24	47,80
Al_2O_3	36,10	2,90	12,94	30,40
Fe_2O_3	1,25	0,83	0,94	6,90
TiO_2	0,29	0,60	0,15	2,0
CaO	0,12	0,03	22,75	7,4
MgO	0,29	0,03	2,77	1,8
K_2O	0,91	0,49	0,26	1,3
Na_2O	0,02	n.n.	0,39	0,6
MnO	0,01	n.n.	0,01	n.n.
P_2O_3	0,02	n.n.	0,02	n.n.
KCl	10,00	10,00	10,00	10,00
H_2O	0,02	0,02	0,02	0,02
N_2	23,86	23,86	23,86	23,86
O_2	7,31	7,31	7,31	7,31
Al_2O_3/SiO_2	0,6	0,03	0,22	0,64



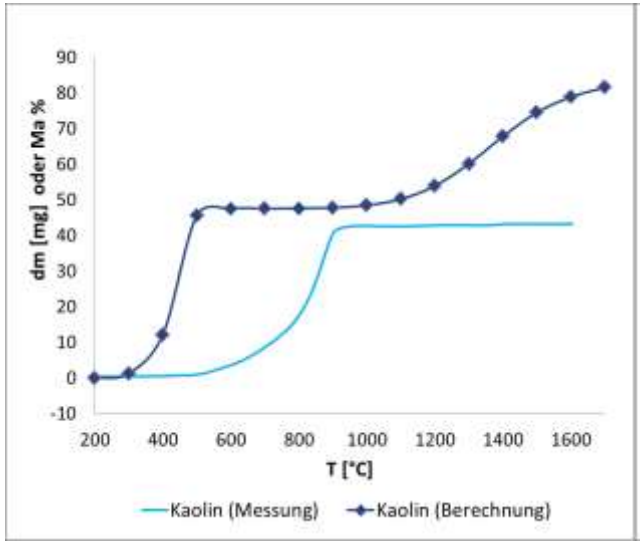
Database:
FT misk-FeLQ
FT oxid SLAGA
FT oxid MeO_A
FT oxid CORU
FT oxid MULF
FT salt ACL_B
FT salt-AMX4A
FT salt SALTB

[Balan 2013]

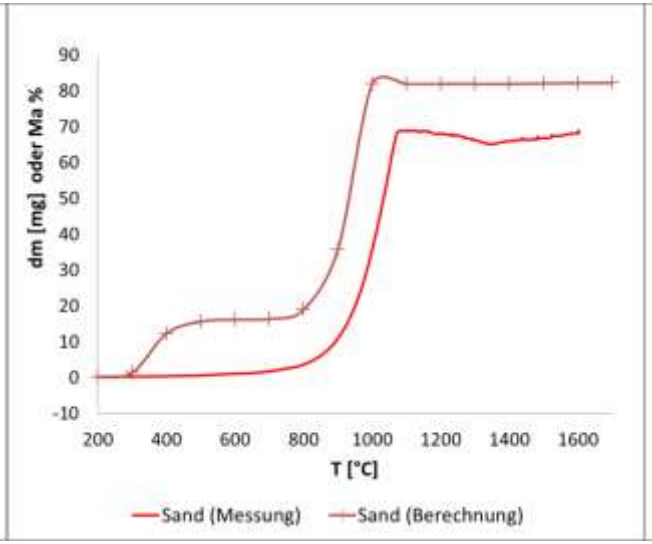
4. Mechanisms of corrosion reduction. Embedding reactions.

Alkali release

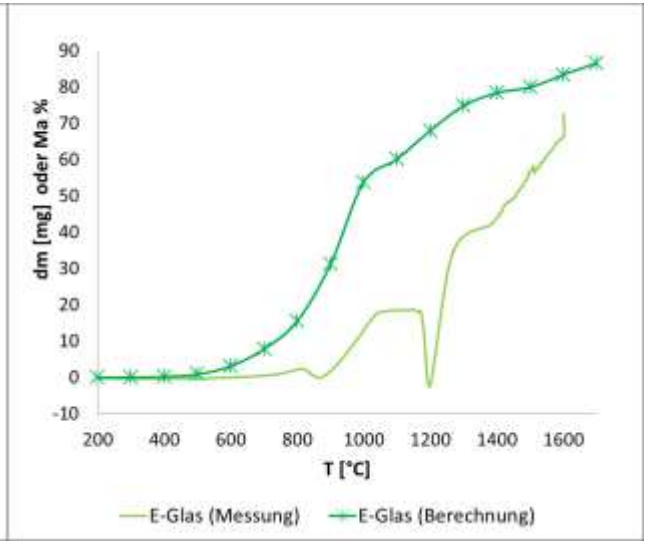
Kaolin



Sand



E-Glas



[Balan 2013]

5. Test facilities.

Biomass power plant – Schkölen.

Fuel:	Wood
Thermal input:	19,5 MW
Turbine power:	5,36 MW_{el}
Use of th. energy:	ca. 75%
Amount of steam:	22 t/h
Hot steam temp.	485 ° C
Pressure:	68 bar

Entrained flow reactor

Constant defined operating conditions

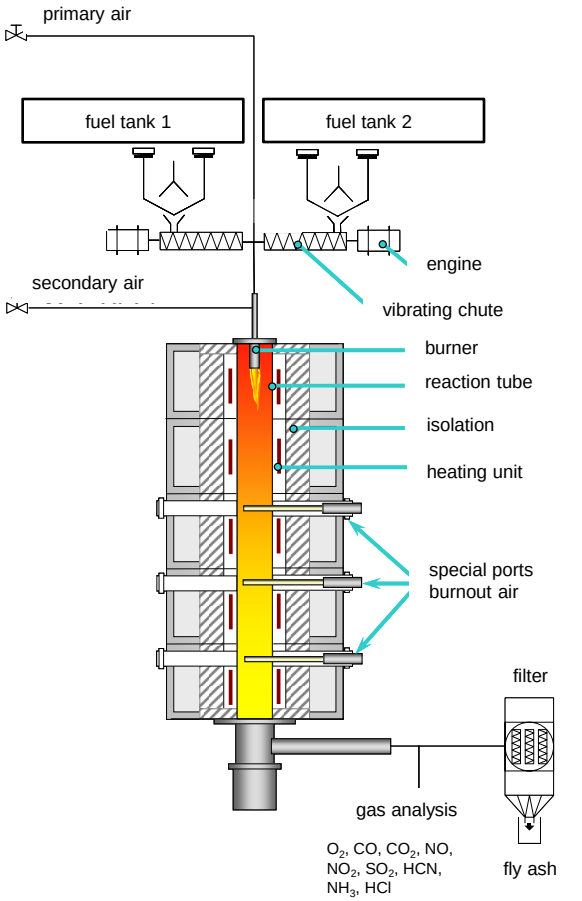
Use of defined fuels (milled)

Minimal damage to risky operating conditions

Fuel mass flow: 2.5 - 5 kg / h

Max. heating temperature 1600 ° C

Heating power: 50 kW



[Balan 2013]

6. Summary.

Pollution.

Pollution and chlorine corrosion are the main cause of the operation time limitation.

Corrosion.

Pollution and chlorine corrosion are the main cause of the operation time limitation.

Investigation of the corrosion reduction by sulfation and reactions with getter material.

- Entrained flow reactor
- Biomass power plant

7. Forecast.

- Simulation and validation of sulfation by FactSage.
- Rating of the gettermaterial by FactSage.
- Development of a corrosion reduction concept.

THANK YOU FOR YOUR ATTENTION.

TU München: Prof. Hartmut Spliethoff
M.Sc. Andreas Stephan

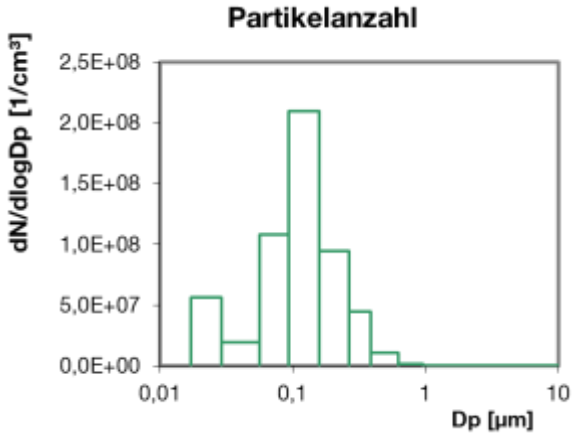
sind die Folien wirklich Backup?

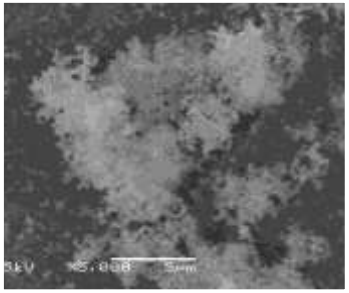
Backup.

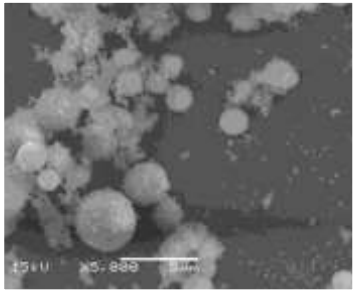
6. Vorstellung der Messtechnik

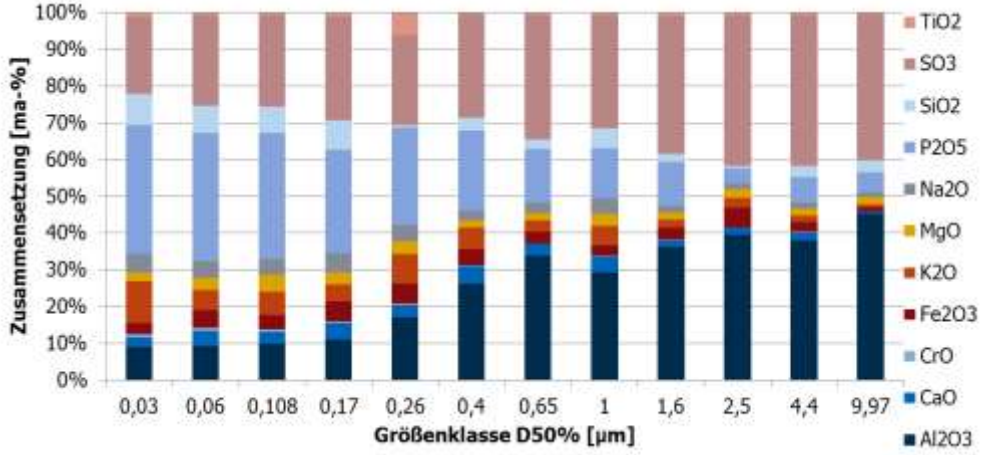
Entnahme von Aerosolen und Partikeln

- Partikelgrößenverteilung: 0,007 µm – 10 µm (Online)
- Partikelmorphologie
- Partikelzusammensetzung
- Entnahme an unterschiedlichen Ebenen im Reaktor









5. Vorstellung der Anlagen

Brennstoffe

- naturbelassen & mit Chemikalien dotiert nach folgenden Kriterien

Dotierung	Kategorie I	Kategorie II	Kategorie III	Kategorie IV	Kategorie V
K	n	↑	↑	↑	↑
Cl	n	↑	↑	↑	↑
S	n	n	↑	n	n
Ca	n	n	n	n	↑
Al-Si	n	n	n	↑	↑

(n) normaler Anteil des Elements, (↑) erhöhter Anteil durch Dotierung

Kategorie I: Naturbelassenen Brennstoffen

Kategorie II: Simulation einer korrosiven Atmosphäre

Kategorie III: Simulation von Sulfatierungsreaktionen an Alkalichloriden

Kategorie IV: Simulation von Einbindungsreaktionen von Alkalien durch Aluminosilikate

Kategorie V: Untersuchung des Einflusses von Konkurrenzreaktionen mit Ca auf die Sulfatierungsreaktionen und die Einbindungsreaktionen durch Aluminosilikate