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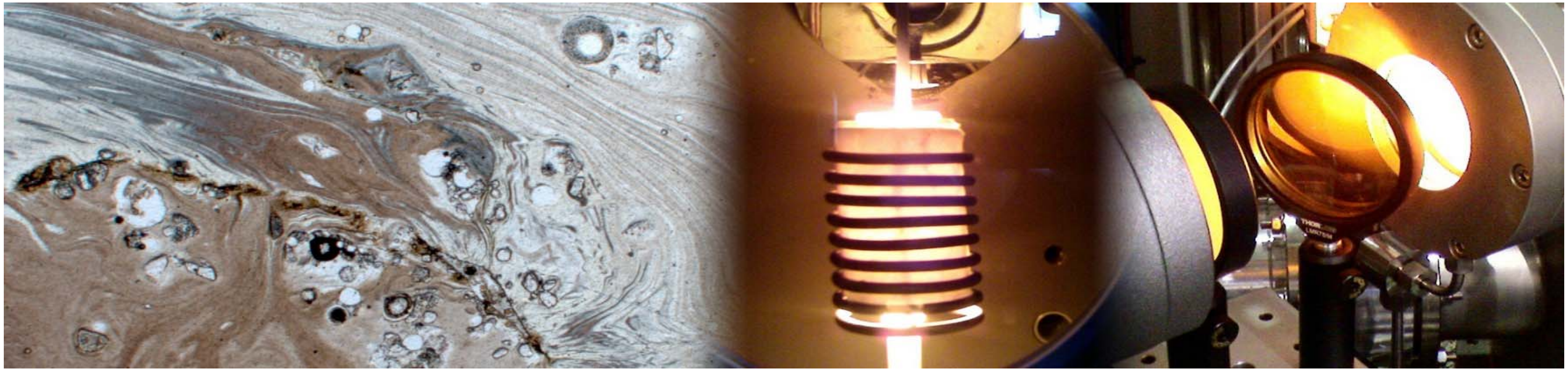
Application of thermochemistry for the prediction of slagging in coal fired boilers



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*Lausitz Energie Kraftwerke AG

GTT Users' Meeting, 26th June 2019, Herzogenrath

R&D Project KORRISTENT

KORRISTENT

- **Funding** by BMWi (Federal Ministry for Economic Affairs and Energy) program „Anwendungsorientierte nichtnukleare F&E im 6. Energie-forschungsprogramm“, Förderbereich „Kraftwerkstechnik sowie CO_2-Abscheidung und –speicherung“
- **time:** 01/01/2016 - 31/12/2019
- **project ID:** 03ET7066A

Cooperation partner

- TU Bergakademie Freiberg
    - Institute of Energy Process Engineering and Chemical Engineering (IEC)
    - Institute of Analytical Chemistry (IAC)
    - Institute of Ceramic, Glass and Construction Materials (IKGB)
- Lausitz Energie Kraftwerke AG

Objective

Development of solutions for reduced slagging of coal fired boilers especially for critical fuels

Power station Boxberg

Issue

- 900 MW el., pulverised fuel firing systems, tower type boiler, **blend of RW/NO lignite**
- **Slagging of boiler wall**, sintered deposits at “Schott” (first horizontal tube bundle heat exchanger)
- Automated cleaning system (water cannons) keeps slagging manageable
- **decreasing coal quality in future** requires R&D

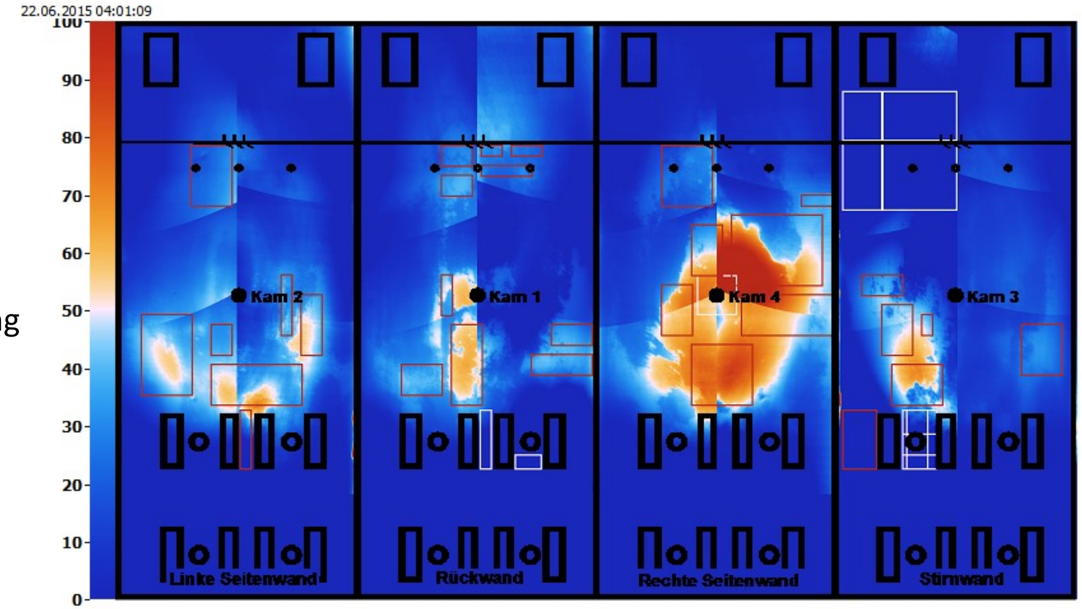


Fig: thermal image, LEAG

Work plan

- Analysing context between coal/ash properties, operation parameters and slagging based on process samples
    - Chemical-mineralogical characterization of proces samples (XRF, REM-EDX/WDX + EBSD, XRD, CT)
    - Development and application of ICP-OES with electro-thermal evaporation
    - experimental investigations (impedance spectroscopy, simulation of slagging in drop tube reactor)
- Modelling via thermochemistry and CFD
- providing applicable proposal for solution

Sample pool

Sample period	blend RW/NO	coal	fly ash	wet ash	deposits
May/June 2015	50/50…70/30…100/0	-	**78**	-	**1** aluminosilicatic slagged
October 2015	70/30	**42 shift samples**	**42 shift samples**	**42 shift samples**	-
December 2015	60/40	-	-	-	1 Fe-dominated
July 2016	100/0	**1** mixed sample	**48**	**103**	**1** aluminosilicatic slagged (large slagged lumps) **+ 34** Fe-dominated
November 2016	0/100	**1** mixed sample	-	-	-
August 2017	50/50	-	-	-	**17** Fe-dominated
December 2016	100	coals and sediments from opencast mine RW			

Coal (set of 42 shift samples RW/NO 70/30)

Oxid	Average Ma.-%	Min. Ma.-%	Max. Ma.-%
SiO_2	**39,8**	**30,0**	**50,2**
Al_2O_3	**14,7**	**7,7**	**20,1**
Fe_2O_3	**12,2**	**7,6**	**15,3**
CaO	**12,2**	**7,7**	**15,8**
MgO	2,5	1,8	3,2
SO_3	16,2	10,4	22,5
Na_2O	0,2	0,2	0,2
K_2O	1,1	0,6	1,8
TiO_2	1,1	0,7	1,5
Summe	100		

Mineral	Formel	Ma.-% coal wf
Quartz	**SiO_2**	**10-13**
Kaolinite	**$Al_2(Si_2O_5)(OH)_4$**	**5-11**
Muscovite	$KAl_2[(OH)_2 \vert AlSi_3O_{10}]$	0-9
Pyrite	**FeS_2**	**2-5**
Marcasite	FeS_2	max. 0,5
Anatase	TiO_2	1-2
Gypsum	$CaSO_4 * 2H_2O$	0-3

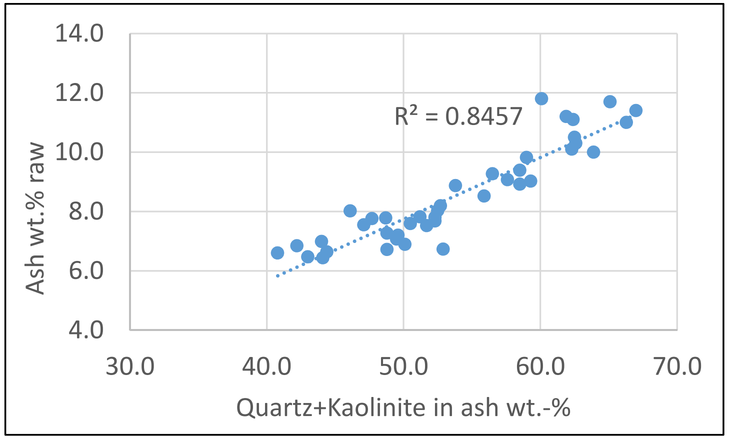
- Ash content 6–12 Ma.-% raw, B/A = 0,3–0,9
- Quartz, clay minerals and pyrite dominate
- Al, Si, 50% Fe, K, Ti → extraneous ash (70%), **sediments**
- Ca, Mg, 50% Fe → inherent ash (30%), humates
- Flow temperature in red. atmosphere in average 1330°C

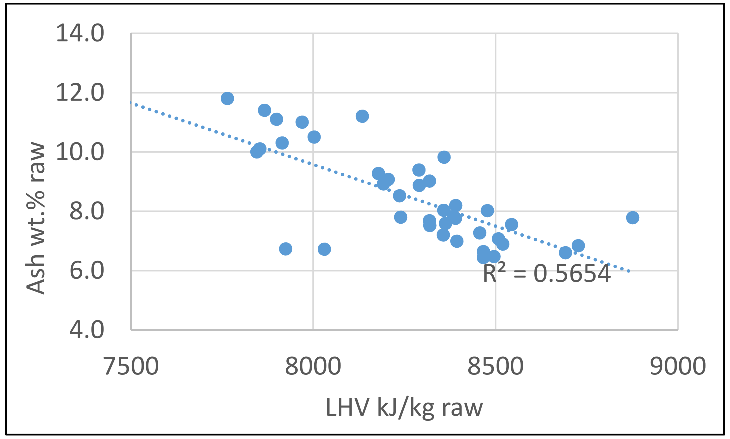
$$\frac{Base}{Acid} = \frac{Na_2O + K_2O + CaO + MgO + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2}$$

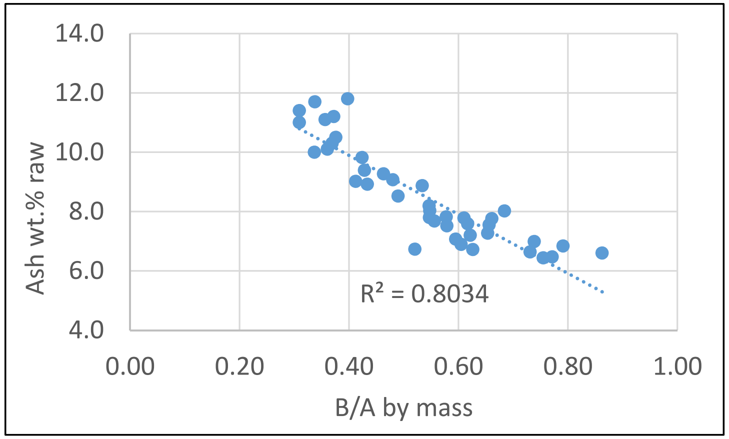
→ highly fluctuating coal properties

Coal (set of 42 shift samples RW/NO 70/30)

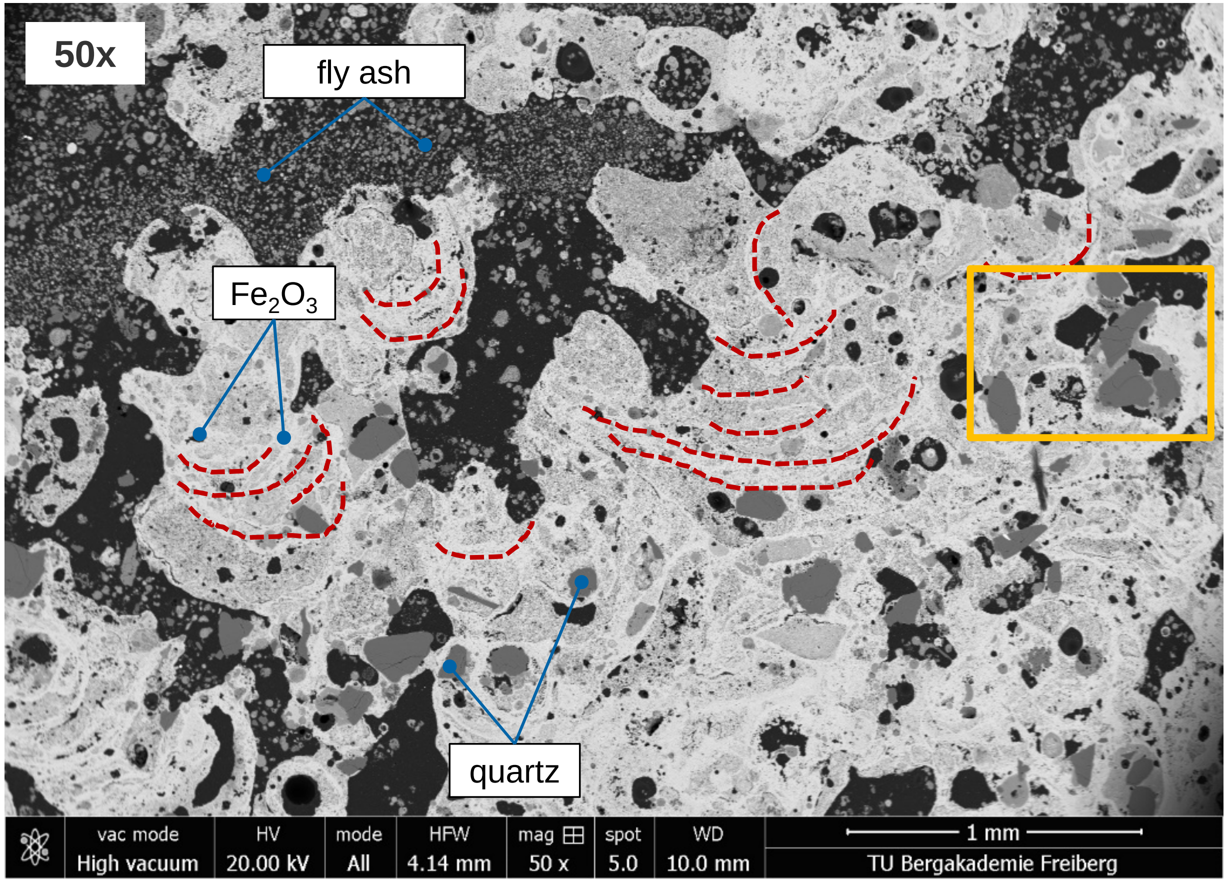
- Sediments quartz and clay minerals (kaolinite, illite, muscovite) determine ash content, LHV and B/A
- quartz and kaolinite can be calculated via XRF-Data and stoichiometry (proven by direct measurement via XRD)



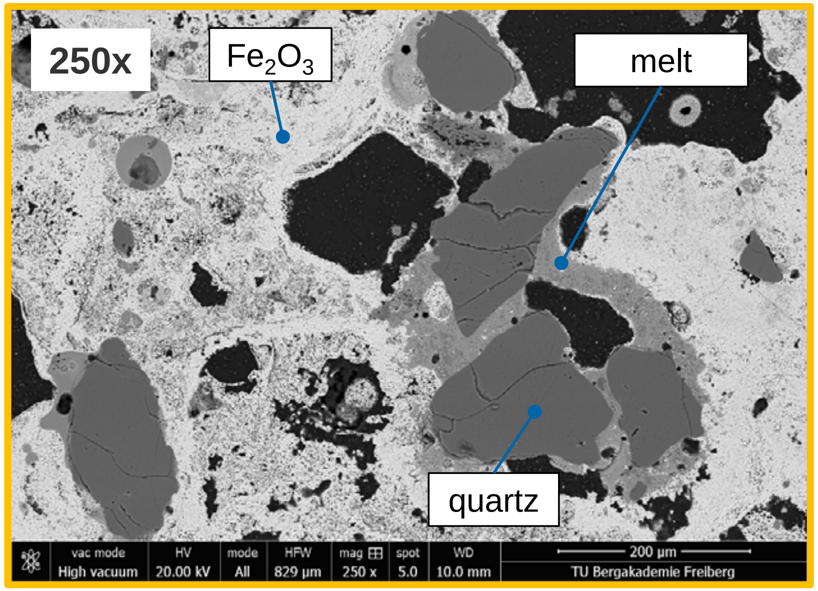




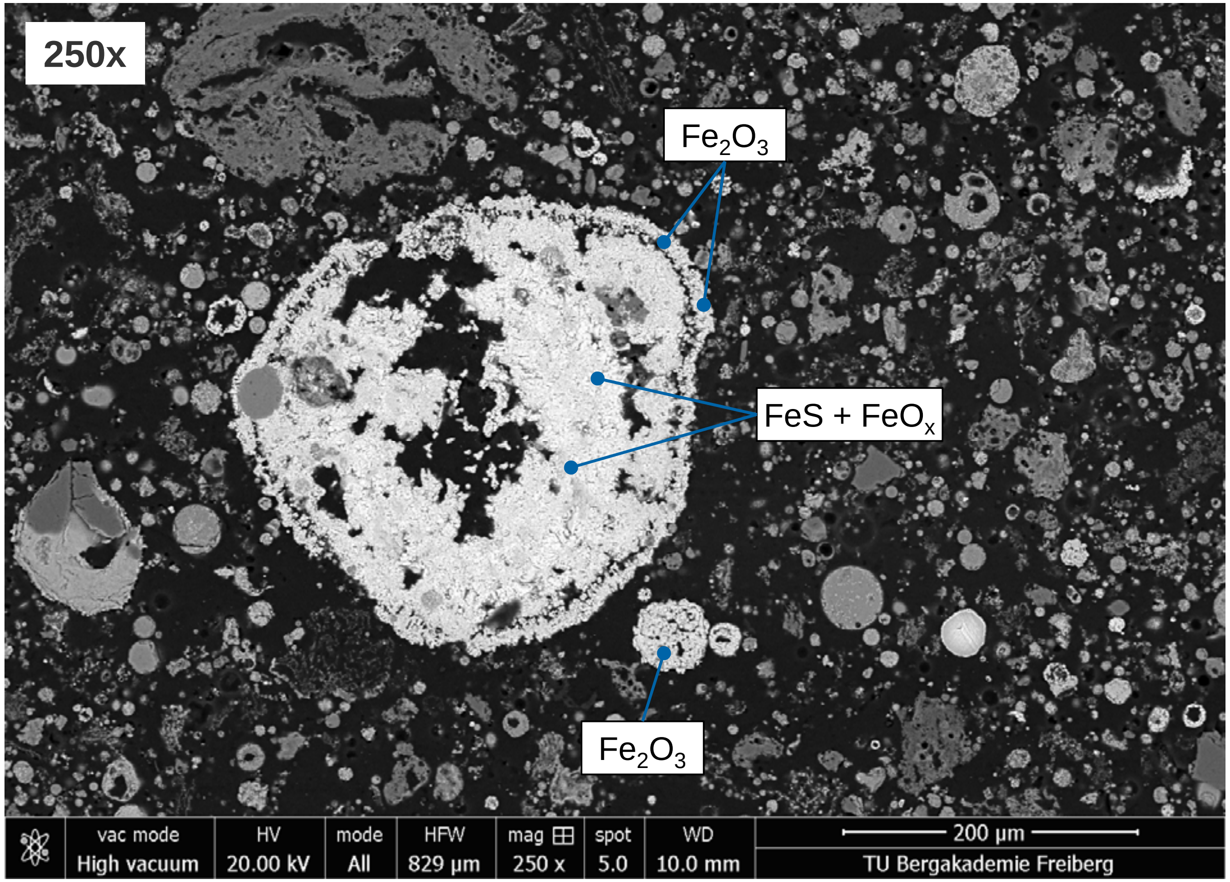
Fe-dominated deposit from boiler wall – SEM



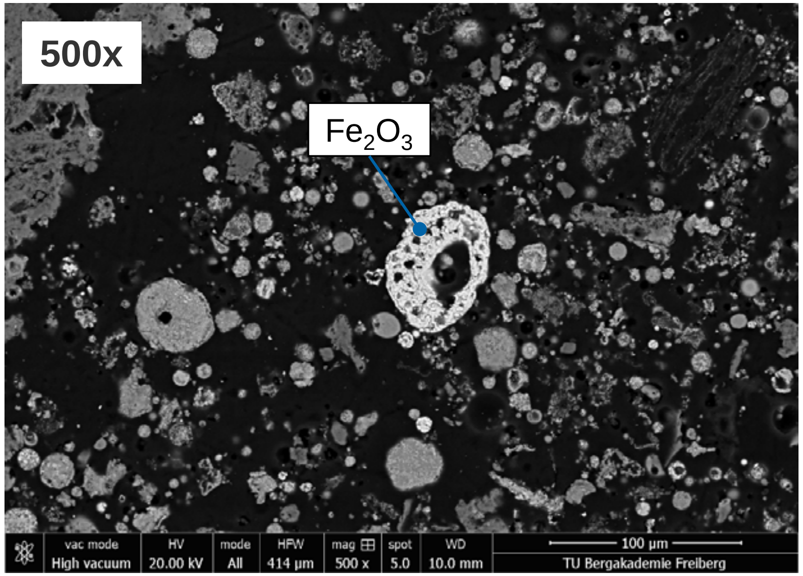
- **Fe_2O_3-Matrix** (layers, formerly melt) with inclusions of alumosilicatic slag and quartz grains
- intermediate layers from fly ash (unspecific composition)



Fly ash



- Fe_2O_3 particles
- in large Fe-rich particles FeS-rich centre
- due to particle form formerly liquid



Wet ash and *„Schlackestürze“ (large slagged lumps)*

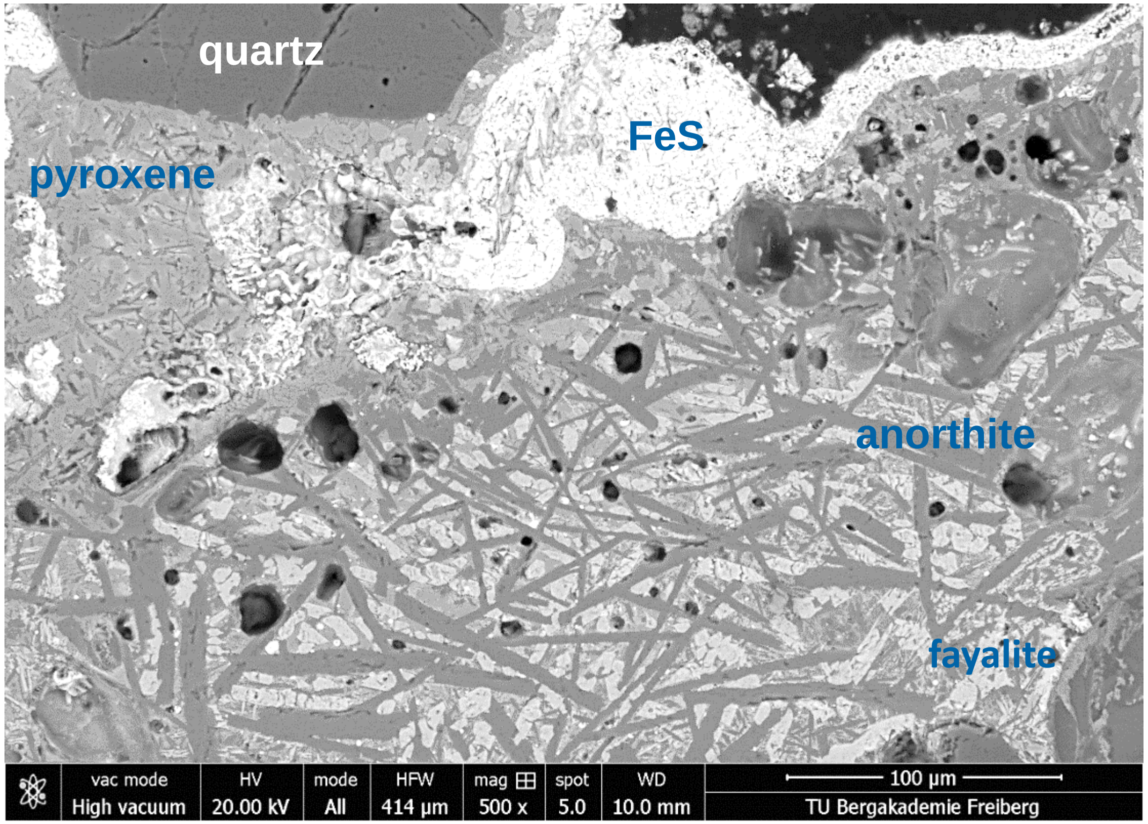


Fig.: coarser wet ash

- relicts of quartz and clay minerals in **recrystallized matrix** (pyroxene ($CaFeSi_2O_6$ and$CaMgSi_2O_6$), anorthite ($CaAl_2Si_2O_8$), fayalite ($Fe_2[SiO4]$)),
- FeS-inclutions
- same composition for alumosilicatic slagged lumps

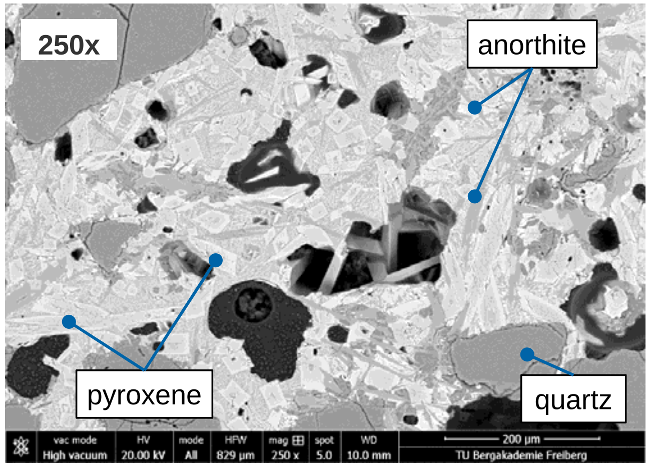
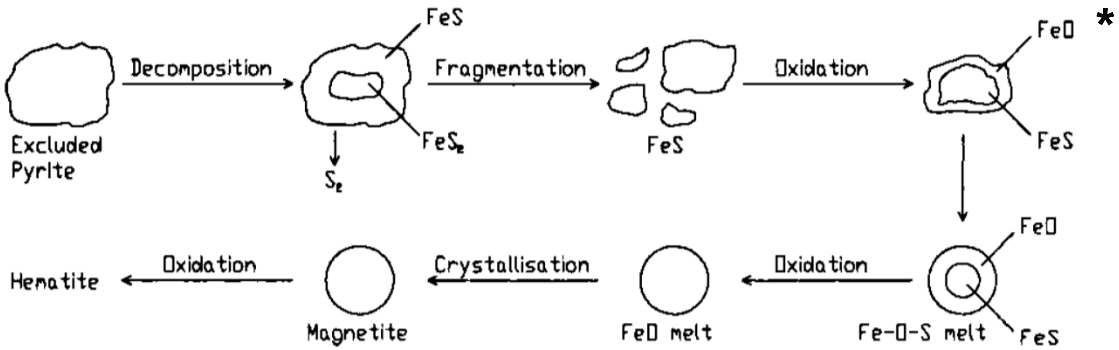


Fig.: Schlackesturz

Mechanism of deposit/slag formation

- formation of FeO-FeS-melt from pyrite
- formation of initial layer on boiler wall, collection of fly ash particles
- mechanism 1: oxidizing of FeO-FeS-melt forms Fe_2O_3 (see SEM results of Fe-dominated deposits)
- mechanism 2: secondary reaction of FeO-FeS-melt with fly ash particles results in alumosilicatic melt with relicts of quartz and decomposed clay minerals (see SEM results of coarser wet ash and *Schlackestürze*)



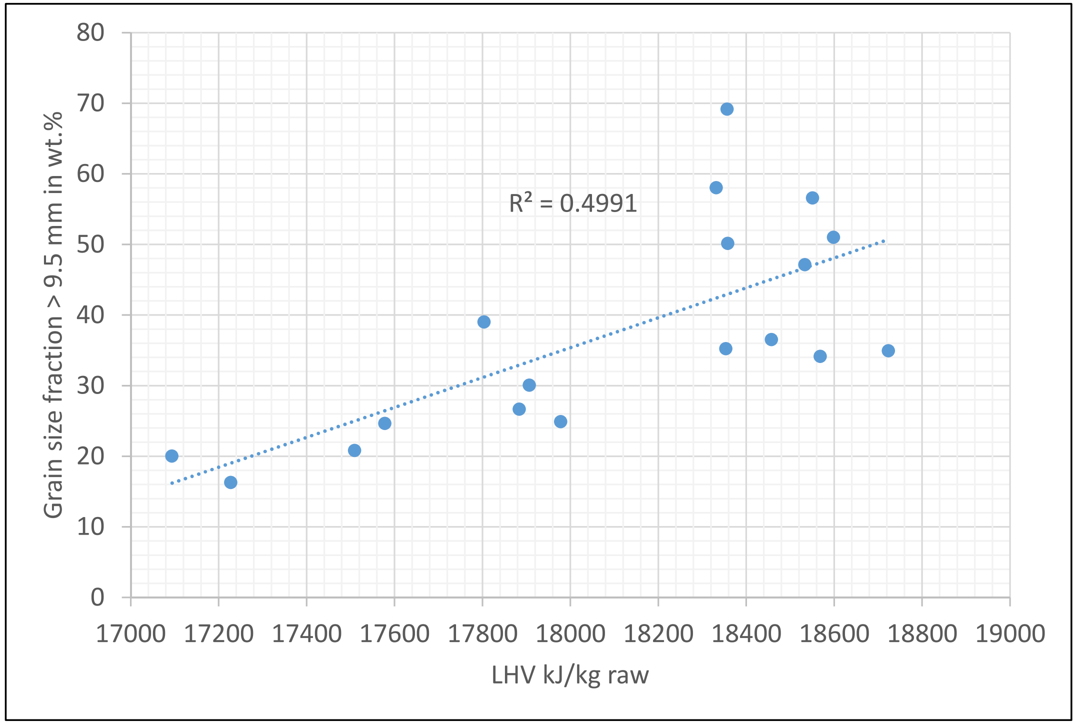
→ **coarser wet ash fraction corresponds to cleaned slag/deposit from boiler wall**

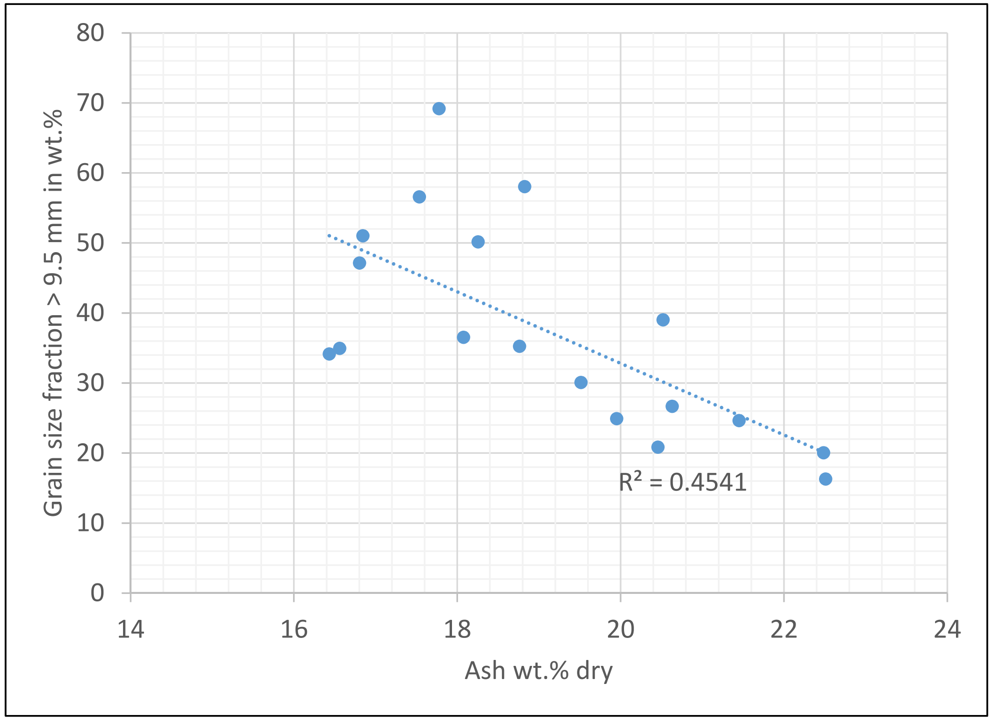
→ **definition of slag index: relative amount of wet ash fraction > 9.5 mm**

*McLennan et al.: Ash formation mechanisms during pf combustion in reducing conditions. Energy Fuels 2000, 14 (1), 150-159

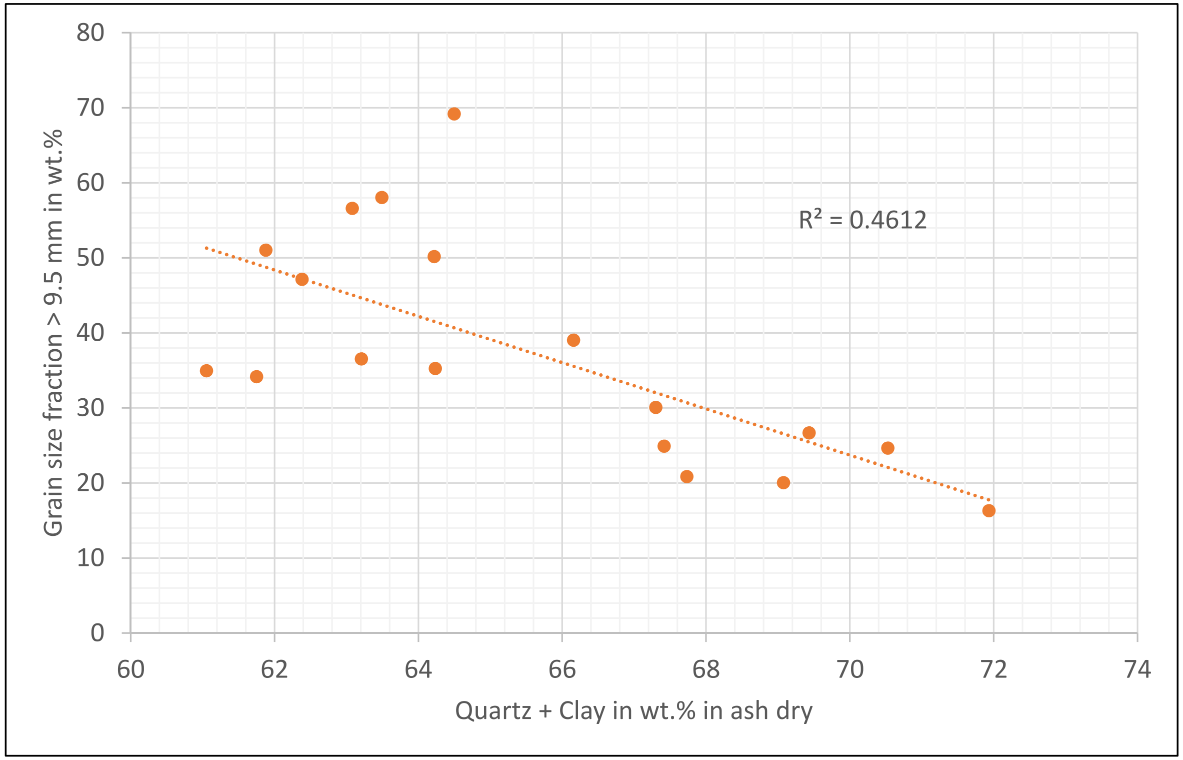
Correlations between slagging and coal properties

- in general a mass balances (coal ash = wet ash + fly ash) is difficult to achieve (Representative samples? Frequency of sampling vs frequency of coal property change? Sampling point before coal distributor!)
  → moving average over two shifts



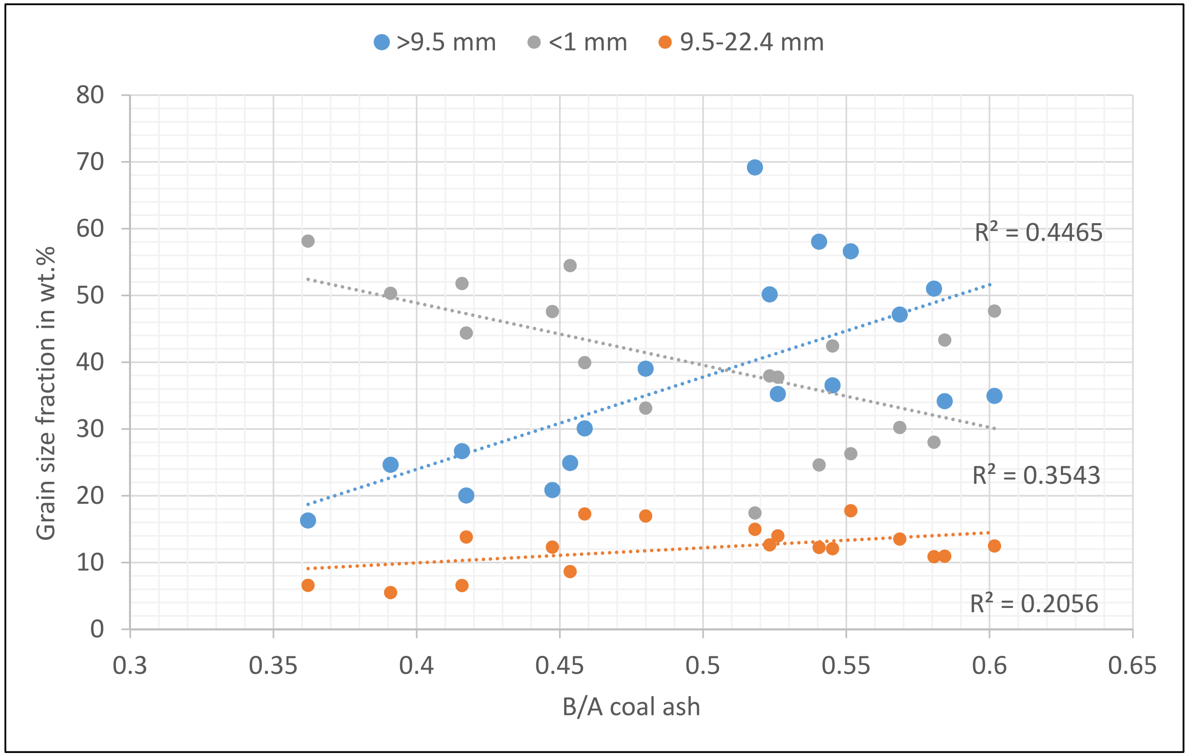


Correlations between slagging and coal properties



- Salgging ~ heating value
- Salgging ~ 1/ash content
- Salgging ~ 1/(quartz + clay minerals)

Correlations between slagging and coal properties

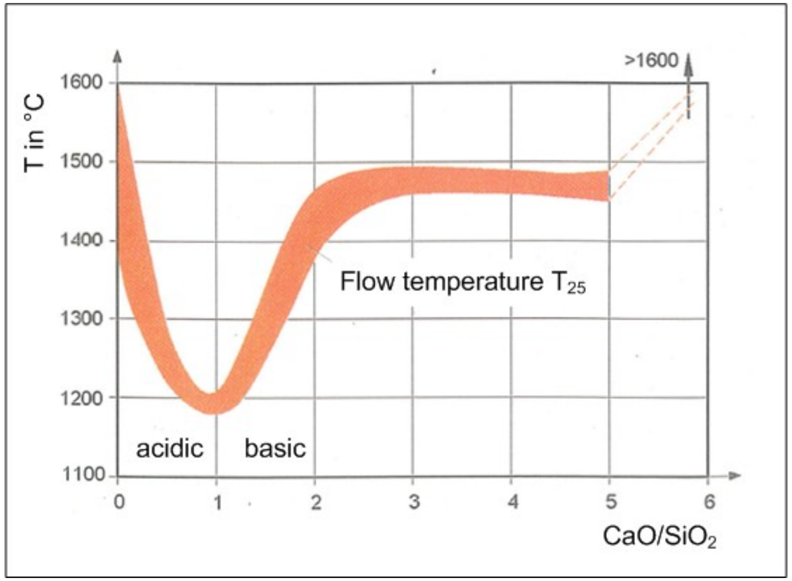


- **Slagging ~ B/A**
- B/A represents indirectly also other slagging sensitive parameters (ash, quartz+clay, LHV, *pyrite*)
- B/A connects ash composition with temperature of slag formation (T_{liq} =f(B/A))

$$\frac{\text{Base}}{\text{Acid}} = \frac{Na_2O + K_2O + CaO + MgO + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2}$$

Basic calculations

- Database: Factsage 7.3 (FToxid; Gtox v2018)
- Calculations in SimuSage (adjustment of T for 100% slag)
- Input:
    - raw coal composition
    - air–fuel ratio = 0.9
    - no flue gas recirculation considered
- validation against AFT (hemisphere temperature at CO/CO_2 40/60 by vol.) and well established correlation of T_{liq}=f(B/A)



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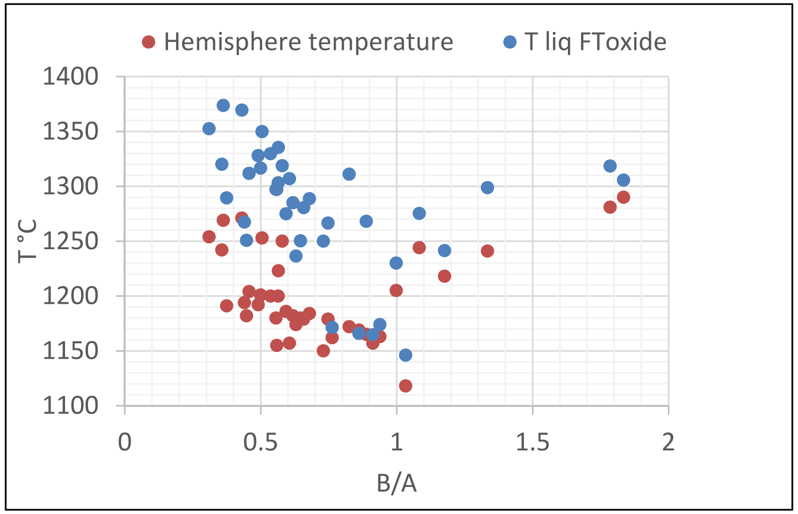
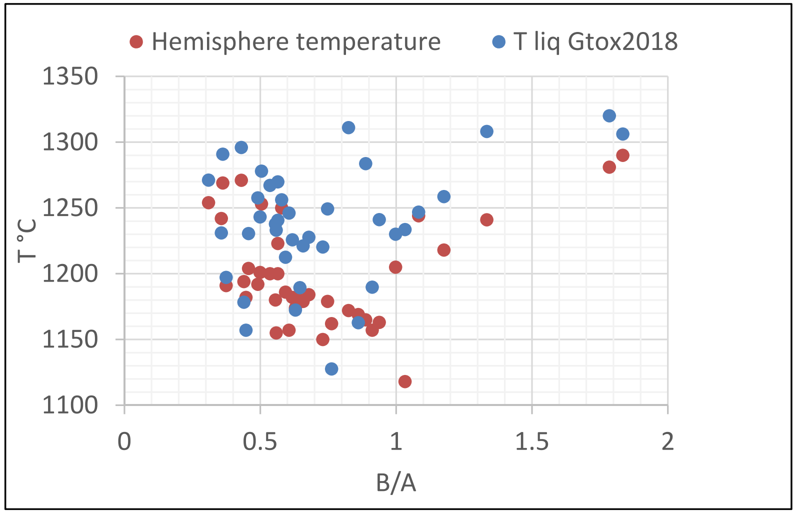
* modified from: J. Schmalfeld: Die Veredelung und Umwandlung von Kohle - Technologien und Projekte 1970-2000 in Deutschland. Hamburg: Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V.. 2008

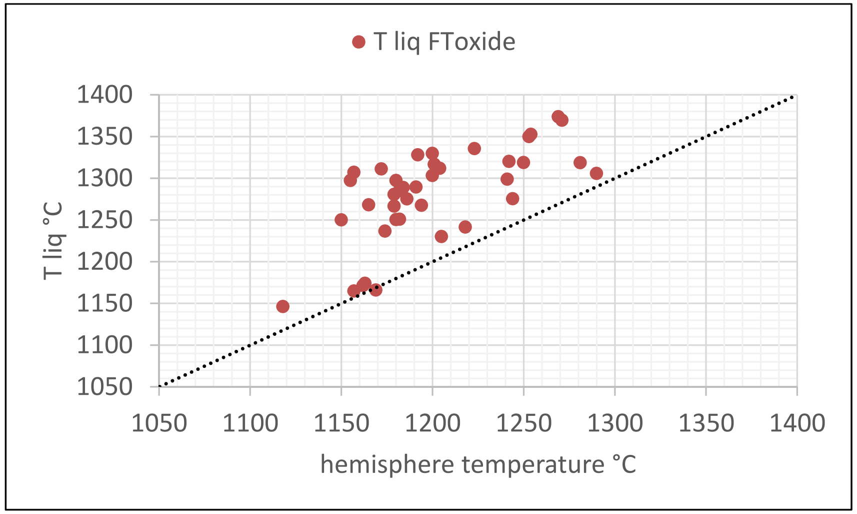
Basic calculations

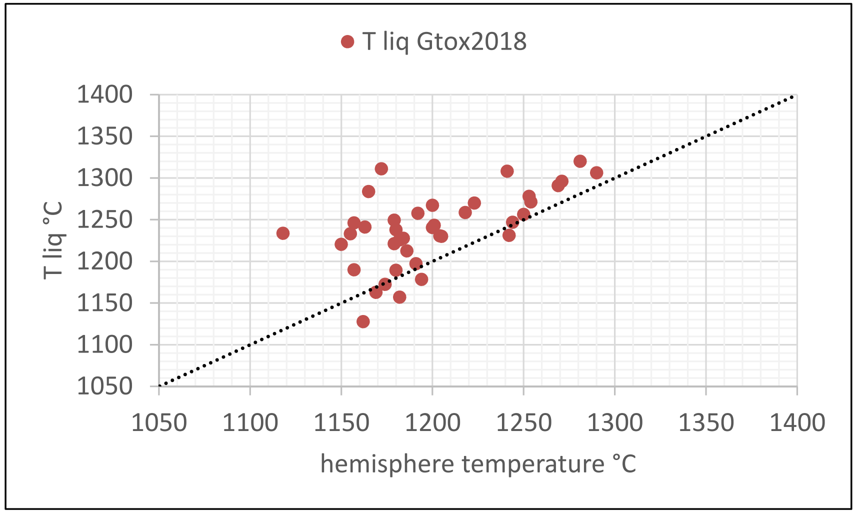




- correlation of T_{liq}=f(B/A) in general visible for both databases

Basic calculations





- Reproducibility of AFT-temperatures for reducing atmosphere 80 K (according to ISO 540: 1995E)
- robust (simple) prediction of slagging as function of temperature and coal ash composition possible
- not considered: special role of pyrite, inert amounts of quartz and clay (mullite)

Extended Model

- FactSage 7.2, FactPS, Ftoxid, FTmisc
- Input data:
    - fuel analysis of 42 coal samples (LEAG-shift data: ultimate analysis, disulphide, XRF of ash)
    - XRF of wet ash fraction > 9.5 mm (average)
- high degree of freedom (air-fuel ratio, inert components, T – range):
    - modeling FeO-FeS-melt
    - reduce number of free parameters (T, reactive SiO_2-content)
    - apply model on 42 coal samples

1. calculation: pyrite induced melts

Input streams:

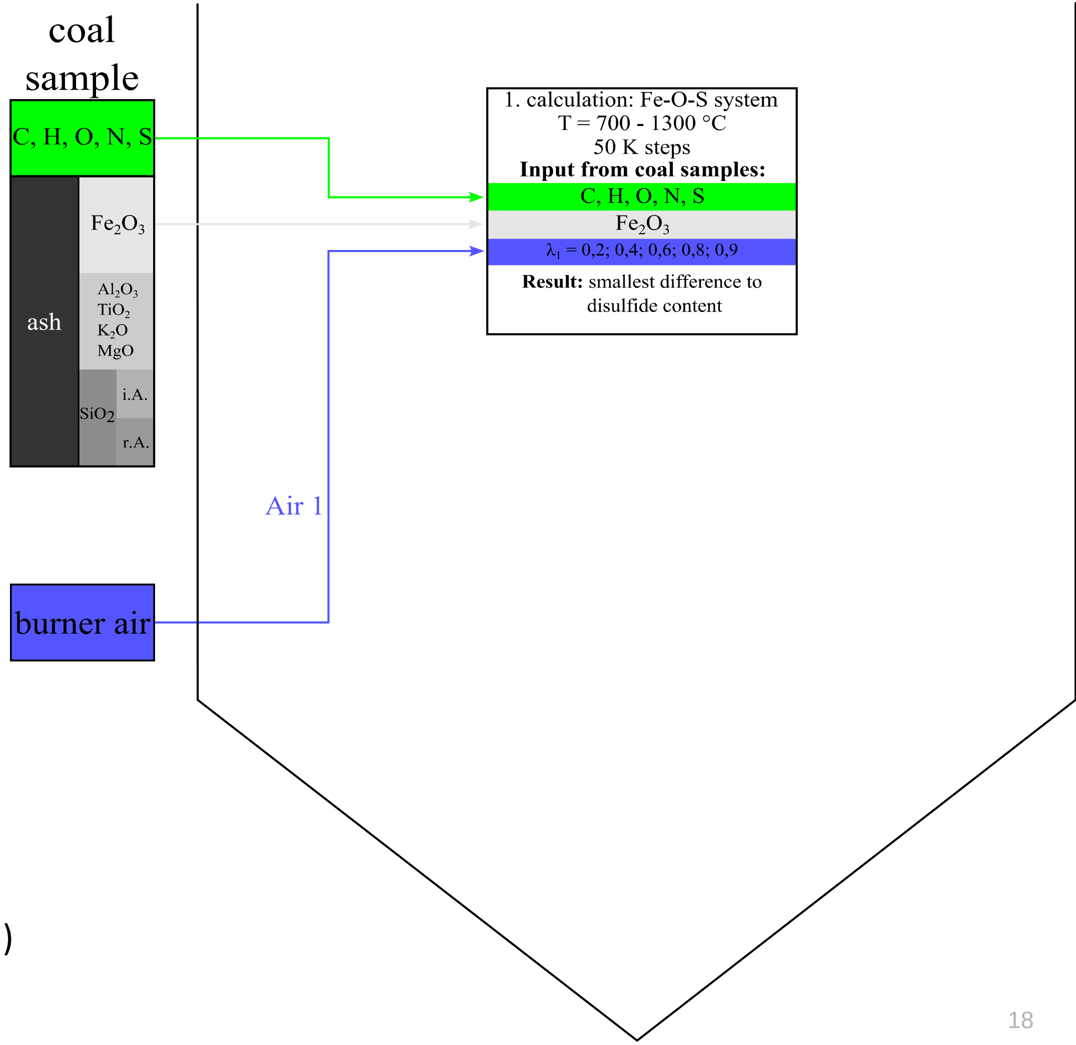
- C, H, O, N, S and water of respective coal sample
- Fe content of the ash (Fe_2O_3)
- Combustion air

Parameter variation:

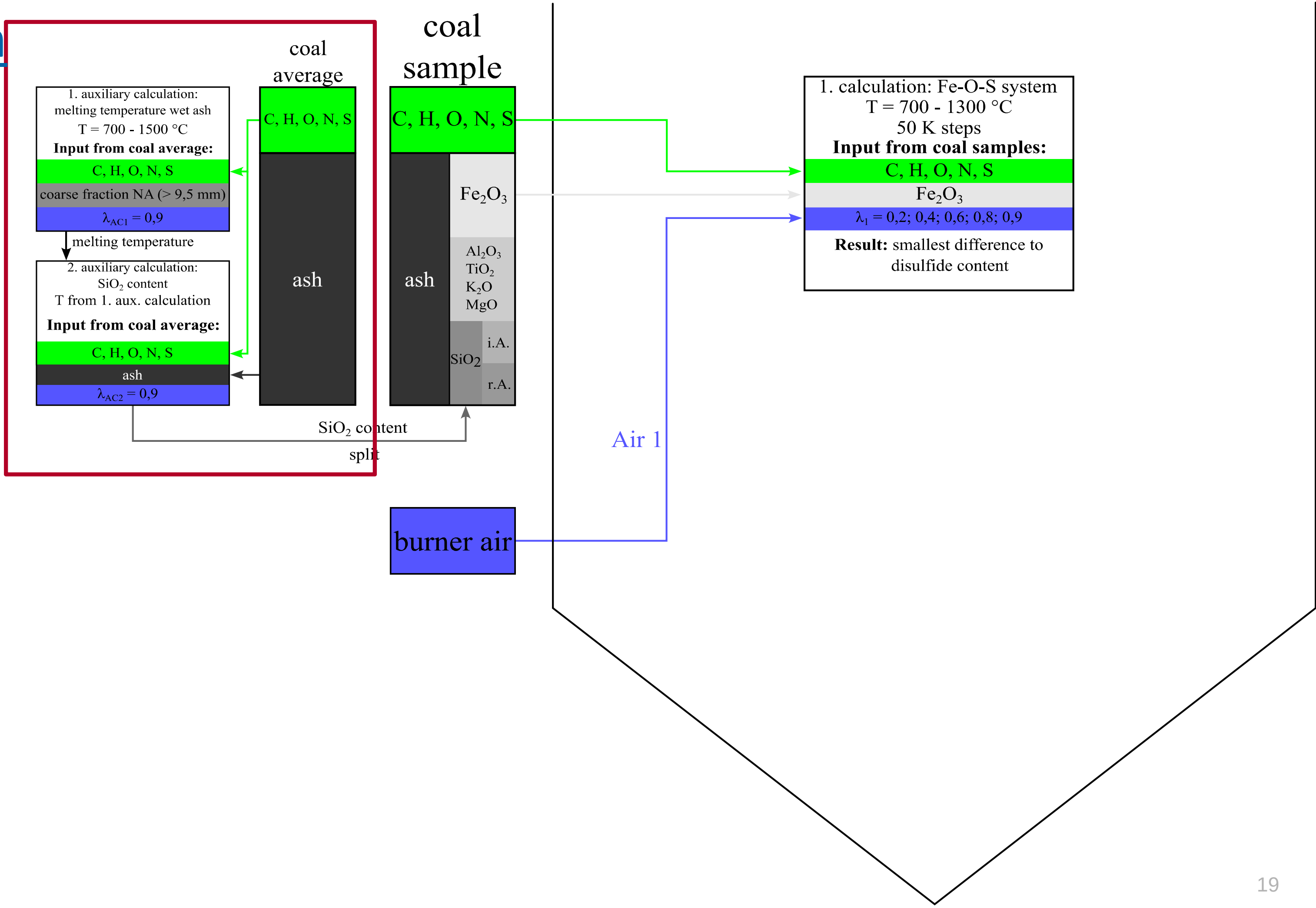
- Air ratio λ_1 = 0,2; 0,4; 0,6; 0,8; 0,9
- Temperature: T = 700 – 1300 °C
- variation of T and λ_1 to minimize the difference between the amounts of
    - disulphide in the coal sample and
    - sulphur in the resulting liquid phase

Result:

T and λ of FeO-FeS-melt formation (ca. 950-1050 °C, λ = 0,2-0,3)



Auxiliary calculation



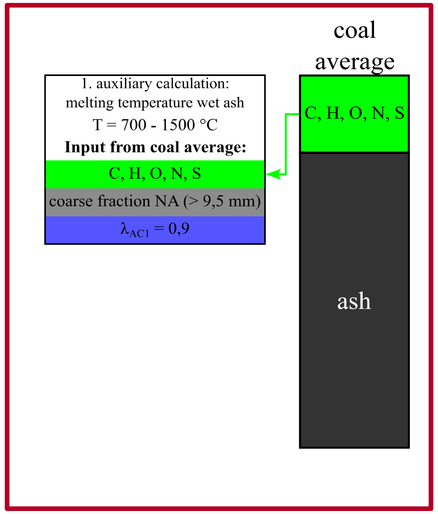
Auxiliary calculation

1. melting temperature of the average slagged wet ash (>9.5mm)

Input:

- C, H, O, N, S and water of the average coal sample
- Ash composition and content of
  the coarse wet ash fraction > 9,5 mm
- Combustion air λ_{AC1} = 0,9 (burner belt section)
- Variation of temperature T = 700 – 1500 °C
  for 100% slag

Result: melting temperature of the average slagged wet ash
1153°C



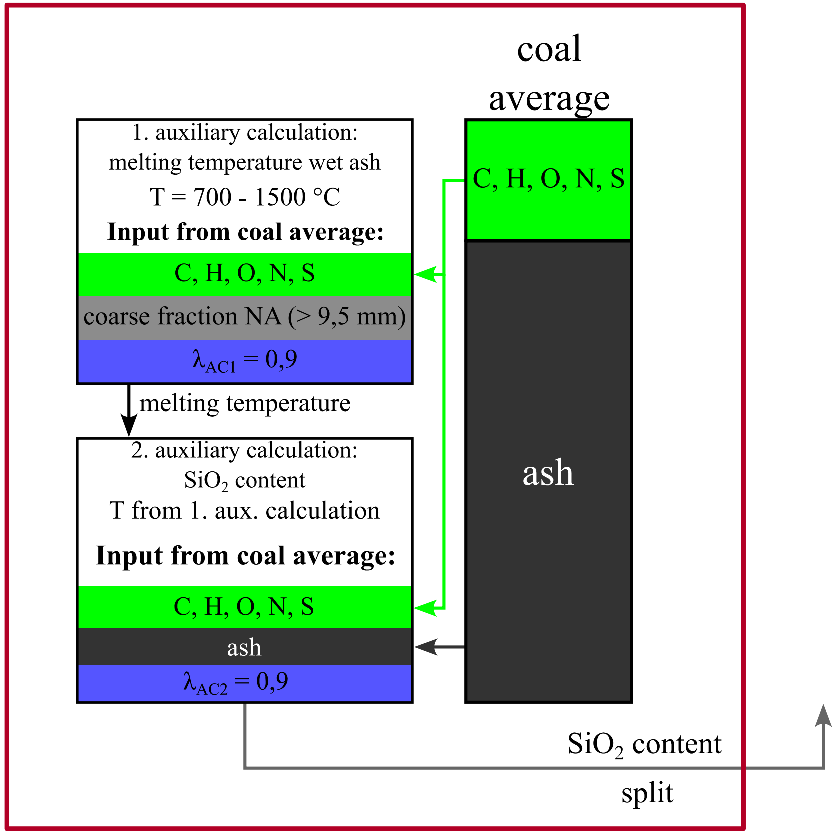
Auxiliary calculation

2. reactive SiO_2 content

Input:

- C, H, O, N, S and water of the average coal sample
- ash composition of average coal sample
- Combustion air λ_{AC2} = 0,9
- Temperature: melting temperature from 1. auxiliary calculation
- Variation of the reactive SiO2 amount to minimize the difference between the composition of the coarse wet ash fraction and the liquid phase

Result: reactive SiO_2 content of 43 wt. %

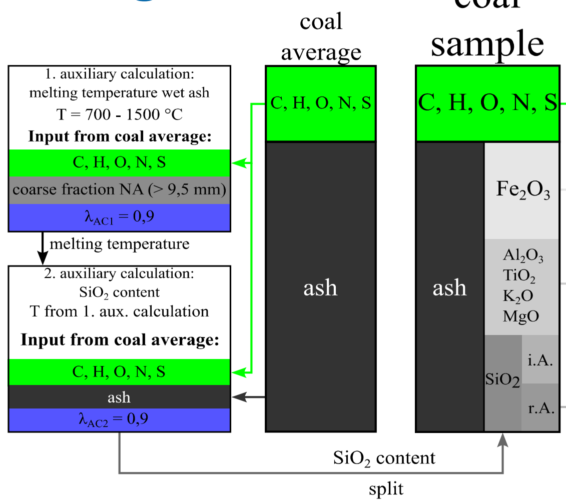


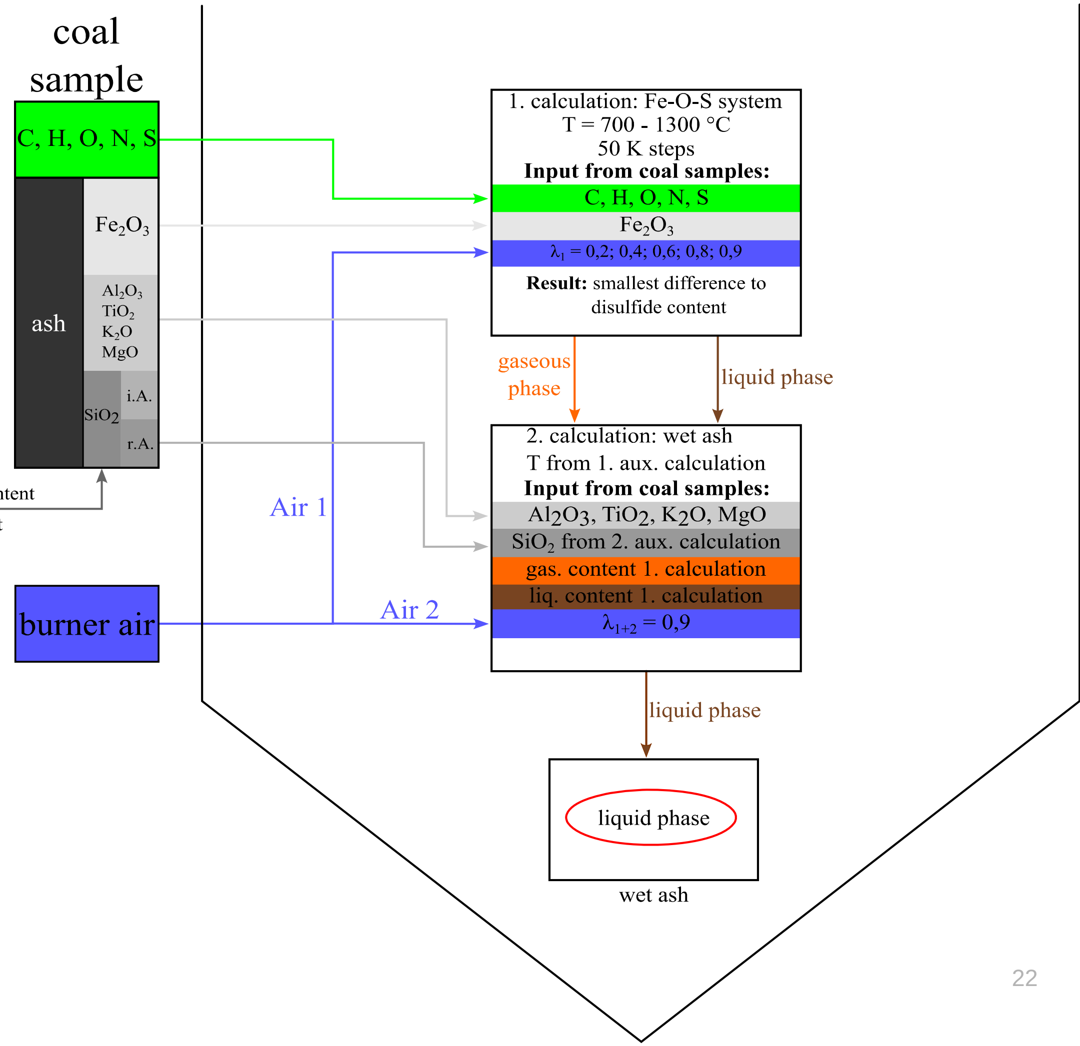
2. calculation: wet ash/slag

Input:

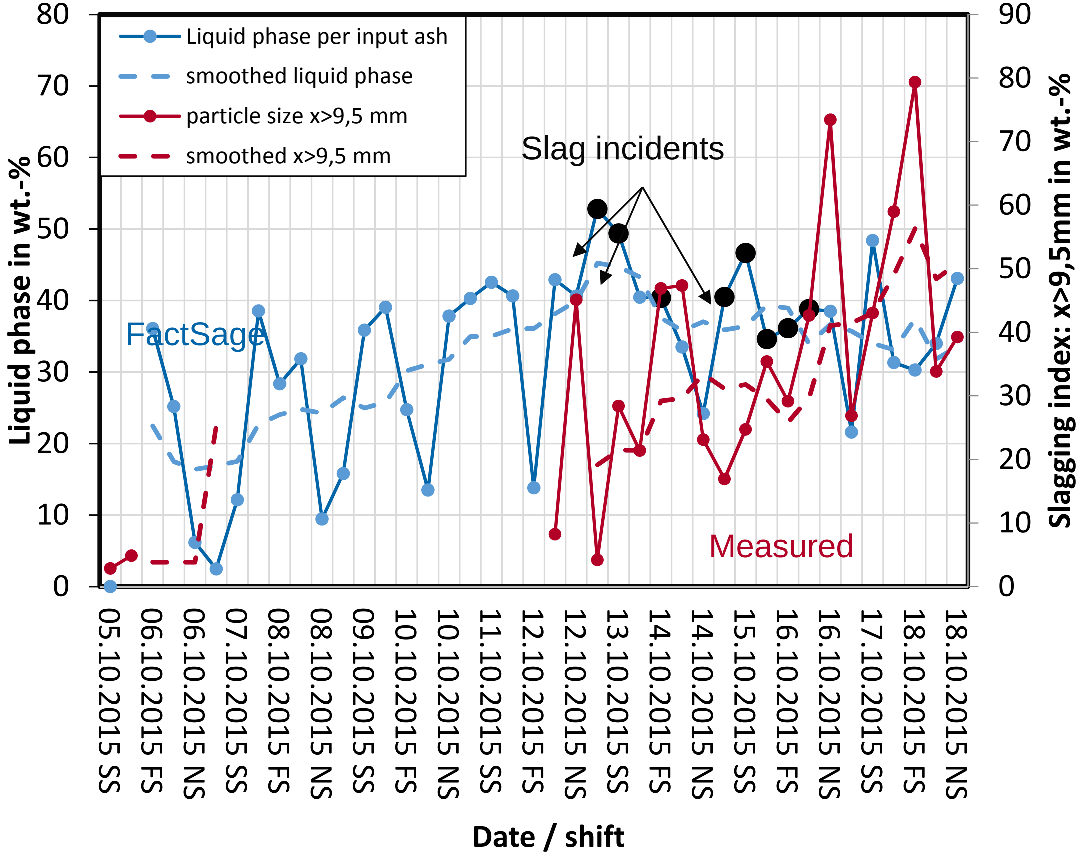
- 42 shift coal samples
- gaseous and liquid phases from 1. calculation
- Remaining ash components of coal samples (excl. Fe)
- reactive amountSiO_2 content based on 2. auxiliary calculation
- Combustion air λ_{1+2} = 0.9
- Temperature from 1. auxiliary calculation

Result: amount of slag phase phase determines slagging tendency





Calculated slag phase vs Slagging index and Slag incidents



Conclusion

- relations between coal properties and slagging extracted (slagging=f(LHV, quartz, clay, *pyrite*)
- B/A allows for robust estimation of slagging propensity, whereas slagging ~ B/A within investigated range of composition
- application thermochemistry allows prediction of T-dependent slag formation
- further improvement of thermochemical model by
    - analysis of inert components (quartz, clay in wet ash and fly ash via XRD)
    - improved estimation of temperature (as function of LHV and boiler load)
- practical application of model (or key figure):
    - simplification of model (have to be based on measurable coal and operational parameters)
    - implementation of ETV-ICP-OES as online measurement (multielement analysis, indirectly detection of quartz, clay minerals and pyrite)

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