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Institute of Energy Process
Engineering and Chemical Engineering
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Evaluation of the ash behaviour of biomasses and waste materials for co-firing with coal



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OUTLINE

- Background
    - Substitute fuels
    - Ash properties of the substitute fuels
    - Ash-related issues in power plants
- Materials and methods
    - Fuel samples
    - Fuel preparation and ashing methods
    - X-ray fluorescence (XRF) analysis
    - Scanning electron microscopy with energy-dispersive X-rays (SEM/EDX)
    - Ash fusion temperatures (AFT)
- Results and discussion
    - Fuel properties
    - Ash composition
    - Ash particles and mineral distribution
    - Ash fusion behavior
    - Evaluation of the ash behaviour for co-firing
- Summary and outlook

BACKGROUND

Substitute fuels

S. V. Vassilev et al., Fuel, 94 (2012) 1-33.

Wood and woody biomass

- wood
- sawdust
- etc.

Herbaceous and agricultural biomass

- grass and flowers
- straw
- stalks
- fibers
- shells and husks
- etc.

Aquatic biomass

- macroalgae
- microalgae
- uni-/multicellular species
- etc.

Animal and human biomass waste

- bone/meat meal
- manure
- etc.

Contaminated biomass and industrial biomass wastes (semi-biomass)

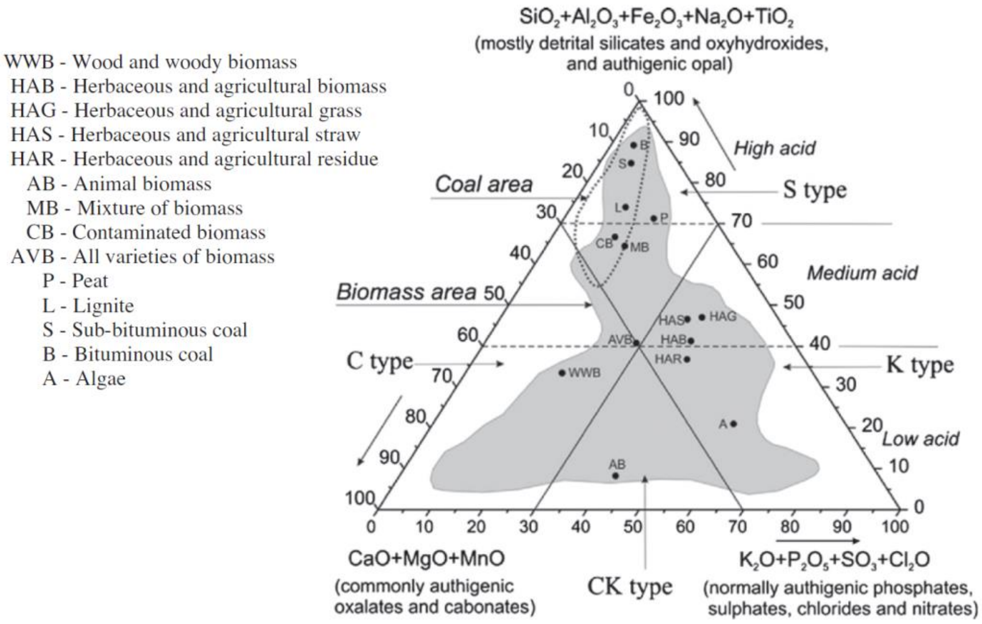
- municipal solid waste
- refuse-derived fuels
- paper-pulp sludge
- railway sleepers
- etc.

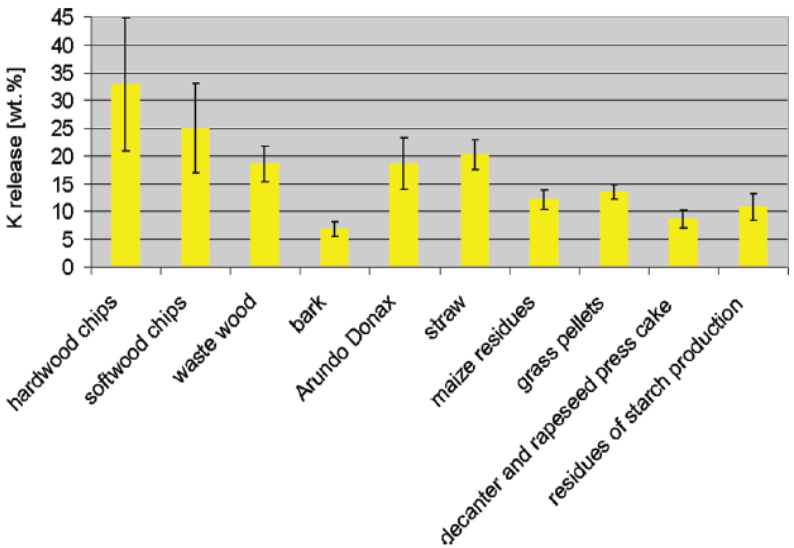
Biomass mixtures

- blends of all mentioned biomass sources

BACKGROUND

Ash properties of the substitute fuels



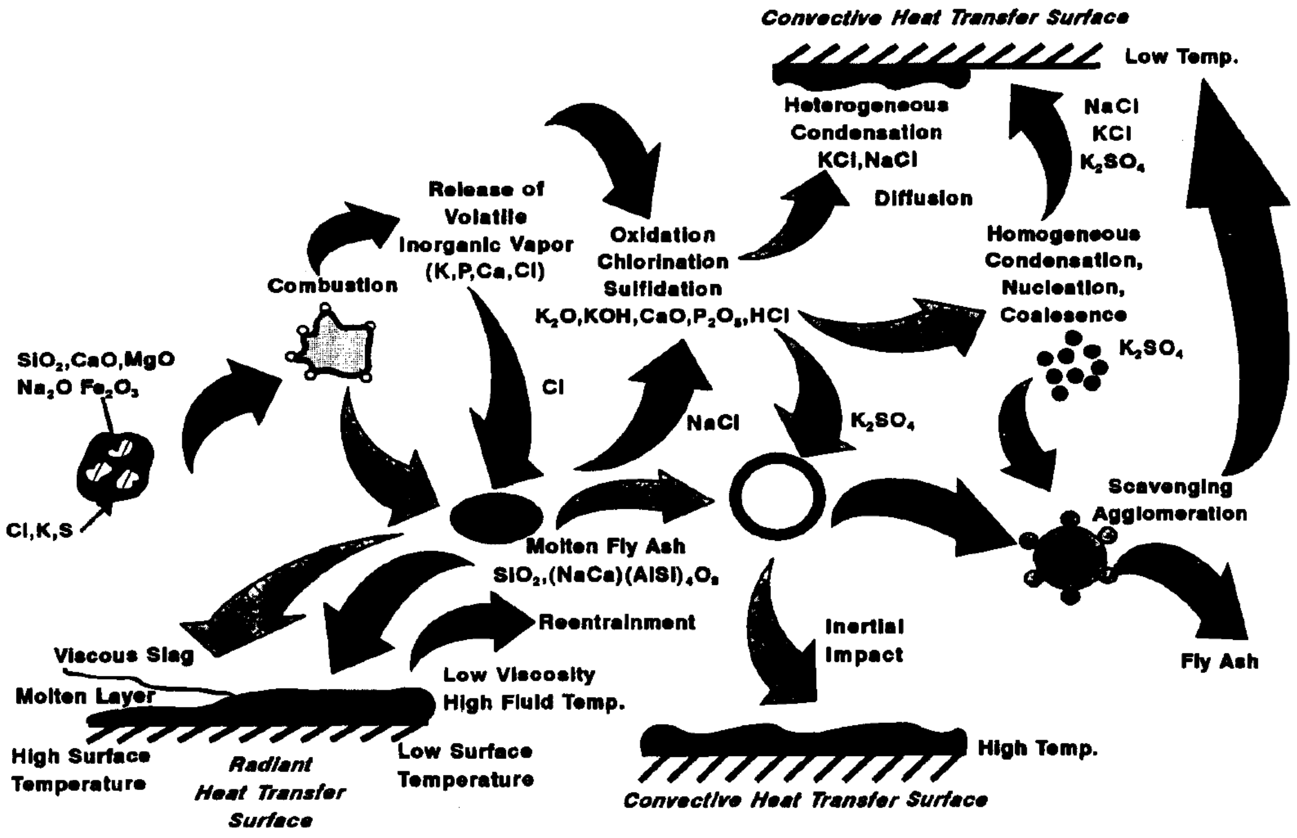


S. V. Vassilev et al., Fuel, 94 (2012) 1-33.

P. Sommersacher et al., Energy Fuels, 26 (2012) 380-390.

BACKGROUND

Ash properties of the substitute fuels

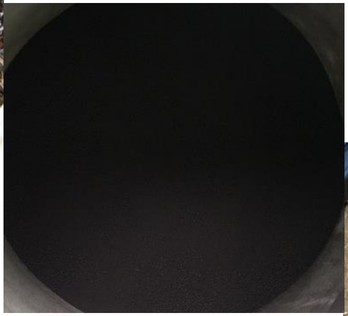


R. W. Bryers, Progress in Energy and Comustion Science, 22 (1996) 29-120.

Fuel samples

Agricultural and woody biomass

Refuse-derived fuel (RDF)



Sewage sludge (SWS)

Oat husks (OAT)

Bamboo (BAM)

Wood pellets (WOD)

Residual/waste materials

Fuel preparation and ashing

- Fuels blended on their raw basis
- Fuel blends dryed at circa 100 °C until constant weight
- Samples are milled to particle sizes ≤200 µm
- Ashed at around 200 °C using a low-temperature plasma (LTA) as well as ashed at 450 °C (MTA) and 815 °C (HTA) under air for 26 h with stepwise heat-up
- Ash ground to particle sizes ≤63 µm

X-ray fluorescence (XRF)

- Bruker S4/S8 Tiger
- Rhodium radiation source
- All elements are given as oxides

Scanning electron microscope (SEM/EDX)

- FEI Quanta FEG 250
- Acceleration voltage 2-5 kV (SE) and 20 kV (BSE)
- SEM/EDX information depth <5 µm
- Magnifications between 100-fold and 500-fold

Ash fusion temperatures (AFT)

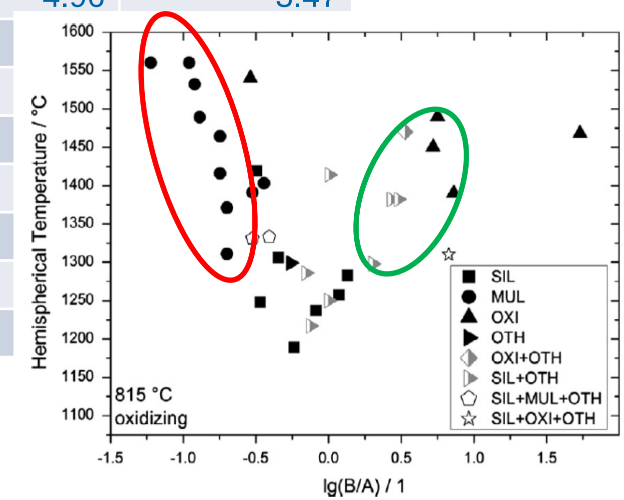
- Ash fusion tests according to DIN 51730
- Leitz heating microscope
- Cylinder from <63 µm ash powder: 3 mm (height) and 3 mm (diameter)
- Atmosphere: air (oxidising)
- Maximum deviation of 50 K under oxidising atmosphere (air)

Fuel properties (proximate / ultimate analysis, LHV)

Property	RDF	SWS	OAT	BAM	WOD
Moisture content / wt.% (raw basis)					
Moisture (raw)	27.66	80.50	10.72	2.41	7.31
Proximate analysis / wt.% (dry basis)					
Ash (815 °C)	27.47	49.89	4.06	0.92	0.57
Volatile matter	65.66	43.33	79.38	81.47	85.27
Fixed carbon	6.87	6.78	16.56	17.61	14.16
Ultimate analysis / wt.% (dry basis)					
C	47.03	25.99	47.72	49.97	50.09
H	5.86	3.72	5.40	5.87	6.34
N	0.84	3.57	0.95	0.27	0.43
S_A	0.43	0.23	0.04	0.02	
S_C	0.18	1.14	0.25	1.70	0.01
O	18.61	15.70	41.41	42.83	42.78
Chlorine content / ppm (dry basis)					
Cl	22,422	n.d.	906	678	31
Lower heating value / MJ/kg (raw basis)					
LHV	14.70	0.12	15.74	17.76	16.70

Ash composition (ashing at 815 °C)

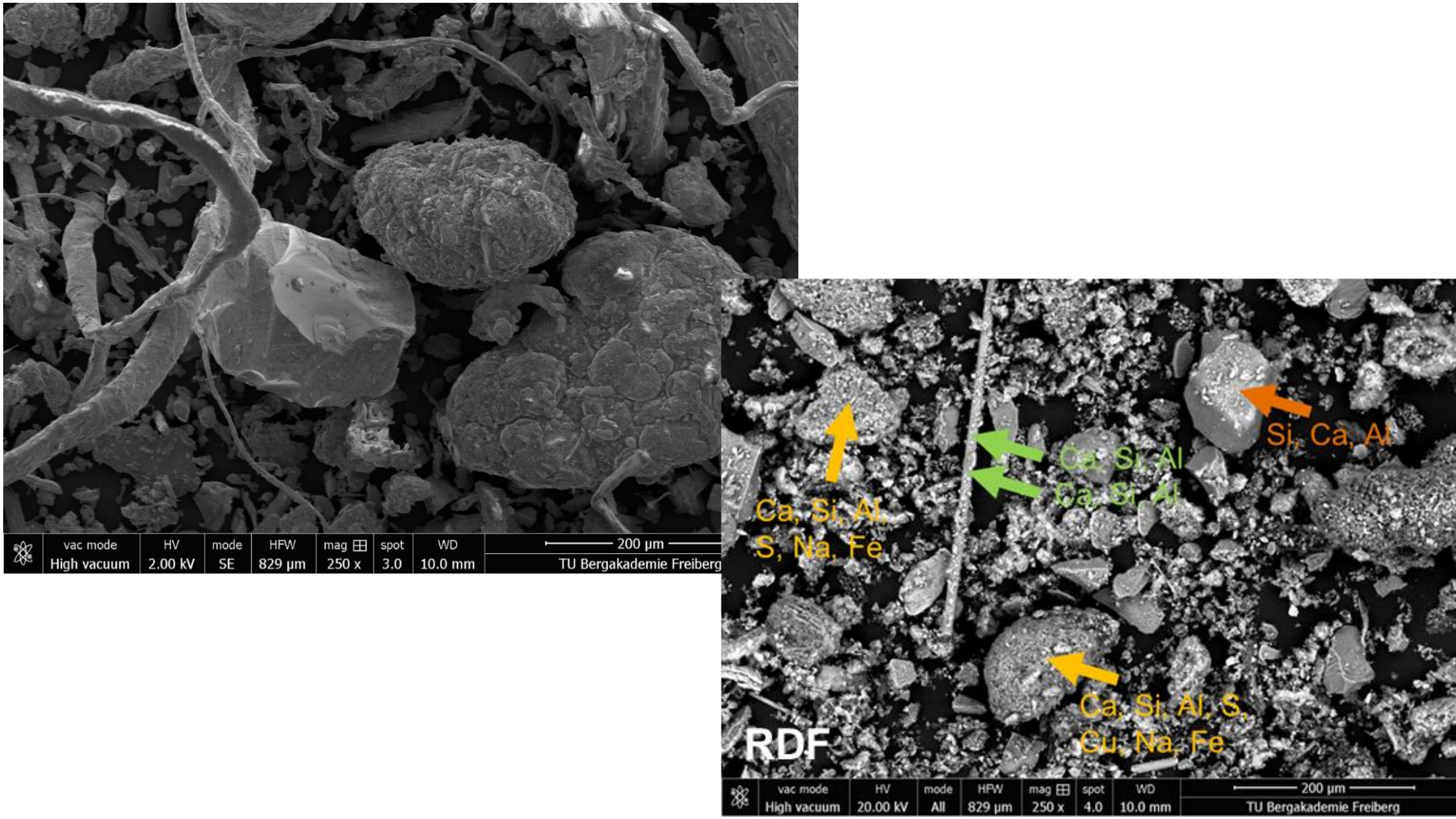
Oxides	RDF	SWS	OAT	BAM	WOD
Normalized mass fraction (XRF, fused tablet) / wt.%					
CO_2	0.72	0.26	0.49	11.60	0.92
Na_2O	1.74	0.54	0.61	7.95	1.57
MgO	1.73	3.88	2.72	5.63	6.67
Al_2O_3	12.04	9.25	0.32	0.51	2.42
SiO_2	53.11	41.48	65.38	7.94	28.20
P_2O_5	0.62	16.99	7.03	19.20	4.01
SO_3	3.75	1.09	2.54	4.96	3.47
K_2O	0.90	1.63	16.93		
CaO	18.90	9.65	3.28		
TiO_2	1.65	1.28	0.02		
Fe_2O_3	3.87	13.42	0.39		
Traces	0.97	0.52	0.29		
Base-to-acid ratio (oxidising conditions) / -					
B/A (mass)	0.40	0.42	0.33		



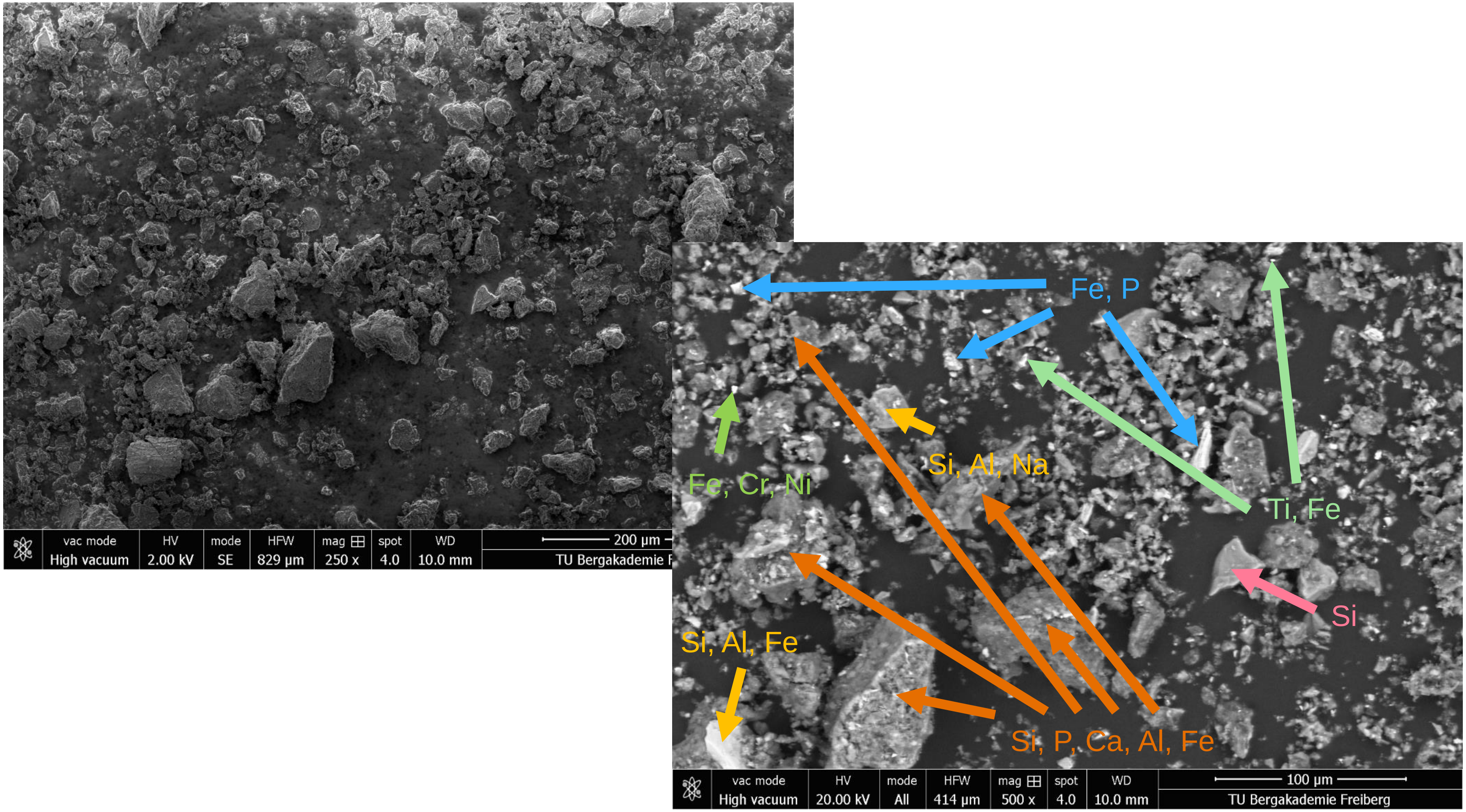
$$\frac{B}{A} = \frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2 + P_2O_5}$$

M. Reinmöller et al., Fuel, 151 (2015) 118-123.

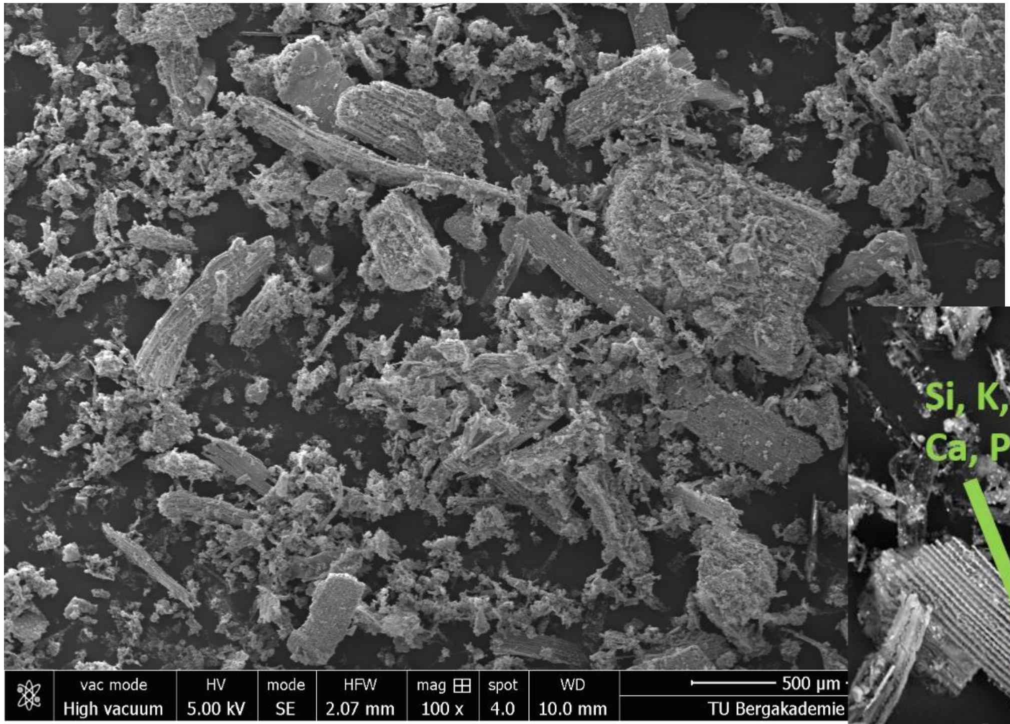
Ash particles and mineral distribution (RDF ashed at 200 °C)

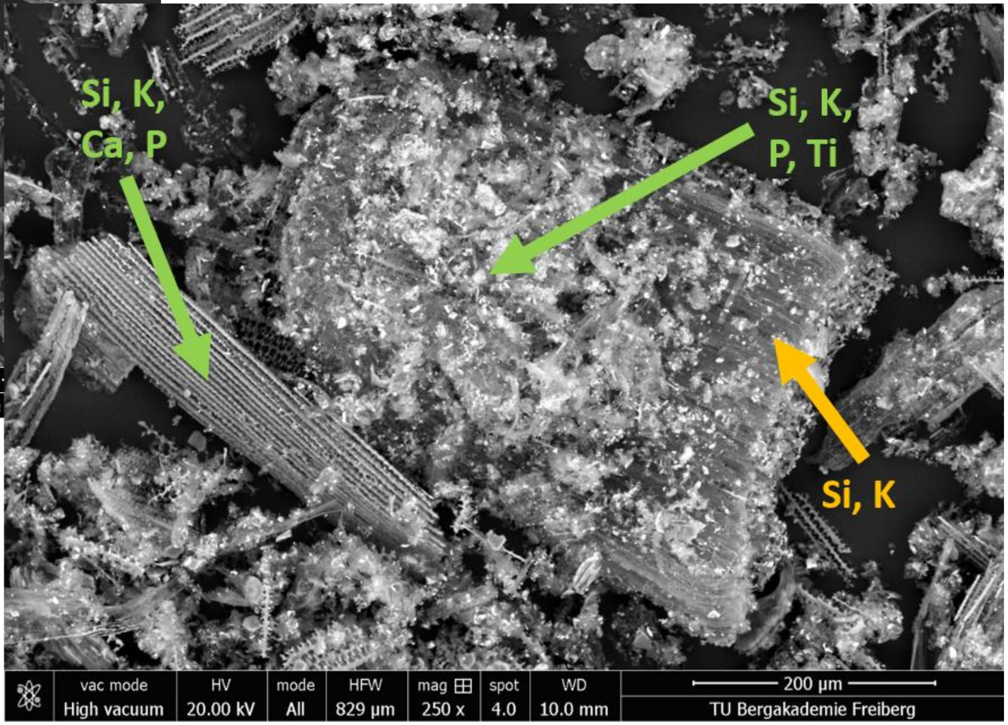


Ash articles and mineral distribution (SWS ashed at 200 °C)

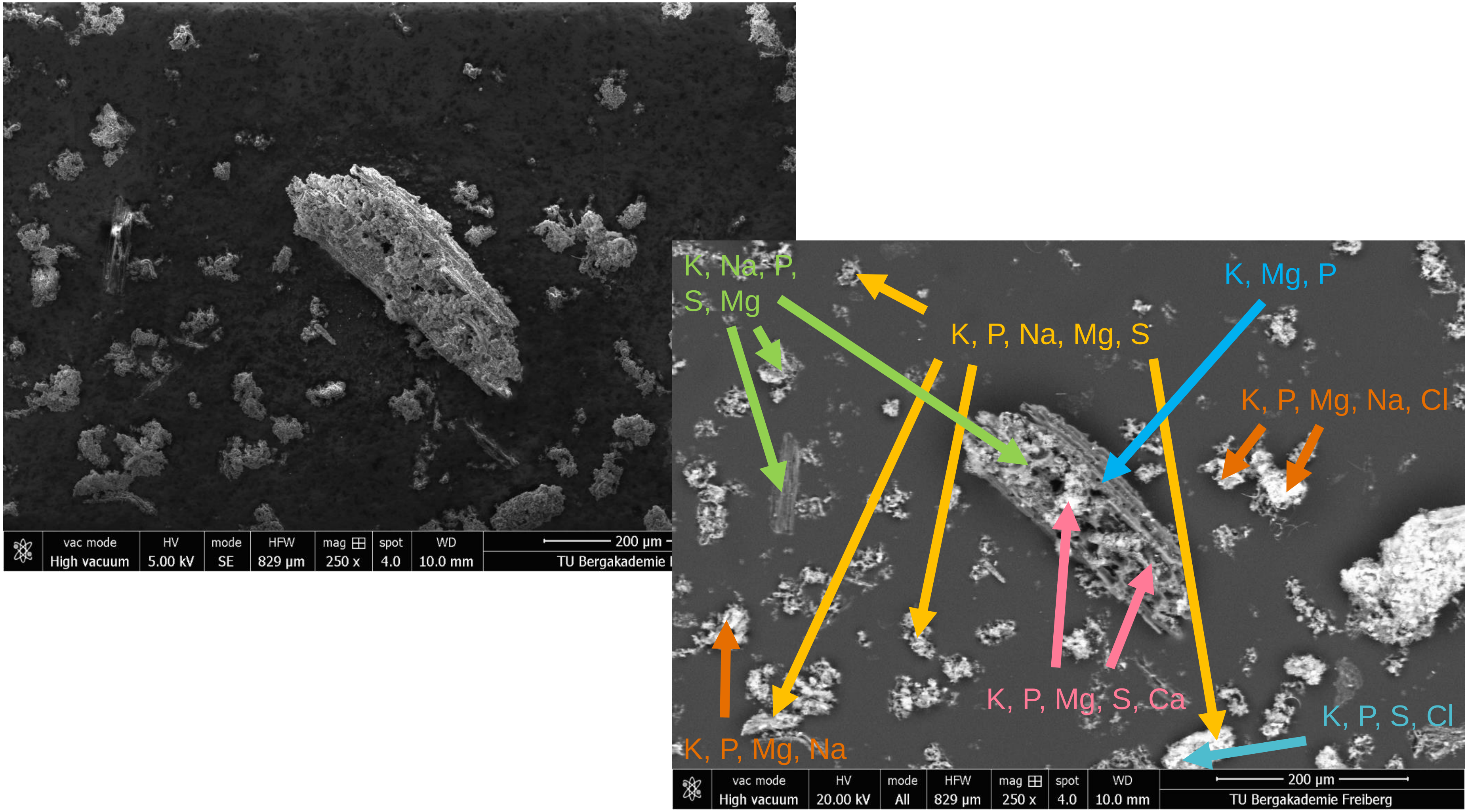


Ash articles and mineral distribution (OAT ashed at 200 °C)

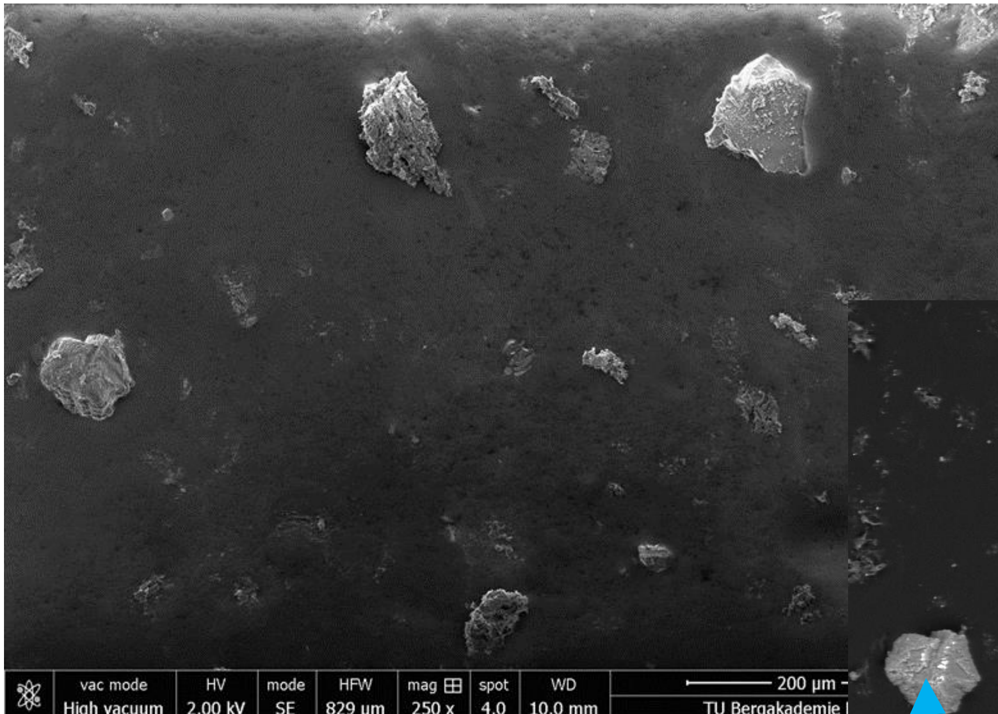


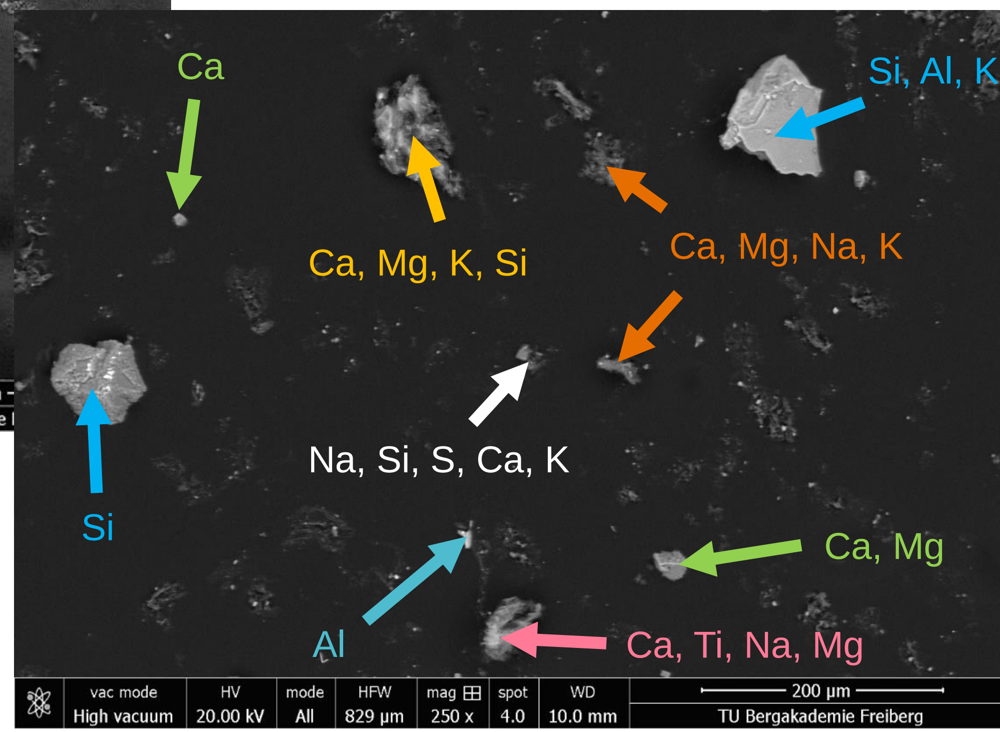


Ash articles and mineral distribution (BAM ashed at 200 °C)

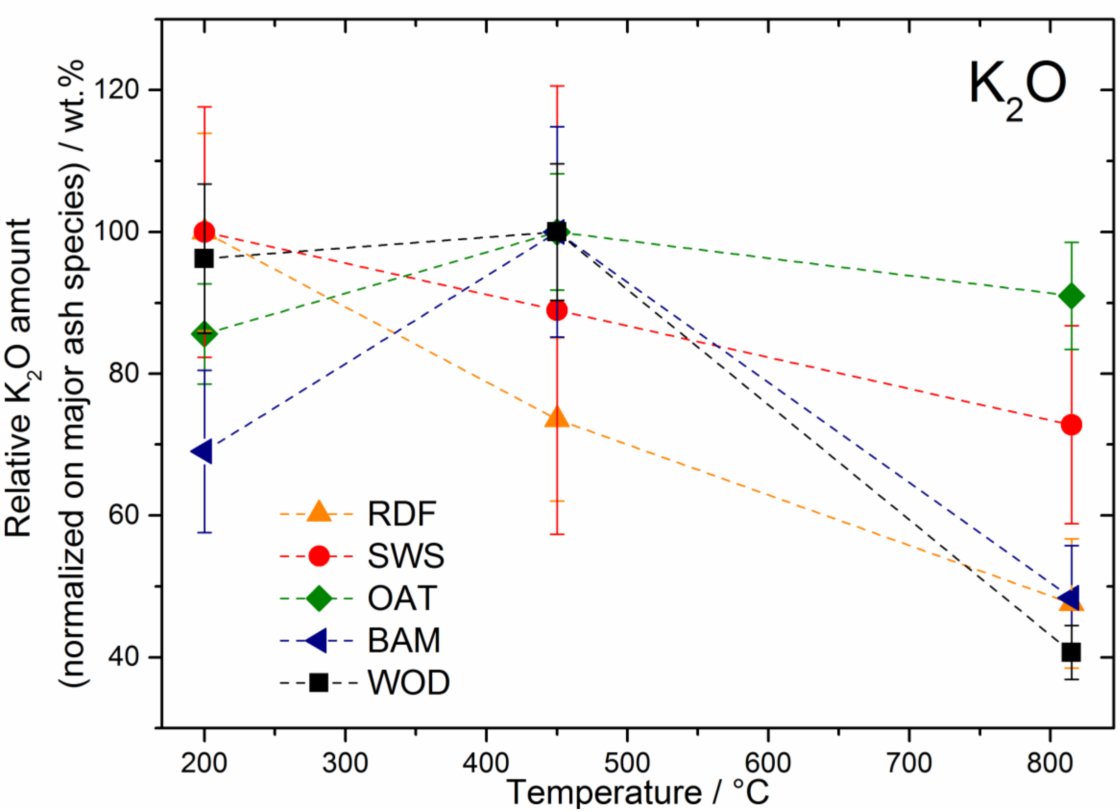


Ash articles and mineral distribution (WOD ashed at 200 °C)





Selective release of ash species



- Release of alkali oxides depends on the availablity of binding partner and their distribution in the ash

Ash fusion behaviour

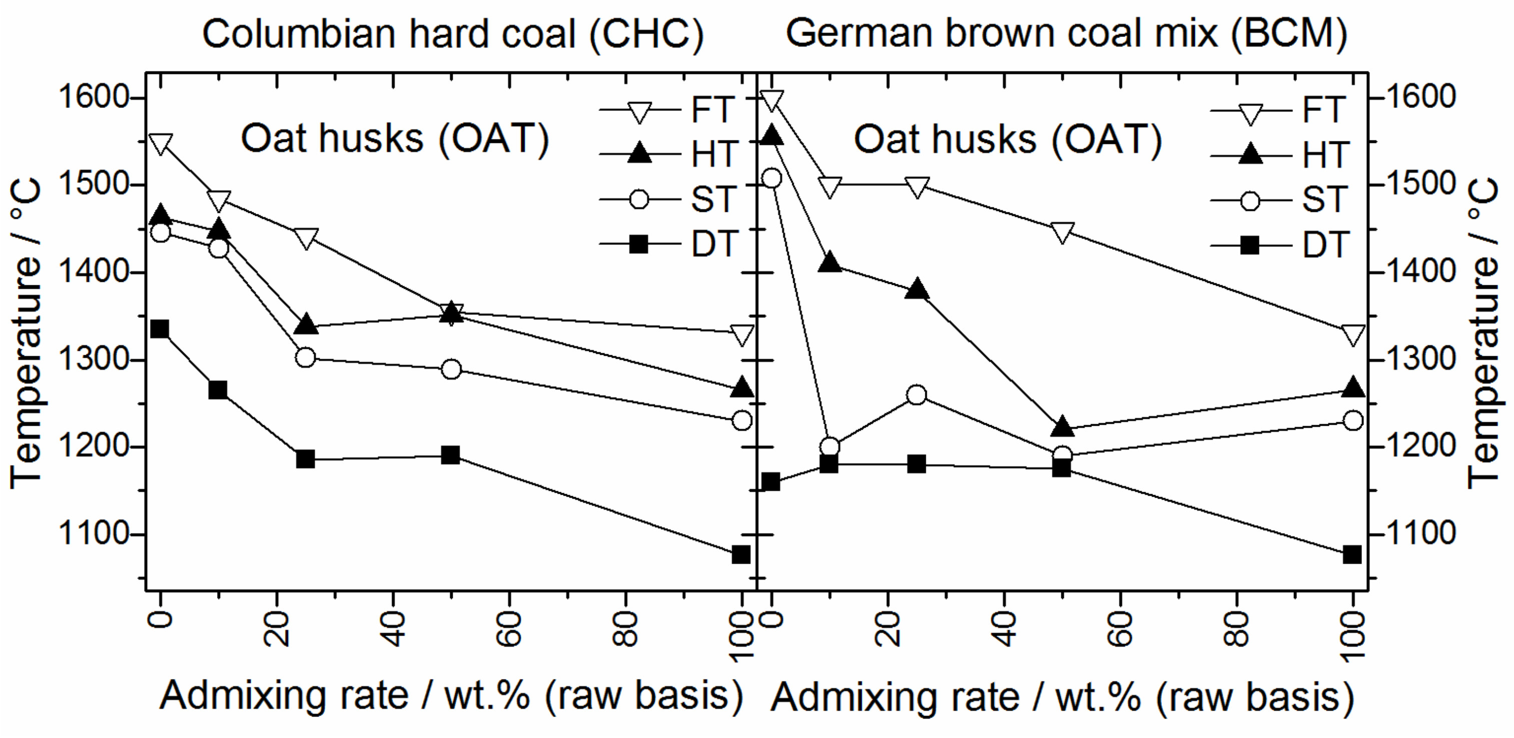
Temperature	RDF	SWS	OAT	BAM	WOD
Ash fusion temperatures – high-temperature 815 °C ash (oxidising atmosphere) / °C					
DT	1150	1130	1080	1210	1330
ST	1160	1190	1230	1270	1340
HT	1170	1250	1270	1290	1370
FT	1410	1330	1330	1300	1400
Ash fusion temperatures – medium-temperature ash (oxidising atmosphere) / °C					
DT	1070	1100	1030	1280	1380
ST	1120	1180	1190	1300	1390
HT	1140	1240	1220	1300	1410
FT	1320	1350	1380	1320	1430

Evaluation of ash behaviour for co-firing

- Water: ↑: LHV (↓), ↓: LHV (↑)
- Ash: ↑: strong impact on ash composition, LHV (↓), ↓: low impact on ash composition, LHV (↑)
- Cl: ↑: release of ash species (↑), ↓: release of ash species (↑)
- Alkalis: ↑: release into gas phase (↑), ↓: release into gas phase (↓)
- LHV: ↑: risk of sintering and slagging (↑), ↓: risk of sintering and slagging (↓)
- DT: ↑: risk of sintering and slagging (↑), ↓: risk of sintering and slagging (↓)
- …

Properties	RDF	SWS	OAT	BAM	WOD
Characteristic properties for co-firing					
Water / wt.%	27.66	80.50	10.72	2.41	7.31
Ash / wt.%	27.47	49.89	4.06	0.92	0.57
Cl / ppm	22,422	n.d.	906	678	31
K_2O / wt.%	0.90	1.63	16.93	37.95	7.00
Na_2O / wt.%	1.74	0.54	0.61	7.95	1.57
LHV / MJ/kg	14.70	0.12	15.74	17.76	16.70
DT (HTA) / °C	1150	1130	1080	1210	1330
Average	bad	poor	riscy	riscy	good

Evaluation of ash behaviour for co-firing



- Columbian hard coal: continous change of DT up to 25 wt.%, a plateau at intermediate admixing rate and a final decrease → maximum tolerable admixing rate of 10 wt.% OAT
- German brown coal: no signifcant change of DT up to 50 wt.% and decrease of about 100 K up to pure oat husks → maximum tolerable admixing rate of 50 wt.% OAT

Summary

- Different fuel properties
- Mineral distribution influences the ash fusion behavior
- Selective release of mineral species depending on binding partners
- Relevant fuel properties for co-firing:
  - Water content
  - Ash content
  - Chlorine content
  - Alkali content
  - LHV
  - DT
  - …
- Final evaluation only with consideration of a coal possible

Outlook

- Modeling of the ash behaviour with respect to the mineral heterogeneity

Acknowledgement

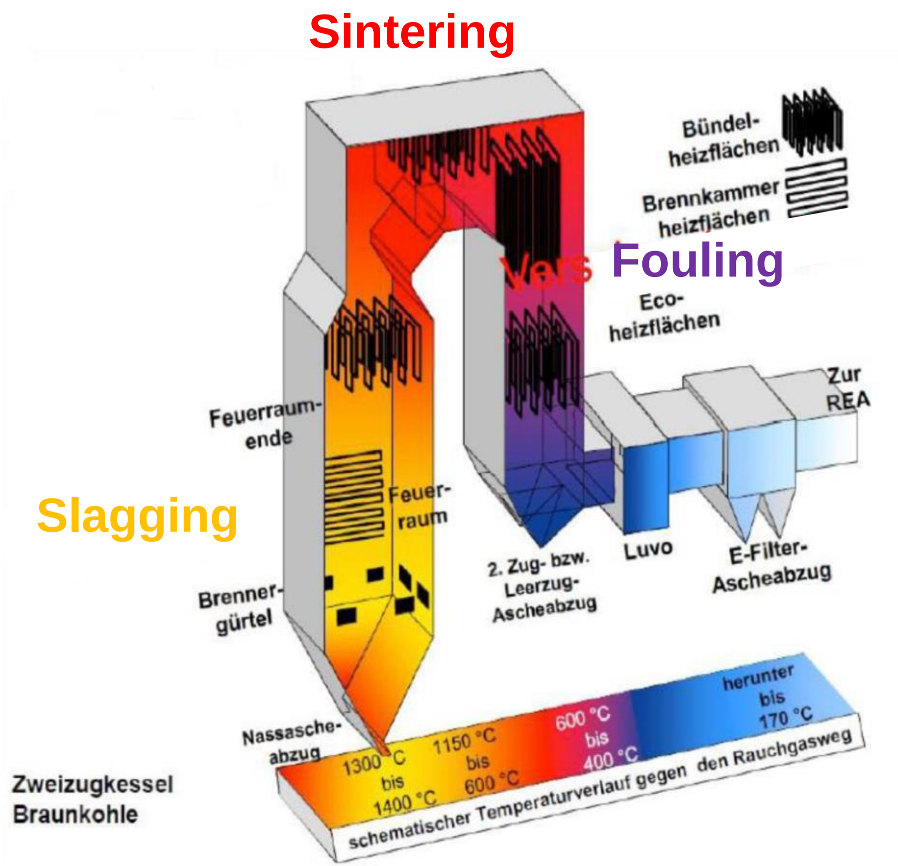
The support of this study by RWE Power AG is gratefully acknowledged.

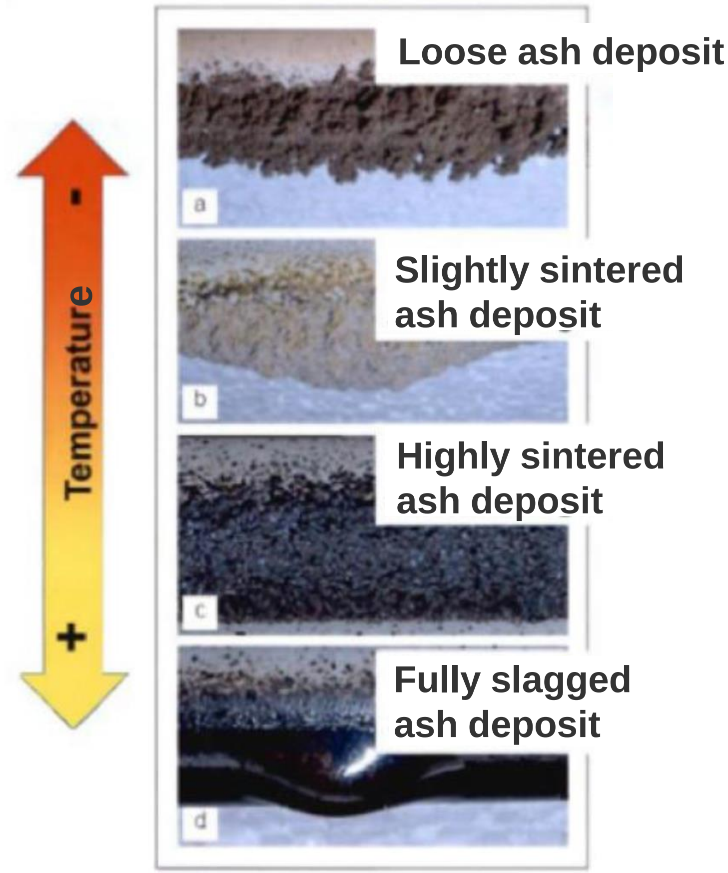
Thank you very much for your kind attention!

Appendix

BACKGROUND

Ash properties of the substitute fuels





M. Muhammadie, PhD thesis, TU Bergakademie Freiberg, (2007). *M. Neuroth, RWE Power AG, personal communication.*

Thermochemical calculations

- FactSage™ version 7.0
- Equilib module

C. W. Bale et al., Calphad, 54 (2016) 35-53.

- Data bases (in the order specified): FToxid, FTmisc, FTsalt, and FactPS
- Solution species: SlagA, AMonoxide, M2O3(Corundum), AMullite, ASpinel, AWollastonite, AMelilite, AOlivine, ACordierite, AOrthopyroxene, Ca(Al,Fe)2O4, Ca2(Al,Fe)2O5, Ca3(Al,Fe)2O6, Ca(Al,Fe)6O10, Ca(Al,Fe)12O19, NaAlO2-HT, (Ca,Na2)Ca8Al6O18, Ca2(Al,Fe)8SiO16, Na,K,[Rb,Cs]//NO3(ss), FeS-liq, AMatte, Ca3Ti2O7-Ca3Ti2O6, and AlkCl-ss_rocksalt
- Input data: stoichiometric ash composition from XRF (except of CO_2 and trace elements)

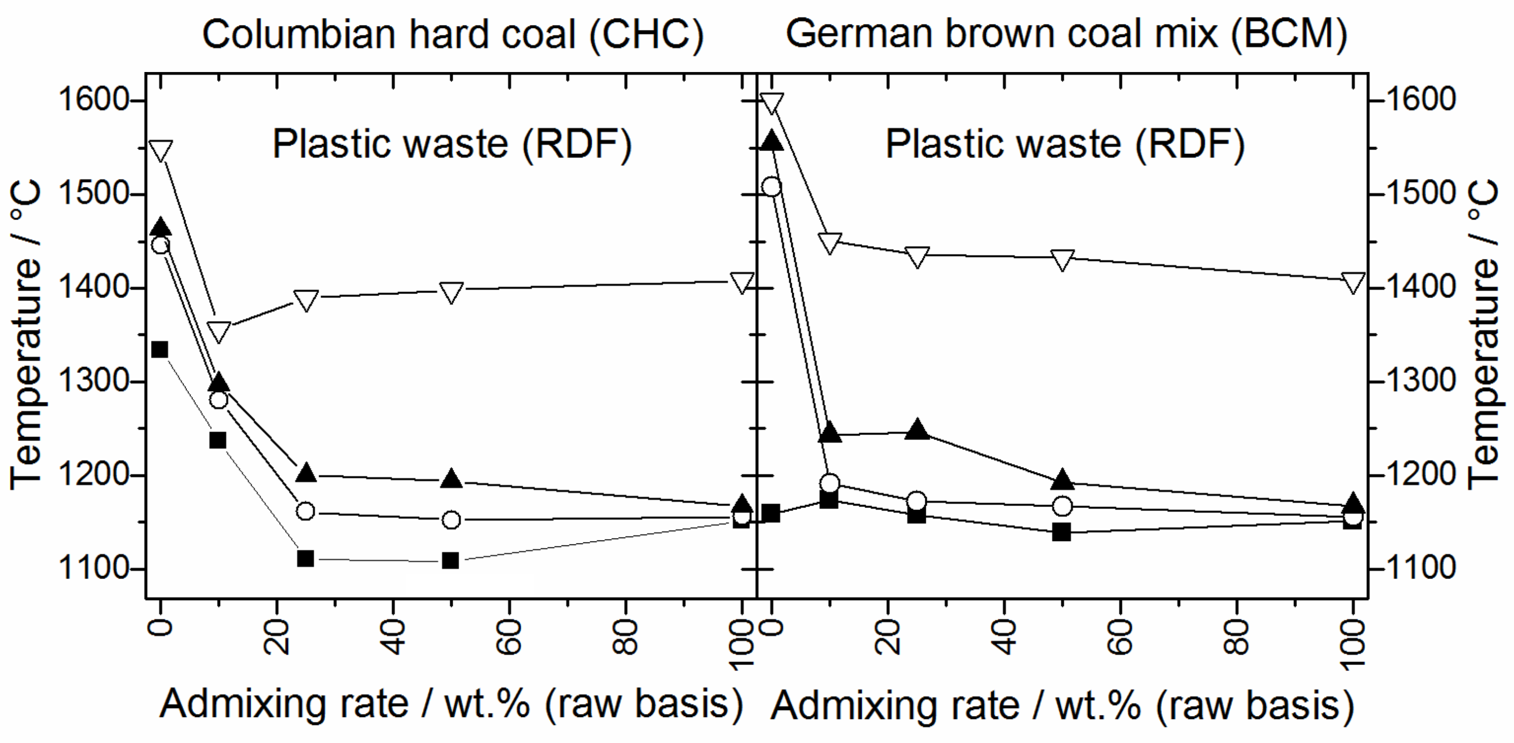
  atmosphere: artificial air using 20-fold mass of ash

  composition of artificial air: N_2, O_2, and Ar
- Analysis: liquidus temperature (T_{liq}) defined by the temperature with 1 wt.% of remaining solid fraction

Mineral phase composition (ashed at 815 °C)

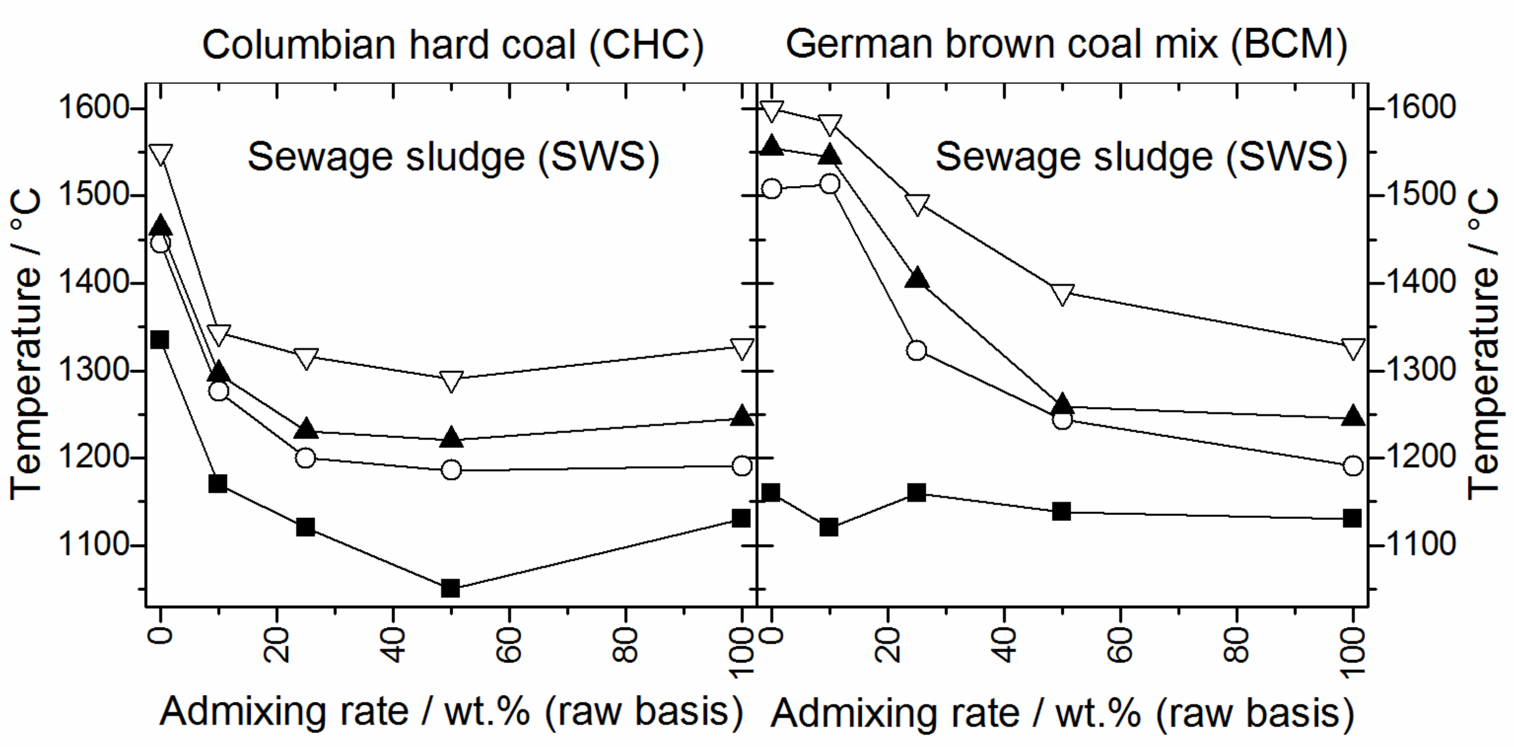
Group	Mineral phase	Stoichiometry	RDF	SWS	OAT
Normalized mass fraction (XRD) / wt.%					
Sulfates	Anhydrite	$CaSO_4$	2	1	-
	Arcanite	K_2SO_4	-	-	12
Carbo-nates	Calcite	$CaCO_3$	1	-	-
	Magnesite	$MgCO_3$	-	-	1
	Huntite	$CaMg_3(CO_3)_4$	-	-	1
Simple oxides	Corundum	Al_2O_3	4	-	-
	Quartz	SiO_2	33	34	10
	Cristobalite	SiO_2	1	-	48
	Rutile	TiO_2	-	-	-
	Maghemite	γ-Fe_2O_3	-	-	-
	Hematite	Fe_2O_3	-	16	-
	Magnetite	Fe_3O_4	-	-	-
Silicates	Wollastonite	$CaSiO_3$	18	-	-
	Diopside	$CaMgSi_2O_6$	8	-	-
	Andradite	$Ca_3Fe_2Si_3O_{12}$	18	-	-
	Hedenbergite	$CaFeSi_2O_6$	-	-	-
	Anorthite	$CaAl_2Si_2O_8$	7	-	-
	Mullite	Al_4SiO_8/Al_2SiO_5	-	-	-
	Albite	$NaAlSi_3O_8$	-	4	-
	Microcline	$KAlSi_3O_8$	-	6	16
	Muscovite	$KAl_3Si_3O_{10}(OH)_2$	-	14	-
	Hauyne	$Na_3CaAl_3Si_3O_{12}(SO_4)$	8	-	-
Phos-phates	Berlinite	$AlPO_4$	-	3	5
	Whitlockite	$Ca_3P_2O_8$	-	21	-
	Amorphous	-	15	20	50

Ash fusion behavior (RDF, ashed at 815 °C)



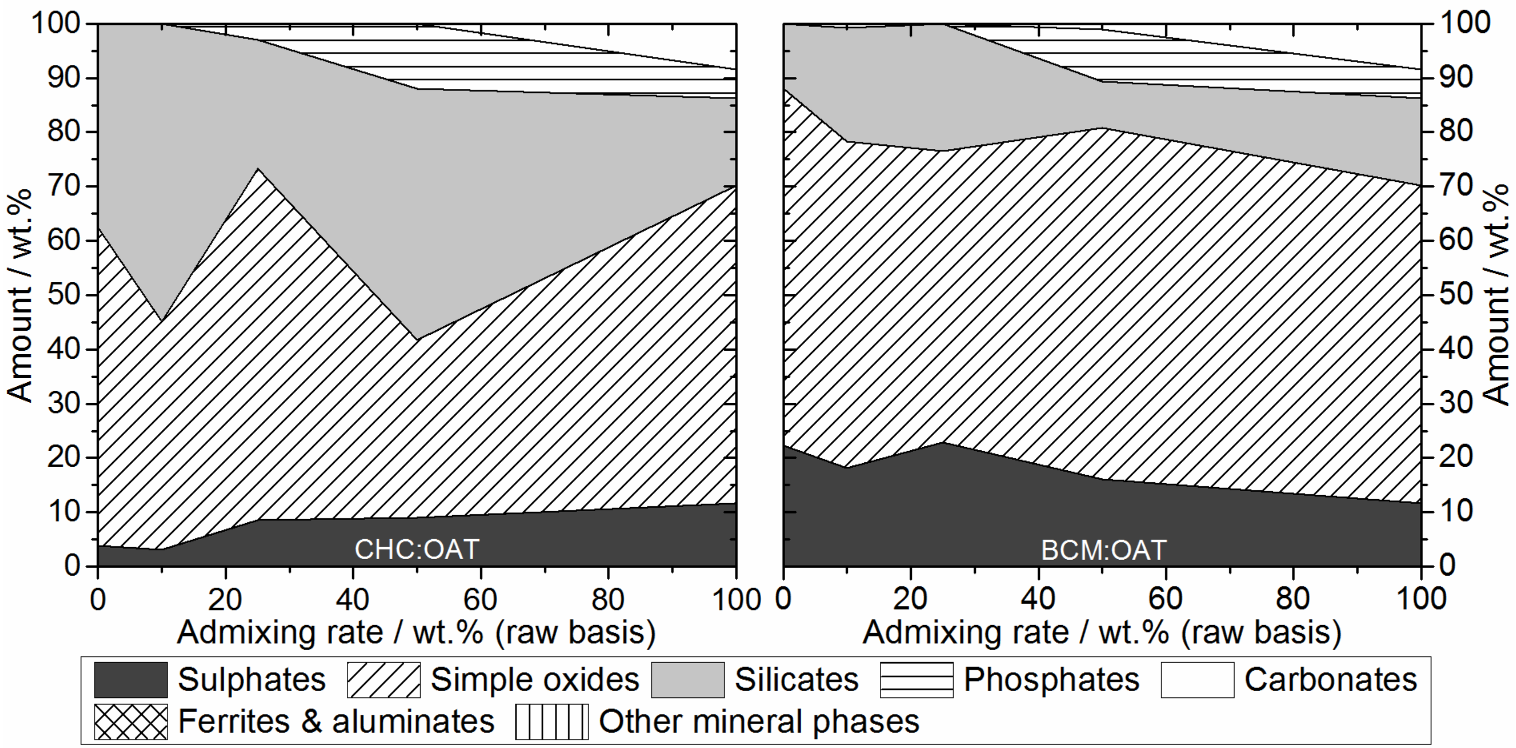
- Strong change of ash fusion temperatures at low admixture rates of RDF
- At 10 wt.% (BCM:RDF) and 25 wt.% (CHC:RDF) the ash fusion temperature already reached the values close to pure RDF

Ash fusion behavior (sewage sludge, ashed at 815 °C)



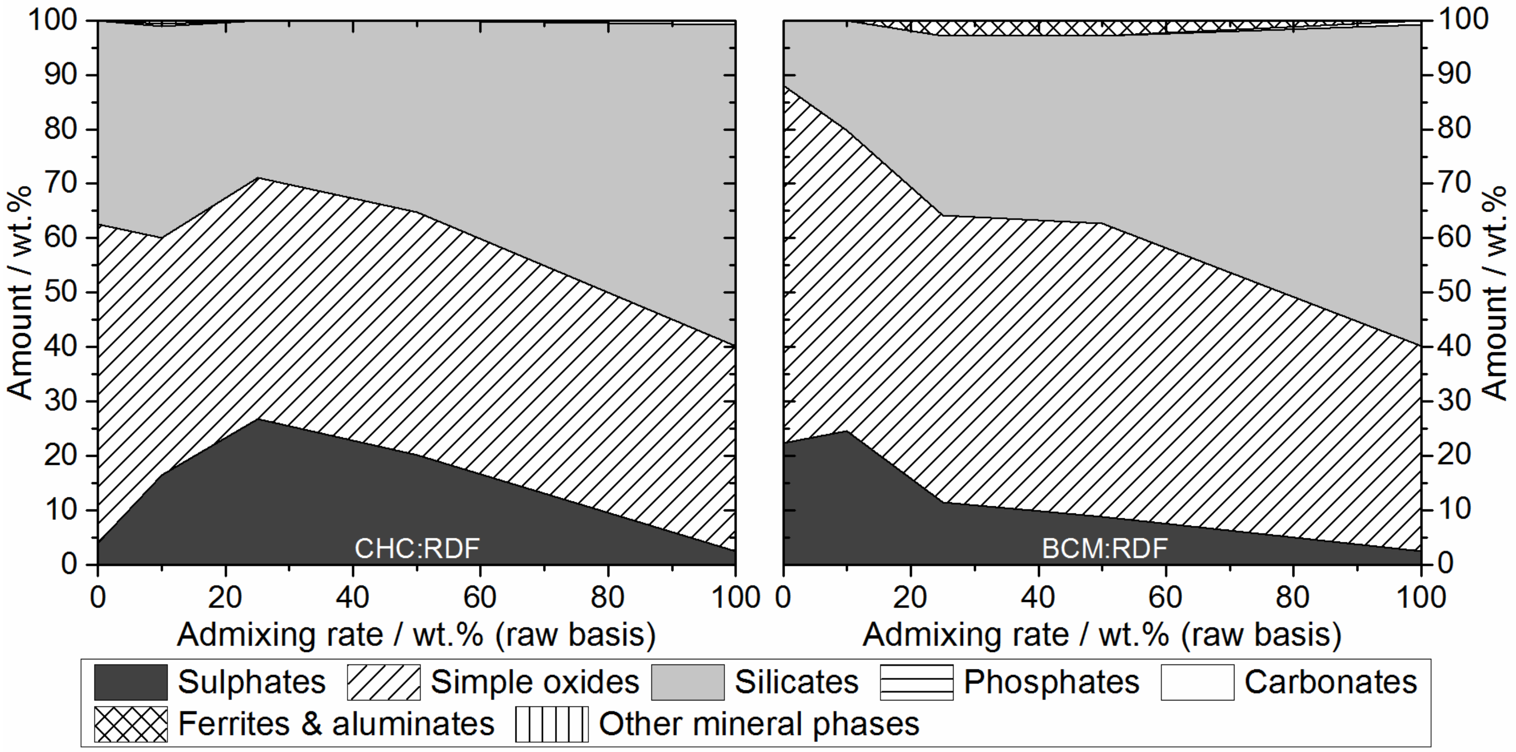
- Strong decrease of the ash fusion temperatures to values of sewage sludge (CHC:SWS)
- Continous change with increasing admixture rates (BCM:SWS)

Mineral phase composition (OAT addition, ashed at 815 °C)



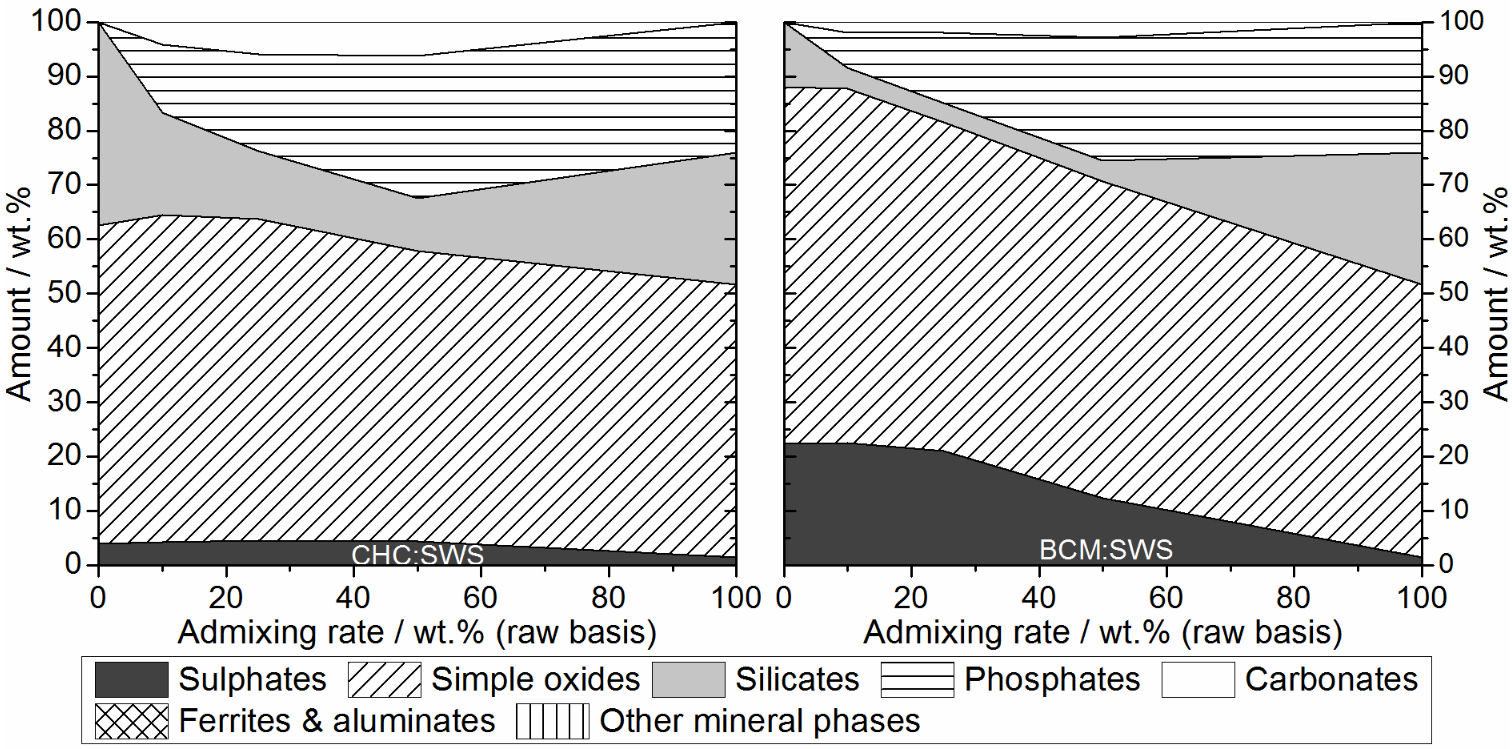
- Amounts of simple oxides are constant with some fluctuations
- Contents of silicates reduced with admixture of OAT
- Sulfates are increased for CHC and reduced for BCM with raising OAT addition

Mineral phase composition (RDF addition, ashed at 815 °C)



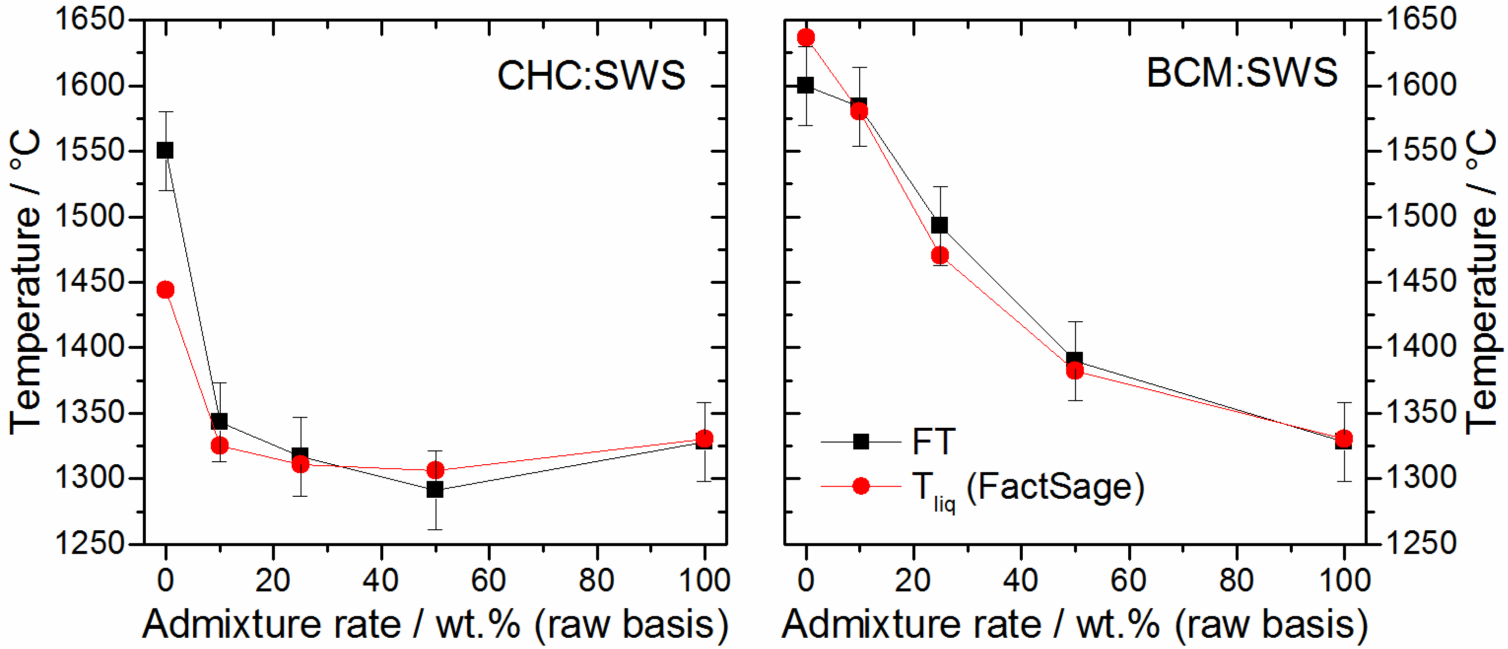
- Amount of silicates clearly increased, while simple oxides and sulfates (BCM) continuously reduced with increasing admixture rate
- Certain mineral phases, e.g. sulfates and ferrites/aluminates, only formed during different admixture range

Mineral phase composition (SWS addition, ashed at 815 °C)



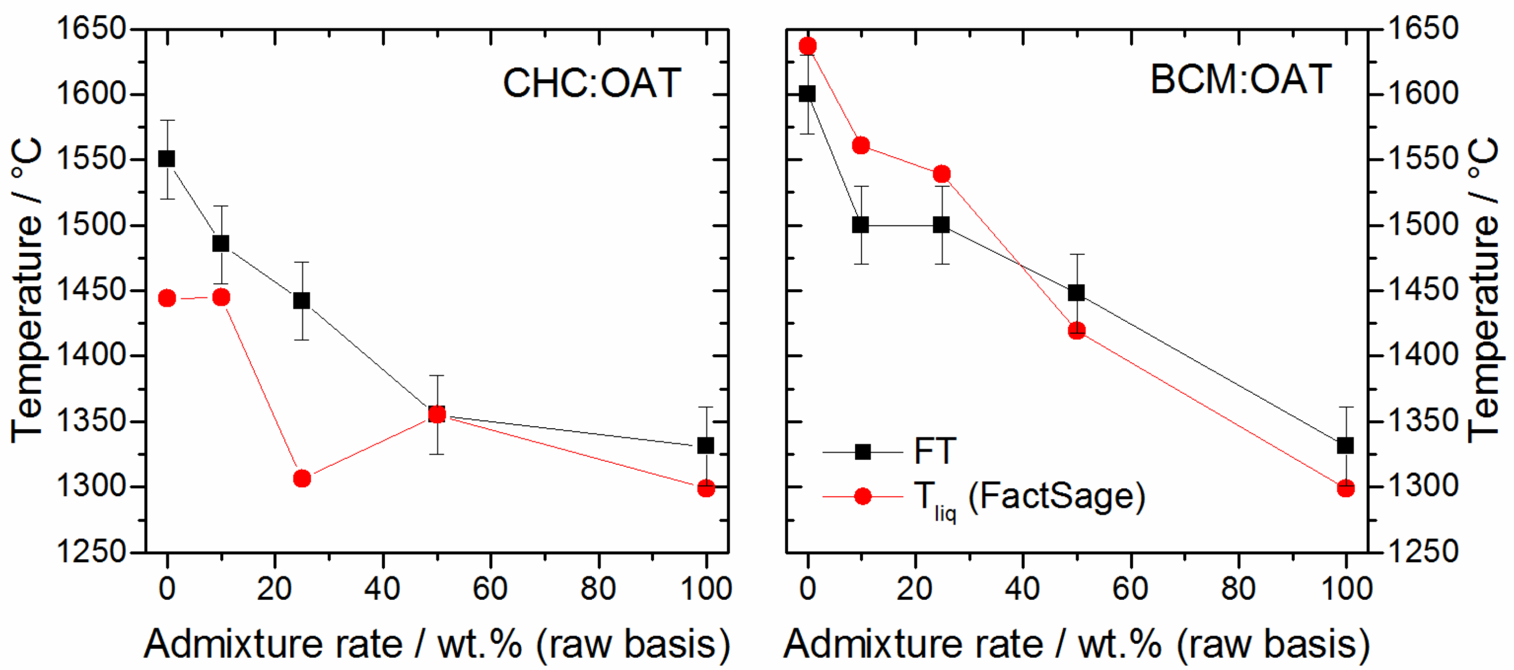
- Amount of simple oxides are slightly reduced with SWS addition
- Silicates found with lowest shares at intermediate admixture rates, while phosphates and carbonates formed
- Sulfates at highest in coal and lowest in pure SWS

FactSage™ calculations (SWS addition, ashed at 815 °C)



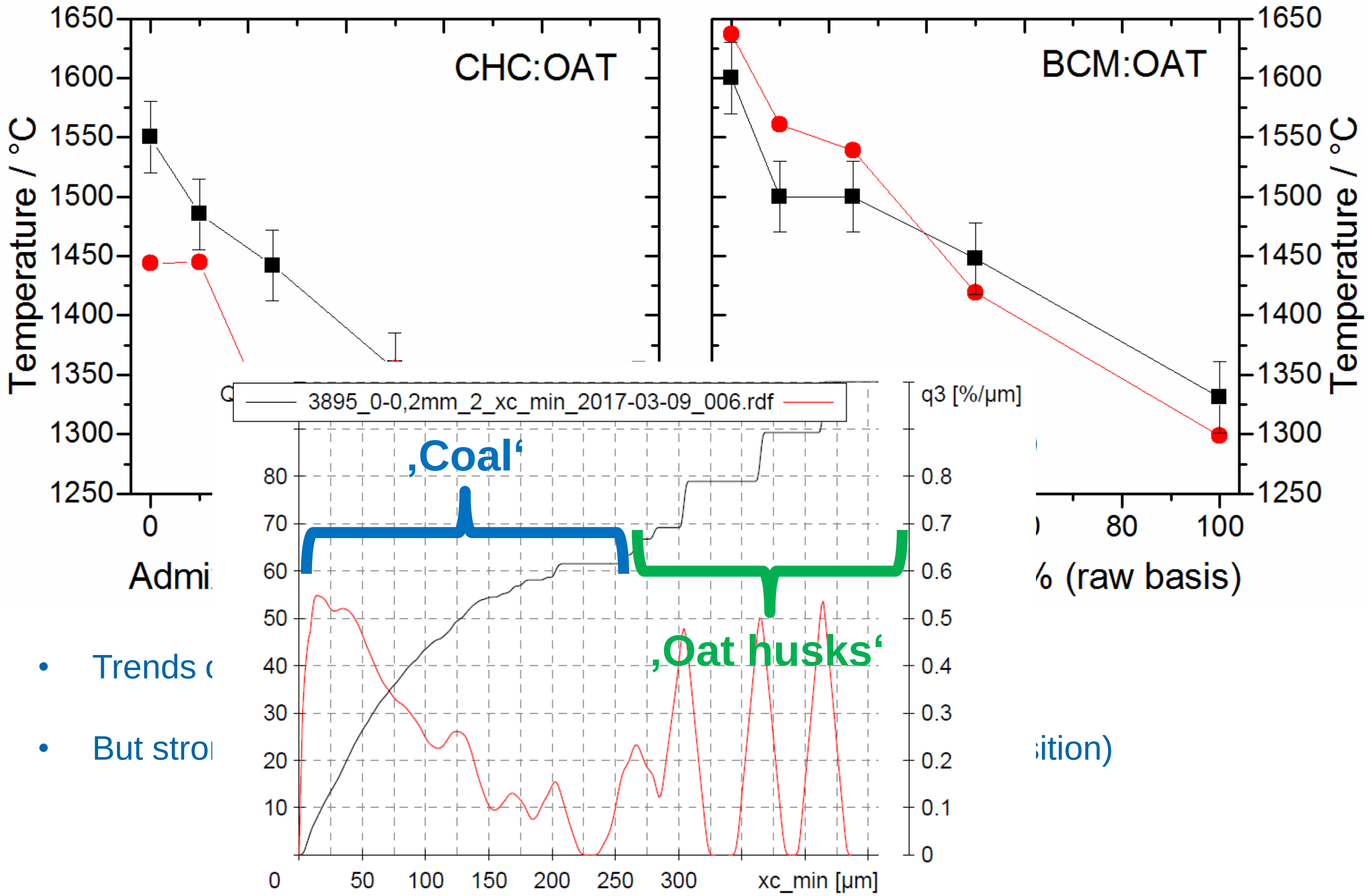
- FactSage™ fits the experimental values well

FactSage™ calculations (OAT addition, ashed at 815 °C)



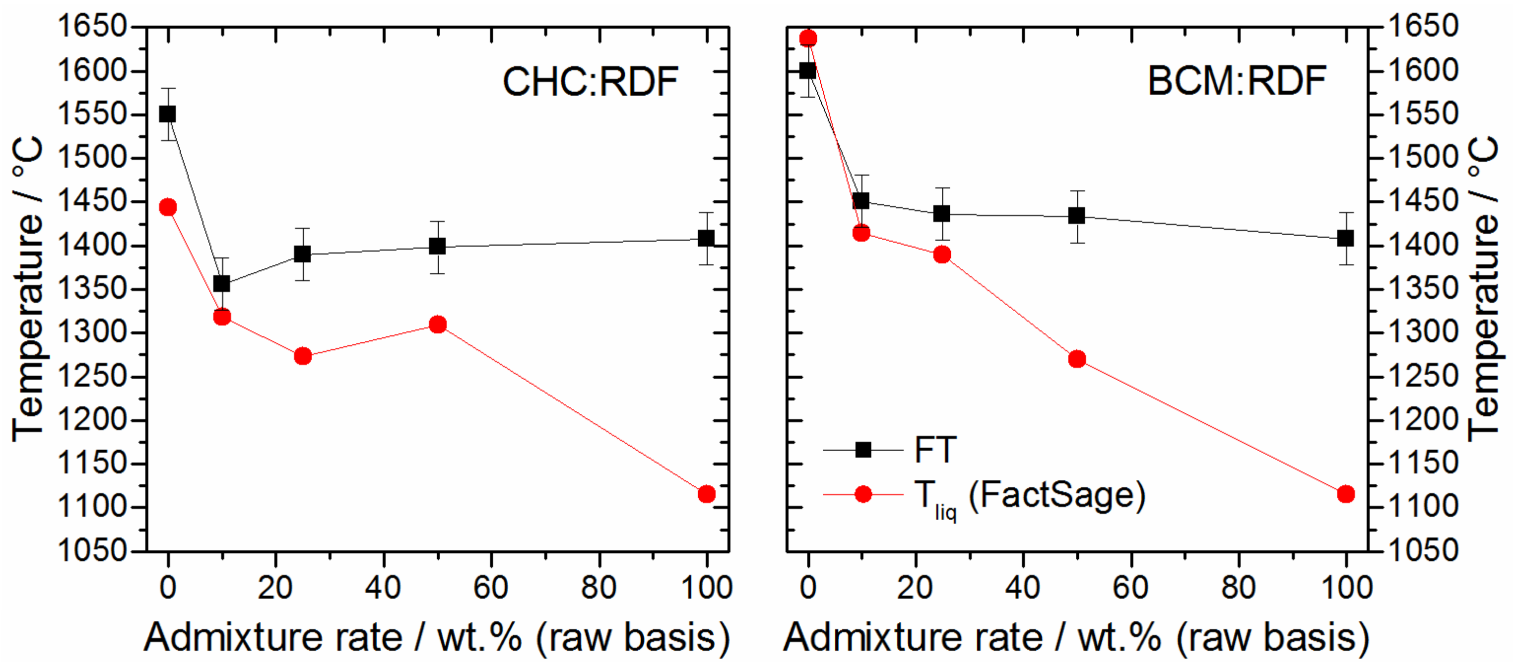
- Trends of the flow temperatures are reproduced by FactSage™
- But strong fluctuations for CHC:OAT (cf. mineral phase composition)

FactSage™ calculations (OAT addition, ashed at 815 °C)



- Trends (
- But stro … sition)

FactSage™ calculations (RDF addition, ashed at 815 °C)



- Agreement at least for low additions of RDF
- FactSage™ fails for higher admixture rates