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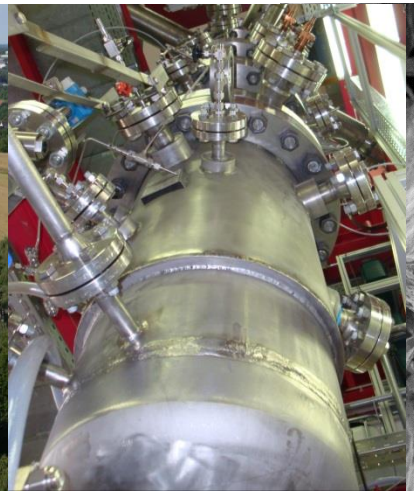
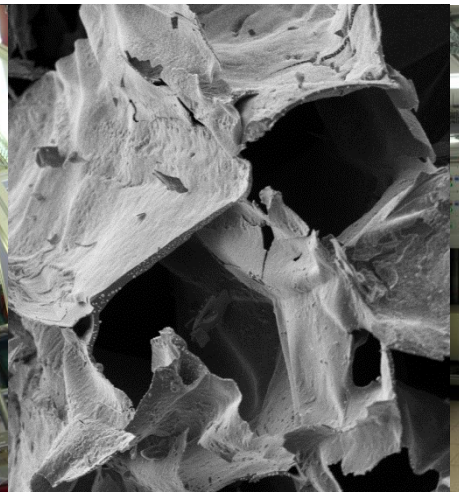
Institute of Energy Process Engineering
and Chemical Engineering
Chair EVT

Slag-induced corrosion of chromium oxide-free refractory materials under simulated gasification conditions: a multi-step modeling approach using FactSage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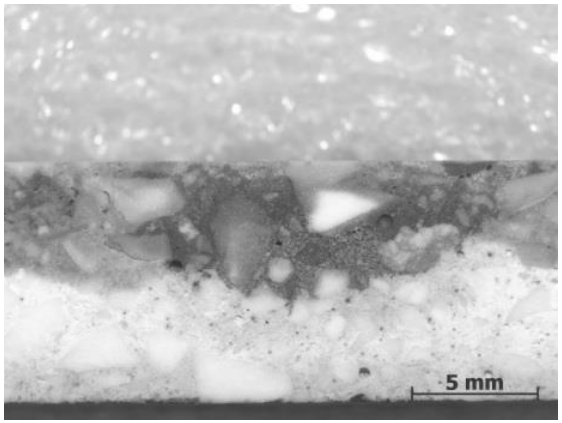
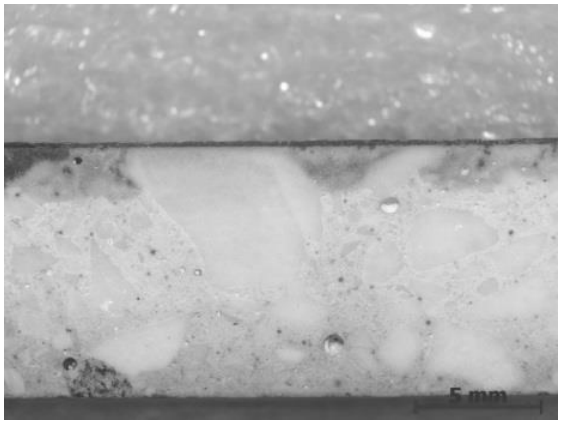
Outline

- Motivation
- Materials and methods
  - Ash and refractory materials
  - Experimental and computational details
  - Multi-step modeling approach
- Results and discussion
  - Ash-refractory interactions
  - Measured infiltration depth vs. calculation steps
- Summary





Motivation

- Rising utilization of coal and biomass in a chemical instead of a pure energetic way
- Higher carbon conversion in entrained flow gasification, but liquid slag
- Environmentally friendly and cheap substitutions of widely used refractories from Cr_2O_3
- Deeper insight into present corrosion mechanisms by means of thermochemical calculations
- Perspective prediction of corrosion resistance prior to refractory development

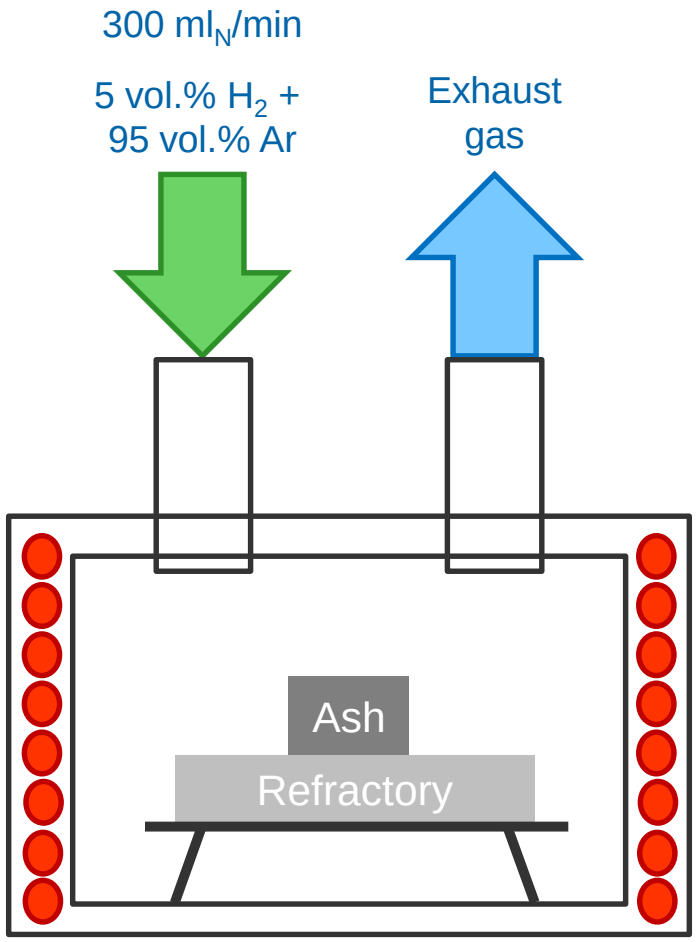
Ash and refractory materials

Component (wt.%)	Acidic Ash (AA)	Intermediate Ash (IA)	Basic Ash (BA)
Residual C	4.3	2.4	-
CO_2	-	2.2	9.9
Na_2O	**5.1**	0.6	0.3
MgO	5.2	3.8	**5.6**
Al_2O_3	**18.4**	2.4	**8.1**
SiO_2	**40.2**	**42.9**	**22.5**
P_2O_5	0.3	0.1	2.3
SO_3	5.1	6.5	2.4
Cl	0.1	0.1	0.4
K_2O	**3.4**	0.2	**6.7**
CaO	**9.4**	**27.0**	**27.9**
TiO_2	0.9	0.2	0.5
Fe_2O_3	7.2	11.1	8.0
BaO	0.1	0.3	0.2
Sum	**99.7**	**99.8**	**94.8**
DT / °C	1094	1260	1160
ST / °C	1157	1280	1210
HT / °C	1192	1289	1214
FT / °C	1304	1300	1246
B/A	**0.52**	**0.94**	**1.58**

Sample	Main Mineral Phases
AR78 AB 1500	60 wt.% spinel ($MgAl_2O_4$), 40 wt.% corundum (Al_2O_3)
AR78 MAC 1450	64 wt.% spinel ($MgAl_2O_4$), 30 wt.% corundum (Al_2O_3), 6 wt.% hibonite ($CaAl_{12}O_{19}$)
CA_6 (Bonite)	86 wt.% hibonite ($CaAl_{12}O_{19}$), 8 wt.% corundum (Al_2O_3), 5 wt.% grossite ($CaAl_4O_7$)
TTA1650	97.5 wt.% corundum (Al_2O_3), 2.5 wt.% titania (TiO_2)

Experimental details

- TOM-AC tests
- Ash cylinder: 4 g, 15 mm diameter, ca. 10 mm height; refractory disc: 50 mm diameter, ca. 10 mm height
- Heat up rate: 20 K/min (up to 800 °C), 10 K/min (800-1450 °C)
- Reducing atmosphere: 5 vol.% H_2 in Ar, 300 ml_N/min
- Slow cool down to room temperature (2-3 h)
- SEM/EDX analysis of sample sections



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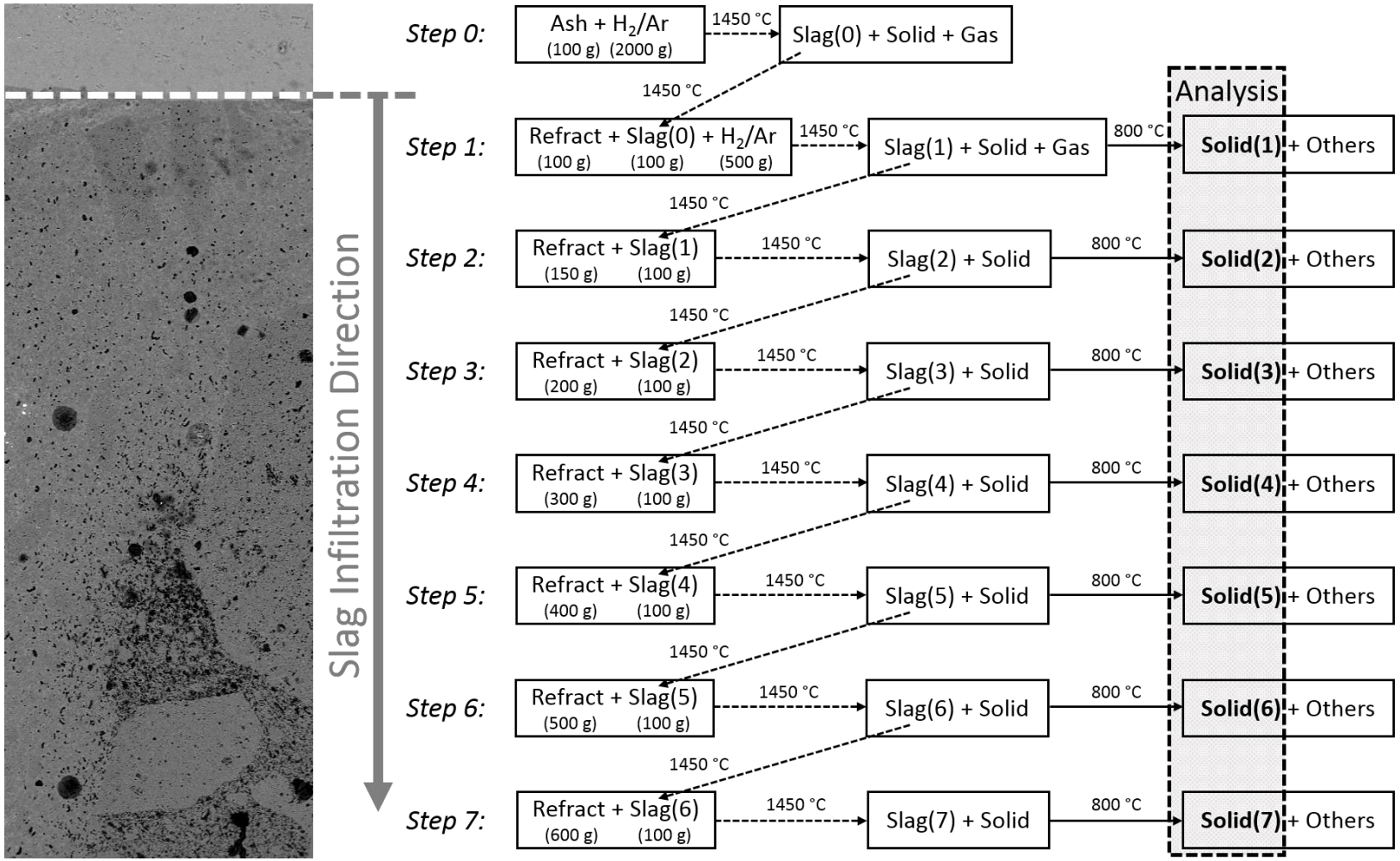
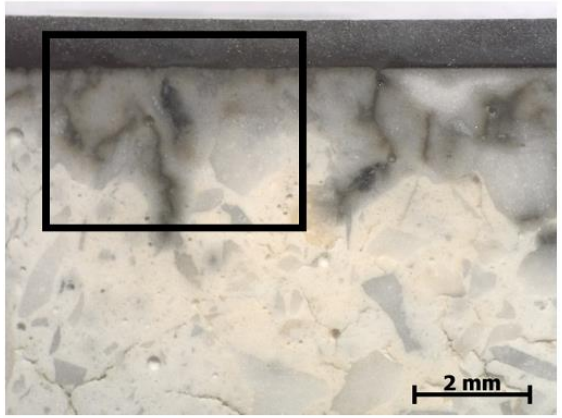
Calculation details

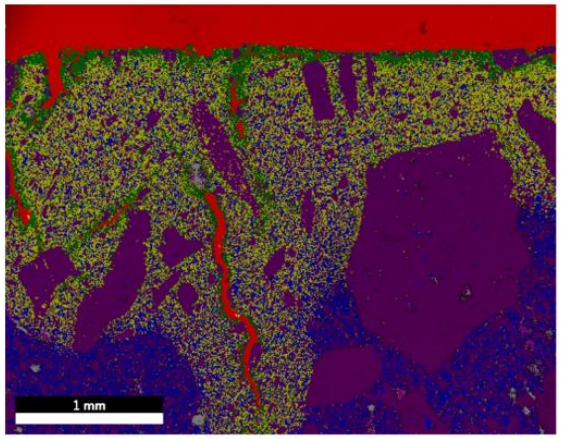
- FactSage™ (version 6.3.1)
- Data bases: FToxid, FTmisc, FTsalt, and FactPS
- Solution species: ASlag, ASpinel, Fe-liq, Mullite
- Input data: ash composition (XRF), composition of refractory (provided by developer / company), reducing atmosphere (H_2, Ar)
- Operation temperature: 1450 °C, determination of mineral phases: 800 °C
- Multi-step modeling approach

Multi-step modeling approach



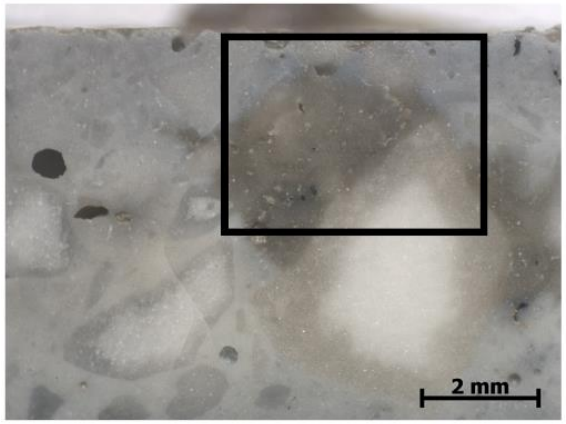
Acidic Ash + AR78 AB 1500

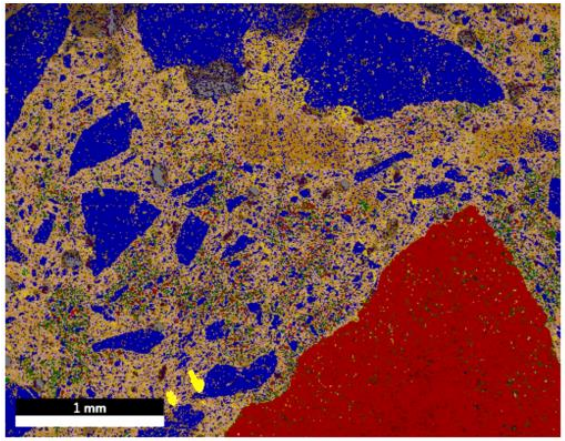




Color bar and concentration (% based on pixels)	Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
12	Si/Al/Ca/O/Mg/K	Slag	A-slag	1–3	4–7
8	Al/Mg/Si/O/Ca	$MgAl_2O_4$ +	A-spinel	6; 7	5
		$CaAl_2Si_2O_8$	$CaAl_2Si_2O_8$ (anorthite)	1	2; 3
18	Al/O/Mg/Si	$Mg_4Al_{10}Si_2O_{23}$ +	$Mg_4Al_{10}Si_2O_{23}$ (sapphirine)	1–7	
		Al_2O_3	Al_2O_3 (corundum)	3–7	2
16	Al/O/Mg	Al_2O_3 +	Al_2O_3 (corundum)	3–7	2
		$MgAl_2O_4$	A-spinel	6; 7	5
45	Al/Mg/O	$MgAl_2O_4$	A-spinel	6; 7	5

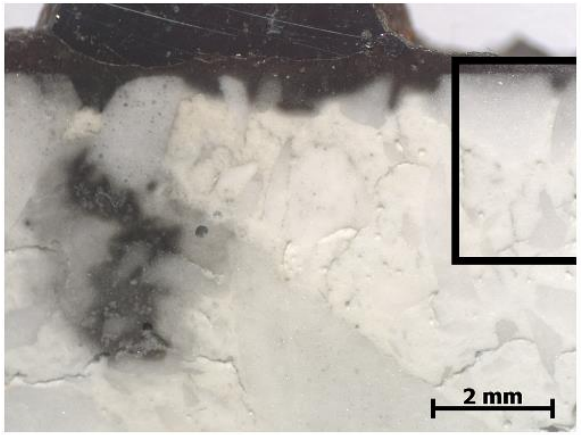
Intermediate Ash + AR78 AB 1500

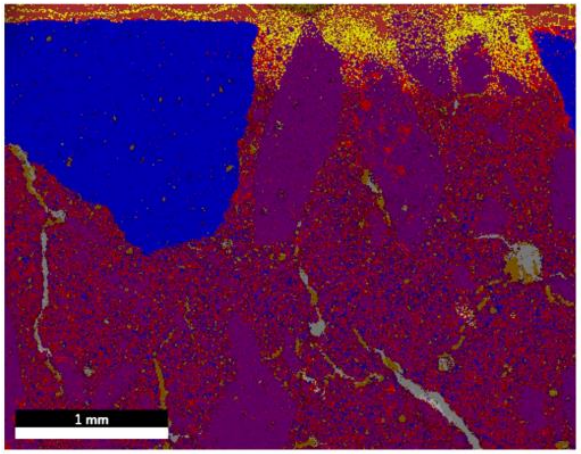




Color bar and concentration (% based on pixels)		Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
	17	Al/Ca/Si/O/Mg	$MgAl_2O_4$ +	A-spinel	1; 2	3; 4; 6; 7
			$CaAl_2SiO_6$	$CaAl_2Si_2O_8$ (anorthite)	1–3	4; 5
	7	Al/Ca/Si/O/Mg	$CaAl_2SiO_6$	$CaAl_2Si_2O_8$ (anorthite)	1–3	4; 5
	20	Al/Mg/O/Ca/Si	$Mg_4Al_{10}Si_2O_{23}$ +	$Mg_4Al_{10}Si_2O_{23}$ (sapphirine)	3–7	2
				no krotite calculatet		
			$CaAl_2O_4$	Al_2O_3 (corundum)	4–7	3
				$CaMg_2Al_{16}O_{27}$ (CAM I)	2–7	
	30	Al/Mg/O	$MgAl_2O_4$	A-spinel	1; 2	3; 4; 6; 7
	5	Al/O/Ca/Si/Mg	Al_2O_3 +	Al_2O_3 (corundum)	4–7	3
			$Ca_2MgSi_2O_8$	$CaMgSi_2O_6$ (diopside)		1
				$CaAl_2Si_2O_8$ (anorthite)	1–3	4; 5
	19	Al/O	Al_2O_3	Al_2O_3 (corundum)	4–7	3

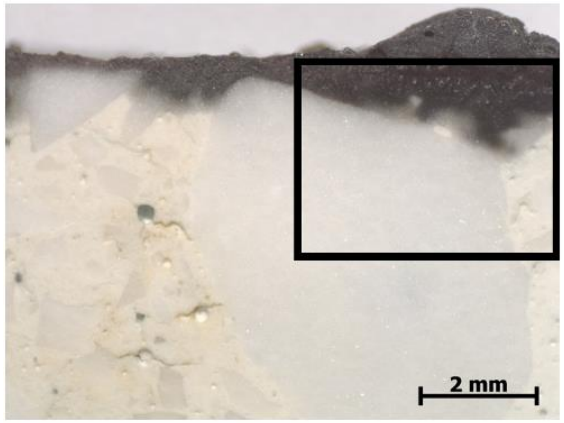
Basic Ash + AR78 AB 1500

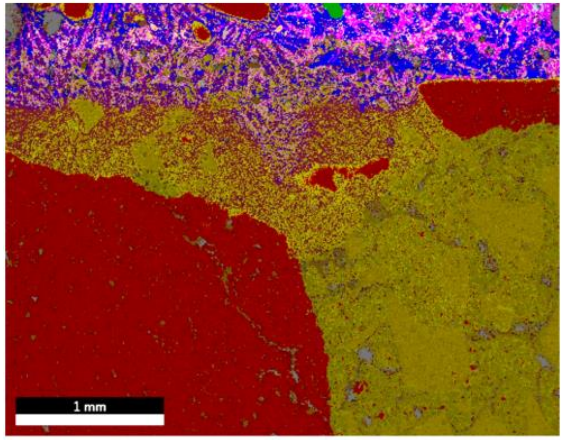




Color bar and concentration (% based on pixels)		Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
	3	Al/Ca/Si/O	$Ca_2Al_2SiO_7$ +	$Ca_2Al_2SiO_7$ (gehlenite)	1	2
			Slag	A-slag		1–7
	4	Al/O/Mg/Ca/Si	$MgAl_2O_4$ +	A-spinel	1–3	4; 6; 7
			$CaAl_2SiO_6$ +	$Ca_3Al_2Si_3O_{12}$ (grossularite)	2	1; 3
			Al_2O_3	Al_2O_3 (corundum)	5–7	
	22	Al/O/Mg	Al_2O_3 +	Al_2O_3 (corundum)	5–7	
			$MgAl_2O_4$	A-spinel	1–3	4; 6; 7
	26	Al/O	$Al2O_3$	Al_2O_3 (corundum)	5–7	
	41	Al/Mg/O	$MgAl_2O_4$	A-spinel	1–3	4; 6; 7

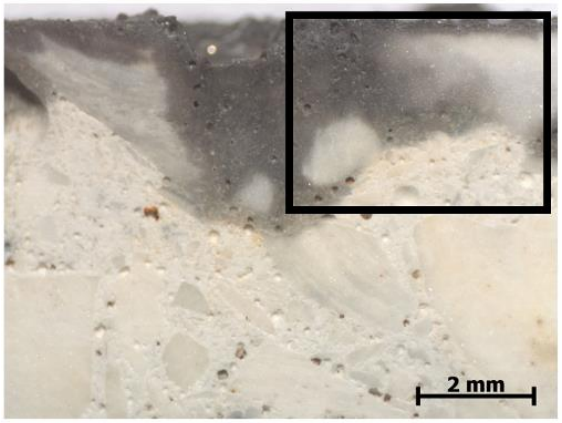
Basic Ash + AR78 MAC 1450

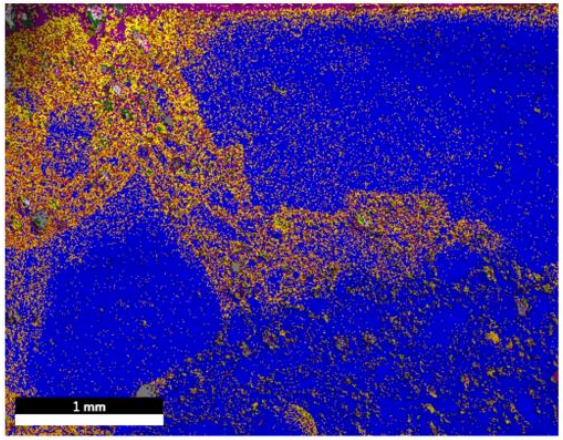




Color bar and concentration (% based on pixels)		Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
	3	Al/Si/Ca/O/K/Mg	Slag	A-slag		1–7
	6	Ca/Al/Si/O	$Ca_2Al_2SiO_7$	$Ca_2Al_2SiO_7$ (gehlenite)	1	2
	5	Al/Ca/O/Si/Mg	$Ca_2Al_2SiO_7$ +	$Ca_2Al_2SiO_7$ (gehlenite)	1	2
			$MgAl_2O_4$	A-spinel	1–4	6; 7
	5	Al/O/Mg/Si/Ca	$MgAl_2O_4$ +	A-spinel	1–4	6; 7
			$CaSiO_3$	$Ca_3Al_2Si_3O_{12}$ (grossularite)	1–3	
	8	Al/O/Mg/Ca/Si	$Ca_2Al_2SiO_7$ +	$Ca_2Al_2SiO_7$ (gehlenite)	1	2
			$MgAl_2O_4$ +	A-spinel	1–4	6; 7
			Al_2O_3	Al_2O_3 (corundum)	7	6
				$CaMg_2Al_{16}O_{27}$ (CAM I)	2–7	
	23	Al/Mg/O	$MgAl_2O_4$	A-spinel	1–4	6; 7
	13	Al/O/Mg	$MgAl_2O_4$ +	A-spinel	1–4	6; 7
			Al_2O_3	Al_2O_3 (corundum)	7	6
	35	Al/O	Al_2O_3	Al_2O_3 (corundum)	7	6

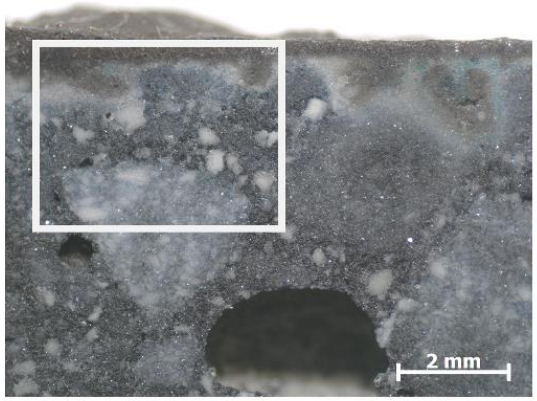
Basic Ash + CA_6 (Bonite)

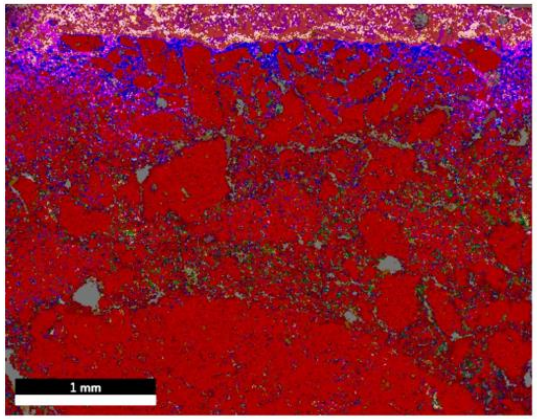




Color bar and concentration (% based on pixels)		Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
	3	Al/Ca/Si/O	Slag +	A-slag	0	1–7
			$Ca_2Al_2SiO_7$	$Ca_2Al_2SiO_7$ (gehlenite)	1–7	
	2	Al/O/Si/Ca/Mg/K	$Ca_2Al_2SiO_7$ +	$Ca_2Al_2SiO_7$ (gehlenite)	1–7	
				A-spinel	1	2–7
			$MgAl_2O_4$			
				$CaMg_2Al_{16}O_{27}$ (CAM I)	1	
	4	Al/Ca/O/Si	$CaAl_2O_4$	no krotite calculated		
	13	Al/Ca/O	$CaAl_4O_7$	no grossite calculated		
	8	Al/Ca/O/Si	$CaAl_4O_7$	no grossite calculated		
	68	Al/O/Ca	$CaAl_{12}O_{19}$	$CaAl_{12}O_{19}$ (hibonite)	4–7	

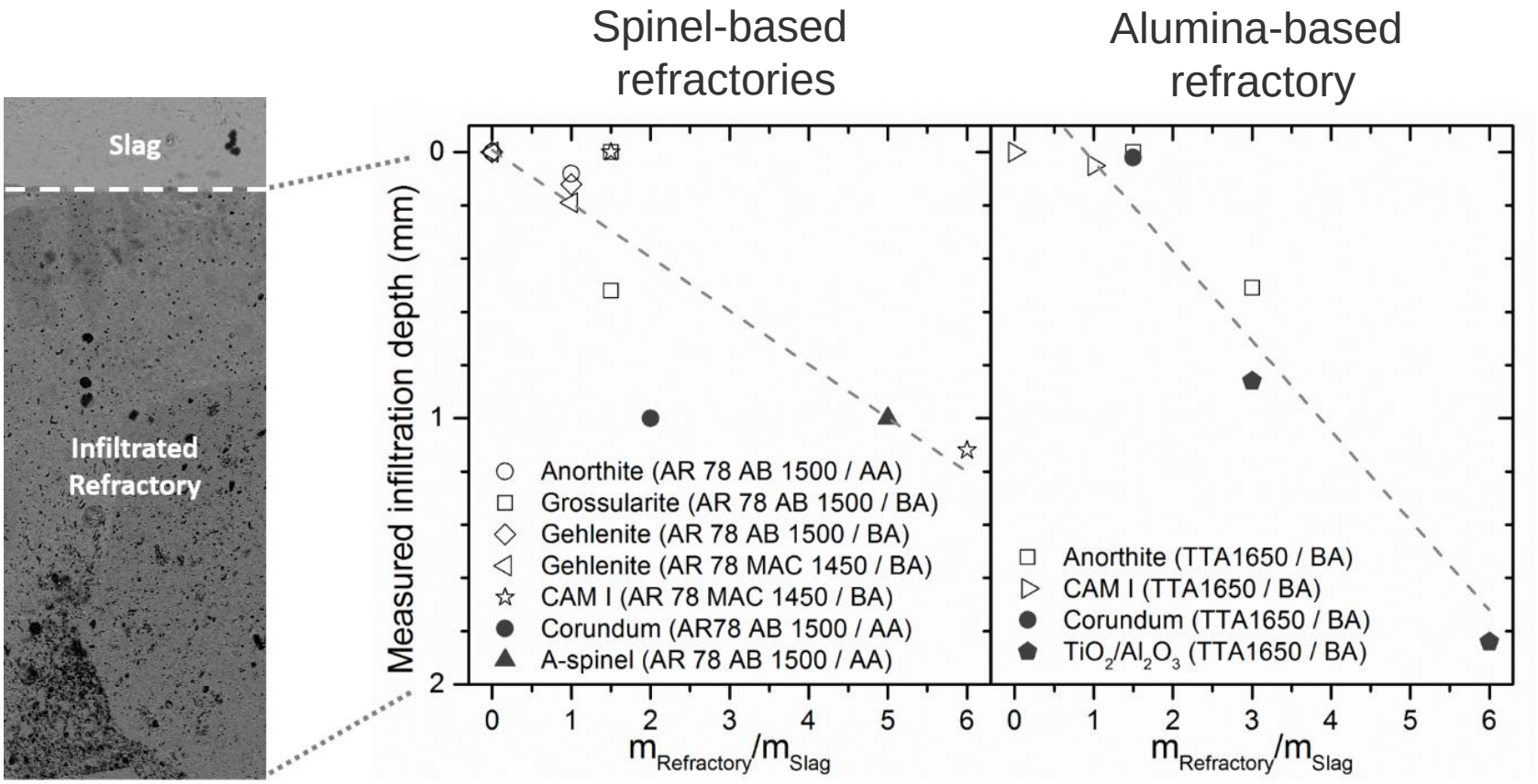
Basic Ash + TTA1650





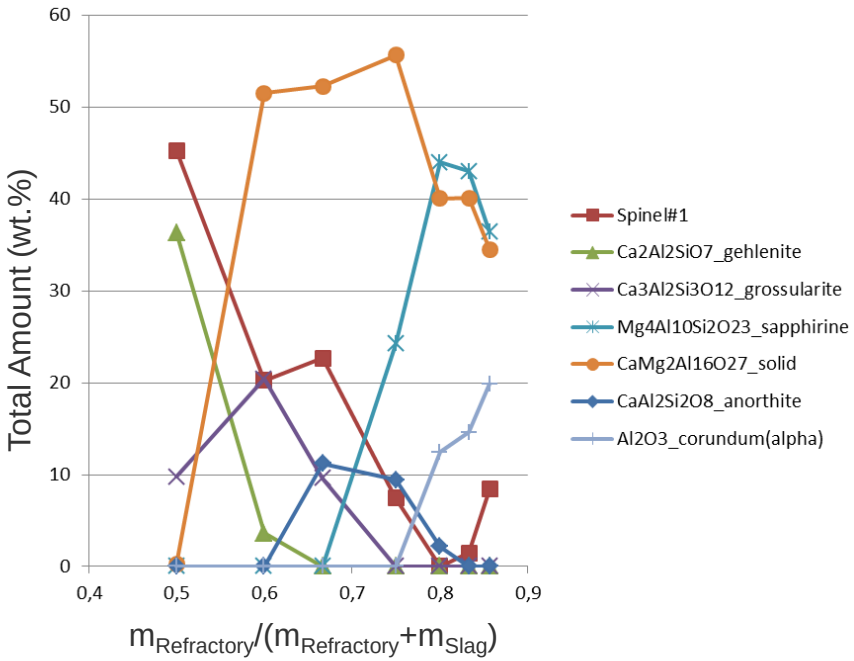
Color bar and concentration (% based on pixels)		Estimated phases	Stoichiometric mineral phases	Similar FactSage™ phases	Steps (>10 wt.%)	Steps (<10 wt.%)
	2	Si/Al/Ca/O/K	Slag	A-slag	0	1–7
	4	Ca/Al/Si/O	$Ca_2Al_2SiO_7$	$Ca_2Al_2SiO_7$ (gehlenite)	1; 2	3
	2	Al/O/Ca/Si/Mg	$MgAl_2O_4$ +	$CaMg_2Al_{16}O_{27}$ (CAM I) +	1	
			$CaAl_2SiO_6$	$CaAl_2Si_2O_8$ (anorthite)	2–4	1; 5–7
	3	Al/O/Ca/K/Si	$CaAl_2SiO_6$ +	$CaAl_2Si_2O_8$ (anorthite)	2–4	1; 5–7
			K-rich Al_2O_3	Al_2O_3 (corundum)	2–7	
	9	Al/O/K/Ti	K-rich Al_2O_3	Al_2O_3 (corundum)	2–7	
			TiO_2	TiO_2 (rutile)		4–7
	68	Al/O	Al_2O_3	Al_2O_3 (corundum)	2–7	
	3	Al/Ti/O	Al_2O_3 +	Al_2O_3 (corundum)	2–7	
			TiO_2	TiO_2 (rutile)		4–7
	2	Al/O/Ti	Al_2O_3 +	Al_2O_3 (corundum)	2–7	
			TiO_2	TiO_2 (rutile)		4–7

Measured infiltration depth vs. calculation steps

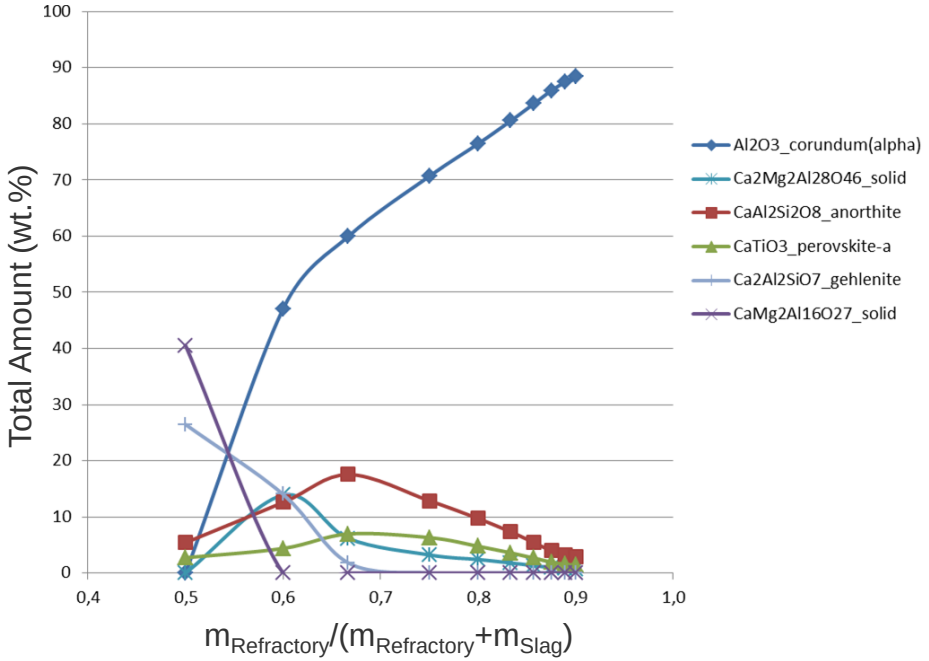


Measured infiltration depth vs. calculation steps

Basic Ash + AR78 AB 1500

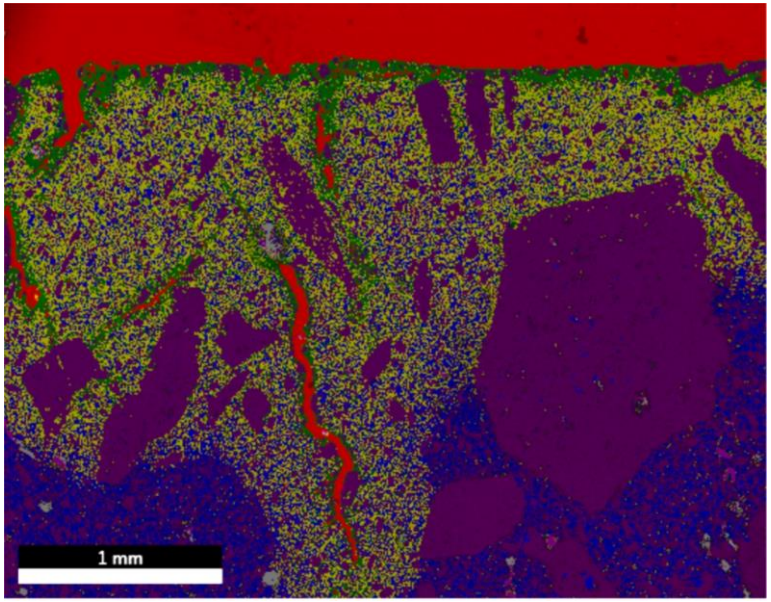


Basic Ash + TTA1650



Summary and outlook

- FactSage™ has calculated mineral phases with similar stoichiometric composition found in SEM/EDX, best agreement for matrix infiltration
- Reconstruction of mineral matter transformations for reactions between slag and refractory
- Decent hints towards the slag infiltration pathways
- Qualitative relationship for slag infiltration depth
- Quantitative prediction of corrosion resistance in the future



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Thank you for your kind attention!