SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

KATHOLIEKE UNIVERSITEIT
LEUVEN

Additions of industrial residues for hot stage engineering of stainless steel slags

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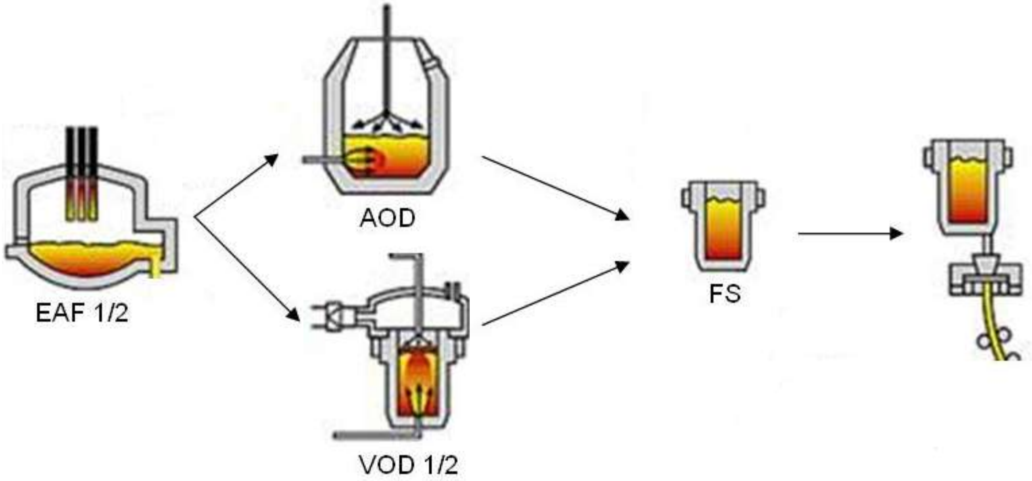
centre

SMART-PRO²

Stainless steel production

- 3-step process (before casting)
  - EAF: scrap melting
  - AOD/VOD: de-C and de-S
  - Ladle refining: de-S



EAF slag
125 kg/ton steel

De-C slag
180 kg/ton steel

Ladle slag
20 kg/ton steel

Steel production sites in Belgium

Stainless steel/slag in Belgium

ArcelorMittal, Genk

- steel: 900 kt/year
- slag: 250 kt/year

ArcelorMittal, Charleroi

- steel: 700 kt/year
- slag: 200 kt/year

Atomium: 1958-2008

Pyramid of Brussels: every 15 years

Slag valorisation chain

Slag valorisation chain

Slag valorisation chain

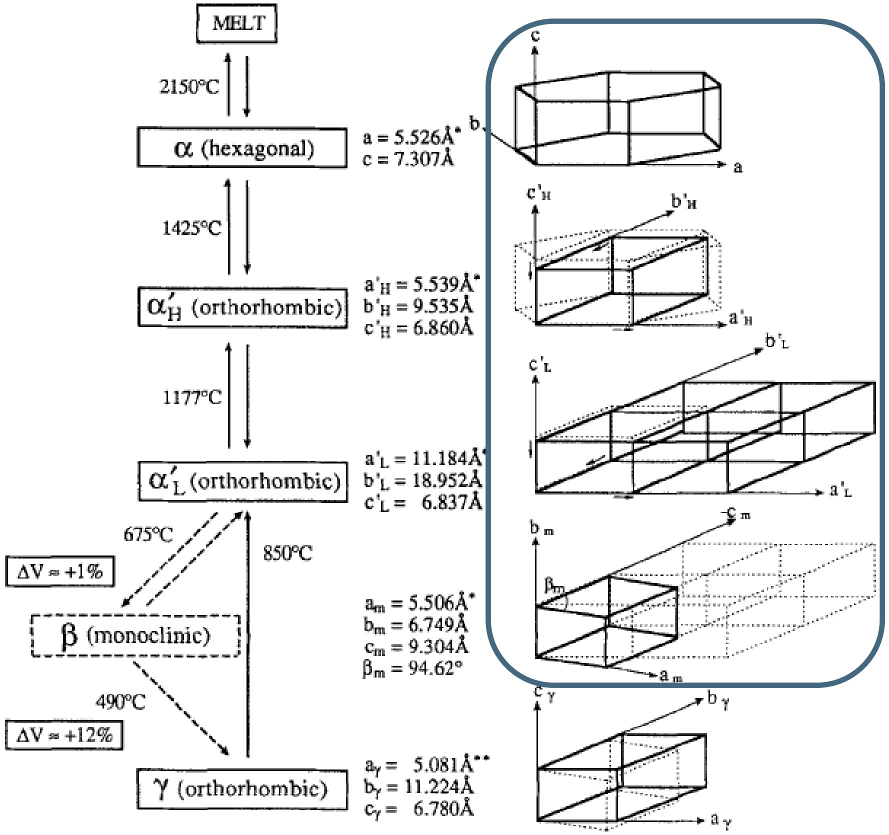
Slag valorisation chain

Slag valorisation chain

Motivation

Slag disintegrates during cooling and can not be used as aggregate.
Goes to land-filling with increased cost per ton.

Transformations of C_2S

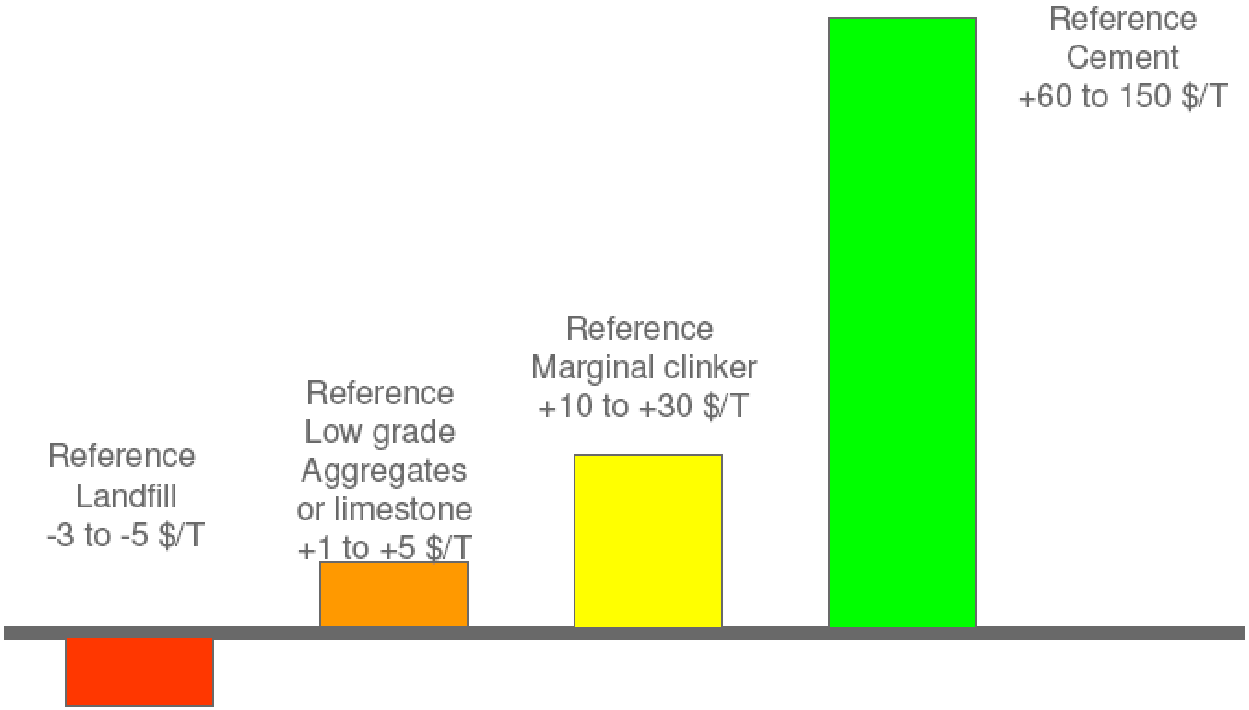


Different unit cells = different ions can stabilise the non-γ phases = Flexibility = opportunities

C. J. Chan, M. W. Kriven and J. F. Young,. J. Am. Ceram. Soc., 1992, 75, (6), 1621-1627.

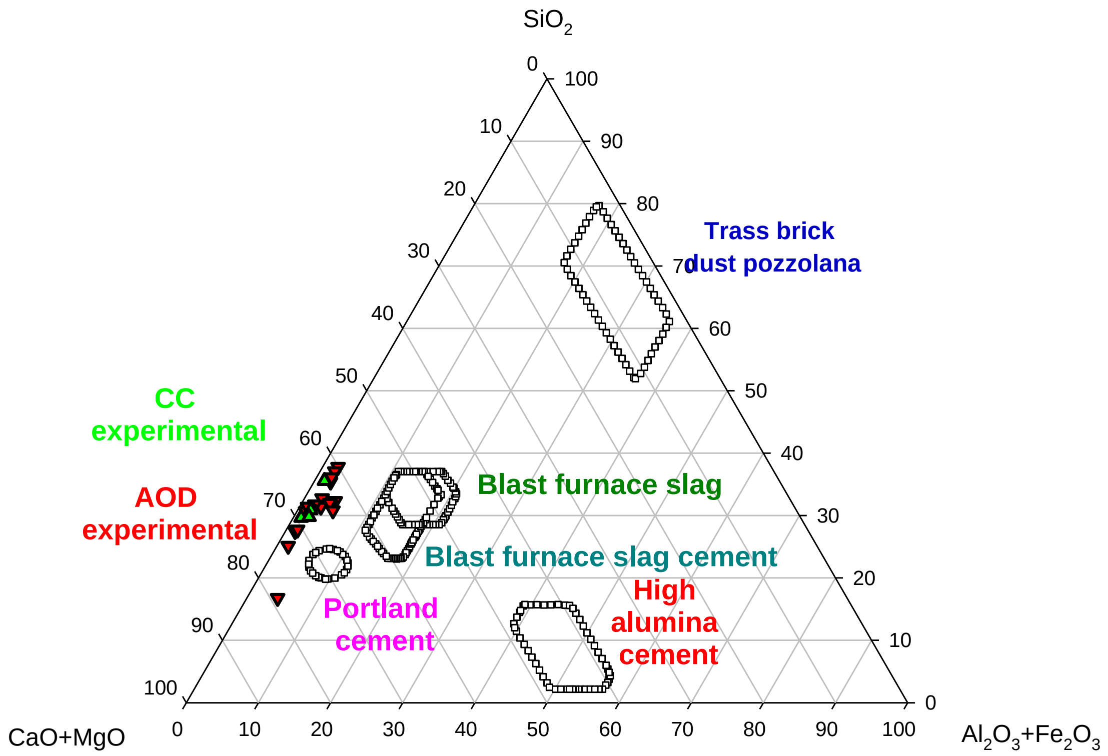
Goal

Stabilise stainless steel slag towards aggregates or a hydraulic binder



Jean-Marie Delbecq, Steel Slags as cementitious materials, Seminário Internacional – Aplicação de Escória de Aciaria, Belo Horizonte, Nov. 22 2010

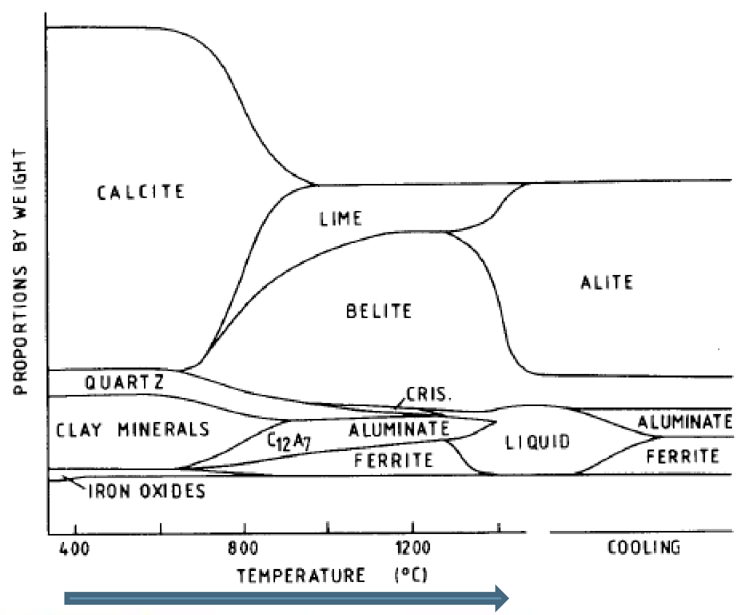
Is a hydraulic binder feasible?

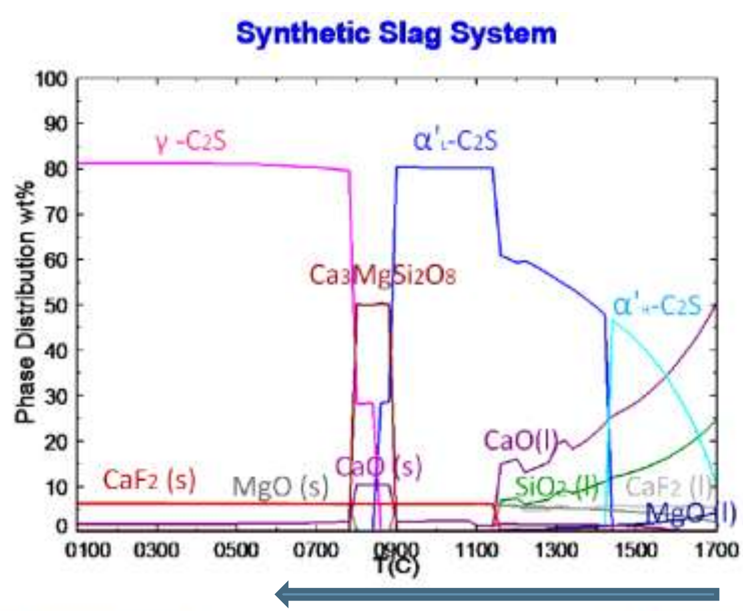


	CaO	MgO	Fe_2O_3	FeO	MnO	SiO_2	Al_2O_3	CaF_2
AOD slag	45-60	5-12	< 1	< 1	< 1	30-40	< 5	4-6
LM slag	60-70	~ 10	< 1	< 1	< 1	15-25	< 1	8-12
Belite-rich clinker	60-63	<1	3-6	-	-	25-30	3-7	-

Cement VS slag

	CEMENT	SLAG
Raw materials	Limestone, shale, clay minerals (bauxite, iron mills, fly ash, blast furnace slag, etc)	Limestone, dolomite, fluorite, quartz sand
Processing	Sintering	Melting
Cooling	Fast	Depends (overlooked)
Post-processing	Milling, additions etc	Depends (overlooked)





Hydration of C_2S

Slow cooling results to γ-C_2S that does not hydrate (activation can change this, see poster by F. Zhang *et al.)*

There is need for β, α′, α forms; β is the one typically found in cement clinkers.

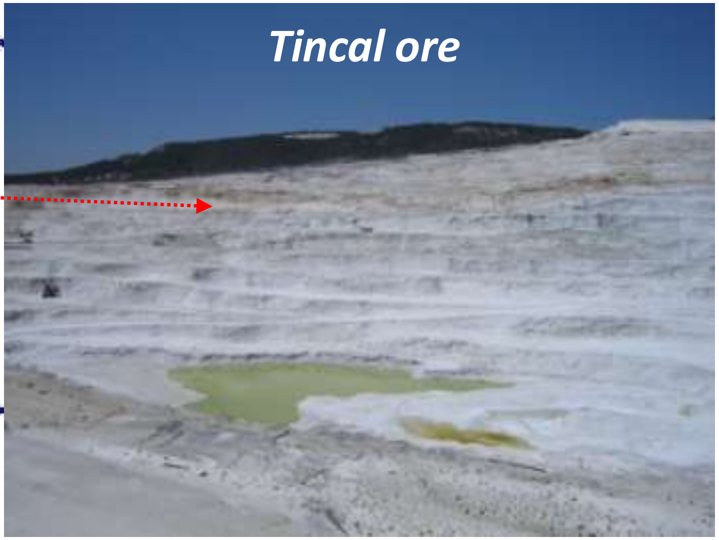
How to stabilise the slag?

- chemical stabilisation by ions
- change in slag chemistry
- fast cooling

Stabilisation by ions

α, α'_H, α'_L	MgO, Al_2O_3, Fe_2O_3, BaO, K_2O, P_2O_5, CrO_3
β	B_2O_3, Na_2O, K_2O, BaO, MnO_2, CrO_3

Boron plants in Turkey



Production in Kirka Plant: 600.000t/y

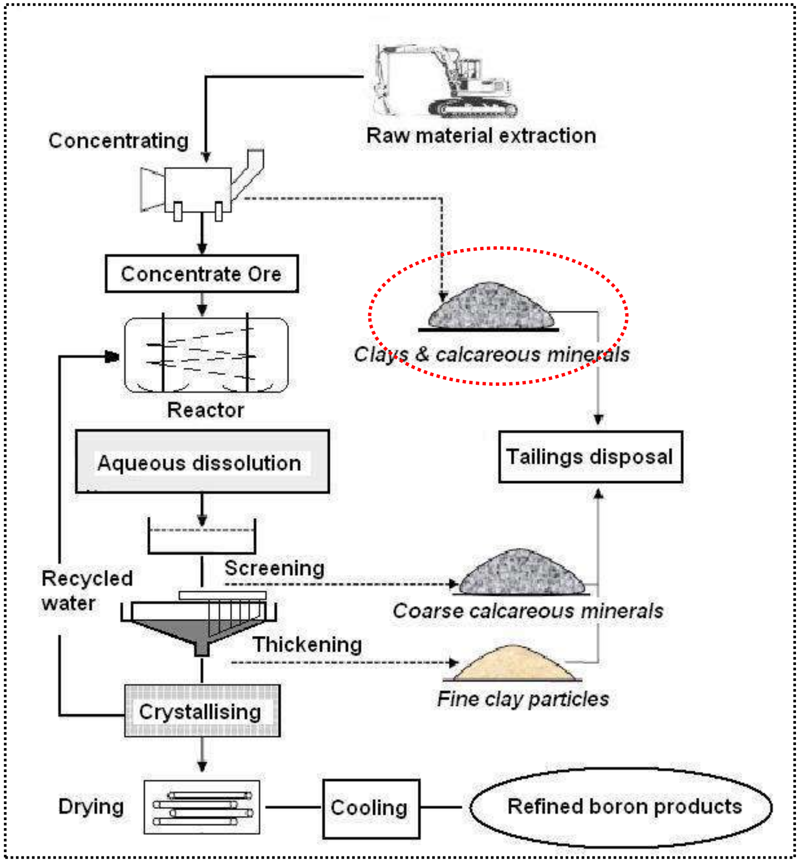
Annual Report - www.etimaden.gov.tr

Production flow sheet of refined borates

- Crushing
- Washing
- Screening

- Dissolving

- Settling



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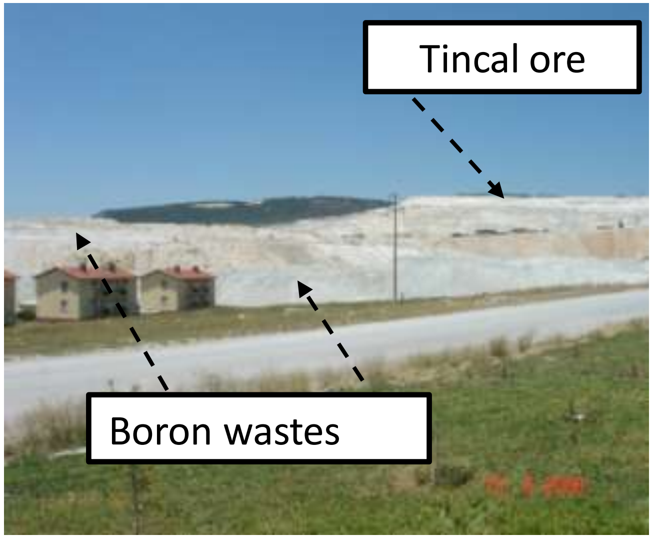


- Annual quantity of solid boron wastes (BW): 300.000 - 400.000t.
- Content of B_2O_3 varies from 3.5wt% to 26wt%.

Fly ash – Lignite combustion

http://www.industcards.com/st-coal-greece.htm

- Megalopolis, Greece
- Fly ash: 10 MT/year
- rich in Al_2O_3 and Fe_2O_3

Raw materials

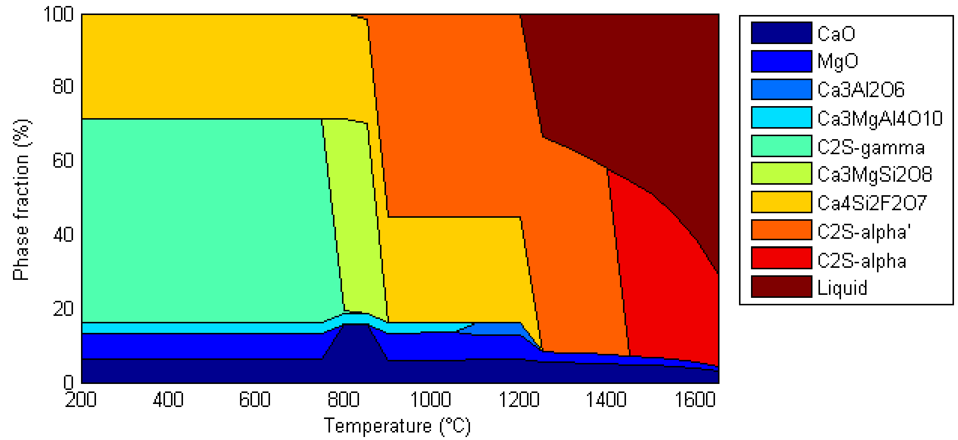
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SrO	K_2O	Na_2O	B_2O_3	SO_3	TiO_2	CaF_2	other
Synthetic slag	28.4	1.3	-	56.7	6.5	-	-	-	-	-	1.1	6.0	-
Boron waste	21.9	3.6	1.0	18.2	14.1	2.8	2.4	9.2	25.8	n.d.	n.d.	n.d.	1.0
Fly ash	50.2	19.5	9.2	11.7	2.5	n.d.	2.2	0.3	n.d.	3.0	0.8	n.d.	0.6

Boron waste is composed of tincalconite $Na_2B_4O_7 \cdot 5H_2O$ and dolomite $CaMg(CO_3)_2$.

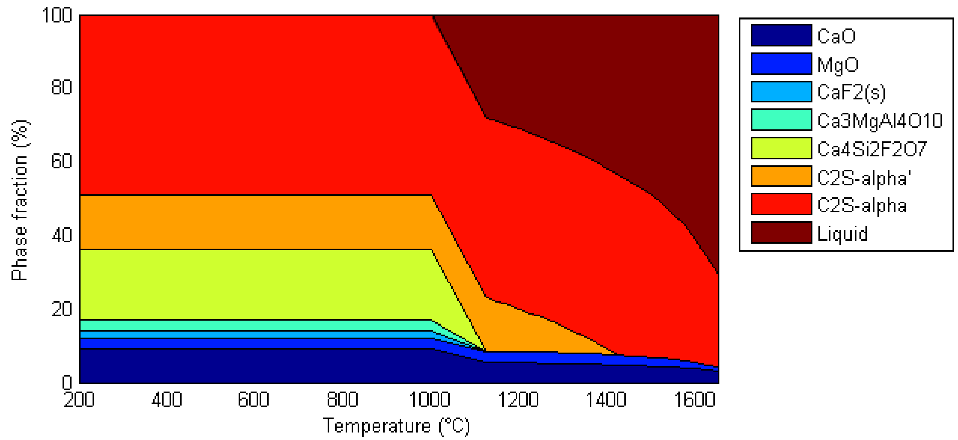
Sanidine $KAlSi_3O_8$, calcite $CaCO_3$, chlorite $(Mg,Fe^{2+})_{10}Al_2[(Si_6Al_2)O_{20}](OH)_{16}$,montmorillonite $(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4 \cdot nH_2O$ and most probably searlesite $NaBSi_2O_5(OH)_2$, are also present as minor phases.

Fly ash is composed of quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), magnetite (Fe_3O_4), anhydrite ($CaSO_4$) and gehlenite ($Ca_2Al_2SiO_7$).

FactSage thermodynamic calculations: reference slag



FactSage
equilibrium cooling

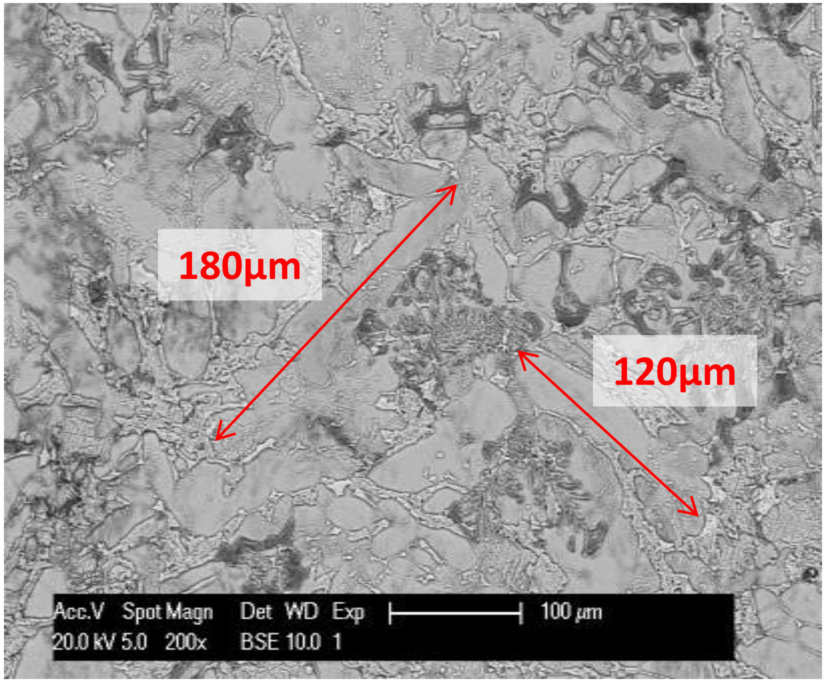


FactSage
Scheil-Gulliver cooling

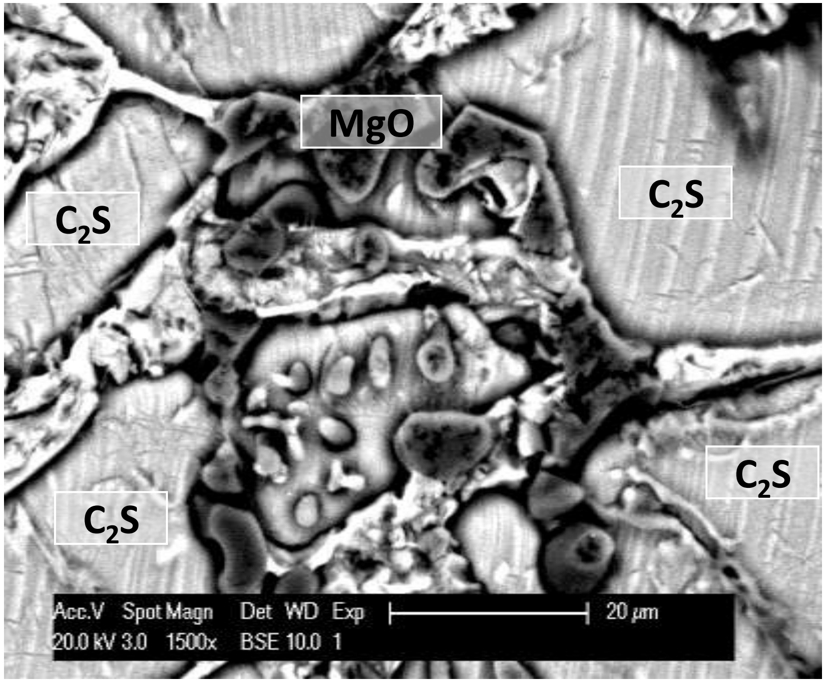
Phase constitution of reference slag

Phase	Thermodynamic calculation (wt%)			XRD analysis 20°C (wt%)
	Equilibrium cooling, 20°C	Scheil-Gulliver cooling, 20°C	1650°C	
CaO	6.3	9.1	1.0	
α-C_2S		49.1	25.1	
α'-C_2S		14.5		
β-C_2S				0.8
γ-C_2S	55.4			42.7
MgO	7.0	3.1	3.3	7.4
$Ca_3Mg(SiO_4)_2$				20.6
CaF_2		1.9		0.5
$Ca_4Si_2O_7F_2$	28.6	19.6		28.1
$Ca_3MgAl_4O_{10}$	2.6	2.6		
Liquid slag			70.6	

Phase distribution in BW stabilised



Backscattered electron image after chemical etching



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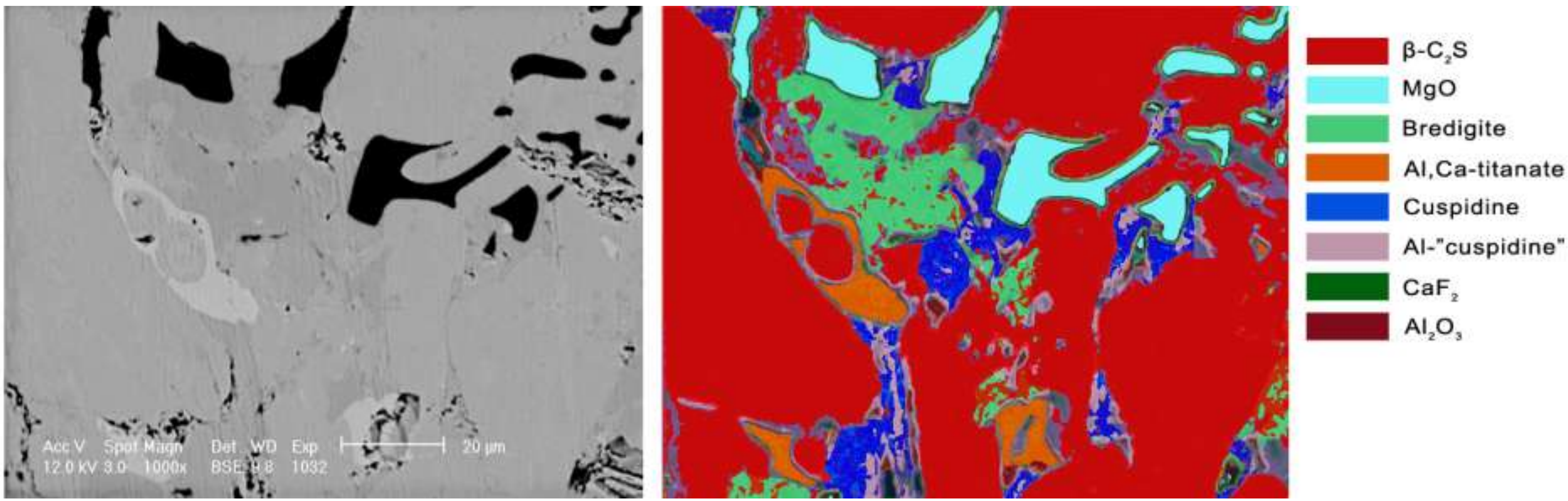
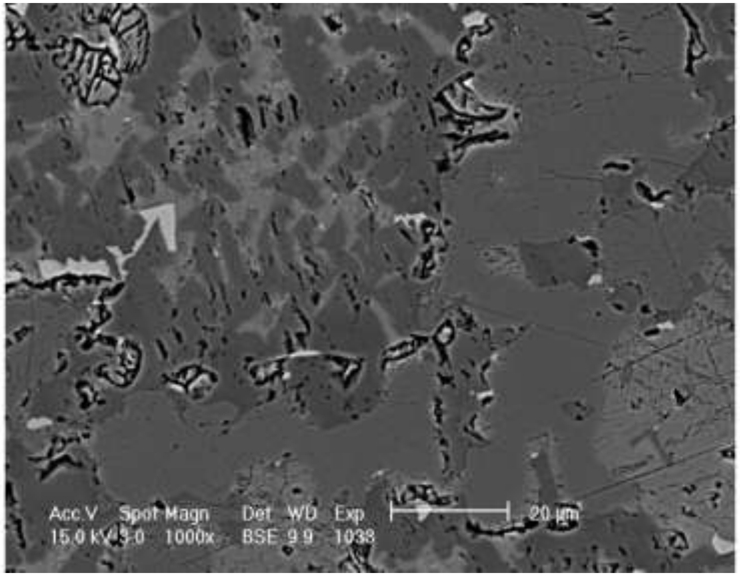


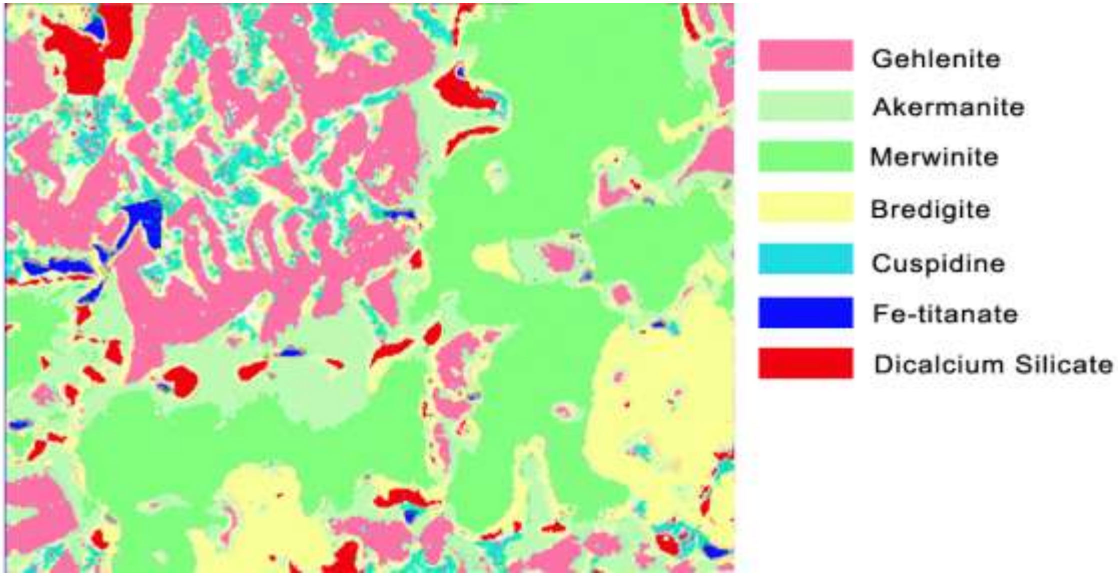
Backscattered electron image (left) and phase distribution based on image stacking from elemental maps (right) of 1 wt% boron waste-stabilized slag.

Phase constitution of BW stabilised slag

Mineral	XRD analysis, 20°C (wt %)
α'-C_2S	8.9
β-C_2S	66.2
MgO	9.1
$Ca_3Mg(SiO_4)_2$	3.2
CaF_2	4.0
$Ca_4Si_2O_7F_2$	8.6

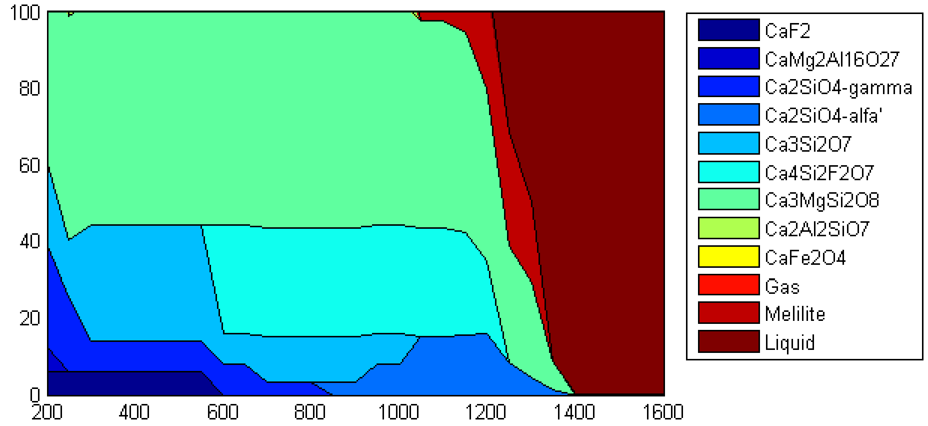
Phase distribution in fly ash stabilised



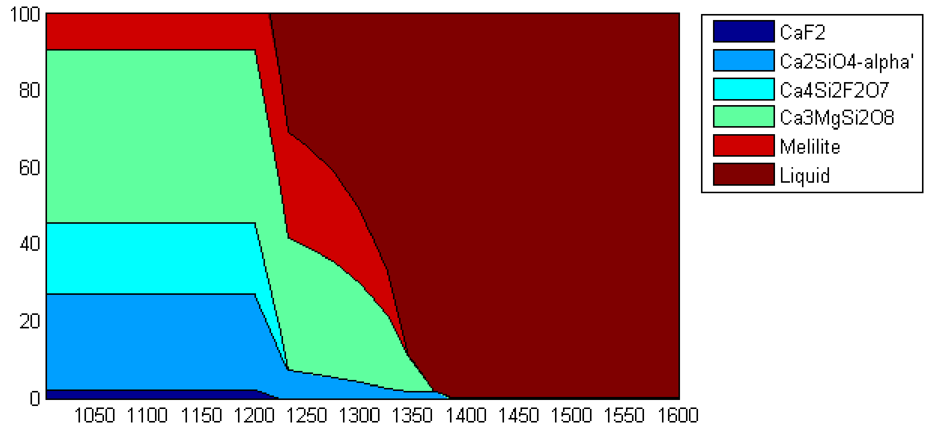


Backscattered electron image (left) and phase distribution based on image stacking from elemental maps (right) of the 22 wt% fly ash stabilized stainless steel slag.

FactSage thermodynamic calculations: fly ash stabilised



FactSage
equilibrium cooling



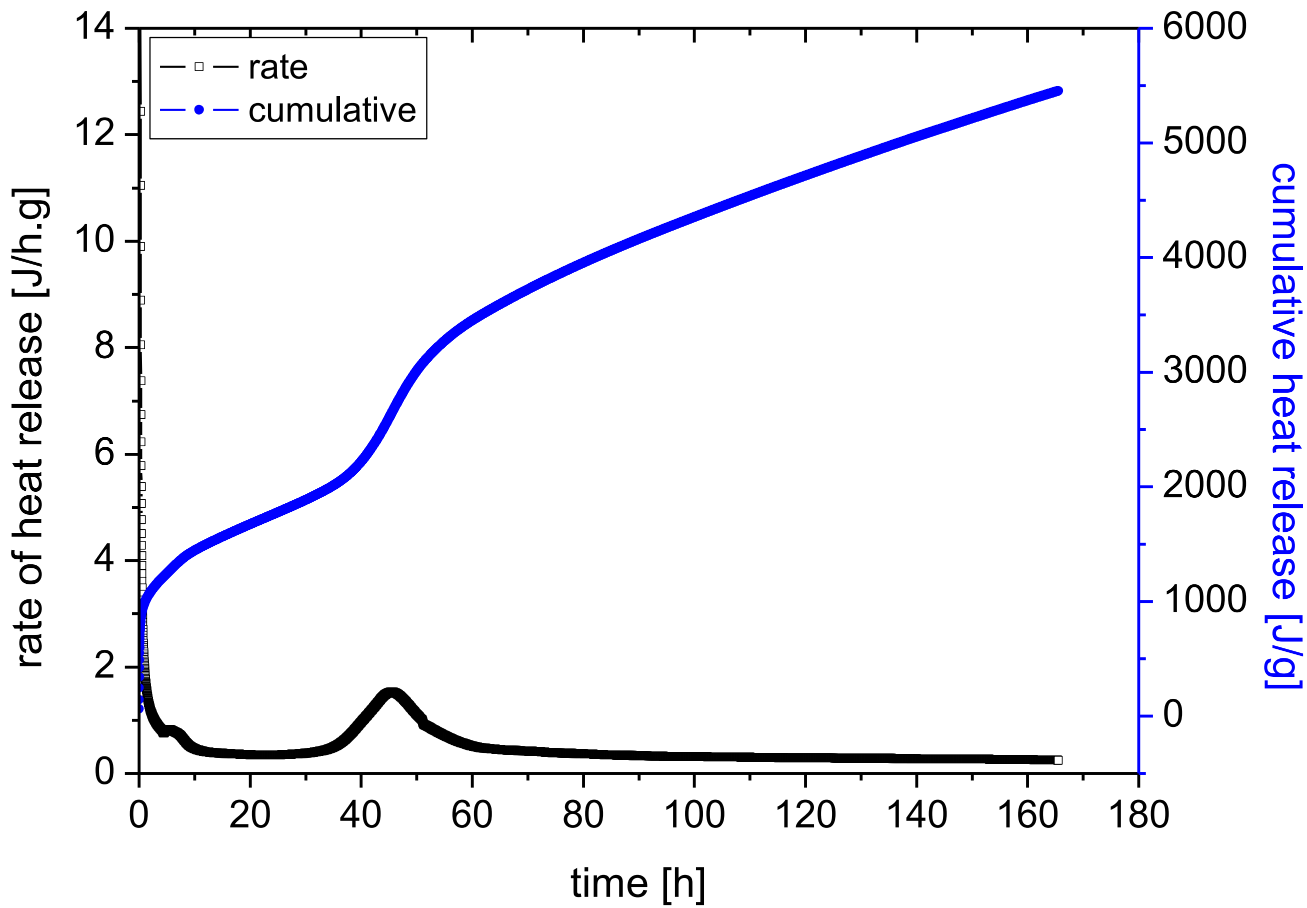
FactSage
Scheil-Gulliver cooling

Phase constitution of fly ash stabilised

Mineral	Thermodynamic calculation (wt%)			XRD analysis, 20°C (wt%)
	Equilibrium cooling, 20°C	Scheil-Gulliver cooling, 20°C	1500°C	
$Ca_2Al_2SiO_7$		24.9 *		30.6
$Ca_2MgSi_2O_7$				3.7
$Ca_7MgSi_4O_{16}$				22.8
$Ca_3MgSi_2O_8$	44.3	37.1		24.9
$Ca_4Si_2O_7F_2$		15.2		18.0
$Ca_3Si_2O_7$	17.5			
$Ca_3Fe_2Si_3O_{12}$	5.5			
$CaMg_2Al_{16}O_{27}$	5.6			
α'-C_2S		20.5		
γ-C_2S	22.0			
CaF_2	5.0	1.8		
Liquid slag			100	

* : the calculated melilite is a solid solution with formula $a_2Al_{1.7}Fe_{0.25}Mg_{0.03}Si_{1.04}O_7$

Will BW stabilised slag react with water?



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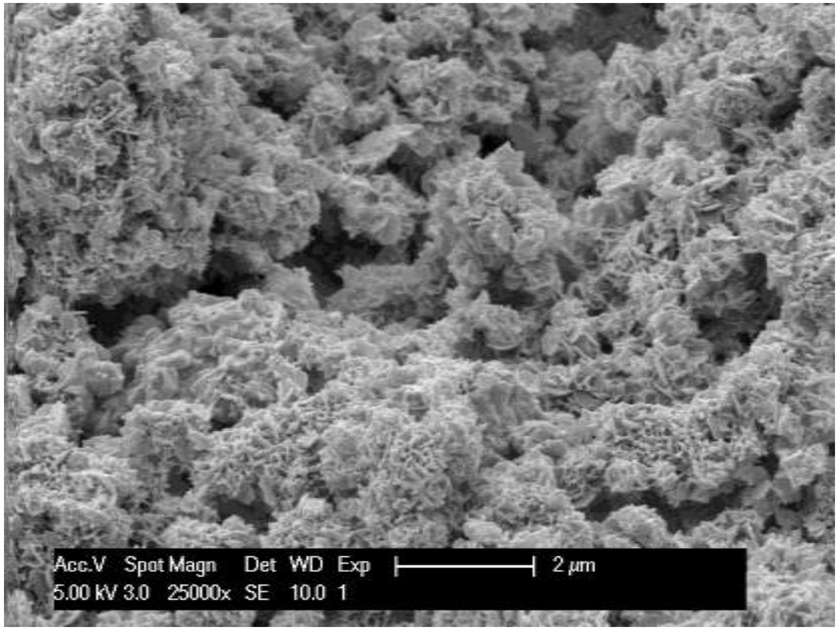
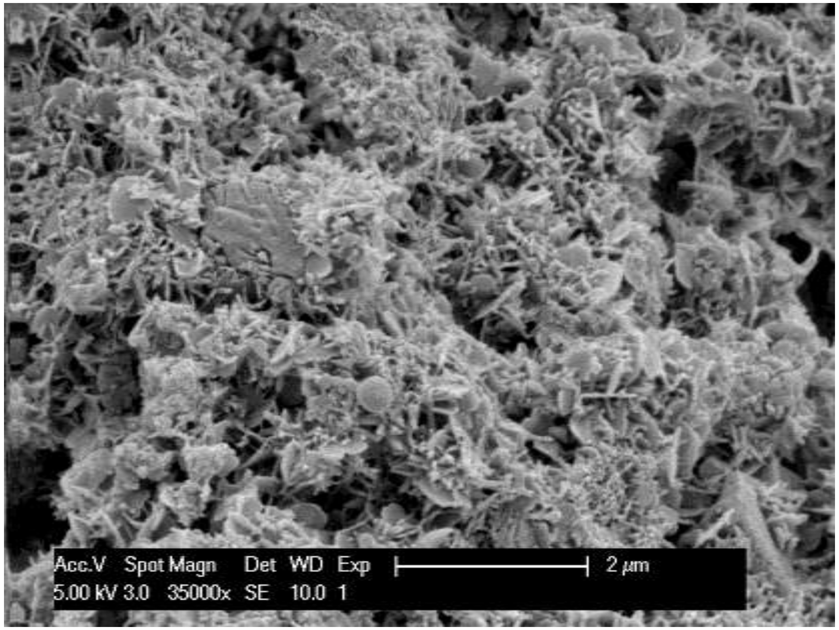




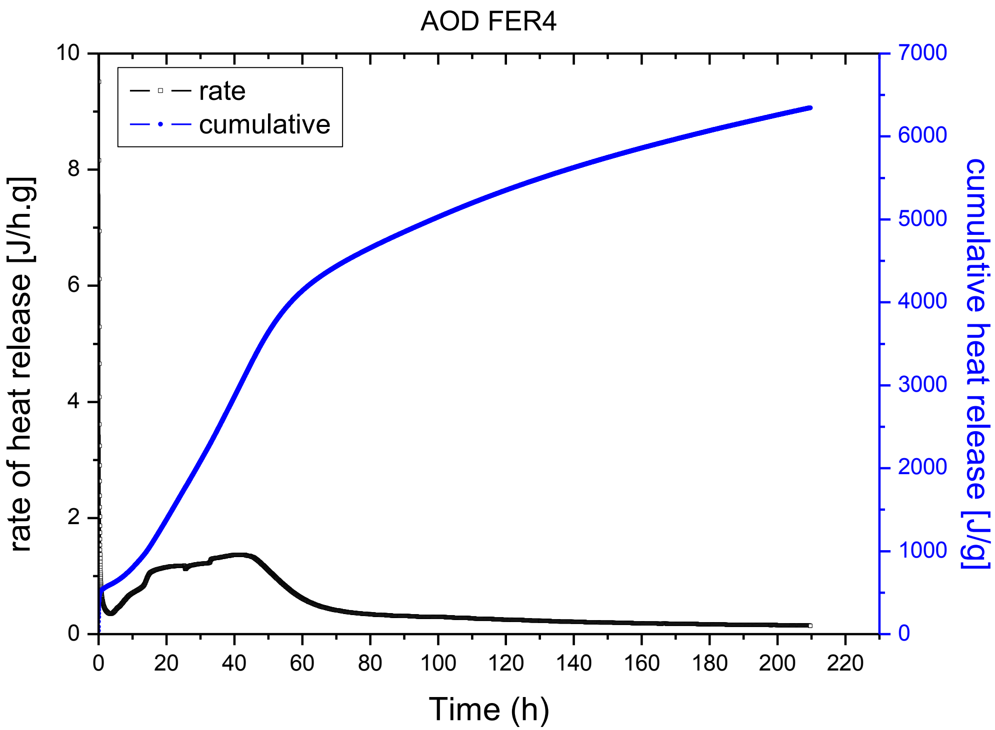
3 days

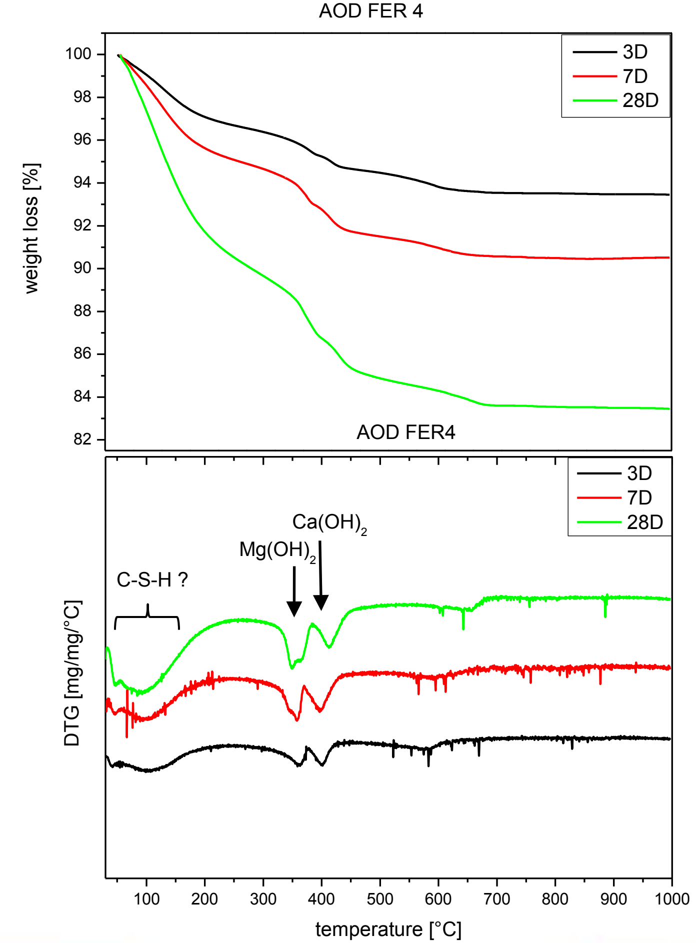
7 days

YES, IT WILL!

Will also B-stabilised AOD slag hydrate?

Industrial sample of AOD from ferritic steel production, stabilised with borates, after 3, 7 and 28 days of hydration





Conclusions

- C_2S-driven disintegration during cooling
- 1 wt% addition of boron: stabilisation of a slag with basicity (CaO/SiO_2) = 2.
- 22 wt% addition of fly ash stabilises the slag
- boron stabilised slag → hydraulic properties.
- Further analysis is required.

Thank you

InsPyro