

The background is a solid teal color. Overlaid on this are several thin, white, curved lines that sweep across the frame from left to right. Small white dots are placed at various points along these lines, creating a sense of motion or data points.

• We enable
materials innovation.



materials
innovation
institute

Understanding carbonation mechanism in alkali-activated fly ash and slag pastes

PhD reseracher: Marija Nedeljkovic

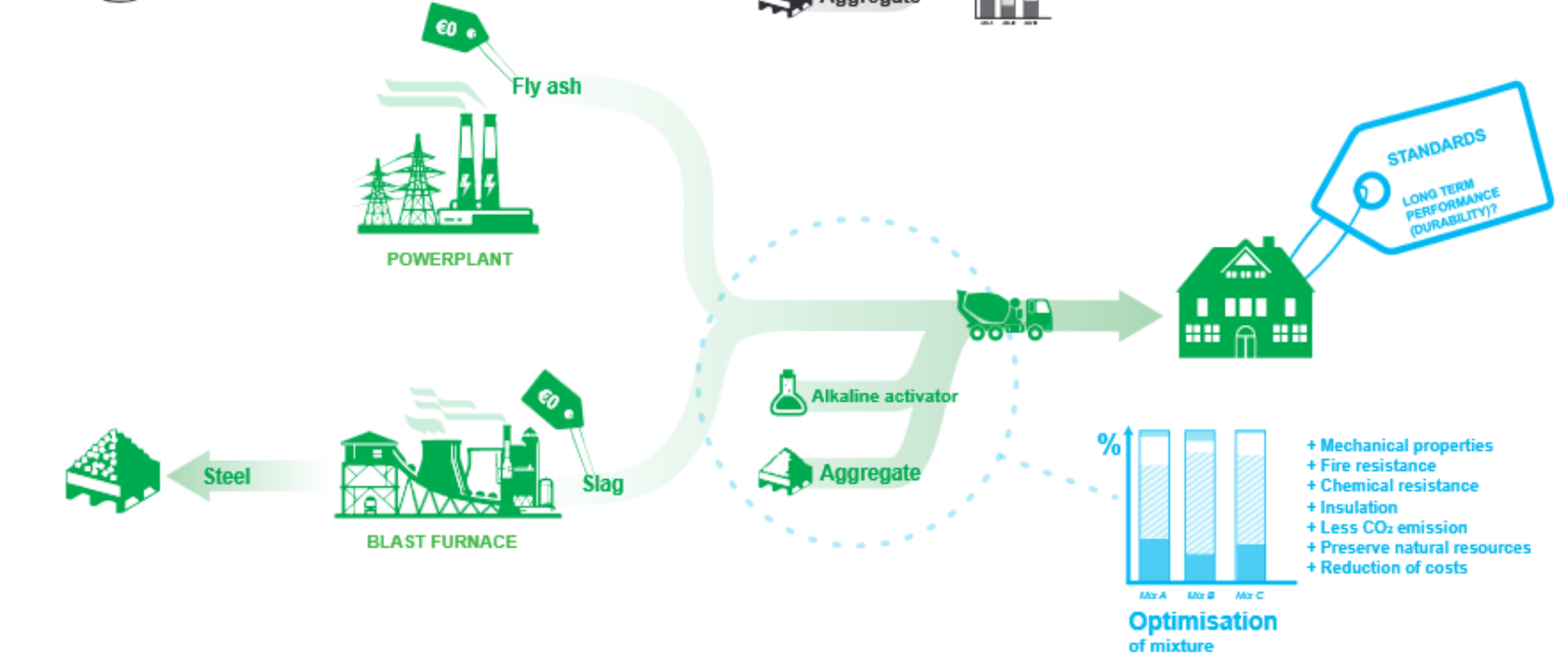
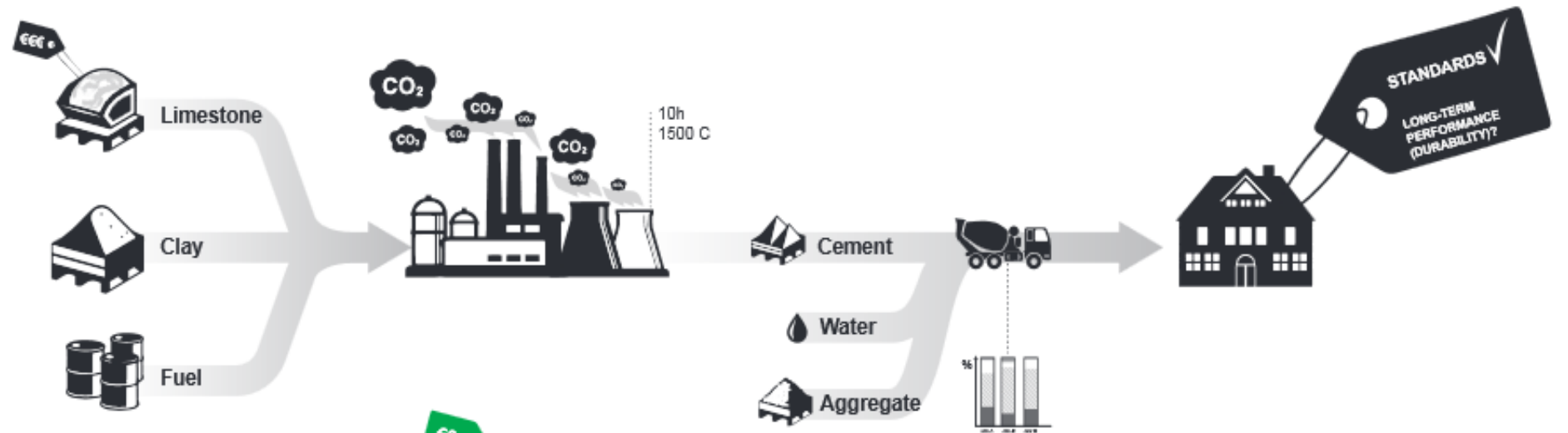
Supervisor: Dr Guang Ye

Promotor: Prof Klaas van Breugel

Outline

- Alkali-activated materials
- Research aim and objectives
- Carbonation mechanism
- Experiments and results
- Conclusions

Cement-based materials



Alkali-activated based materials

Alkali-activated materials (AAM)

AAM are binders that can be produced by (suitable) alkaline activation ($-\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$) of industrial by-products ($\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$) such as:

- fly ash (thermal power plants),
- blast furnace slag (steel making),
- waste glass,
- agricultural waste,
- incineration waste, ...



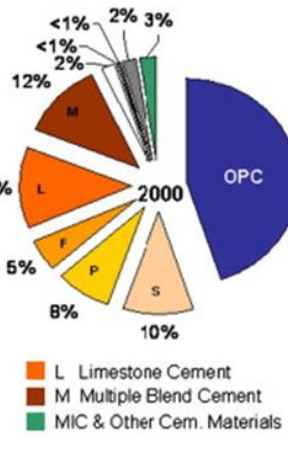
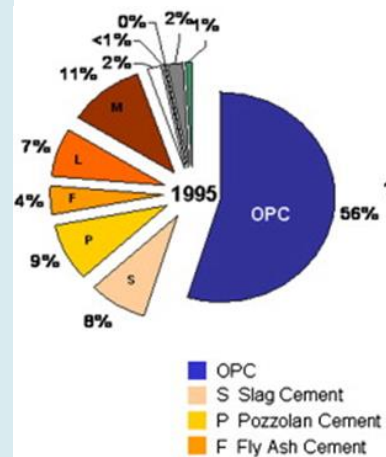
Maastricht Enci Quarry, The Netherlands



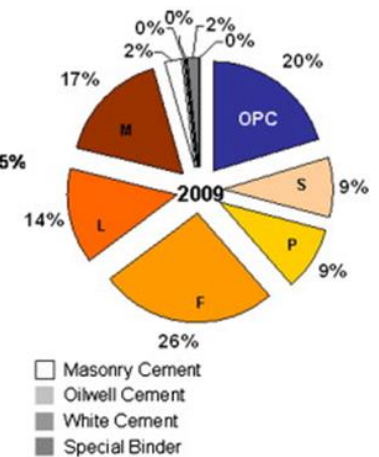
CEMENT



Tata STEEL, IJmuiden, The Netherlands



Eemshaven-coal-power-plant



Standards

Cement-based materials

Alkali-activated based materials

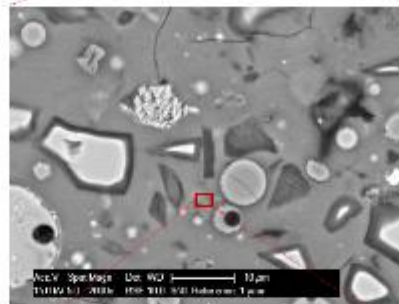
upscale

Level III
Alkali-activated **concrete**
paste + aggregates



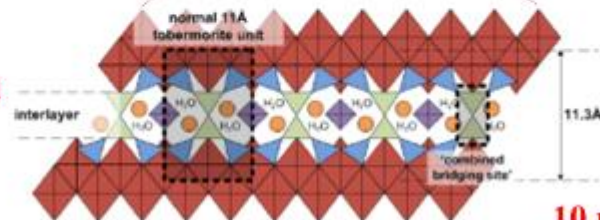
10 mm

Level II
Alkali-activated
fly ash and slag **paste**
Ca-(Mg-)Na-Al-Si-H
unhydrated
fly ash and slag



10 μ m

Level I
Alkali-activated **gel**
Ca-Na-Al-Si-H



10 nm

Summary

Alkali-activated concrete:

- ✓ Use of by products from industrial processes
- ✓ Environmentally friendly (low CO₂ emission, energy consumption)
- ? Raw materials
- ? Standards
- ? Long-term performance

Research aim and objectives

Aim: to develop alkali-activated concrete mixtures and to investigate the degradation mechanism of alkali-activated concrete due to carbonation.

Objectives:

- to propose methodology for investigation of carbonation,
- to study the mechanism that drives the carbonation front,
- to investigate the effects of carbonation,
- to predict the service life of alkali activated concrete due to carbonation.

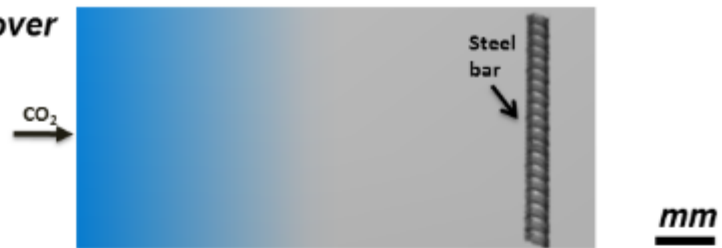
1.
Problem

2.
Simplification

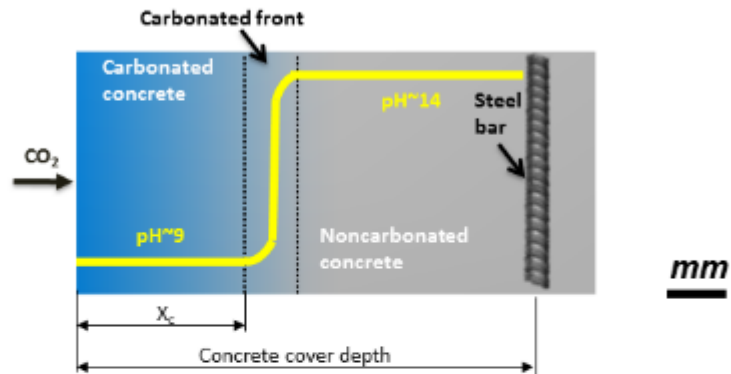
3.
Understanding

4.
Modelling

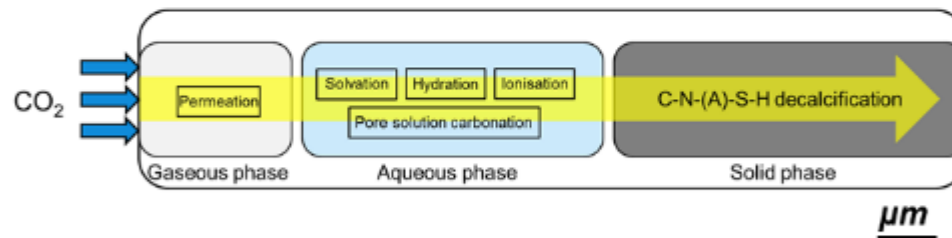
Concrete cover



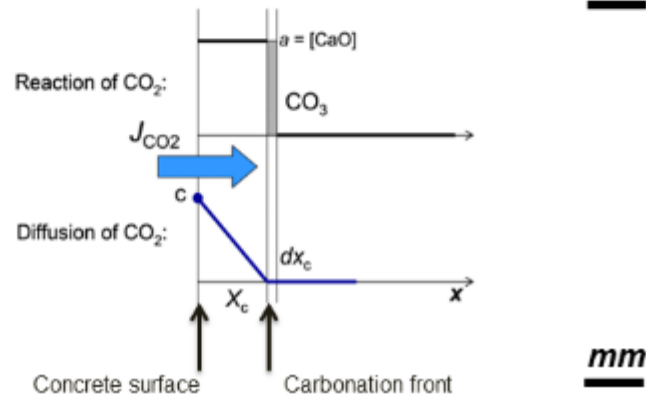
pH Profile



Mechanism



Modelling



Research boundaries:

Carbonation mechanism

Carbonation rate (**kinetics**)

Carbonation degree (**thermodynamics**)

Carbonation effects

Chemical (reaction products and pH of the pore solution)

Physical (pore structure and porosity change)

Mechanical (E_m , compressive, tensile, flexural strength)

Carbonation model

Kinetics: pH of the pore solution (Na, K)_diffusion

Thermodynamics: phases of the microstructure (density, Ca content)

Methodology

Case 1: Carbonation of the pore solution

Case 2: Carbonation of the microstructure



Alkali-activated paste mixtures

Raw materials:

1. Ground granulated blast furnace slag
2. Low CaO fly ash

Alkaline activator:

4.8 wt.% Na₂O

Liquid/binder ratio:

l/b=0.5

	FLY ASH	SLAG
PASTE	(wt.%)	(wt.%)
S0	100	0
S30	70	30
S50	50	50
S70	70	30
S100	0	100

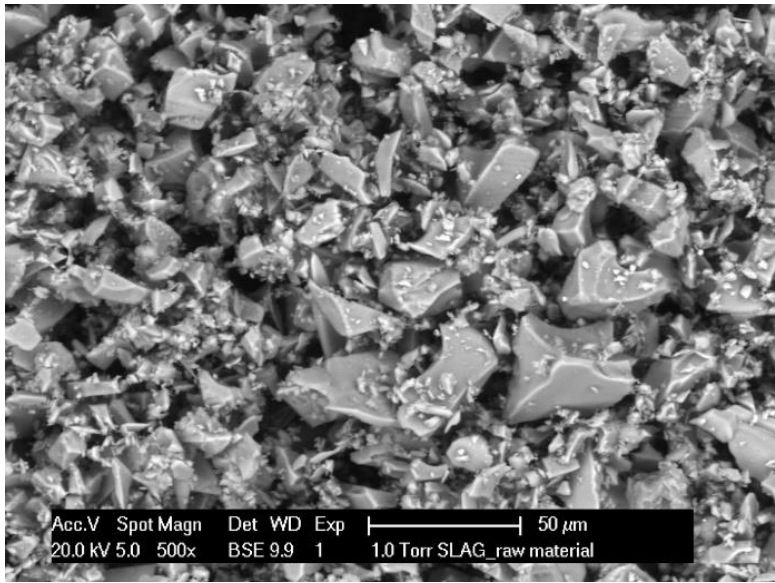
Ref: Nedeljkovic et al. 2017, Conbuildmat, Volume 161, Pages 687–704

MATERIAL PROPERTIES

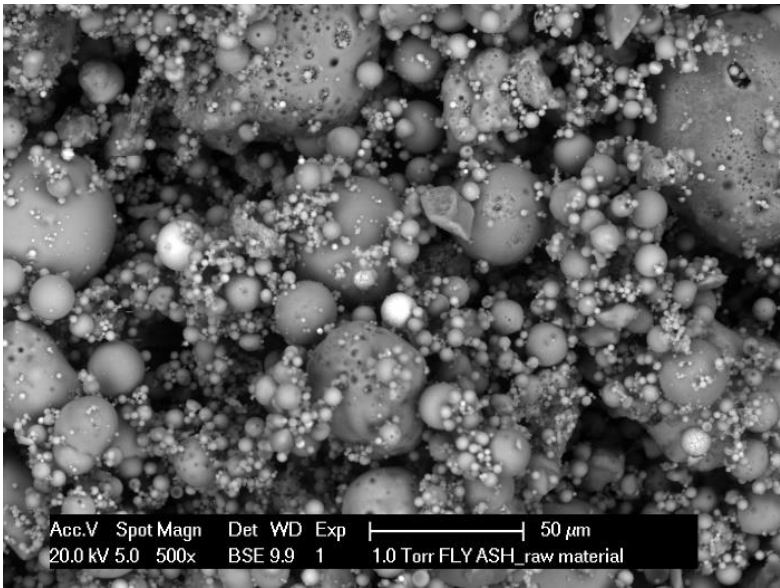
XRF-CHEMICAL COMPOSITION

	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	S	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	L.O.I.
BFS	35.5	13.5	39.8	8.0	0.64	1.04	0.4	0.53	1.0	0.009	-1.3
FA	56.8	23.8	4.8	1.5	7.2	0.3	0.8	1.6	1.2	0.51	1.2

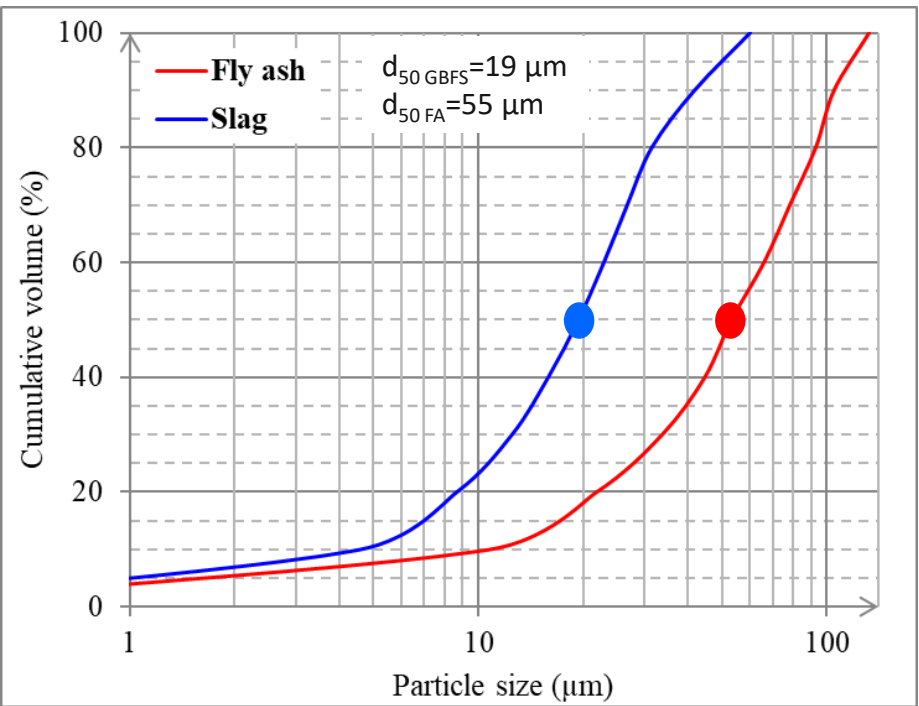
SEM-BSE→PARTICLES SHAPE



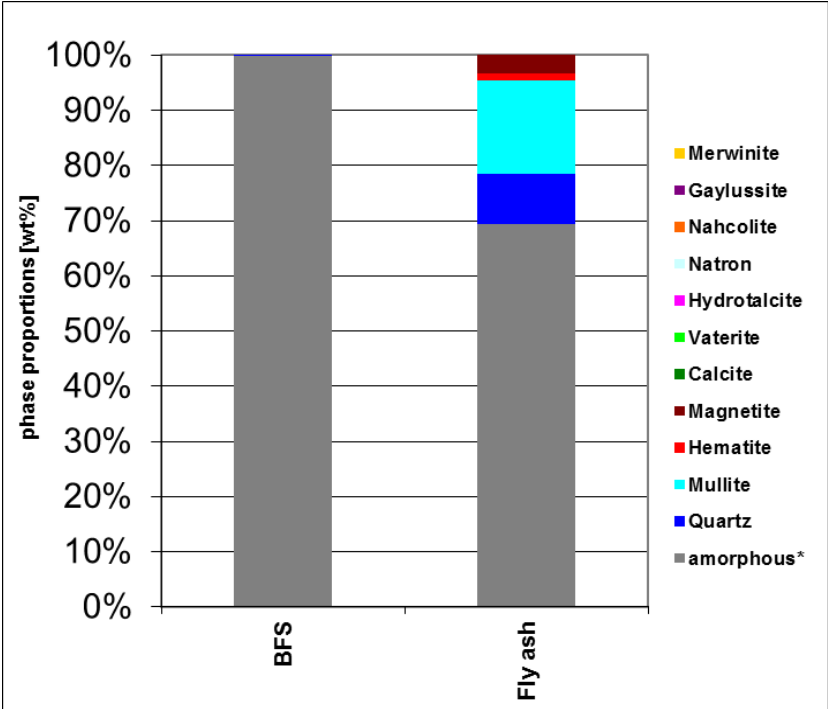
SLAG



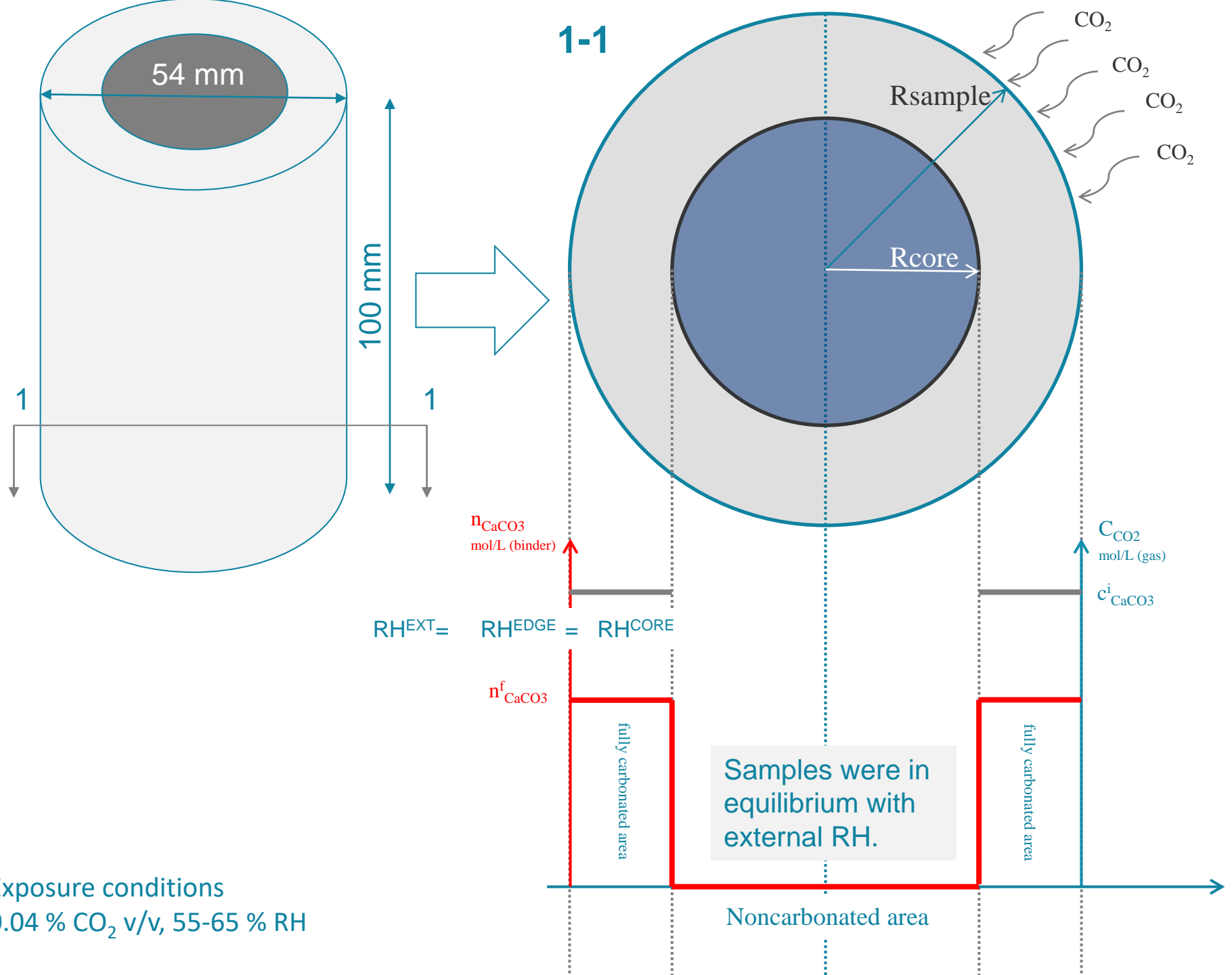
FLY ASH



Particle size distribution of fly ash and slag.



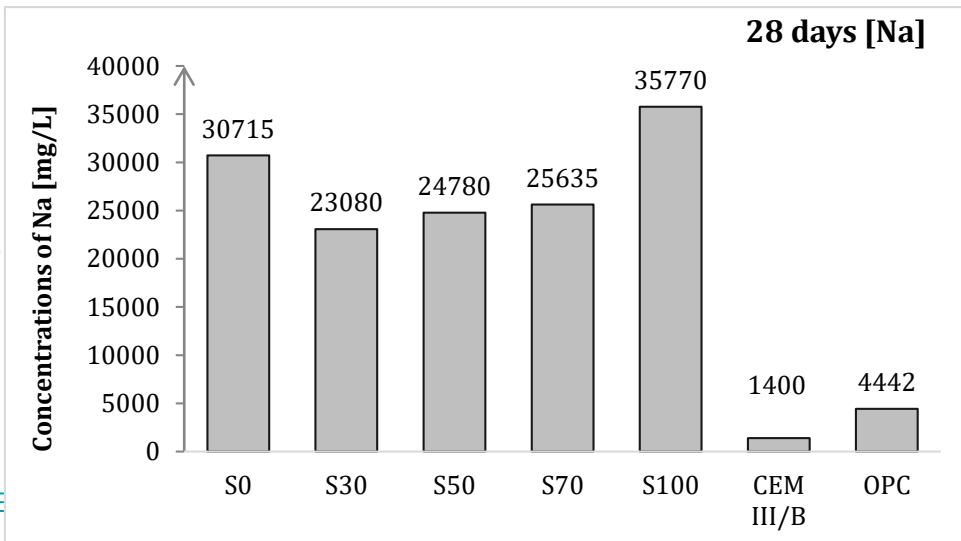
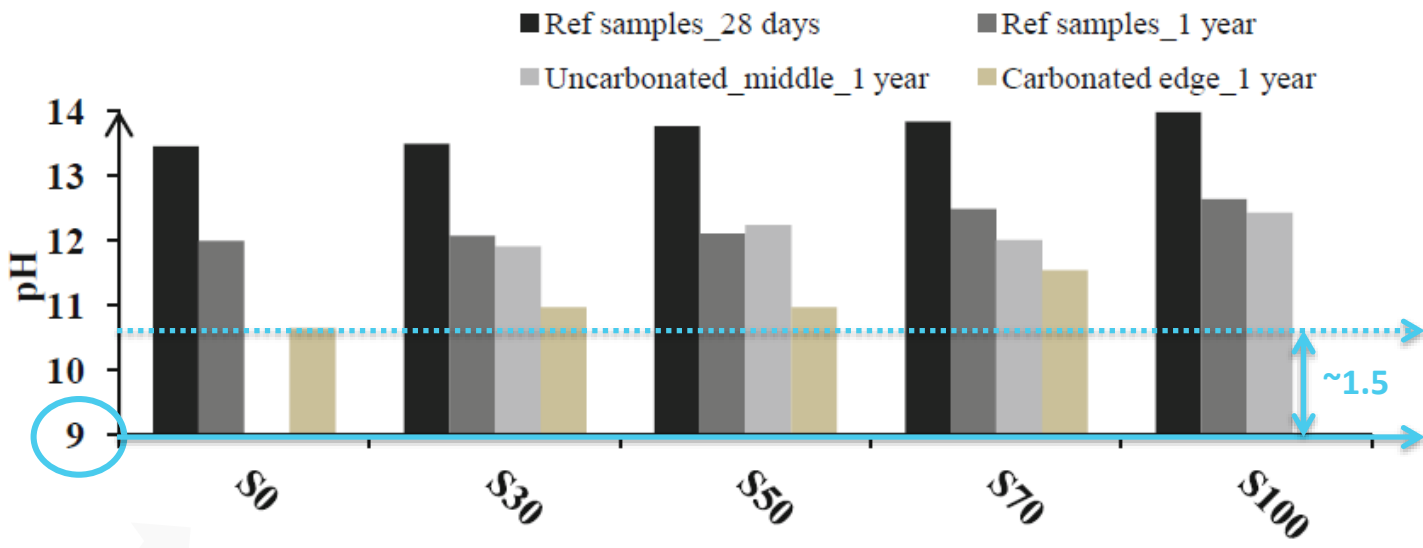
Rietveld refinement method- Phases and their proportions



Case 1: Carbonation of the pore solution

pH preservation

Test done by: Ex-situ
leaching method
powder suspension



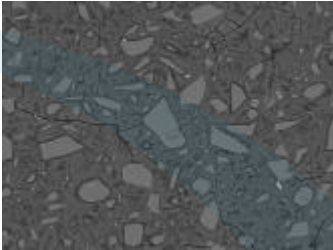
Case 2: Carbonation of the microstructure



SEM JEOL JSM7001F



Elemental chemical composition

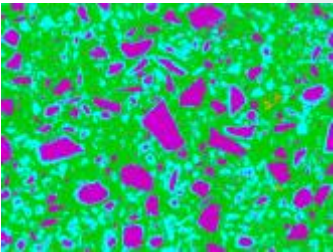


Frame size: 512x384 pixs
(Σ : 196 608)
Field size: 1536x1152 pixs
(Σ : 1 769 472)
Pixel size: 0.49 μm
Field size: 750x0.565 μm^2

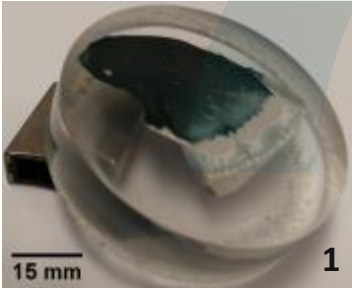
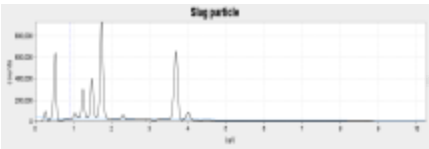
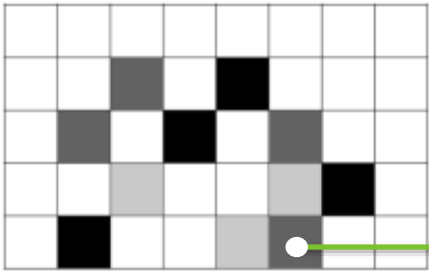
SEM-BSE



Phase recognition and characterization
TATA STEEL



PARC MAP



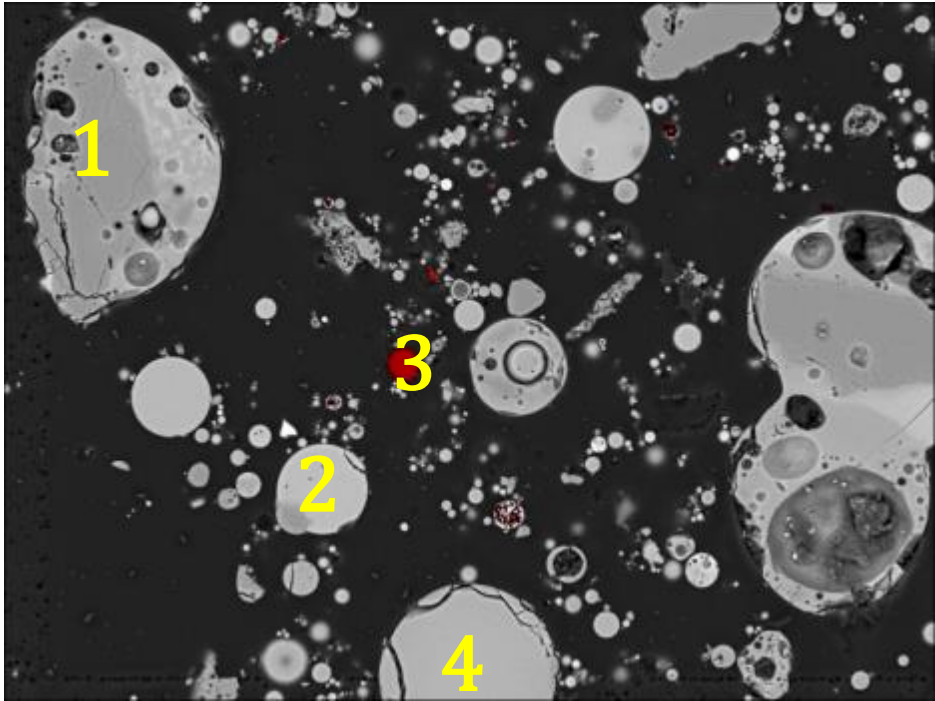
Polished sample

Bulk chemistry comparison
between PARC and XRF

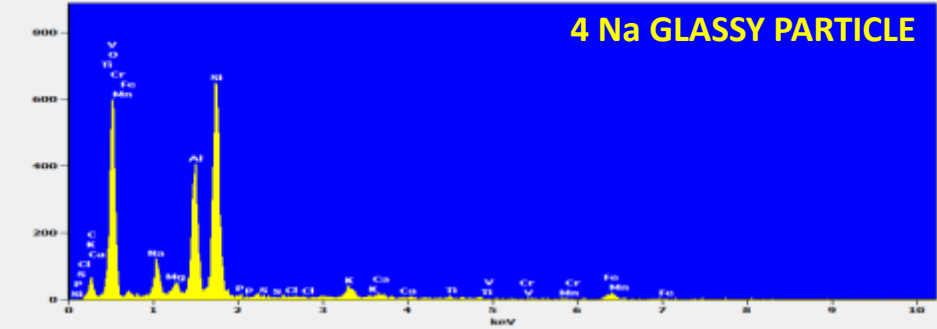
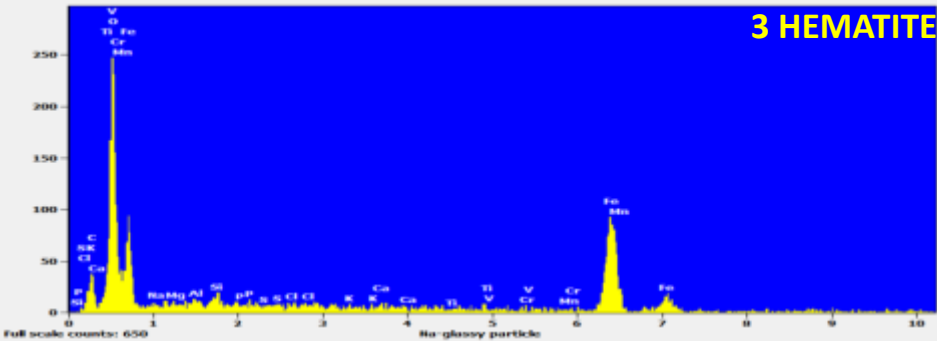
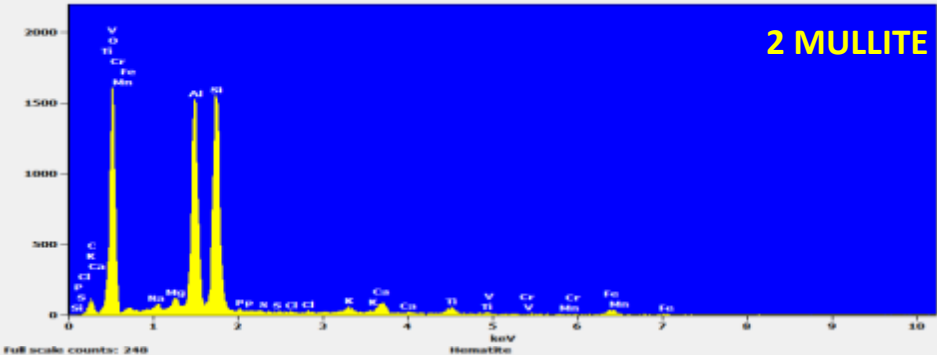
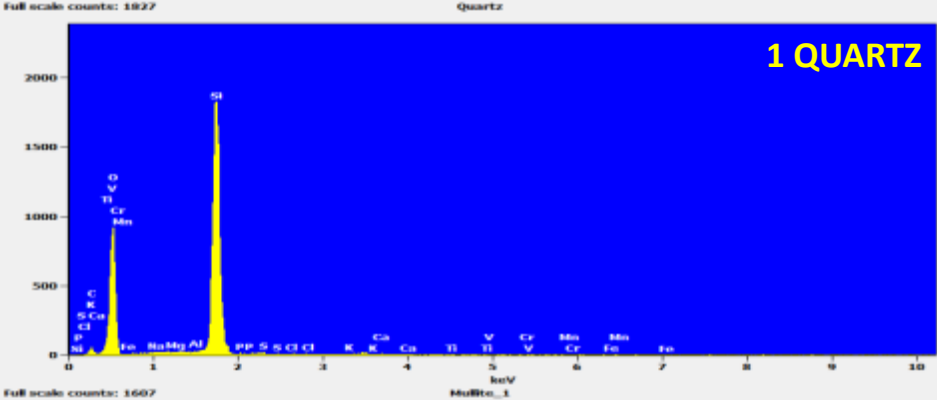


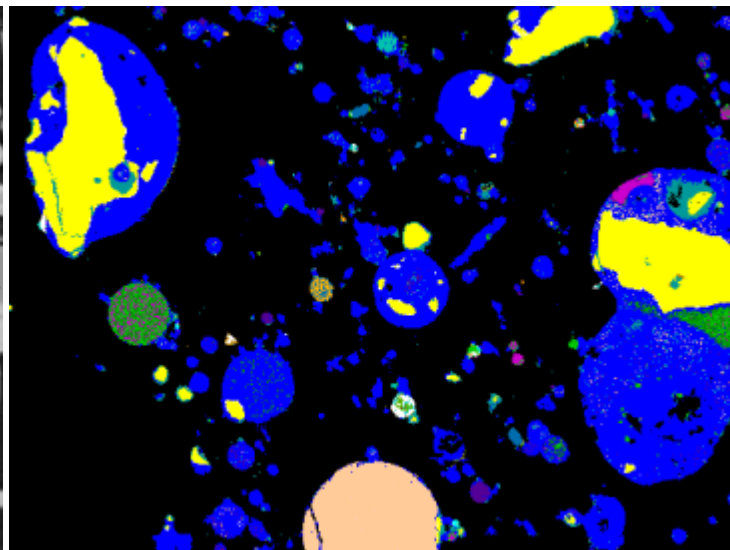
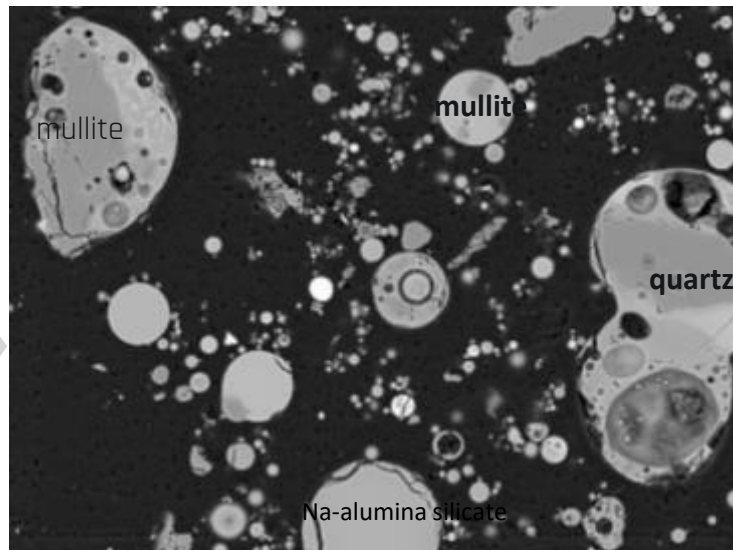
Determination of the bulk chemistry

Raw FLY ASH



256x192 μm





color	label
	embedding
	empty spectra
	AlSi
	unclassified
	Quartz_extracted
	NaAlSi-Particle
	MgAlSiCa grain
	AlSiCa-grain 1
	MgAlSi
	Mix Quartz AlSi
	AlSiTi-grain 2
	AlSiCa
	Dolomite
	AlSiK
	P-glass4
	MgSCa
	Calcite
	AlSiFe
	P-glass1
	AlSiPCa
	P-glass5
	NaAlSiK
	P-glass2
	MgSiCa
	NaMgAlSi
	Fe
	SiCa
	Al2O3
	SiFe-oxide
	P-glass3
	MgSi
	MgAlSiCaFe
	MgAlSiFe

256x192 μm

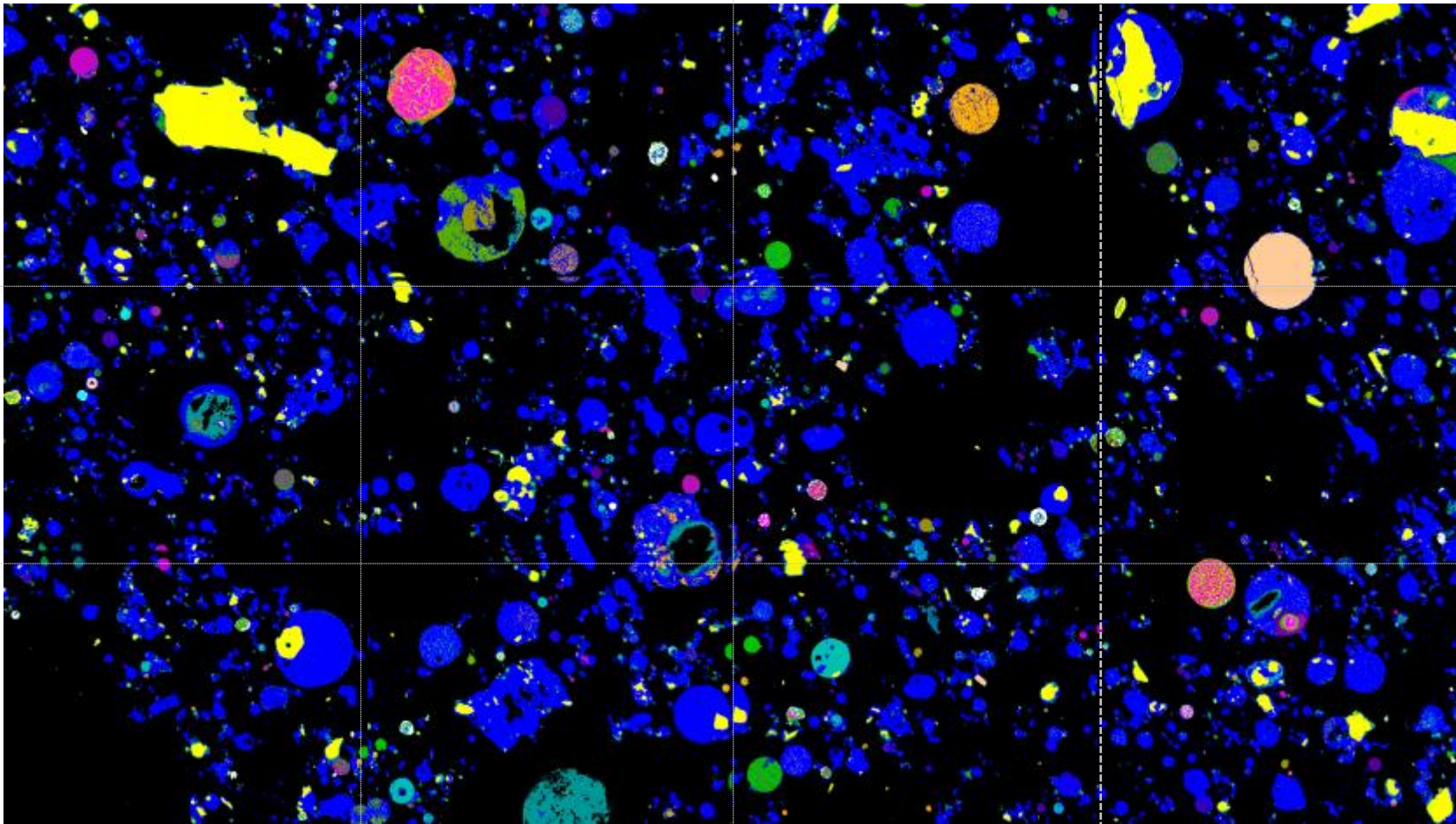
Phase model map
raw fly ash

Compositional domain	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃
01 Mullite/Glass (AlSi)	0.92	1.04	28.33	58.67	0.44	0.26	1.97	0.87	1.11	0.03	6.37
02 Quartz (SiO ₂)	0.31	0.09	0.09	98.35	0.14	0.63	0	0	0	0	0.39
03 Hematite	0.33	0.46	0.76	3.04	0	0	0.2	0.59	0	0.36	94.27
04 Na, K-alumina silicate	5.36	0.78	25.58	61.24	0.57	0.16	2.03	0.6	0.58	0.2	2.9
05 P-glass	0	6.09	11.6	17.14	24.01	0.07	0.3	36.6	0.88	0	3.31
06 Ti-alumina silicate	1.27	1.22	29.71	43.39	0	0	1.51	2.77	14.45	1.24	4.45
07 Ca-alumina silicate	0	0.37	35.18	41.74	0.7	0.15	0	17.45	0.56	0	3.85
08 Mg-alumina silicate	0.65	5.14	10.2	61.09	0.61	0.61	0.94	1.57	0.34	0.32	18.52
09 Ca, Mg-alumina silicate	0.14	8.24	20.64	39.17	2.34	0	0.02	21.03	0.53	0.11	7.78
10 Calcite	0	0	0.82	0.43	1.54	2.33	0	94.38	0	0	0.49
11 Dolomite (CaMg(CO ₃) ₂)	0	32.17	1.3	2.09	0.97	3.75	0.07	57.65	0.09	0.14	1.78



Ref: van Hoek, C., Small, J., and van der Laan, S., 'Large-Area Phase Mapping Using PhAse Recognition and Characterization (PARC) Software', Microscopy Today, 24 (5) (2016) 12-21.

RAW FLY ASH

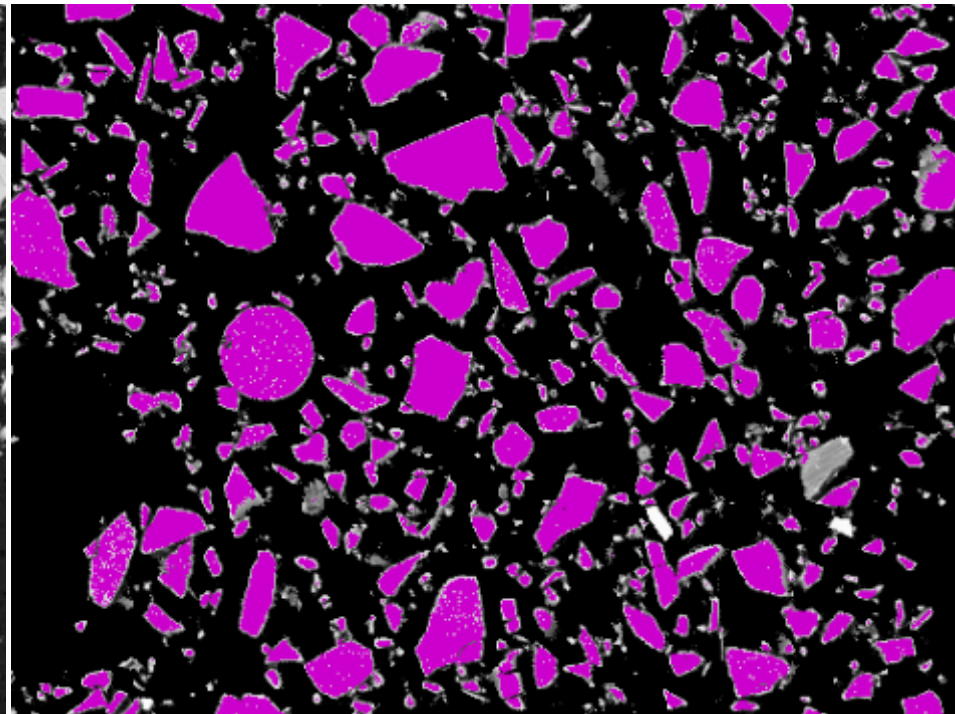
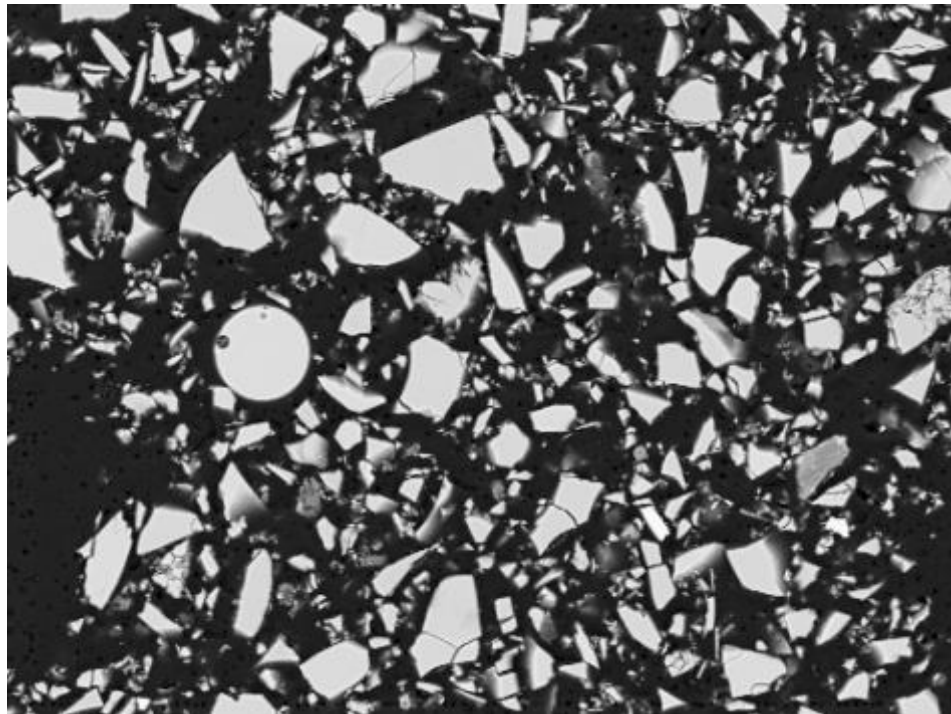


color	label
	embedding
	empty spectra
	AlSi
	unclassified
	Quartz_extracted
	NaAlSi-Particle
	MgAlSiCa grain
	AlSiCa-grain 1
	MgAlSi
	Mix Quartz AlSi
	AlSiTi-grain 2
	AlSiCa
	Dolomite
	AlSiK
	P-glass4
	MgSCa
	Calcite
	AlSiFe
	P-glass1
	AlSiPCa
	P-glass5
	NaAlSiK
	P-glass2
	MgSiCa
	NaMgAlSi
	Fe
	SiCa
	Al2O3
	SiFe-oxide
	P-glass3
	MgSi
	MgAlSiCaFe
	MgAlSiFe

1024x576 μm



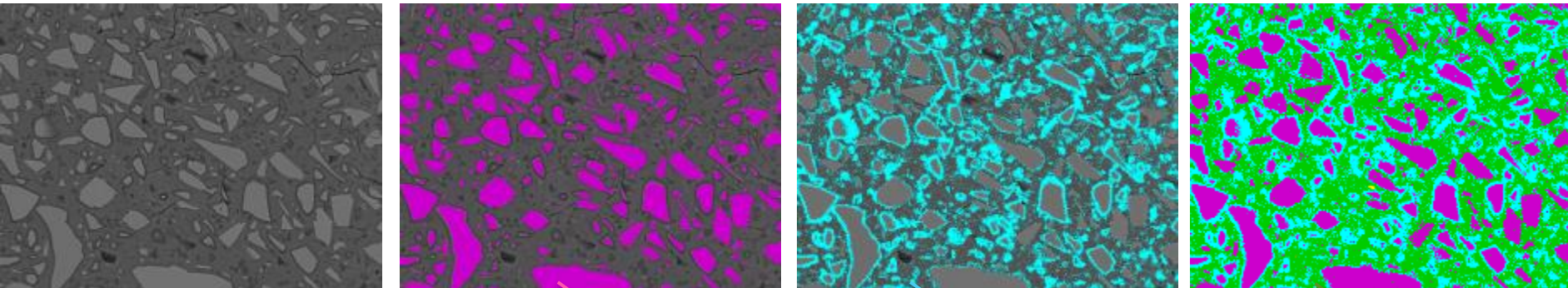
Raw ground granulated blast furnace slag



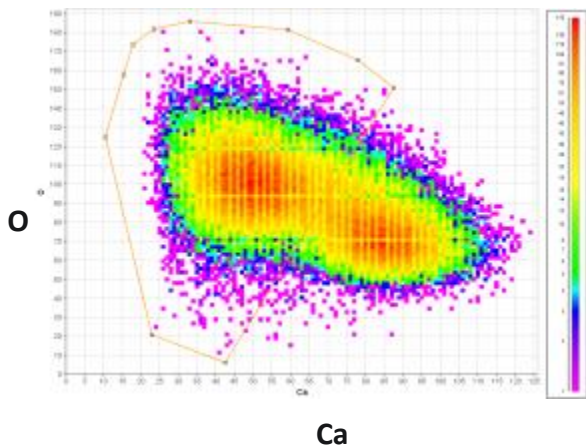
color	label
white	unclassified
black	empty spectra
dark gray	embedding
magenta	Slag_MgAlSiCa

Alkali-activated slag paste (S100)

28 days cured sample



Density plot



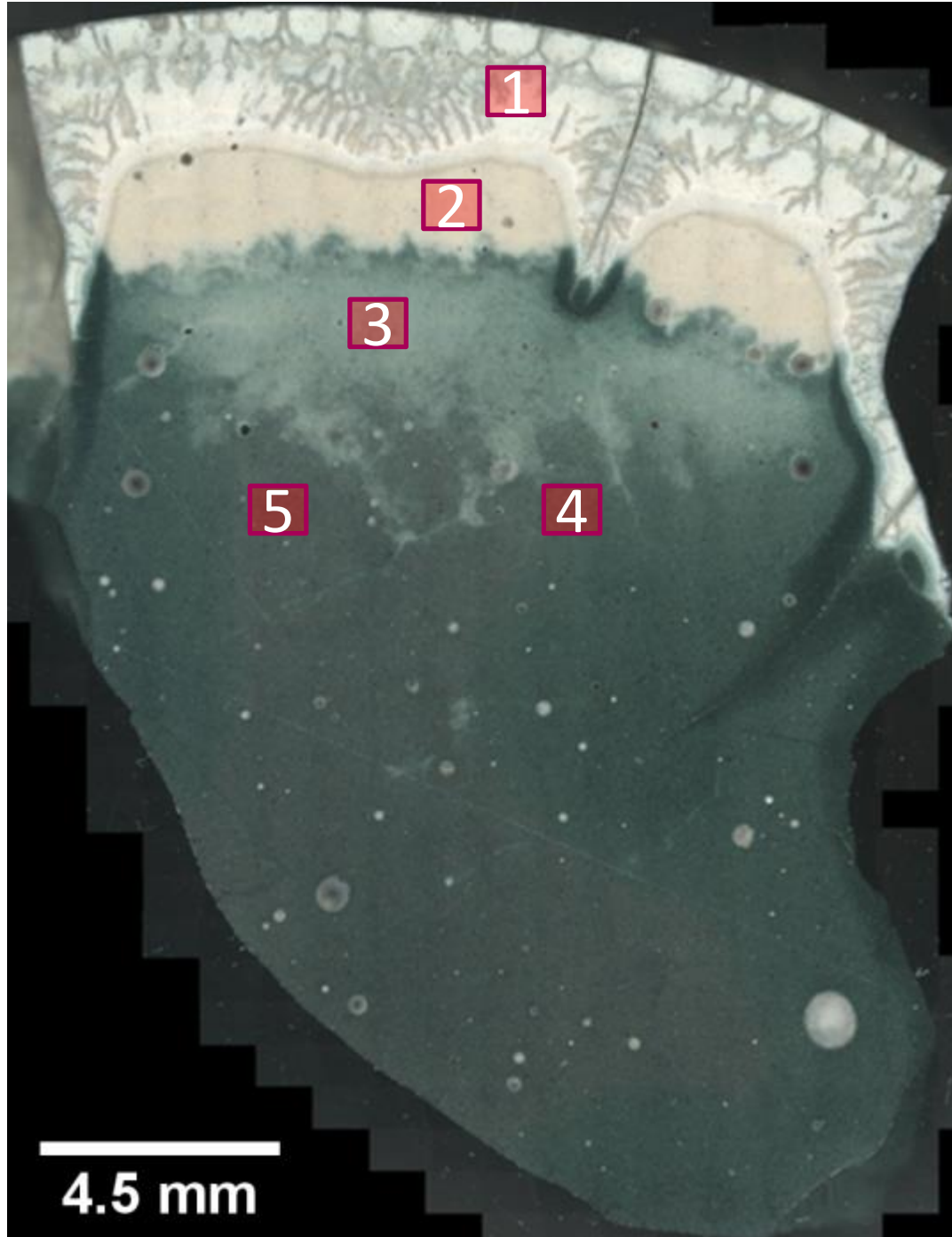
	Raw slag	NaMgAlSiCa gel (28d)	NaAlSiCa gel (28d)
	Wt %	Wt %	Wt %
Na ₂ O	0.49	5.31	7.47
MgO	8.99	14.8	2.88
Al ₂ O ₃	14.66	14.77	9.51
SiO ₂	36.81	33.59	43.48
P ₂ O ₅	0.22	0.21	0.25
SO ₃	2.5	2.36	0.83
K ₂ O	0.35	0.3	0.38
CaO	34.31	26.38	34.09
TiO ₂	1.18	1.53	0.77
MnO	0.35	0.45	0.17
Fe ₂ O ₃	0.14	0.32	0.16

BULK SAMPLE_S100



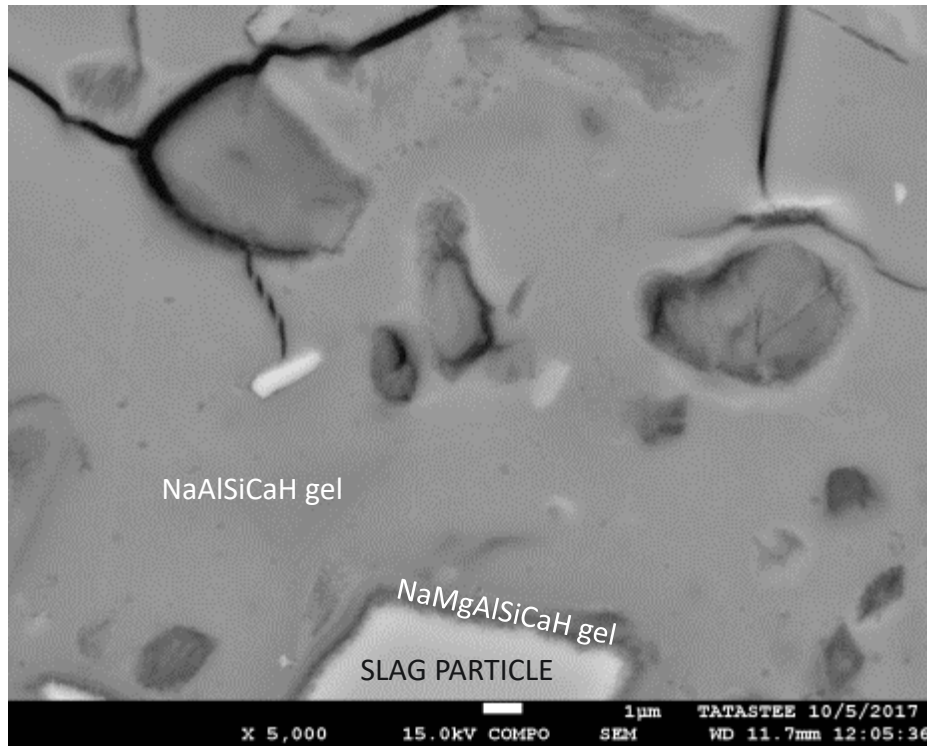
25 mm

Stereoscope mosaic

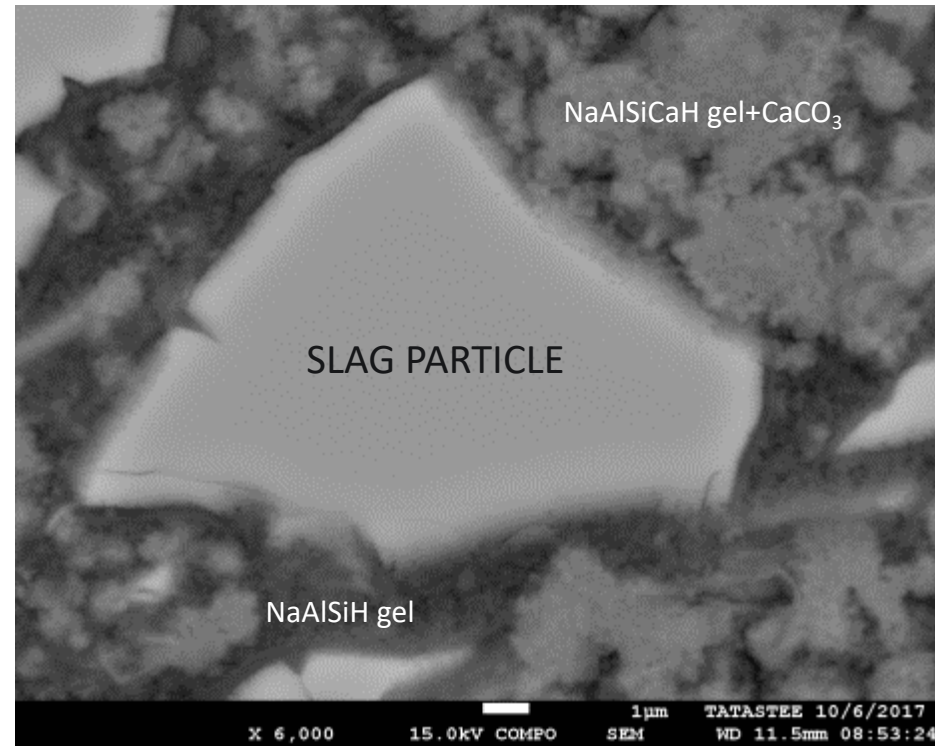


1. Carbonated zone
2. Oxidated zone
3. Blue zone
4. Green zone
5. Dark green zone

Alkali-activated slag mixrostructure after 2YR of exposure to natural carbonation
(0.038 % CO₂ v/v, 55-65 %RH)



Noncarbonated zone

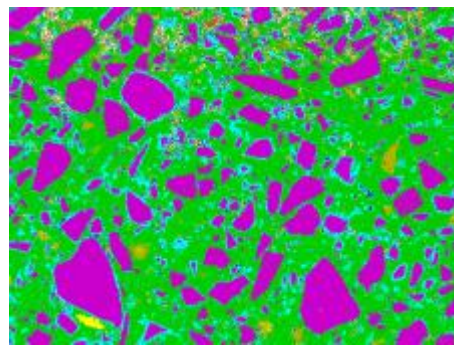
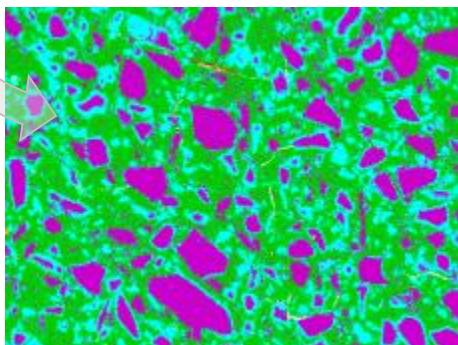
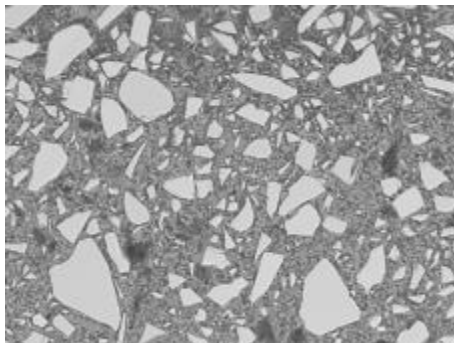
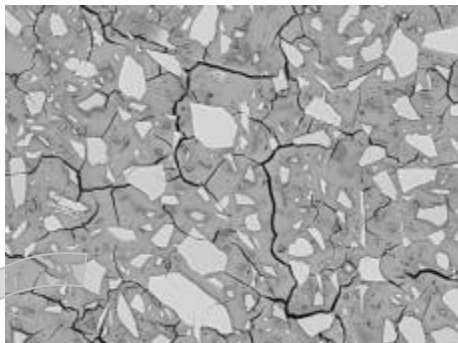


Carbonated zone

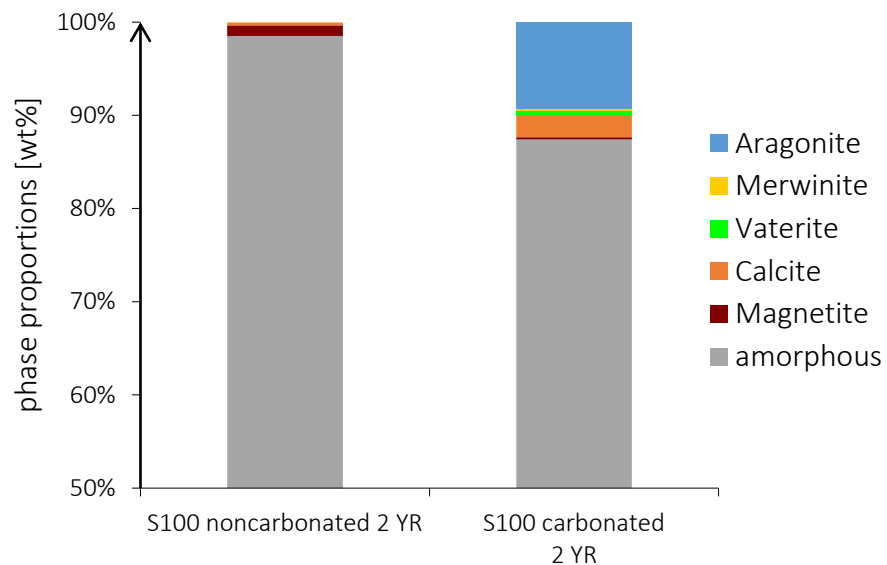
SEM-BSE scans

Noncarbonated zone

Carbonated zone

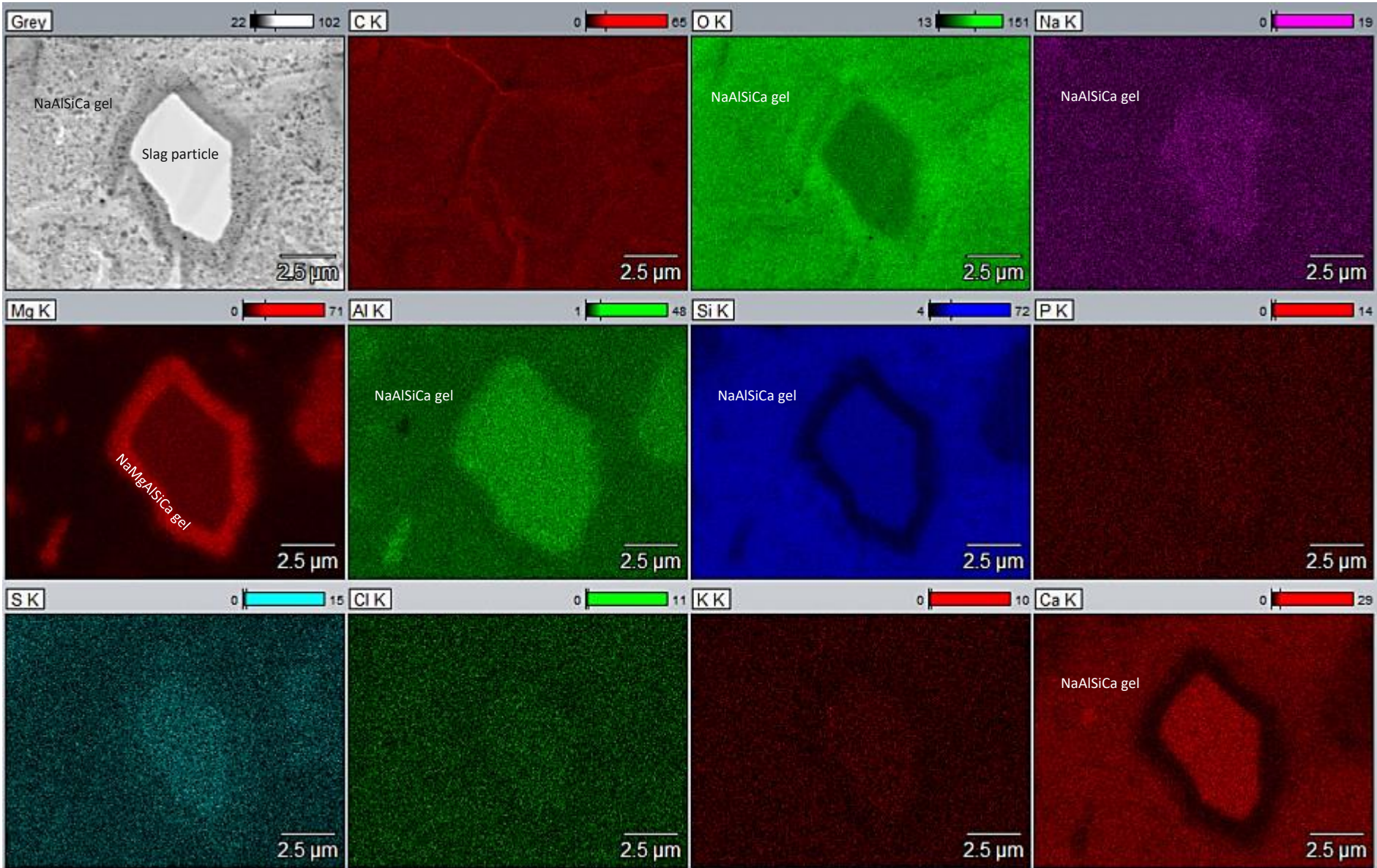


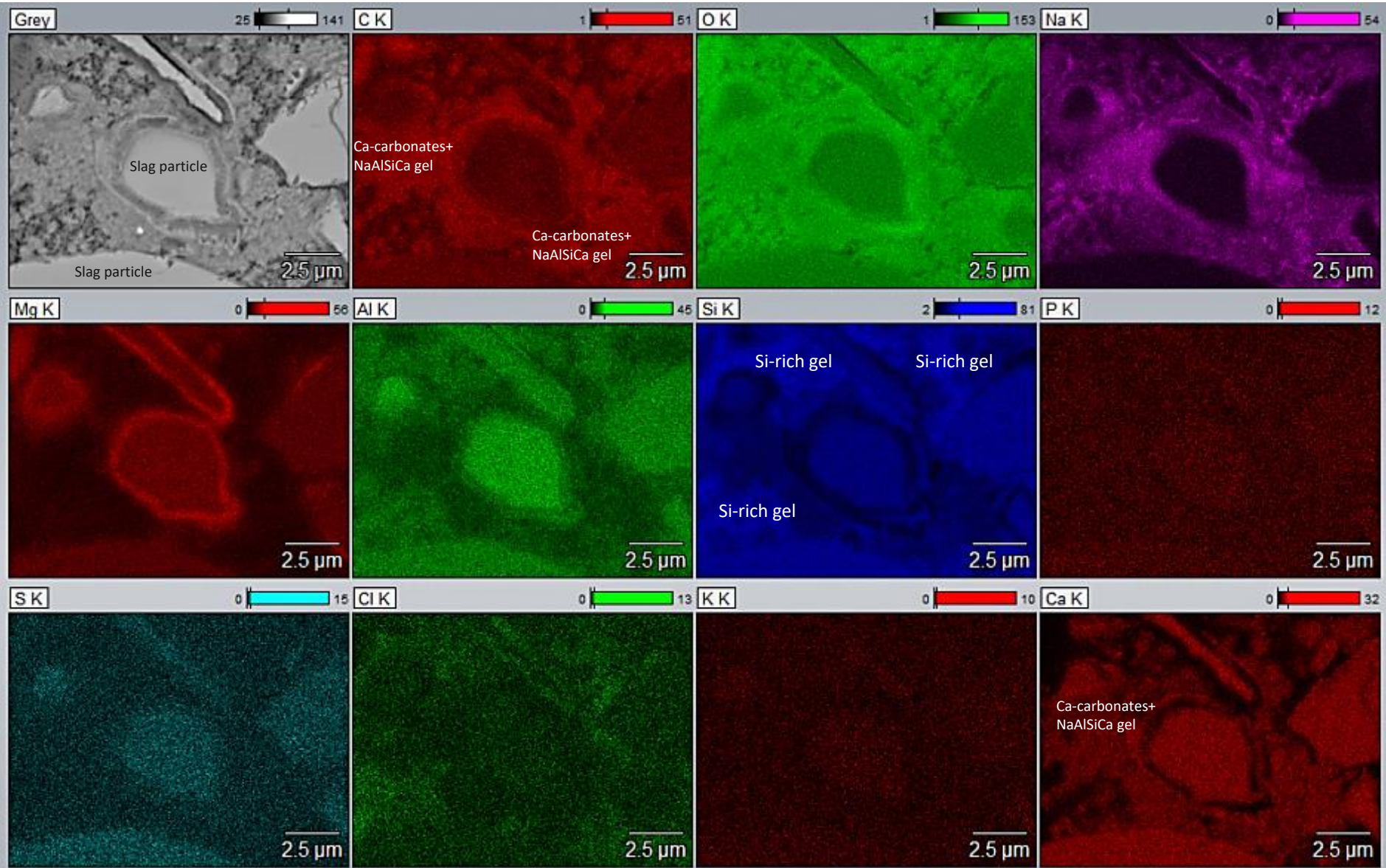
250x192μm²

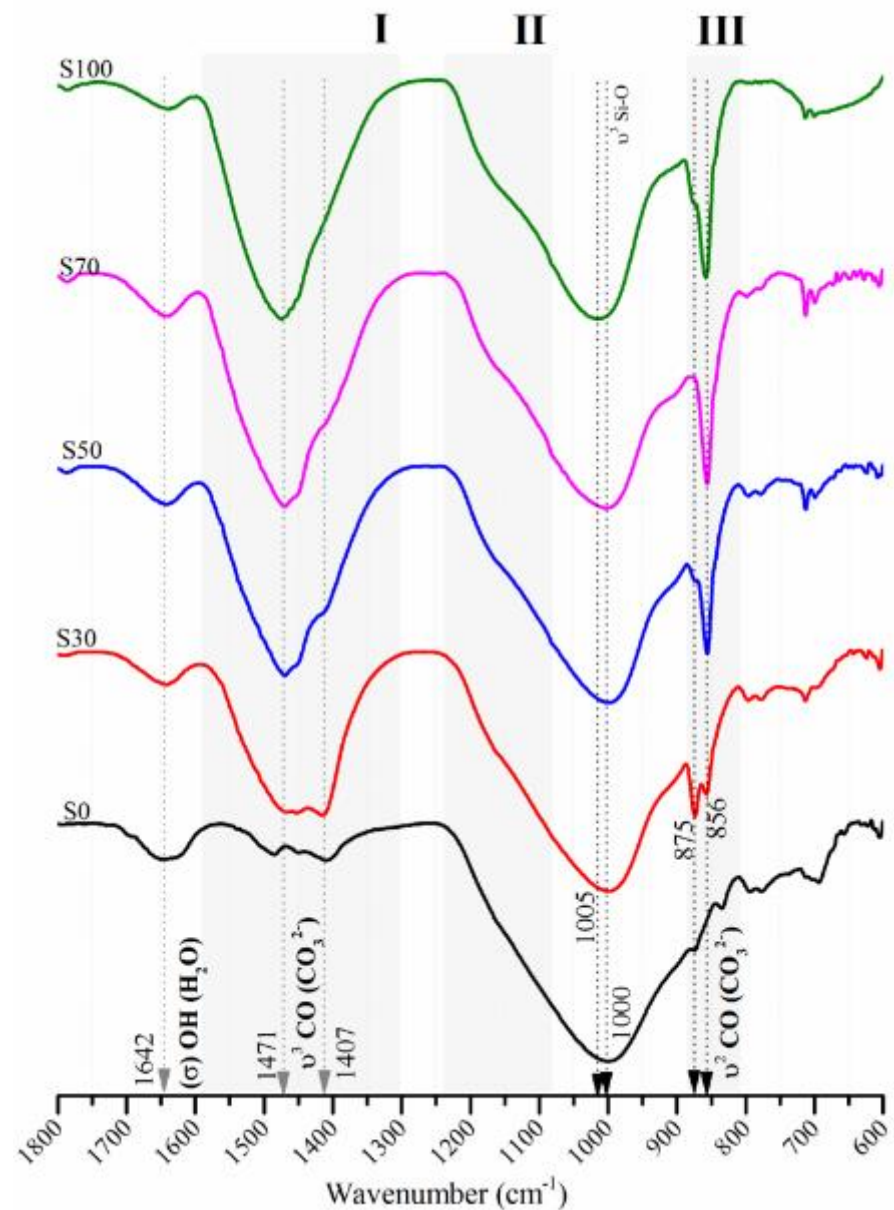
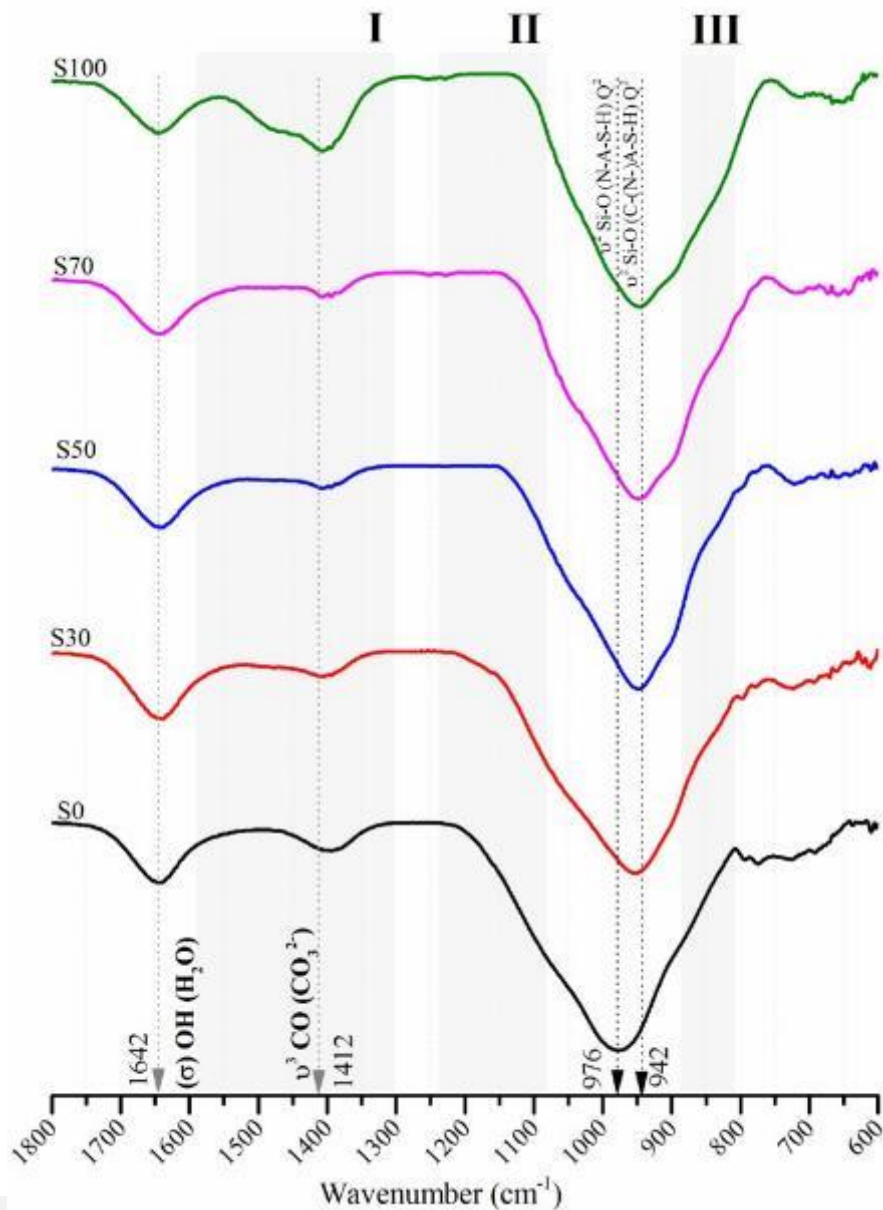


	NaMgAlSiCa gel noncarbonated zone	NaMgAlSiCa gel carbonated zone
	Wt %	Wt %
Na ₂ O	12.1	5.51
MgO	15.13	12.46
Al ₂ O ₃	13.85	13
SiO ₂	30.6	38.72
P ₂ O ₅	0.21	0.17
SO ₃	1.61	1.54
K ₂ O	0.34	0.45
CaO	24.14	26.25
TiO ₂	1.24	1.18
MnO	0.44	0.43
Fe ₂ O ₃	0.33	0.29

	NaAlSiCa gel noncarbonated zone	NaAlSiCa gel carbonated zone
	Wt %	Wt %
Na ₂ O	6.67	7.9
MgO	2.64	3.71
Al ₂ O ₃	8.87	8.76
SiO ₂	41.72	48.81
P ₂ O ₅	0.22	0.26
SO ₃	0.69	0.64
K ₂ O	0.23	0.56
CaO	36.01	35.19
TiO ₂	0.66	0.83
MnO	0.17	0.21
Fe ₂ O ₃	0.12	0.13







noncarbonated

carbonated

30

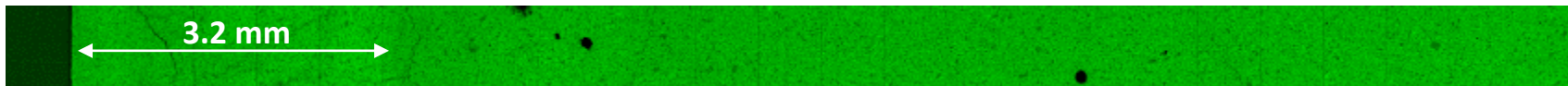
Comparison of Fourier-transform infrared spectra between different pastes for time zero of exposure and complete carbonation at 28 days.



Mosaic



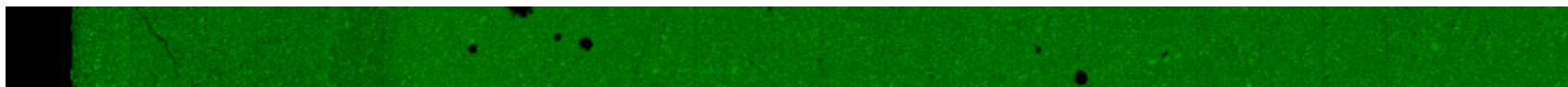
Grey



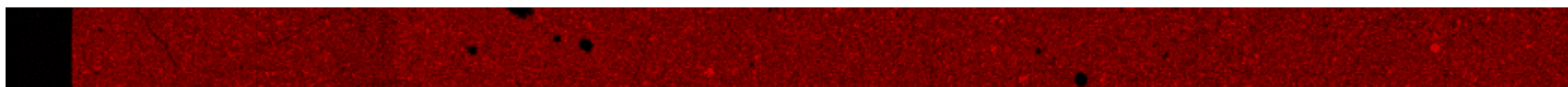
O



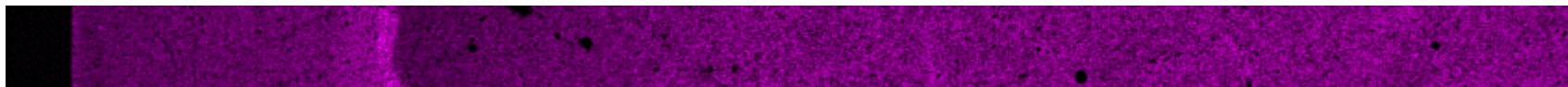
C



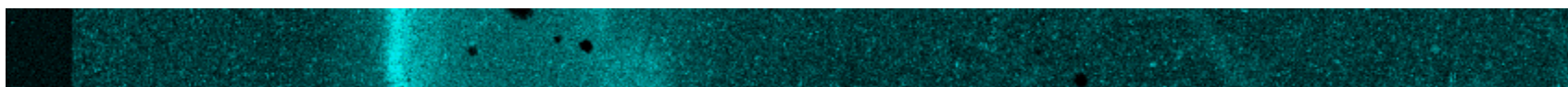
Ca



Mg



Na



S



Si

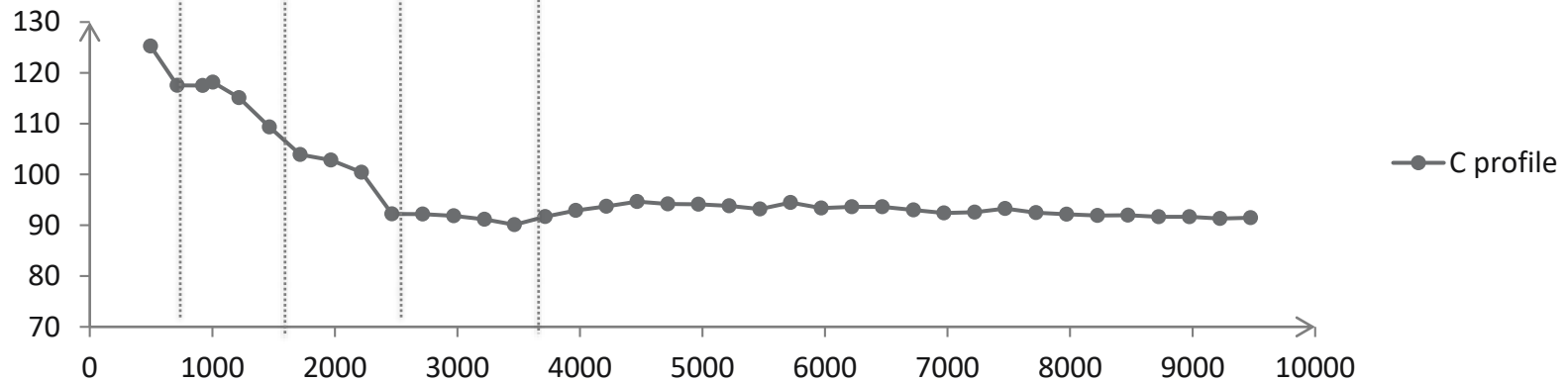
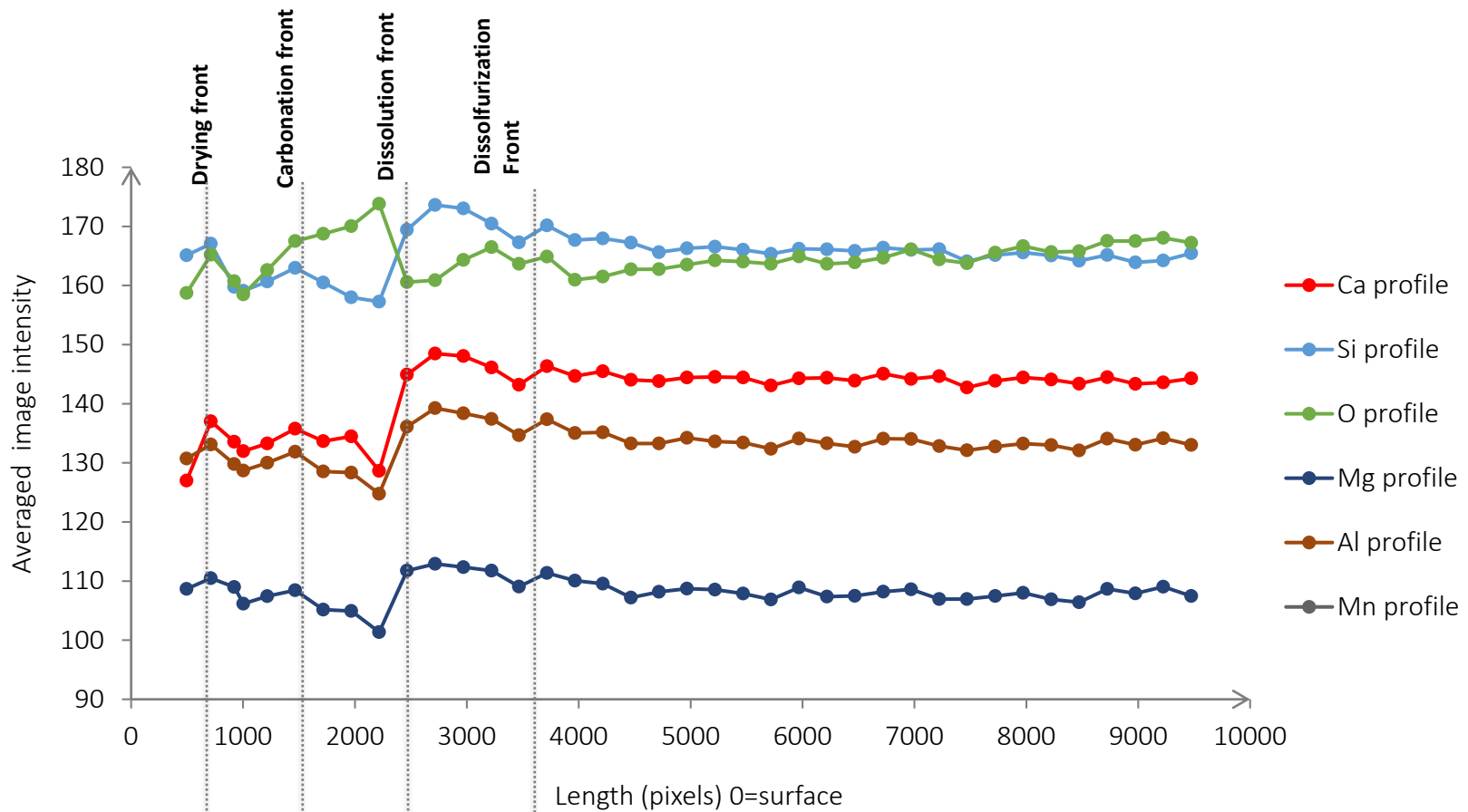


Al

12 mm

M21 NWO

SEM-EDX element profiles_S100



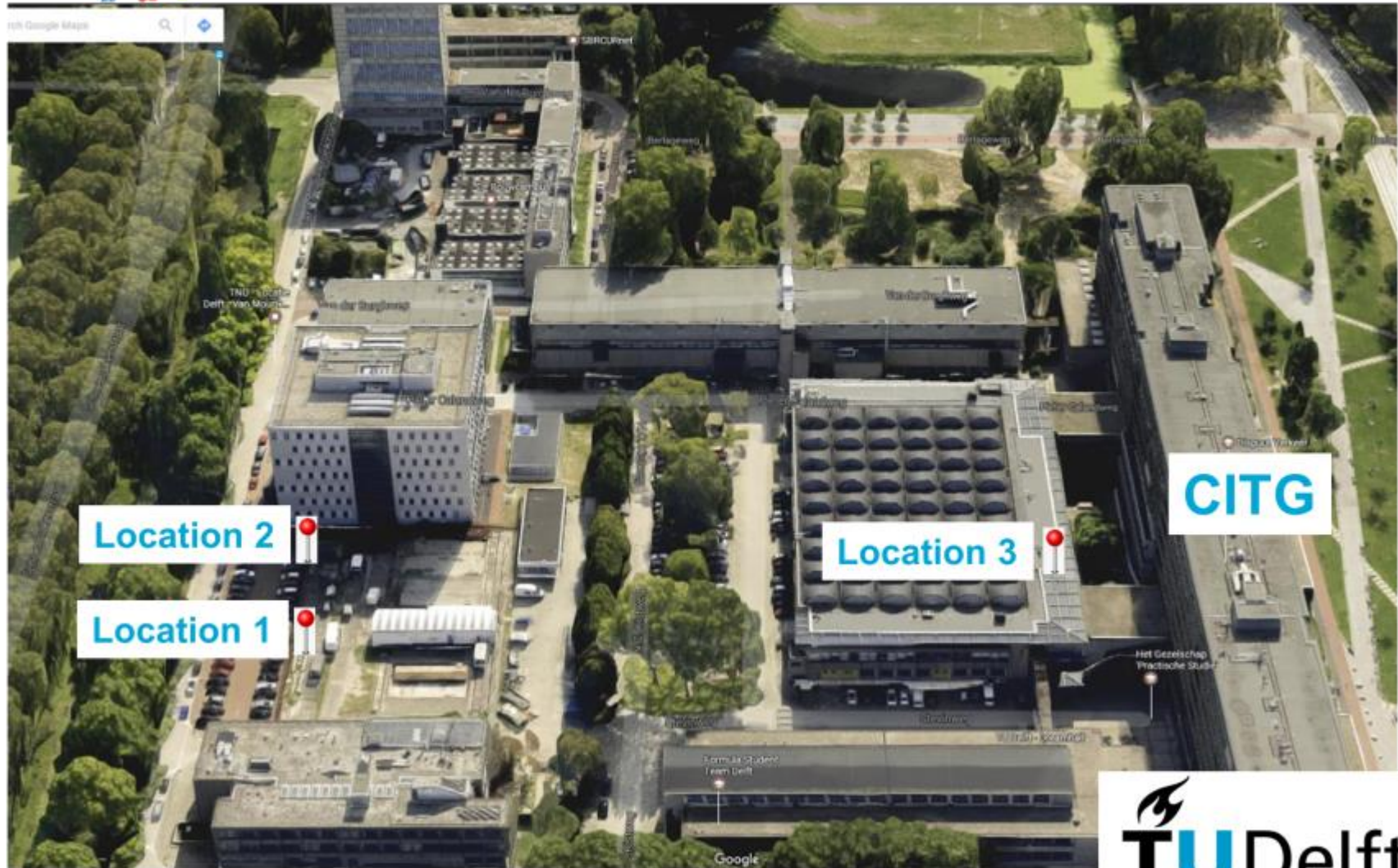
From the edge towards the core, the altered paste consists of:

- **carbonated zone** (contains altered gel: calcium carbonates, silica gel and calcium-depleted silicate phases),
- **carbonation front** (the carbonation front is a thin layer (50 to 200 μm wide) of very low porosity, in which abundant calcium carbonates have precipitated),
- **dissolution front** (is a zone of high porosity where phases (calcium sodium aluminate silicate hydrate phases) progressively dissolve to form calcium carbonates backwards, in the carbonation front,
- **the core of sample** (unaltered gel phases).

The dissolution of the gel phases provides OH^- and Ca^{2+} ions towards the carbonated area.

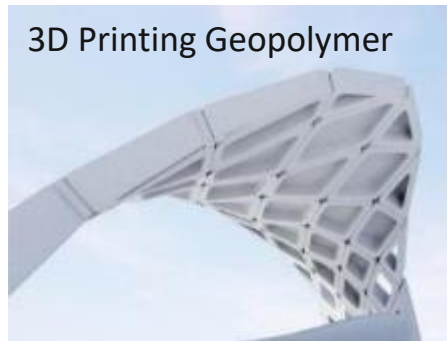
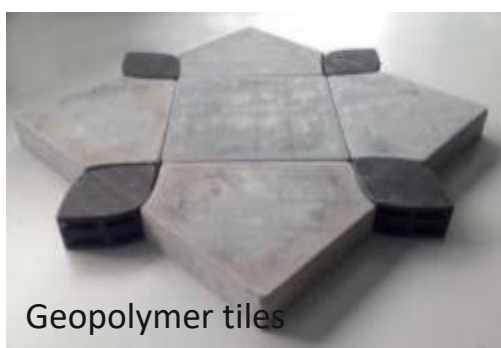


EXPOSURE OF GEOPOLYMERS

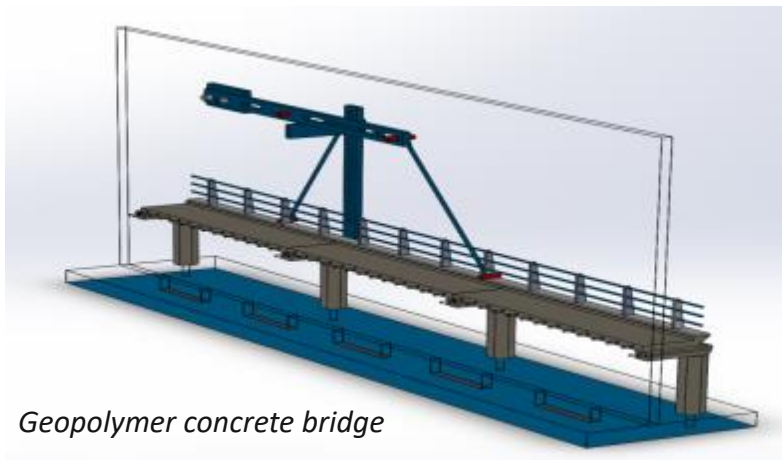


Late lab scale demonstrations at concrete level.

Aim: durability testing, structural applications.



- Geopolymer pavement tiles, 0.05 m³
- 3D geopolymer printed elements, 0.02 m³
- Geopolymer fibre reinforced canoe, 0.12 m³
- Geopolymer reinforced cantilever bench, 1.2 m³
- Geopolymer bridge, XY m³



Conclusions

1. Recognition and characterization of different phases before and after carbonation were successfully completed by PARC. However, carbonates could not be identified as a single phase, due to their *nanometer* size.
2. Carbonation mechanism has a rather bulk scale than a local occurrence. The chemical reactions are the driving force for carbonation in AAM.
3. Carbonation leads to removal of Ca from the gel, forming aragonite and calcite, depending on the supersaturation level, ionic ratio of $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$ in solution and the pH of solution.
4. Element profiles showed immobile (Mg) and locally mobile chemical elements with different spatial distribution favoured by carbonation, leading to reduction of bulk density in carbonated zone.

Thank you



Toegepaste en
Technische Wetenschappen