Granulation and coating with Geopolymer Binders

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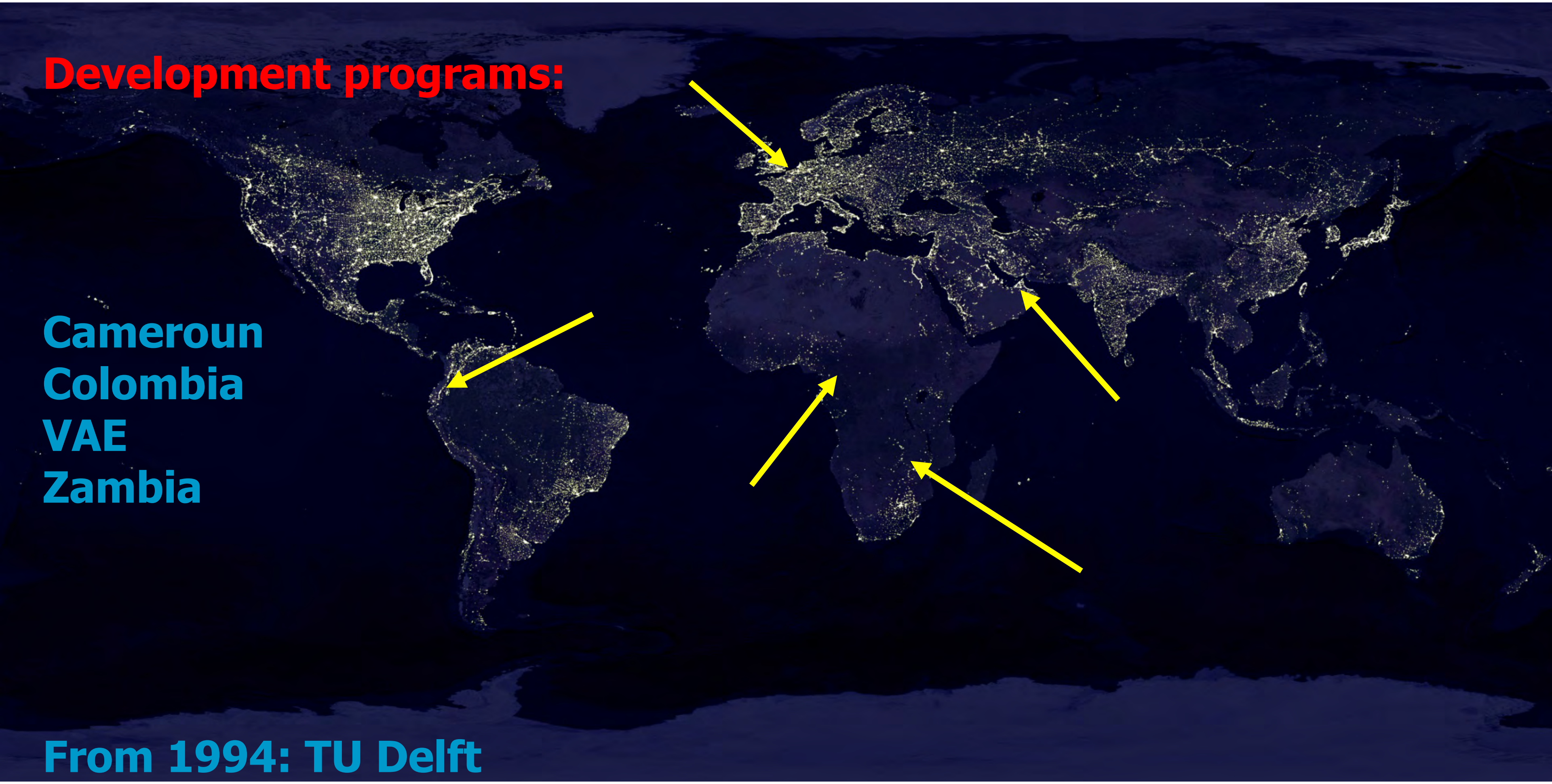
GEOPOLYMER CAMP, SAINT-QUENTIN, FRANCE
07 – 07 - 2015

TU Delft
Delft University of Technology

Henk Nugteren

Study Geology, Mineralogy, Ore Deposits at VU Amsterdam 1978



Development programs:

Cameroun
Colombia
VAE
Zambia

From 1994: TU Delft

Research: New Products from waste materials (PhD in 2010)

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GRANULATION

GOAL

TECHNOLOGY OF GRANULATION

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TECHNOLOGY OF GRANULATION

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TECHNOLOGY OF GRANULATION

Or is it an art?

Liquid content is crucial

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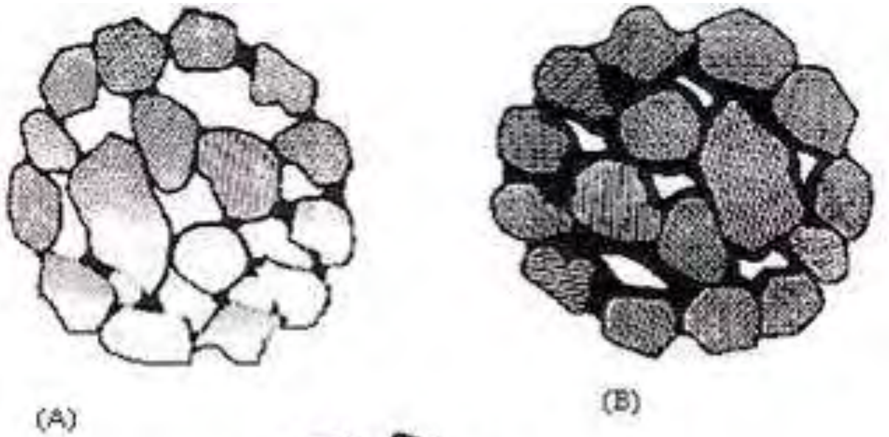
STAGES OF WETTING

A) Pendular state

B) Funicular state



C) Capillary state

Growth regimes:

- Steady Growth
- Induction Growth

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High shear granulator

(Eirich R-02)

Raw Materials and Activator Liquids

SOLIDS:

- Type C Pulverised Fuel Ash
- Peat and Wood Ash (Netherlands and Finland)
- Granulated Blast Furnace Slag
- Polluted Sand
- Metakoalin

LIQUIDS:

- Water
- Potassium Silicate Solution
- Sodium Aluminate Solution (Waste from Aluminium Etching)

THE LIQUID CHALLENGE

$$[4SiO_2 \cdot Al_2O_3] + 10\,OH^- + 3\,H_2O \longrightarrow 2\,[Al(OH)_4]^- + 4[SiO_2(OH)_2]^{2-}$$

$$[Al(OH)_4]^- + [SiO_2(OH)_2]^{2-} \xrightarrow{-H_2O} \left[\begin{array}{ccccc} & O^- & & HO & \\ & | & & | & \\ HO - & Si & -\,O\,- & Al^- & -\,OH \\ & | & & | & \\ & O^- & & HO & \end{array}\right] \longrightarrow$$

$$\xrightarrow{polycondensation} \left[\begin{array}{cccccc} | & & | & & | & \\ -Si- & O & -Al^-- & O & -Si- & O\,- \\ | & & | & & | & \\ O & & O & & O & \\ | & & | & & | & \end{array}\right]_n$$

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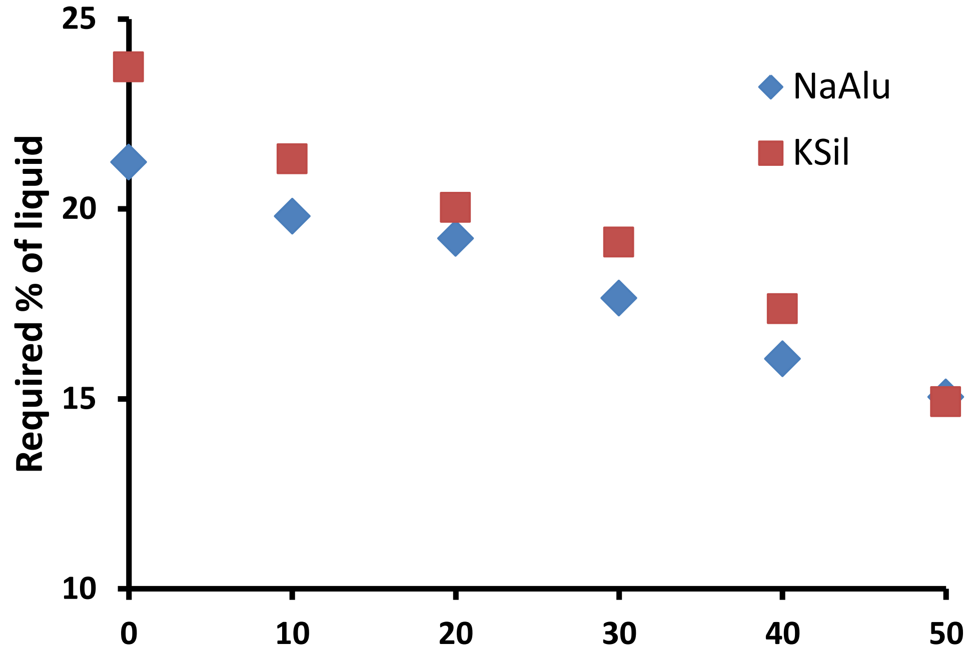
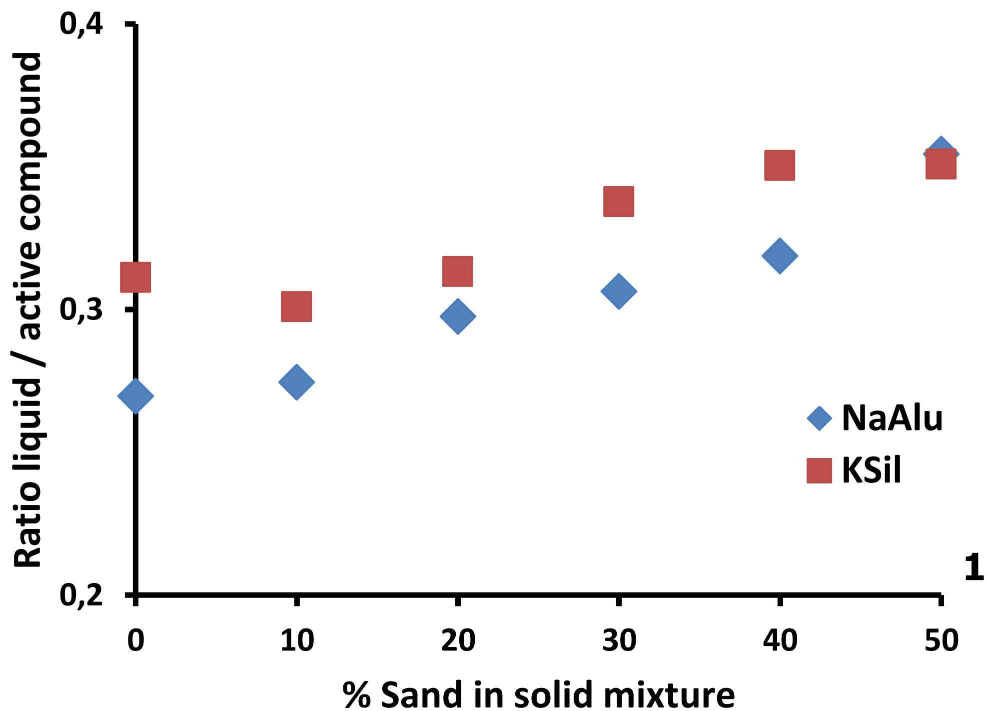
LIQUID REQUIRED

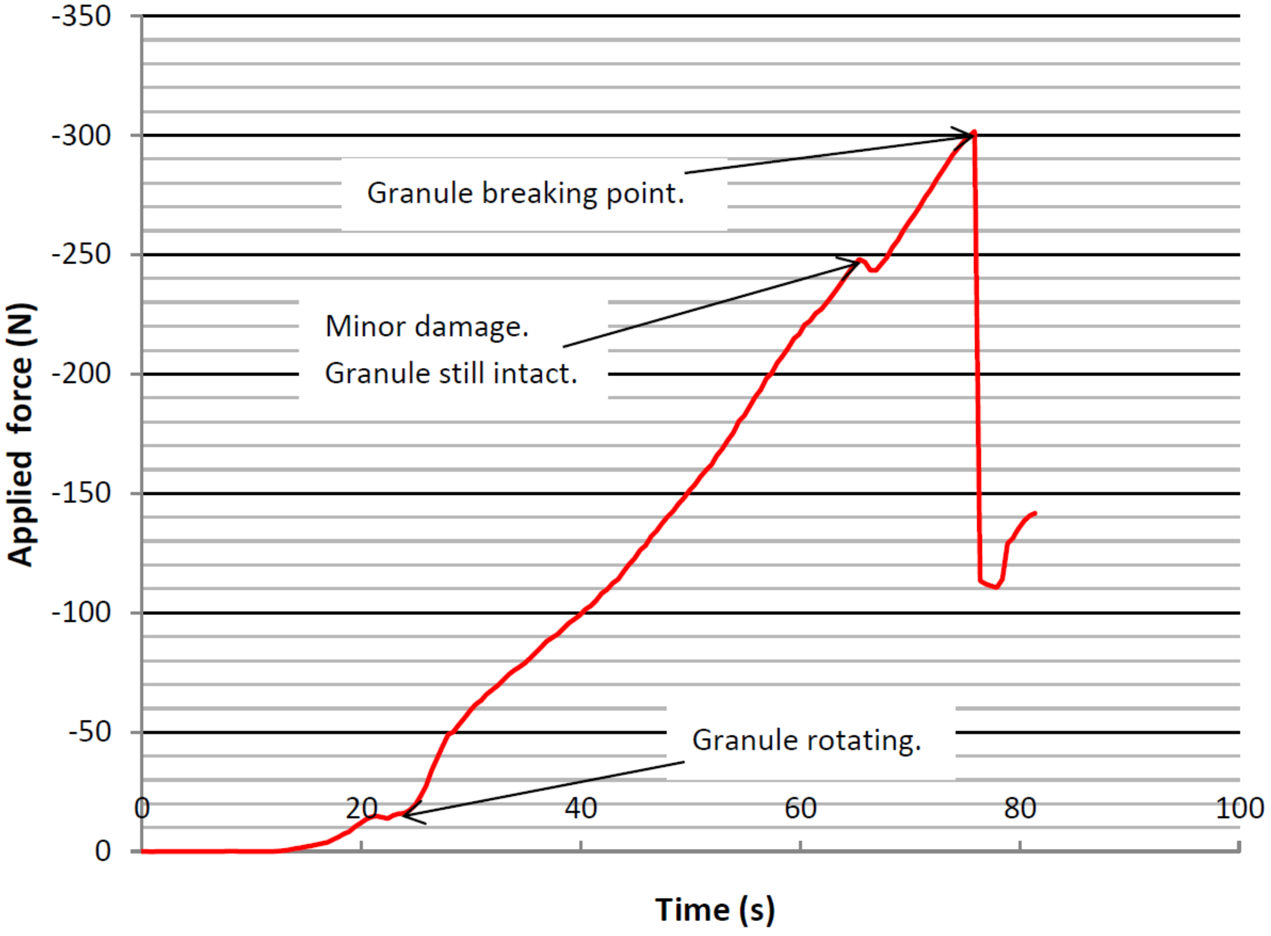
More sand:

- **less liquid in mix**
- **higher liquid to precursor ratio**





STRENGTH MEASUREMENTS



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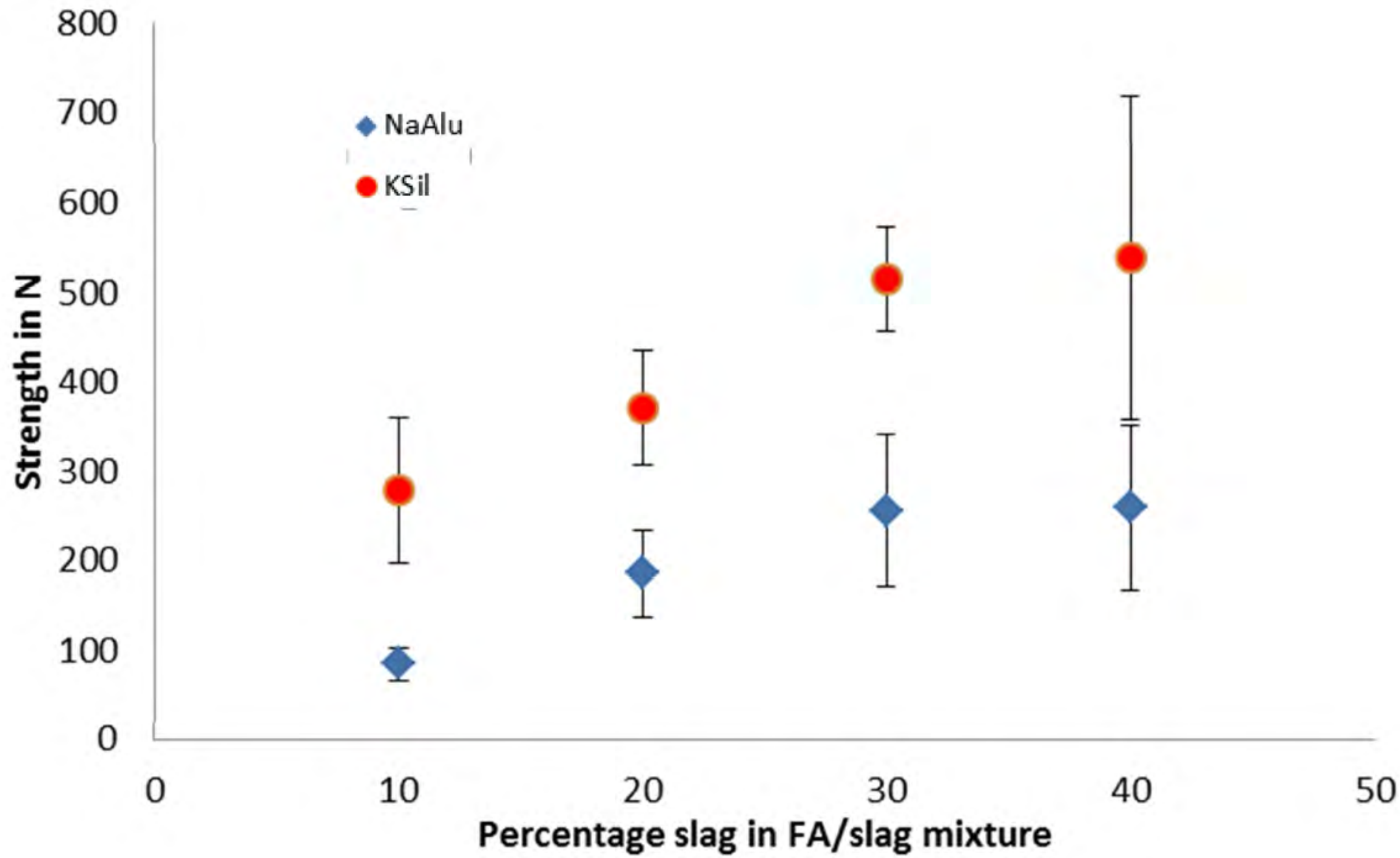
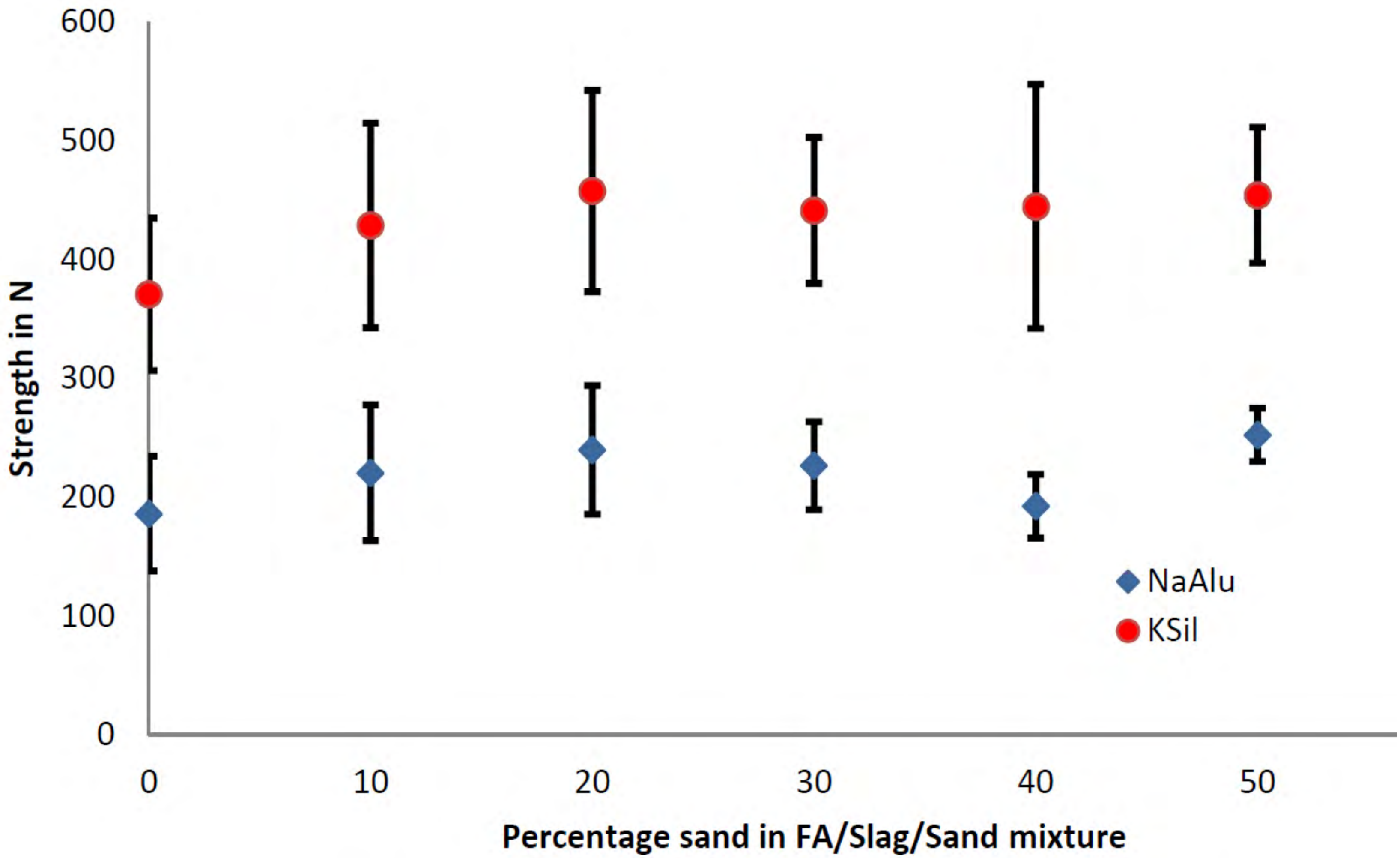
STRENGTH OF GRANULES



STRENGTH OF GRANULES



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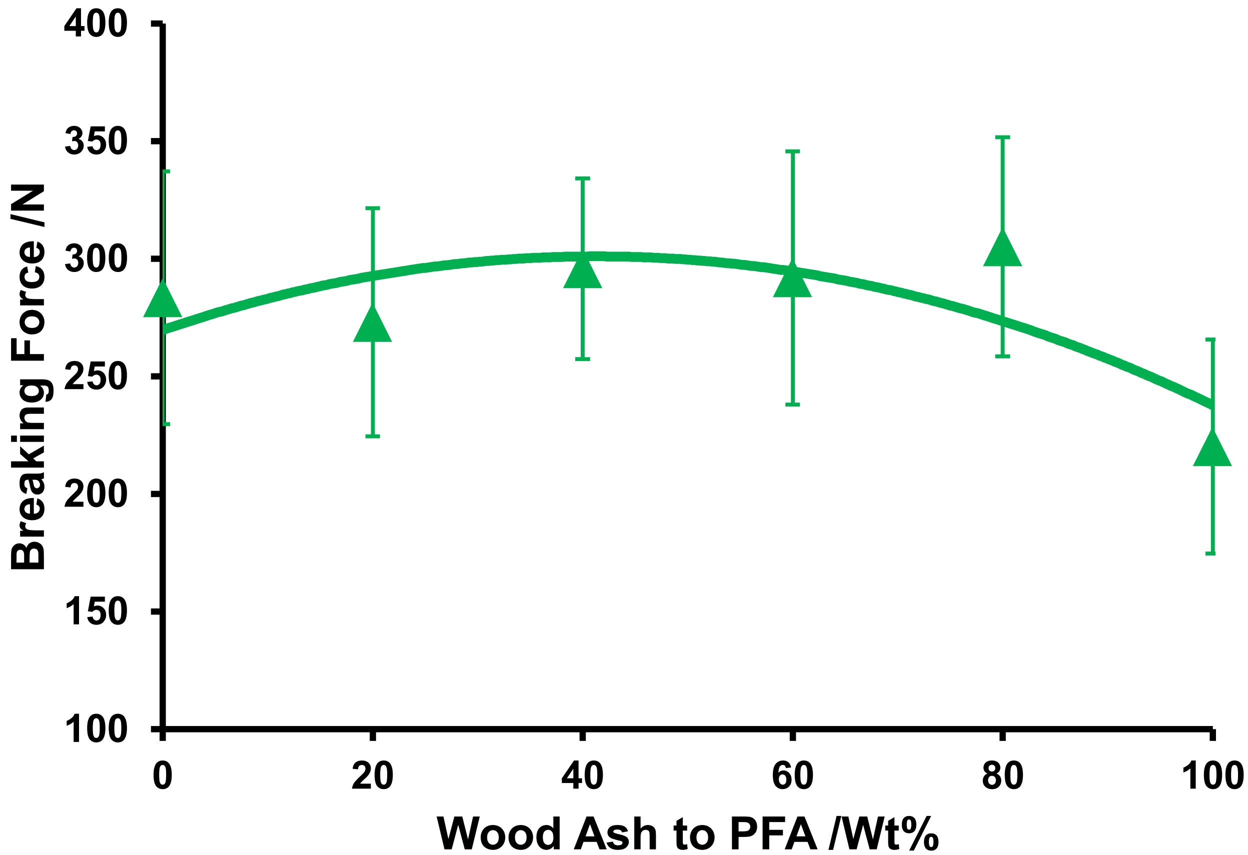
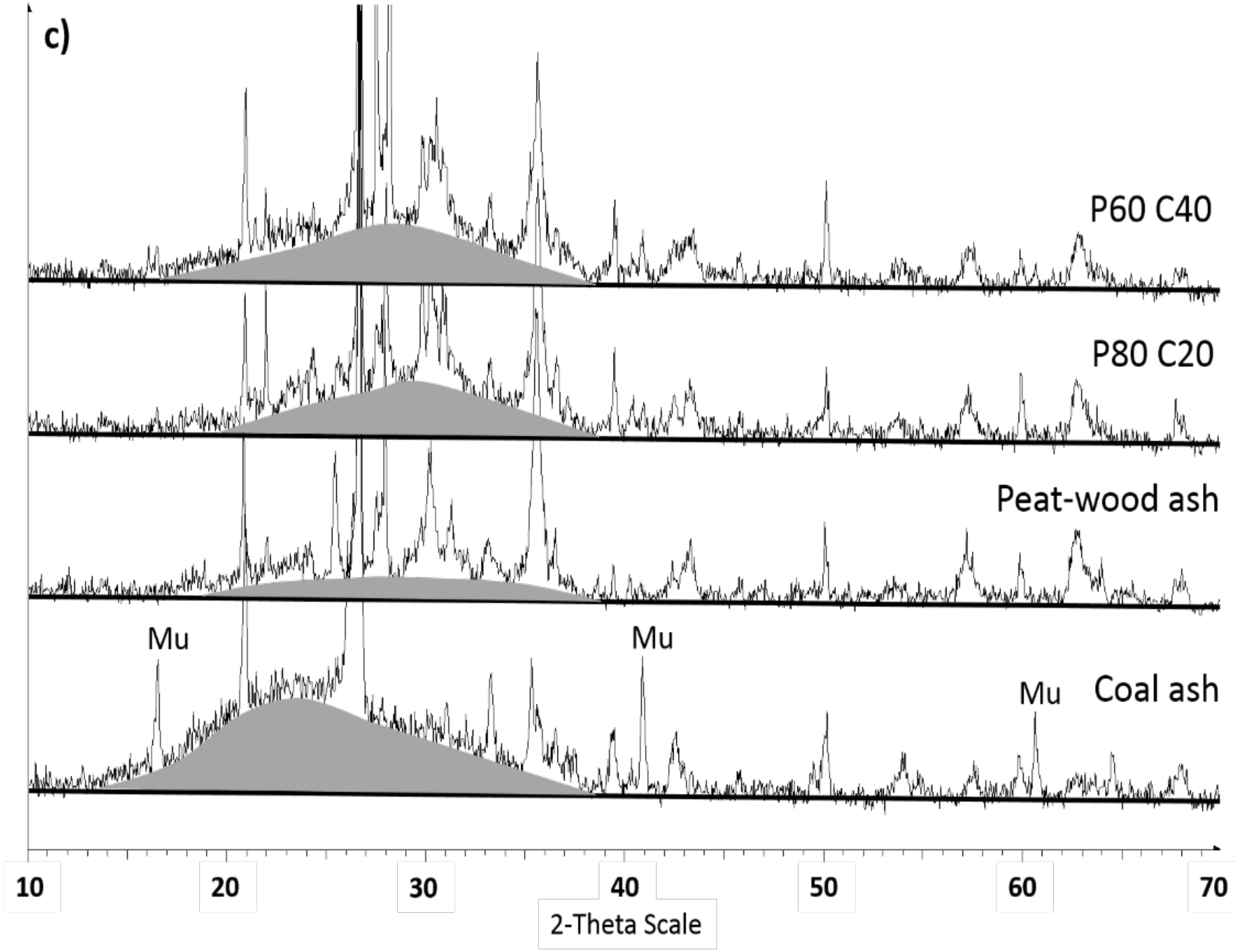
WOOD ASH PERFORMANCE



But:

Do we really have chemical reaction?

XRD



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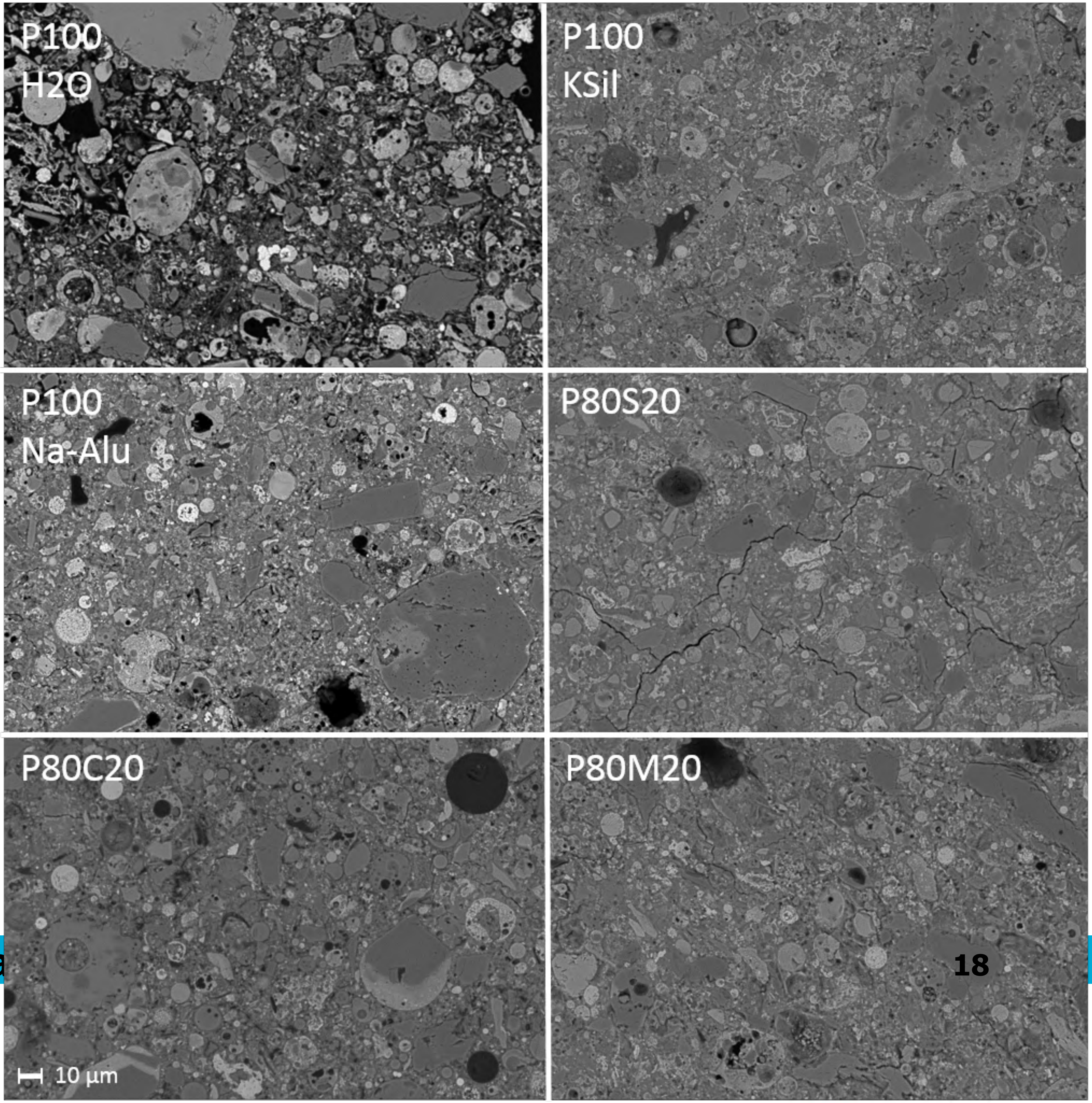
But:

Do we really have chemical reaction?

FESEM BSE



CONCLUSIONS

- **Granulation of geopolymer precursors with spraying liquid activators is feasible**

- **Peat / wood ash with relatively small amounts of silica and alumina can still produce strong granules**

- **Operating windows (liquid / solid ratio) are narrow but can be maintained even when the geopolymeric reaction takes place simultaneously**

- **High amounts of polluted inerts can be added without losing strength**

- **XRD and FESEM show that geopolymeric binders have formed**

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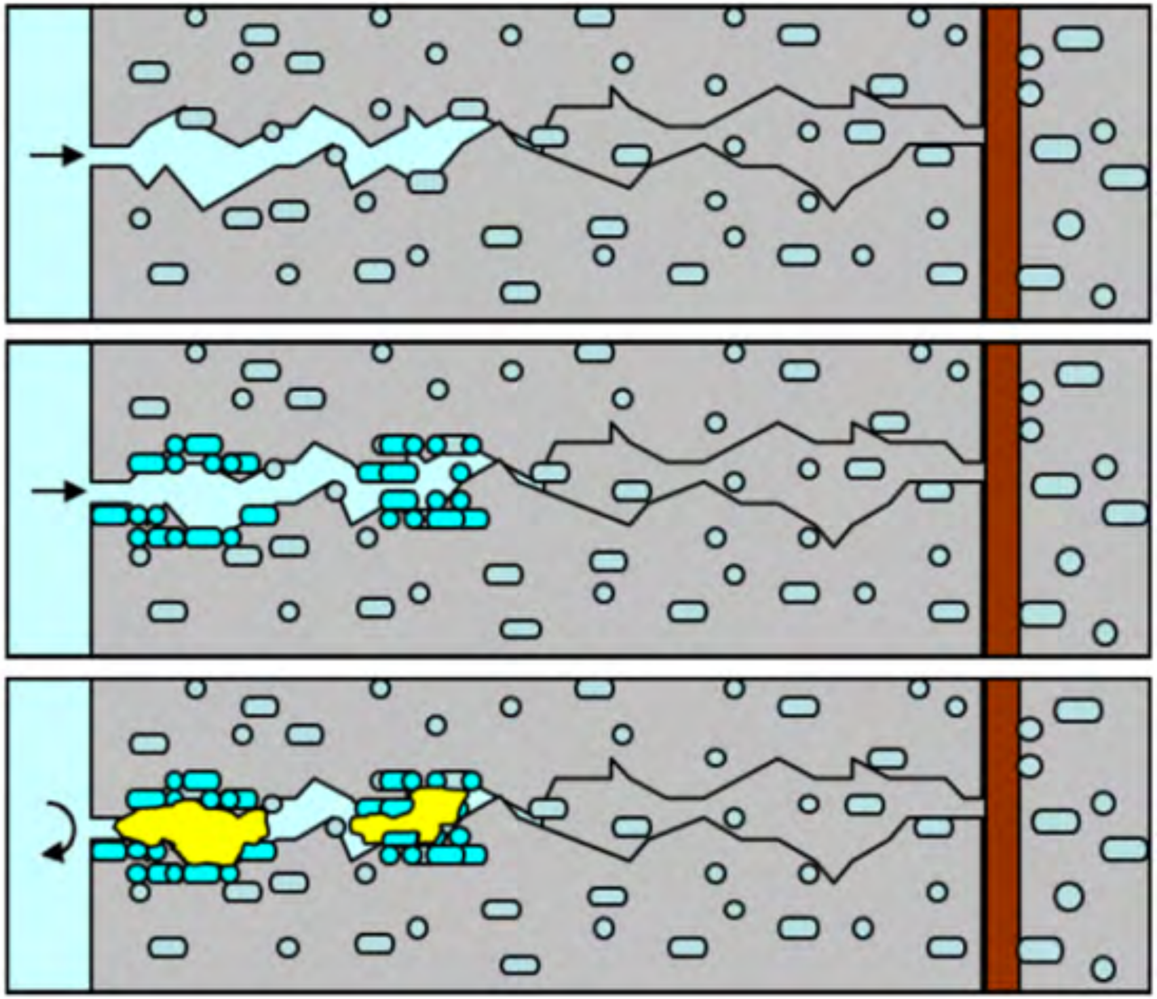
COATING OF SELFHEALING PARTICLES

PRINCIPLE OF SELF-HEALING



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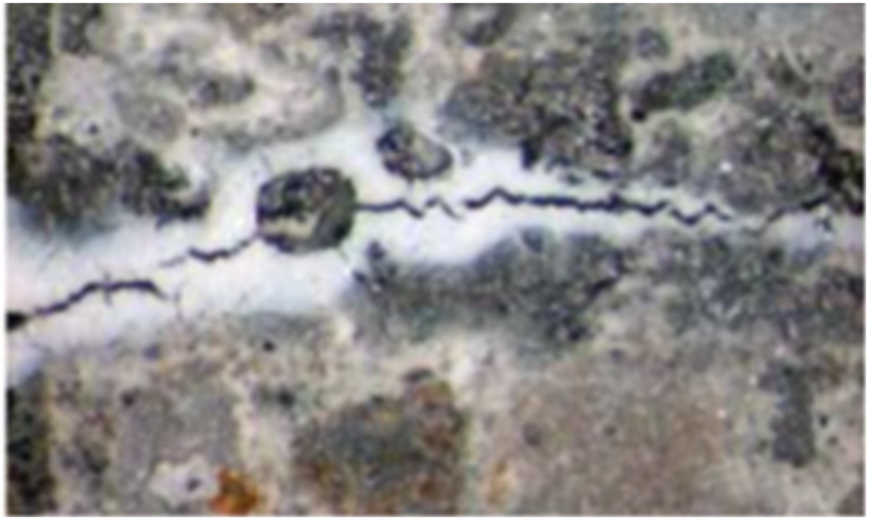
Concrete without healing agent

Just cracked



After healing period

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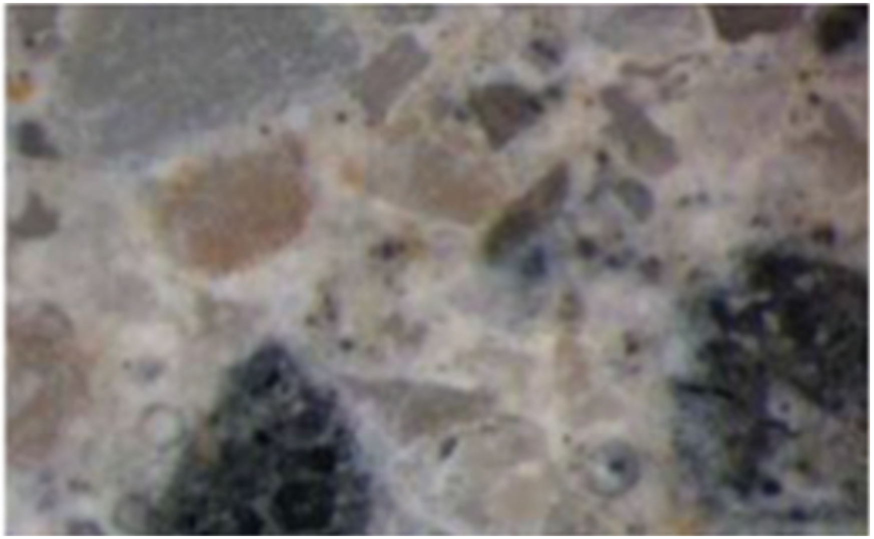
Concrete with healing agent

Just cracked



After healing period

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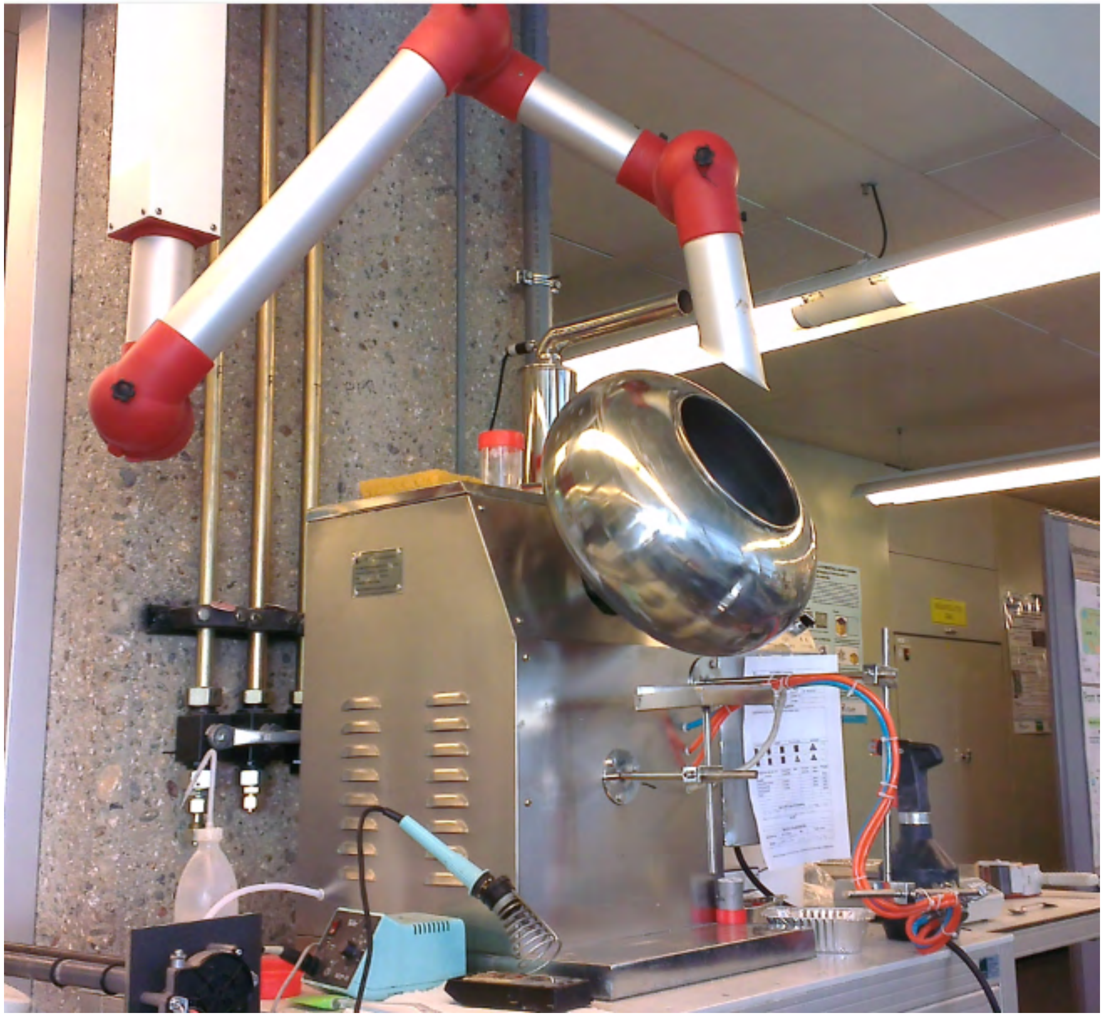
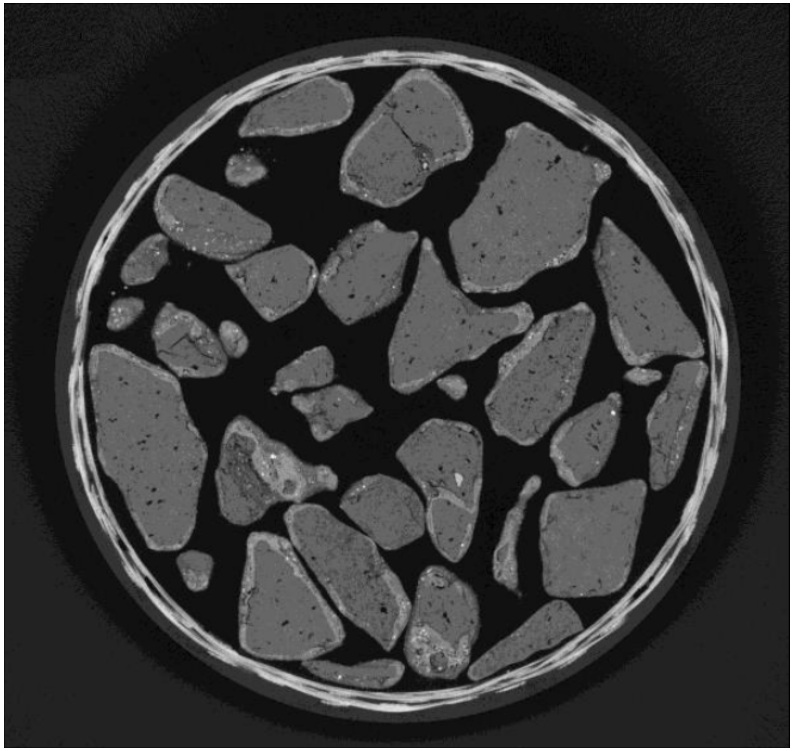
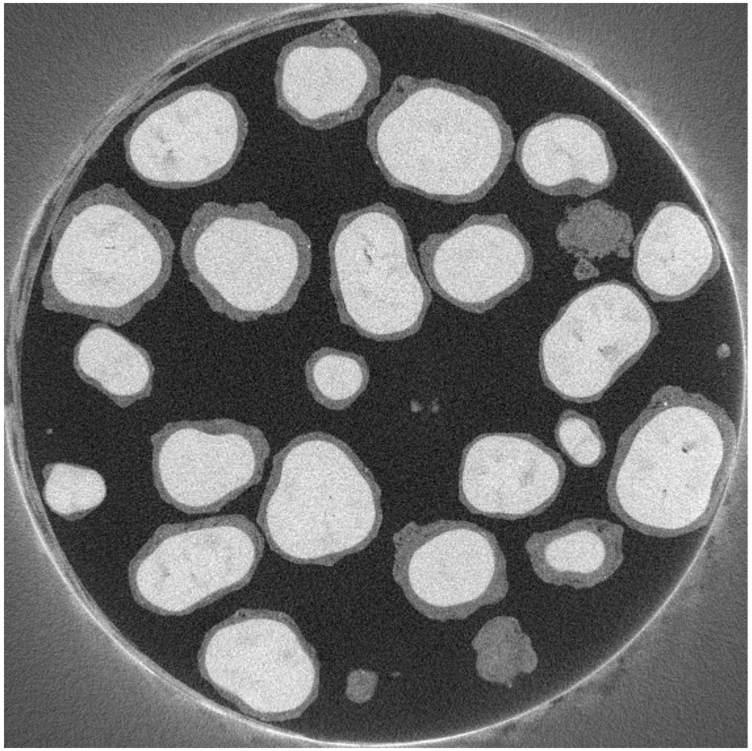
Low Shear Pan Granulator



Shape of particles to be coated
CT Scans





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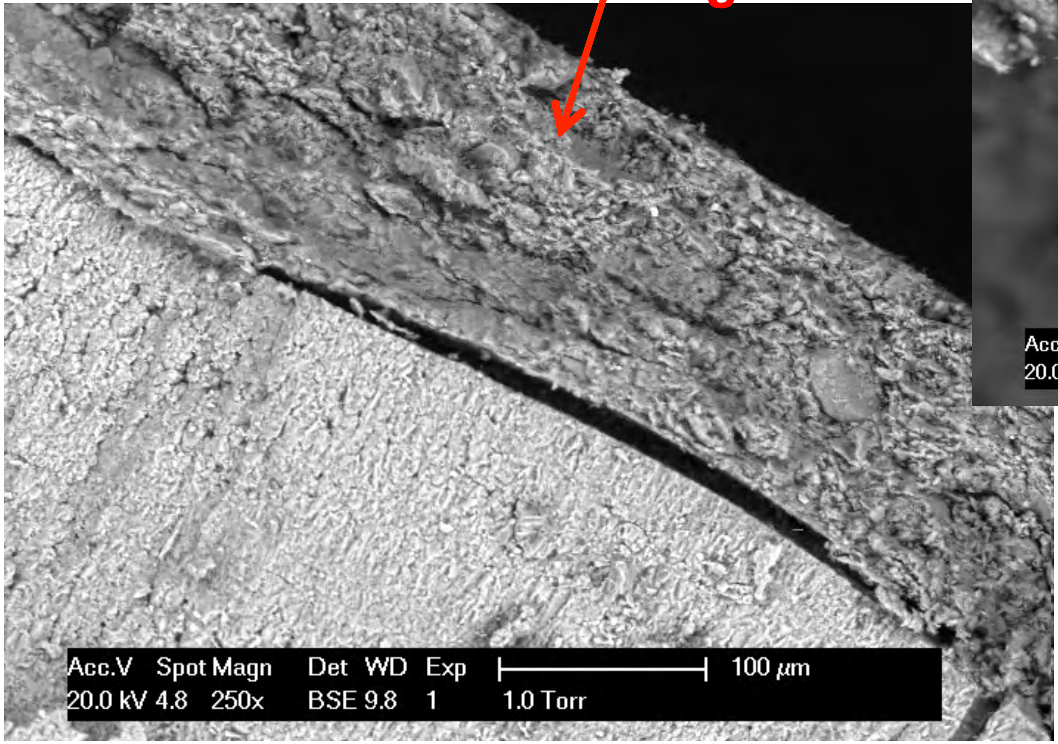
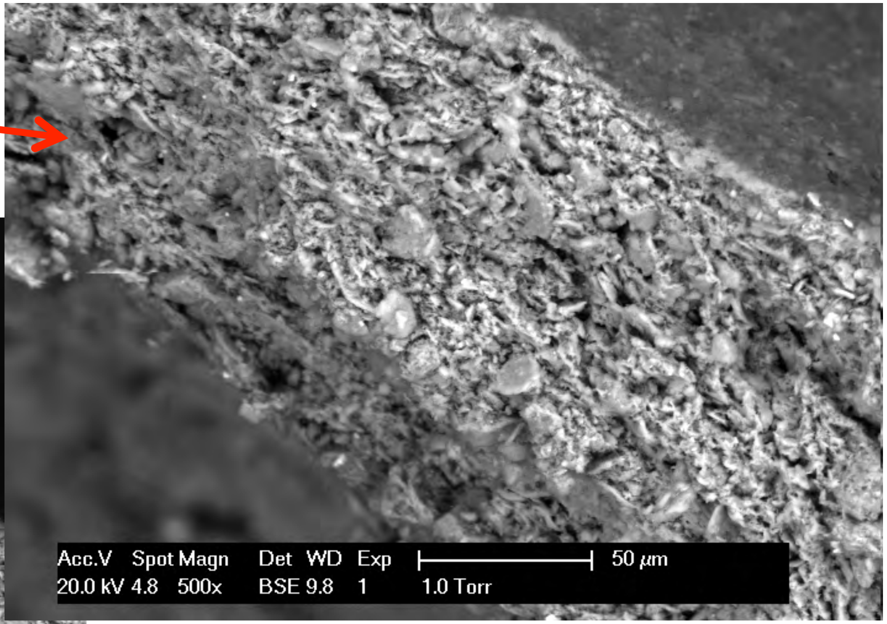
Coated particles

Metakaolinite geopolymer coating





ESEM images

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Water tightness

Leaching solution	Sample	Ca (mg/l)	Al (mg/l)	Si (mg/l)
6 M HCl	Coated core	28.2	15.7	2.4
	Coating only	3.4	31.3	2
1 M NaOH	Coated core	1.6	85.5	629
	Coating only	1.9	248	1123

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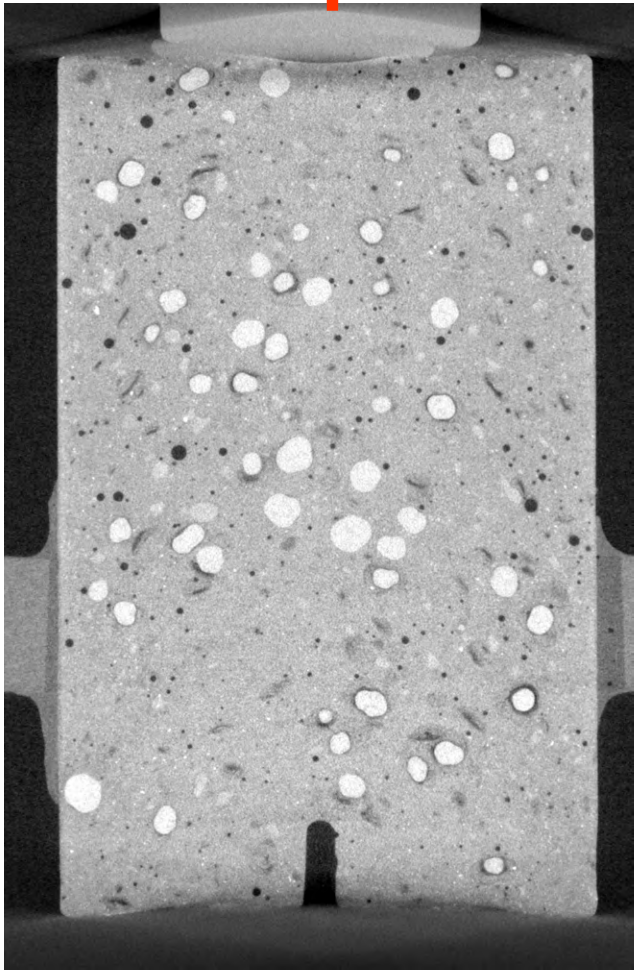
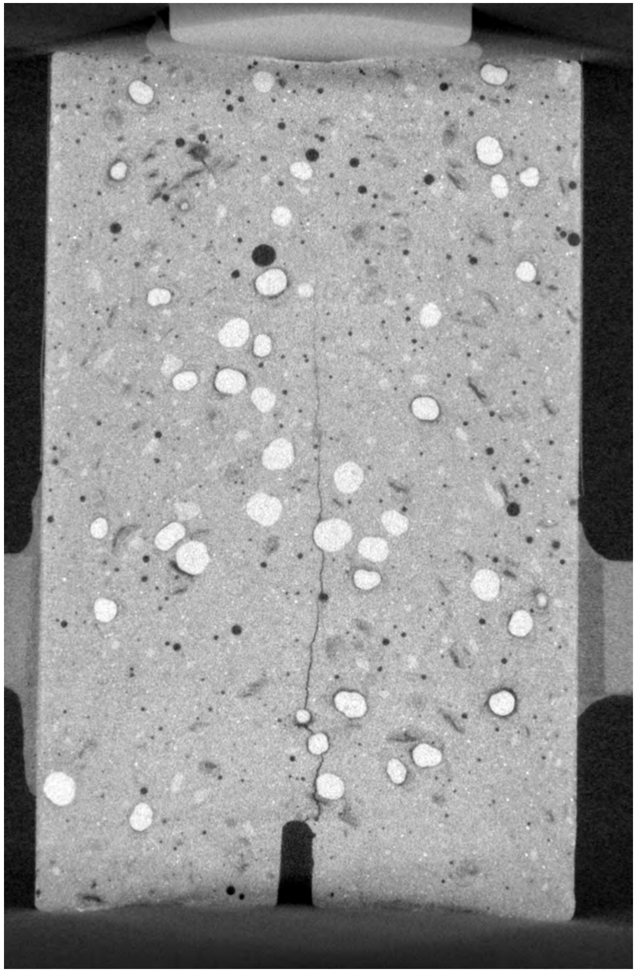
Adhesion to cement paste



Cracking behaviour



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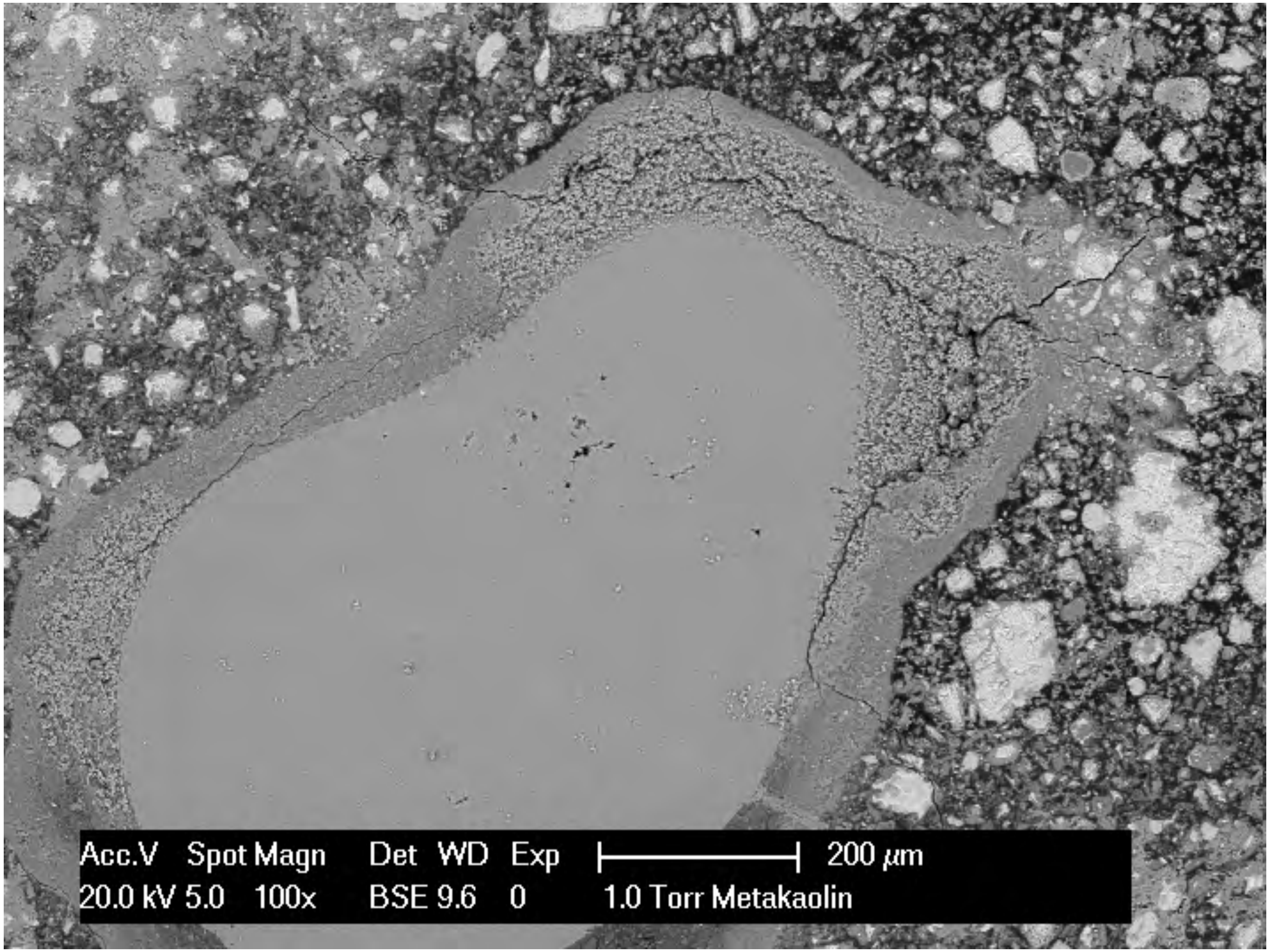
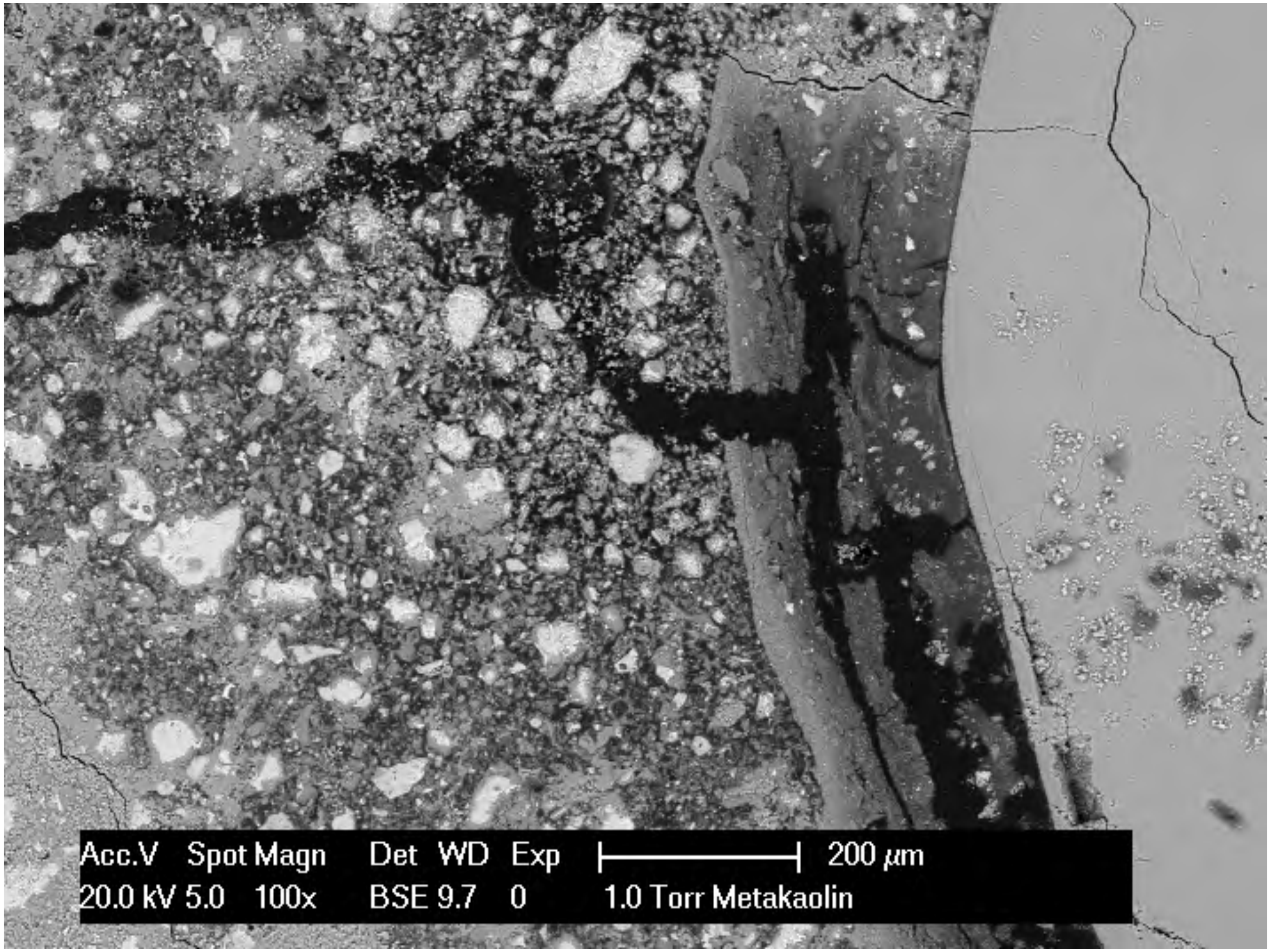
Cracking of coating



Cracking of coating



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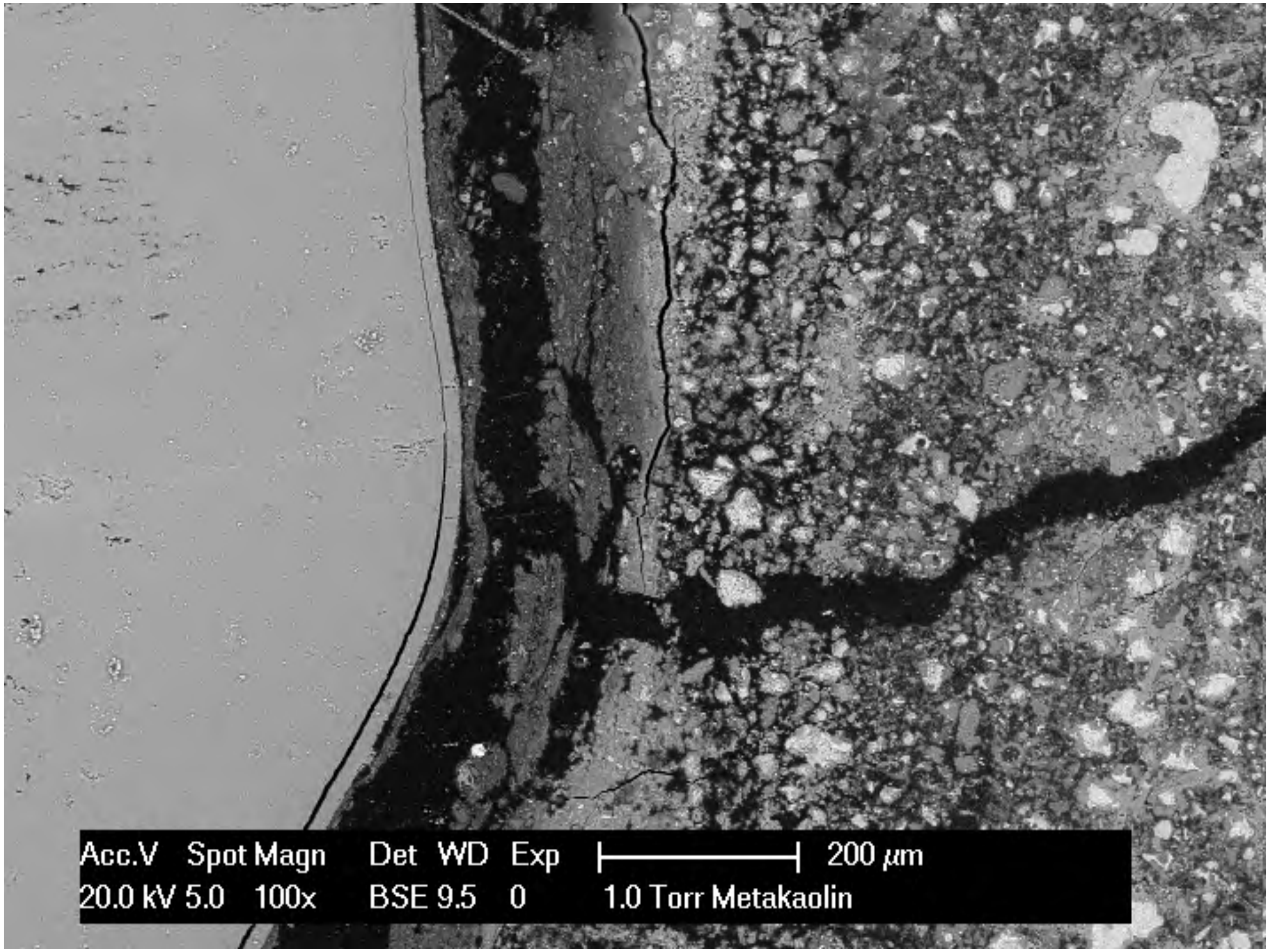
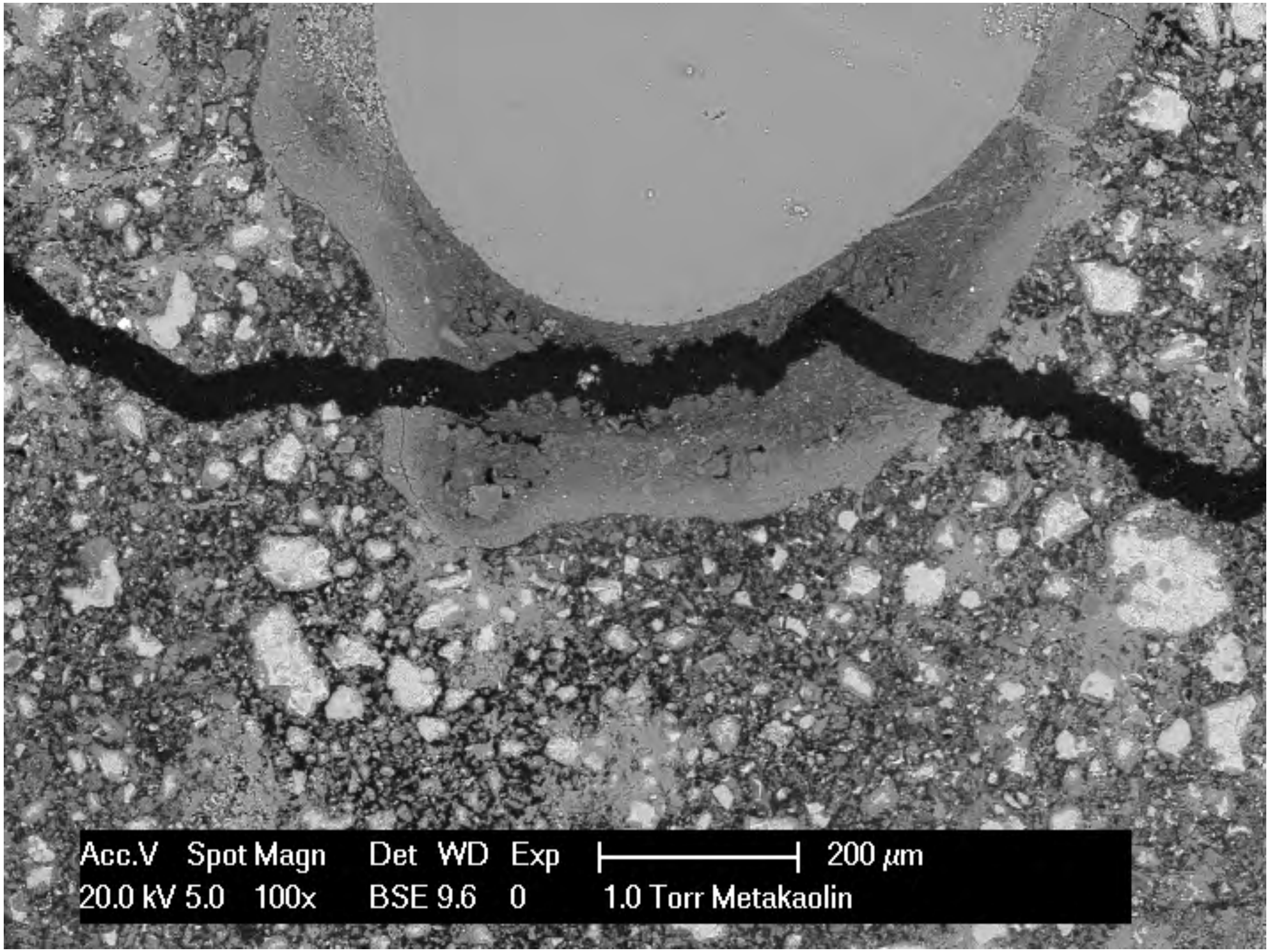
Cracking of coating



Cracking of coating



CONCLUSIONS

- Geopolymer coatings were obtained by carefully dosing metakaolinite powder and spraying liquid activators

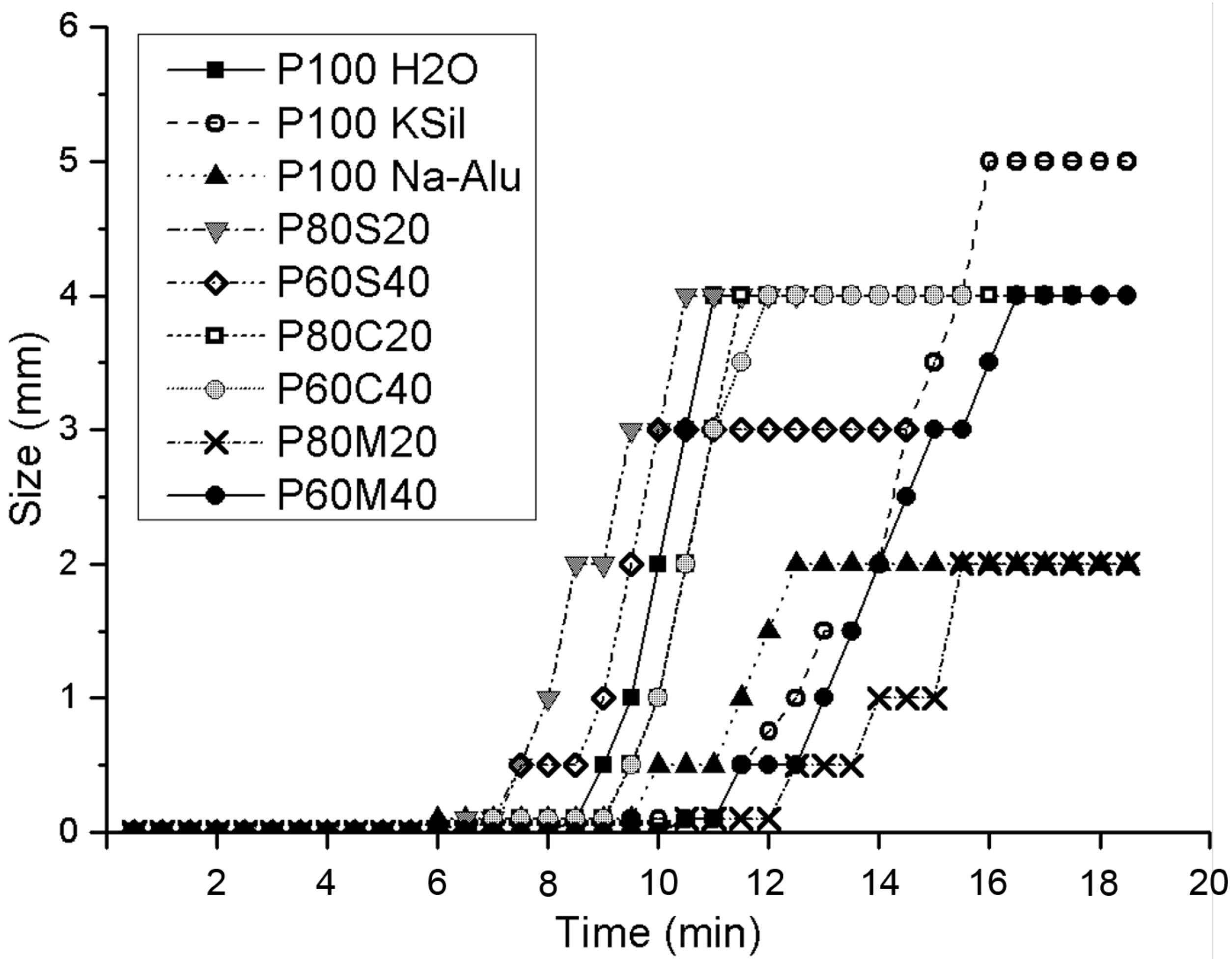
- Coatings are uniform and water tight

- Adhesion to cement paste is excellent

- Cracks developed in the cement paste follow paths connecting the embedded particles

- Coatings will also crack and make selfhealing agents available when required

Induction Growth



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Composition of solid precursors

Sample	Chemical composition, %										Particle size		
	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	P_2O_5	TiO_2	SO_3	<10% [μm]	<50% [μm]	<90% [μm]
P	11.6	44.9	10.7	20.1	1.5	2.1	3.0	2.6	0.4	2.0	2.4	17.4	135.6
S	39.5	34.5	9.9	0.5	0.4	0.3	8.1	0.0	1.1	3.4	1.0	10.3	31.9
C	4.9	54.3	22.9	8.0	1.1	1.7	1.8	0.7	1.2	0.8	3.0	30.2	133.7
M	0.1	59.5	32.8	1.4	0.1	0.6	0.1	0.0	1.9	0.0	1.0	8.0	53.1

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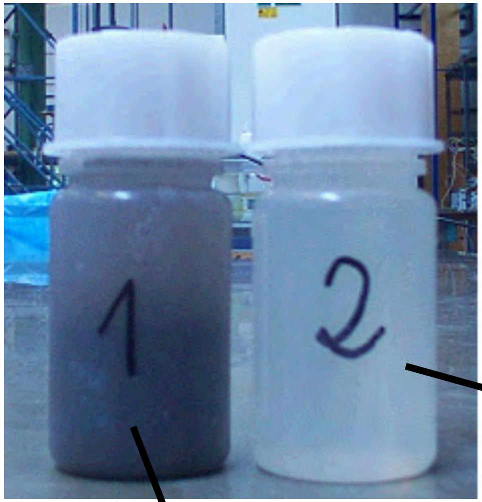

SODIUM ALUMINATE ACTIVATOR

Waste rinsing bath from aluminium etching:

Al	69-85 $g.kg^{-1}$
NaOH (free)	17-30 $g.kg^{-1}$
Si	0.3 $g.kg^{-1}$
S	2 $g.kg^{-1}$
Cr	4 $mg.kg^{-1}$
Others	<1 $mg.kg^{-1}$

Black particles are $NaAlO_2$ with:

Minor quantities: Mg, Fe, Si, Ca and S (0.5-5%)
Mn, Zn and Cu (± 2000 ppm)
Traces: Cr, Pb, Ti, V and Ni (<350 ppm)

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