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Procedia Engineering 102 (2015) 475 – 484

**Procedia  
Engineering**[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)

The 7th World Congress on Particle Technology (WCPT7)

## Geopolymer coating of bacteria-containing granules for use in self-healing concrete

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### Abstract

Concrete structures are often reinforced with steel. In order for the reinforcement to take over tensile forces, concrete has to crack. Through such cracks, water and compounds that are harmful to concrete can enter. This can cause durability issues like leakage, concrete degradation and reinforcement corrosion. In situ repair of cracks is often labour-intensive and inefficient.

Preferentially, cracks are autonomously healed from the inside out in an early stage, preventing the ingress of water. This can be achieved by incorporating healing agent particles composed of nutrients and bacterial spores into the concrete matrix. The bacteria will germinate when water is available, plugging cracks with calcium carbonate. However, a coating is needed to protect the water-soluble healing agent from water during mixing. In order to allow the bacteria access to water for activation after the concrete has hardened, such a coating should break whenever a crack occurs in the concrete. Therefore, it should adhere well to the concrete matrix. It is possible to achieve this by protecting the particles with a brittle geopolymer coating.

For this study, healing agent particles are coated with geopolymers following different mixture recipes. Metakaolin is used as an aluminosilicate source and sodium silicate as well as sodium aluminate are used as activator liquids. The particles are coated by granulation in a low-shear granulator. In order to improve the coating process, the operating window and the granulation mechanism are determined for all activator liquids used. Leaching and strength tests are performed and coated particles are incorporated in cement paste in order to determine the feasibility of application of the particles in concrete.

Results show that the prepared particles are better protected from leaching than untreated particles. Using a high pressure single-fluid nozzle to improve nebulisation when coating produces more particles of the desired size than coating with a low pressure single-fluid nozzle with poor nebulisation. Furthermore, particles prepared with a high pressure nozzle sprayer perform better when incorporated into cement paste than particles prepared with a low pressure nozzle sprayer.

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Selection and peer-review under responsibility of Chinese Society of Particuology, Institute of Process Engineering, Chinese Academy of Sciences (CAS)

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*Keywords:* Self-healing concrete; Geopolymer; Coating; Low-shear granulation; Operating window; Mechanism; Bacteria

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## 1. Introduction

Concrete is one of the most produced materials in the world [1]. The amount of cement, the binder in concrete, produced in 2012 totalled an astounding 3.6 billion tonnes [2]. Although concrete has high compressive strength, it is weaker to tensile forces [1]. Therefore, concrete is often reinforced with steel bars. In order for the reinforcement to take over tensile forces, concrete has to crack [3]. Unfortunately, water entering through cracks in concrete can cause corrosion of the steel reinforcement and deterioration of the concrete matrix [1]. Concrete repair is inefficient, as generally only manual inspection and repair techniques are used [4, 5]. Consequently, it is necessary to find a non-labour-intensive method to repair concrete from the inside out. Ideally, concrete should be made in such a way that it is self-healing: making it heal itself without any external aid [6].

One of the possible methods to achieve this is to add calcium carbonate producing bacteria of the genus *Bacillus* to the concrete mixture [7]. This type of bacteria forms spores, allowing it to survive without nutrients and water for up to hundreds of years. Hence, incorporating nutrients and spores into the concrete matrix can make the material self-healing. Whenever a crack forms, water will enter the crack, causing the bacteria to germinate and start producing calcium carbonate. In this way, cracks are plugged and further water ingress is prevented. A schematic representation of this process is shown in Figure 1.

Although this method looks promising, incorporating bacteria into the concrete in such a way that the highly water soluble nutrients are not dispersed throughout the concrete matrix is complicated [5]. Simply adding bacteria and nutrients to the concrete mixture is ineffective, as water is one of the major components of the mixture [1]. By encapsulation of particles made of bacterial spores and nutrients, it is possible to prevent water from dissolving the nutrients while keeping a wide range of applications open [8]. One way of achieving encapsulation is by coating a mixture of compressed nutrients and bacterial spores. The resulting coated particles can be added directly to the concrete mixture. The coating should be strong enough to survive the mixing process, but brittle enough to crack whenever a crack appears in the concrete. In order to make sure the cracks go through instead of around the particles, the coating should form a sufficiently strong bond with the concrete matrix.

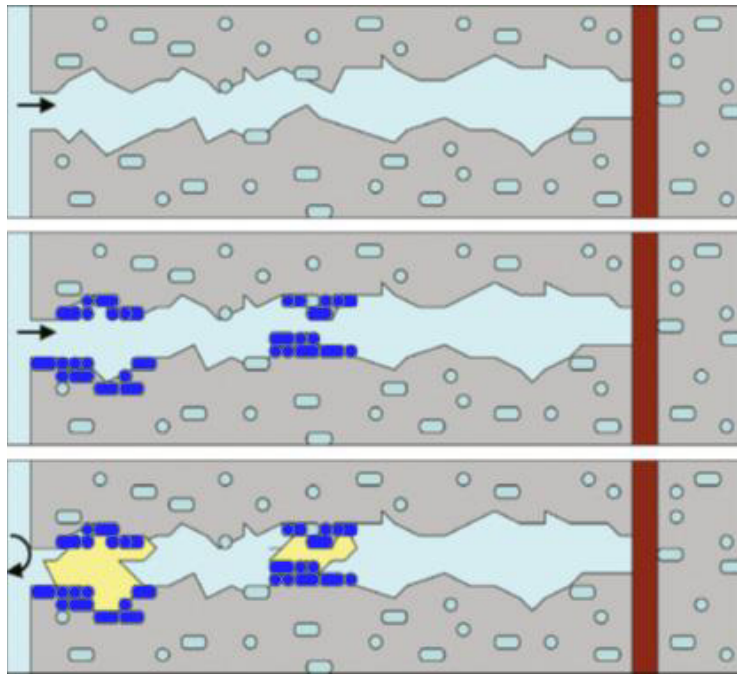


Figure 1: Schematic representation of healing by bacteria. Calcium carbonate (yellow) is formed by bacteria (dark blue) incorporated into concrete (grey). The black arrows represent water flow and the red bar represents the steel reinforcement. After Jonkers [7].

Earlier work at Delft University of Technology indicated that the coating of such particles by geopolymers via granulation is a possible route [9], although in these preliminary investigations only partial coating was achieved. The coating process was complicated by the geopolymerisation reaction, and guidelines for the coating process were needed.

The purpose of this study is to determine the main factors influencing the product specifications. This should be done by gaining more knowledge on the coating process. Therefore, the operating windows of the used geopolymer coatings are obtained first. With the operating windows, the granulation mechanisms of the different coatings are determined. Using the information obtained in these two experiments, the healing agent particles are coated using different activator liquids. Coated particles should replace the sand fraction in concrete, and should therefore be 1-4 mm in diameter [1].

Metakaolin is the only solid aluminosilicate source used in order to reduce complexity of the reaction. The coatings are tested for water tightness and compressive strength. Furthermore, the coated particles are incorporated into cement paste and tested by splitting the hardened cement in order to investigate the behaviour of the coating. After discussing the results, conclusions regarding the validity of using geopolymer coated particles in cement are drawn and recommendations for improving the process are presented.

## 2. Experimental

In order to coat the healing agent particles, the operating window and granulation mechanism were determined. After coating, leaching and strength tests were performed on the particles. Furthermore, coated particles were incorporated into cement paste and analysed using X-ray tomography in order to determine the behaviour of the particles in a cementitious phase. In this chapter, the procedures of the experiments are explained.

### 2.1. Coating healing agent particles with a geopolymer coating

Healing agent particles, composed of 95-99 wt% nutrients and bacterial spores (genus *Bacillus*) [4] were coated

with a geopolymer coating. Coatings were produced from metakaolin (AGS Mineraux sample, ARGICAL-M 1000) and five different activator liquids. The compositions and nomenclature of the activator liquids can be found in Table 1.

Batches of 100 g of healing agent particles were coated in a rotating disk granulator (MINHUA Pharmaceutical Machinery Co., BY-400 Coating Machine. Metakaolin and activator liquid were added in an alternating fashion. Either a low pressure single-fluid nozzle (Gardena 806 sprayer) or a high pressure single-fluid nozzle (Wagner W 450 SE airless paint sprayer) were used to nebulise activator liquid. Acceptable liquid/metakaolin ratios had been determined by investigating the minimum and maximum amounts of activator liquid that could be added for granulation. The obtained values are referred to as the *operating window*. The used ratios are listed in the last row of Table 1.

Table 1: Compositions, nomenclature and amounts of activator liquids used. X.XX R stands for the molar ratio of Na/Si or Na/Al.

<b>Activator liquid</b>	<b>0.3 R Na-Si</b>	<b>0.5 R Na-Si</b>	<b>0.8 R Na-Si</b>	<b>2.74 R Na-Al</b>	<b>3.91 R Na-Al</b>
<b>Na<sub>2</sub>O/SiO<sub>2</sub> (mol)</b>	0.29	0.50	0.80	-	-
<b>Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> (mol)</b>	-	-	-	2.74	3.91
<b>wt% Na<sub>2</sub>SiO<sub>3</sub></b>	34.90	32.44	29.49	0.00	0.00
<b>wt% Na<sub>2</sub>AlO<sub>3</sub></b>	0.00	0.00	0.00	21.81	10.77
<b>wt% NaOH</b>	0.00	7.05	15.49	12.90	11.60
<b>wt% H<sub>2</sub>O</b>	65.10	60.51	55.02	65.30	77.63
<b>g liquid/5 g MK</b>	4.3	3.0	3.0	2.9	3.0

Table 2: Names and properties of all batches prepared.

Batch	Activator	Spraying nozzle	MK (g)
1	0.3 R Na-Si	Low pressure	60
2	0.5 R Na-Si	Low pressure	60
3	0.8 R Na-Si	Low pressure	60
4	2.74 R Na-Al	Low pressure	60
5	3.91 R Na-Al	Low pressure	60
6	0.3 R Na-Si	High pressure	60
7	0.5 R Na-Si	High pressure	60
8	0.8 R Na-Si	High pressure	60
9	2.74 R Na-Al	High pressure	60
10	3.91 R Na-Al	High pressure	60
11	0.3 R Na-Si	High pressure	200

A total of 11 batches of coated particles were prepared. The used activator liquids, spraying methods and amount of metakaolin added can be found in Table 2. Five batches were prepared with a low pressure nozzle sprayer. In order to improve nebulisation, a high pressure nozzle sprayer was used to prepare another five batches. Batches 1, 2, 3, 4 and 5 were produced using the same activator liquids as batches 6, 7, 8, 9 and 10, respectively. Therefore, the performance of the use of low and high pressure nozzle sprayers in the process can be compared. Additionally, one batch was produced using 200 g of coating material in order to increase coating thickness.

### 2.2. Leaching of calcium ions from the coated particles

All batches produced were tested for leaching of calcium lactate by using a Tetra test for general hardness. 3 g of coated particles were added to 1 L of demineralised water. A 2 cm stirring magnet was used at 100 rpm to provide some convection without damaging the particles. After 5, 15, 30, 45, 60 and 180 minutes, a 1 mL sample was taken. Next, the particles were crushed, the stirring speed was increased to 900 rpm for 10 minutes and a final 1 mL sample was taken. Samples were diluted with 4 mL of demineralised water and tested for a colour change. For batch 11, samples were not diluted since the maximum calcium concentration was lower than that of the other batches. Instead, 5 mL samples were taken.

### 2.3. Compressive strength testing of coated particles and geopolymer cubes

In order to compare the strength of coated particles to the strength of uncoated particles, particles from all batches were tested in a compression stage (Kammrath & Weiss tension/compression stage). The stage was displacement controlled. For batches 1-5, 15 particles from each batch were tested with a displacement rate of 0.02 mm/s. In order to quickly verify the suspicion that all coated particles were about equally strong, 6 particles from batch 6 and 3 particles from batches 7-11 were tested. A displacement rate of 0.005 mm/s was used in order obtain more accurate results.

The compressive strengths of the five different coating materials were compared by preparing eight 20x20x25 mm geopolymer cubes for each different activator liquid. The used metakaolin to activator liquid ratios were those used for the coating process. In order to increase workability, demineralised water was added. A sixth series of 8 cubes was prepared without the addition of demineralised water in order to determine the effect of increasing the water content on compressive strength. A list of the compositions of the geopolymers can be found in Table 3.

After one week of curing, 3 cubes were tested for compressive strength in a Macben hydraulic press. The press was load controlled with a slope of 0.5 kN/s. After three more weeks of curing, the remaining 5 cubes were tested.

Table 3: Compositions of geopolymer mixtures used for strength testing.

Series	Solution	g MK/g activator	g water/g activator
I	0.3 R Na-Si	1.16	0.00
II	0.5 R Na-Si	1.67	0.50
III	0.8 R Na-Si	1.67	0.50
IV	2.74 R Na-Si	1.72	1.00
V	3.91 R Na-Si	1.67	1.00
VI	0.3 R Na-Si	1.16	0.50

#### 2.4. Incorporation of coated particles in cement paste

Particles from batches 1 and 6 were incorporated in cement paste in order to investigate both the interaction between the coating material and the cementitious phase and the dissolution of the healing agent in a realistic situation. For both batches, particles larger than 2 mm and particles between 1 and 2 mm were used. For the cement paste, a water to Ordinary Portland Cement (CEM I 42.5 N) mass ratio of 0.5 was used.

The cylindrical cement paste sample was divided in four layers. The bottom and layers contained coated particles larger than 2 mm from batches 1 and 6, respectively. For the second and fourth, particles between 1 and 2 mm from batches 1 and 6 were used. The sample was scanned in its mould after eight days of curing using X-ray tomography. After three weeks, the sample was split with a hydraulic press in order to test splitting behaviour of the coating.

### 3. Results and discussion

In this chapter, we will first treat the coating process, Next, the results from the leaching and compressive strength testing and the incorporation of particles in cement paste are summarised and analysed.

#### 3.1. Coating of healing agent particles with a geopolymer coating

During coating with the low pressure nozzle sprayer, agglomerates were clearly formed due to poor nebulisation. The high pressure nozzle sprayer nebulised the liquid better than the low pressure nozzle, although droplets formed at the tip of the nozzle. Such droplets occasionally fell into the granulator, causing additional agglomeration.

Table 4: Particle size distributions of produced batches.

Batch	d<1 mm (wt%)	1<d<4 mm (wt%)	d>4 mm (wt%)
1	3.2	41.1	55.7
2	3.1	33.7	63.3
3	2.8	23.2	74.0
4	2.1	35.1	62.8
5	3.0	44.5	52.5
6	10.1	47.5	42.4
7	13.3	46.5	40.2
8	2.2	41.6	56.3
9	8.9	31.9	59.2
10	10.8	39.4	49.7
Batch	d<2.24 mm (wt%)	2.24<d<4 mm (wt%)	d>4 mm (wt%)
11	24.2	50.7	25.1

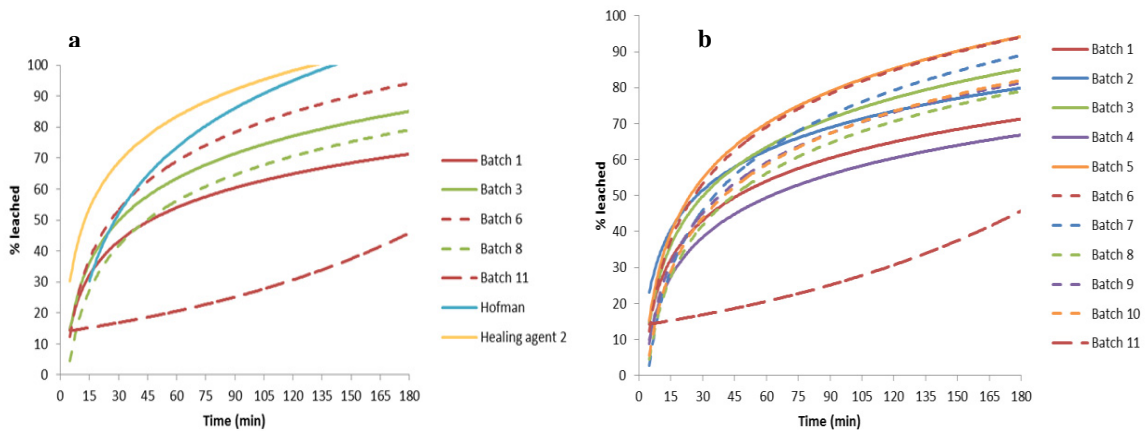


Figure 2: (a) Comparison of leaching from prepared particles compared to uncoated healing agent and Hofman's coated healing agent. (b) Percentage calcium lactate leached from the coated particles as a function of time for all batches. Batches prepared with the same activator liquids but different spray methods are represented by the same colour.

Another disadvantage of the high pressure nozzle sprayer was the lack of control over the spray pattern. For the prepared batch sizes, the spray cone was too wide. Therefore, activator liquid and coating material stuck to the wall of the granulator. Despite these two disadvantages, batches prepared with the high pressure nozzle sprayer contained fewer agglomerates than batches produced with the low pressure nozzle sprayer. This difference can be clearly observed from the particle size distributions shown in Table 4. Particle size distributions were obtained by sieving. For batch 11, a sieve with a mesh size of 2.24 mm was used in order to prevent overloading of the sieve.

Batches 1, 2, 3, 4 and 5 should be compared to batches 6, 7, 8, 9 and 10, respectively, since those batches were prepared with the same activator liquid. The fraction of particles larger than 4 mm, which mainly consisted of agglomerates, decreased for all batches. The fraction of particles with a desired diameter of 1-4 mm did not necessarily increase, as observed from the behaviour of batches 9 and 10. This is likely caused by the spray pattern of the high pressure nozzle sprayer, which results in loss of fluid to the wall, reducing the actual amount of liquid used for coating.

### 3.2. Leaching of calcium ions from the coated particles

Figure 2a shows how well coated particles from batches 1, 3, 6, 8 and 11 performed compared to healing agent particles and particles produced by Hofman [9]. Under low convection, uncoated healing agent particles were fully dissolved after two hours. Coated healing agent particles were better protected against dissolution than untreated healing agent particles. All coated particles outperformed those prepared by Hofman [9]. Particles from batches 1-10 appear to lose 65-100 % of the coated healing agent after 3 hours regardless of the nebulisation method used in the coating process, as demonstrated in Figure 2b. Particles from these batches all fall within this range, but in order to better compare the performances of the different batches produced, a more accurate method should be used.

Particles from batch 11 were more resistant to leaching than particles from other batches. This result shows that increasing coating thickness leads to better protection of the healing agent.

### 3.3. Compressive strength testing of coated particles

For the breakage behaviour of particles, two events were discerned. The first event was defined as loss of coating material. Loss of loose powder was not included in this definition. Breakage of the healing agent core was considered the second event. The results of the test are shown in Table 5. Numbers between brackets indicate the number of particles tested.

Table 5: Average strength of coated particles and standard deviations. Numbers between brackets indicate the number of particles tested. Healing agent is abbreviated as HA.

<b>Batch</b>	<b>1 (15)</b>	<b>2 (15)</b>	<b>3 (15)</b>	<b>4 (15)</b>	<b>5 (15)</b>	<b>6 (6)</b>	<b>7 (3)</b>	<b>8 (3)</b>	<b>9 (3)</b>	<b>10 (3)</b>	<b>11 (3)</b>
Load at event 1 (N)	2.85	2.52	2.69	1.20	2.24	1.96	3.00	2.16	2.21	1.29	2.12
Std. Dev. (N)	1.20	1.19	0.90	0.60	1.20	1.03	0.86	1.18	1.34	0.66	0.82
Load at event 2 (N)	15.18	14.58	12.46	8.70	11.11	12.44	12.73	11.10	10.59	8.76	10.22
Std. Dev. (N)	6.26	5.27	4.50	4.68	4.94	5.18	2.26	0.84	2.31	4.80	1.83

Loss of coating occurred at relatively low loads, between 1 and 3 N. In order to damage the healing agent core, loads above 10 N were generally required. Batches 1-5 all showed similar behaviour. This observation implies that the coating material was much weaker than the healing agent particle core. A coating weaker than the particle core is acceptable as long as the coating fulfils its purpose of protecting the healing agent from dissolution until it is incorporated into the concrete matrix.

Particles from batches 6-11 were tested in order to compare the results to support the observation that all particles behave similarly, regardless of the coating material. As expected, values comparable to those of the other coated particles were found. Since such values are based on only 3 measurements, the values only serve as an indication to support the conclusions.

Compressive strengths of the geopolymer cubes are listed in Table 6. After seven days of curing, all cubes had reached similar compressive strengths, except for those prepared with a 0.8 R Na-Si solution. After 28 days of curing, however, all strengths were comparable. This shows that most of the compressive strength develops within the first seven days for five of the six series prepared. Moreover, the final strengths were close. For the samples prepared with and without the addition of demineralised water, series I and VI, strengths are comparable.

Since coating strengths are similar and the coating does not contribute to the strength of the coated particles, the strength of the particles does not have to be taken into account when selecting the coating material.

### 3.4. Incorporation of coated particles in cement paste

CT-scans, shown in Figure 3, revealed that particles coated with a high pressure nozzle sprayer (A and B) retained healing agent, whereas particles prepared with a low pressure nozzle sprayer were completely hollow (C). Agglomerates prepared with the high pressure nozzle (D) also retained healing agent. This was in agreement with visual observations, since the agglomerates consumed most of the activator liquid and metakaolin during the coating process.

Considering the leaching results from section 3.2, the difference between particles from batch 1 and 6 was noteworthy. Although batch 1 outperformed batch 6 slightly in the leaching experiments, actual incorporation of particles in cement clearly showed that particles from batch 6 protected the healing agent better from dissolution. This result shows that the conditions in cement paste were completely different from the conditions in demineralised water. Therefore, leaching tests should not be used as the sole basis for making a decision about the optimal coating.

Since no air was observed between the coating material and the cementitious phase, the interaction between cement paste and the coating appeared to be sufficient. This observation was supported by splitting the cement sample. The crack interface went straight through the particle.

Table 6: Average strength of geopolymer blocks after 1 and 4 weeks of curing.

<b>Series</b>	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>	<b>VI</b>
Average strength (MPa) after 1 week	29.24	27.13	17.85	28.80	28.79	29.51
Std. Dev. (MPa)	2.94	0.82	1.55	0.37	2.93	3.13
Average strength (MPa) after 4 weeks	29.85	29.32	25.25	28.32	28.38	27.12
Std. Dev (MPa)	0.92	0.28	1.97	0.94	0.83	0.80



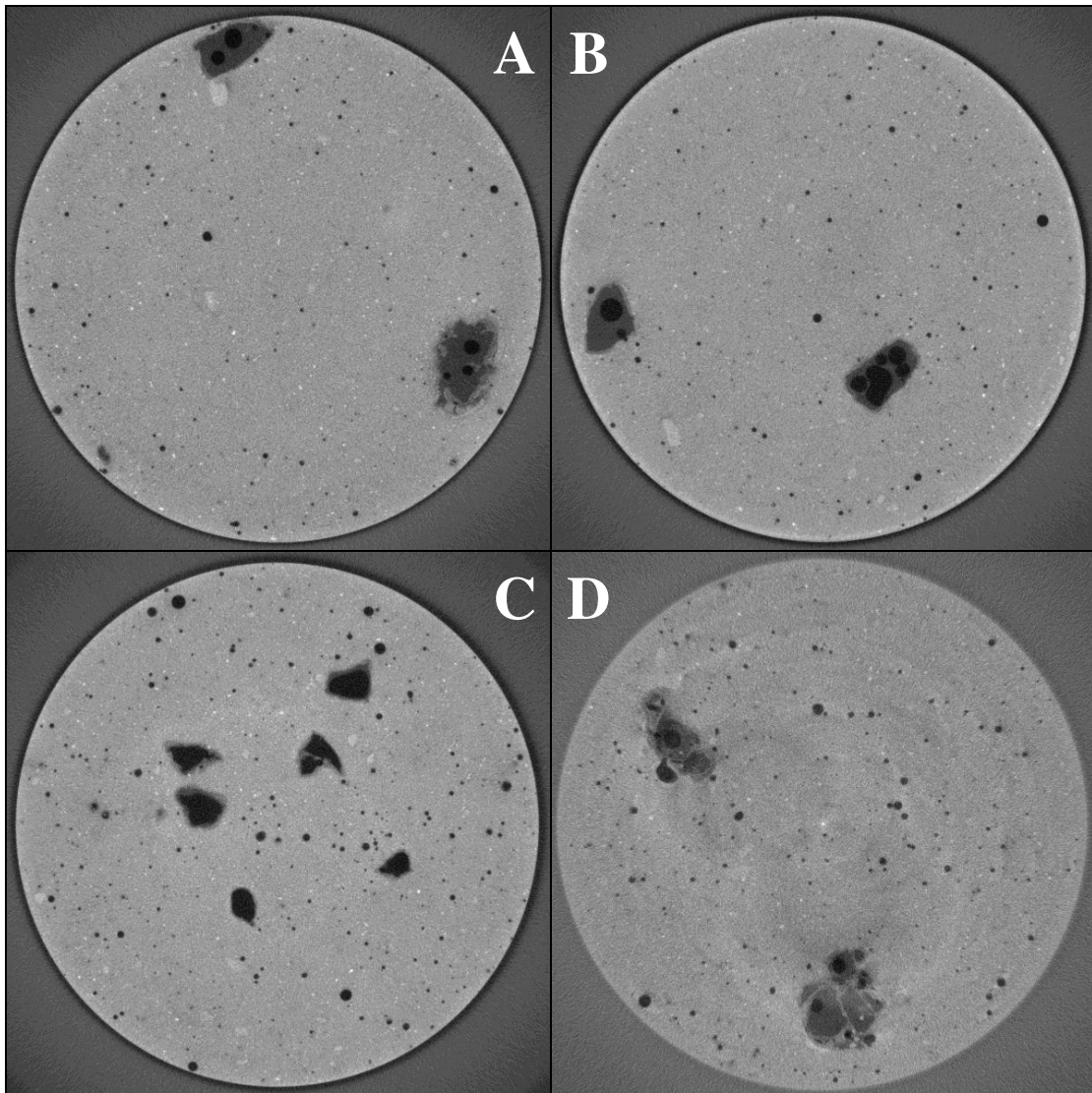


Figure 3: Top view CT scans of (A) and (B) particles larger than 2 mm from batch 6, (C) particles between 1 and 2 mm from batch 1 and (D) agglomerates from batch 1. In order of increasing black saturation: cement paste (light grey), coating, healing agent and air (black).

### 3.5. Outlook

In future research, a better control over the width of the spray is recommendable. Moreover, one should aim at increasing the coating thickness, either by coating multiple times or by coating for a longer amount of time with more material. For the former option, there is more risk of the formation of agglomerates. For the latter option, the coating might crack due to shrinkage of the geopolymer layer. Since agglomeration causes unwanted loss of materials and the particles from batch 11 were cracked but still showed good leaching behaviour, coating for a longer time is probably the best option. As the particles were incorporated into cement paste, the performance of the particles in a concrete mixer in which aggregates might damage the particles has not yet been determined. Cracking tests so far have only focused on splitting, whereas such cracks rarely occur in reality. Bending tests and other more realistic experiments should be performed in order to determine the cracking behaviour of the particles. To ensure

coated particles were broken by cracks and not by taking the samples apart, the cracks can be investigated with computed tomography first. When finally deciding which material to apply in practice, other considerations than just the best performance have to be taken into account. The 0.3 R Na-Si solution used is relatively cheap and safe, which makes this solution more attractive for industrial use than the other activator liquids.

#### 4. Conclusions

This study has provided a theoretical base in order to achieve a well-defined geopolymer coating of healing agent particles. By determining the operating window and coating mechanism, the coating process is no longer a black box that has to be monitored closely in order to achieve coating. Furthermore, nebulisation has been improved in order to create a better distributed coating, reducing agglomeration. The coated particles are better protected from leaching than untreated particles. Finally, the coating material appears to interact sufficiently with the concrete matrix.

#### Acknowledgements

The authors would like to thank AGS Mineraux for generously providing the metakaolin sample used for this study. Furthermore, we would like to express their gratitude to Rijk Zwaan Production B.V. for sharing knowledge on coating processes in low-shear granulators.

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