Granulation and coating with Geopolymer Binders

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Study Geology, Mineralogy, Ore Deposits at VU Amsterdam 1978

Development programs:

Cameroun
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From 1994: TU Delft
Research: New Products from waste materials (PhD in 2010)

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GRANULATION

GOAL
TECHNOLOGY OF GRANULATION
TECHNOLOGY OF GRANULATION
TECHNOLOGY OF GRANULATION

Or is it an art?

Liquid content is crucial
STAGES OF WETTING

A) Pendular state

B) Funicular state

C) Capillary state

Growth regimes:
- Steady Growth
- Induction Growth
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

\[ [4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3] + 10 \text{OH}^- + 3 \text{H}_2\text{O} \rightarrow 2 \text{[Al(OH)]}_4^- + 4\text{[SiO}_2\text{(OH)}_2]^{2-} \]

\[ \text{[Al(OH)]}_4^- + \text{[SiO}_2\text{(OH)}_2]^{2-} \xrightarrow{-\text{H}_2\text{O}} \begin{pmatrix} \text{HO} & \text{O}^- \text{Si} & -\text{O}^- & \text{Al}^- & -\text{OH} \end{pmatrix} \]

polycondensation

\[ \begin{pmatrix} -\text{Si} & -\text{O} & -\text{Al}^- & -\text{O} & -\text{Si} & -\text{O} & - \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \end{pmatrix} \]

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LIQUID REQUIRED

More sand:
- less liquid in mix
- higher liquid to precursor ratio

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STRENGTH MEASUREMENTS

Granule breaking point.
Minor damage.
Granule still intact.
Granule rotating.
STRENGTH OF GRANULES

![Graph showing strength of granules vs percentage of slag in FA/slag mixture. The graph compares NaAlu and KSil samples.](image)

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STRENGTH OF GRANULES

![Graph showing the strength of granules in relation to the percentage of sand in the FA/Slag/Sand mixture. The graph compares NaAlu and KSil samples.](image-url)
WOOD ASH PERFORMANCE

![Graph showing the relationship between Wood Ash to PFA/Wt% and Breaking Force/N. The graph indicates a peak breaking force at approximately 60 Wt% of Wood Ash to PFA.](Image)

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But:

Do we really have chemical reaction?

XRD
But:
Do we really have a 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
COATING OF SELFHEALING PARTICLES

PRINCIPLE OF SELF-HEALING
Concrete without healing agent

Just cracked

After healing period
Concrete with healing agent

Just cracked

After healing period
Low Shear Pan Granulator
Shape of particles to be coated
CT Scans
Coated particles

Metakaolinite geopolymer coating

ESEM images
## Water tightness

<table>
<thead>
<tr>
<th>Leaching solution</th>
<th>Sample</th>
<th>Ca (mg/l)</th>
<th>Al (mg/l)</th>
<th>Si (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 M HCl</td>
<td>Coated core</td>
<td>28.2</td>
<td>15.7</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Coating only</td>
<td>3.4</td>
<td>31.3</td>
<td>2</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>Coated core</td>
<td>1.6</td>
<td>85.5</td>
<td>629</td>
</tr>
<tr>
<td></td>
<td>Coating only</td>
<td>1.9</td>
<td>248</td>
<td>1123</td>
</tr>
</tbody>
</table>
Adhesion to cement paste

Cracking behaviour
Cracking of coating
Cracking of coating
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

![Graph showing the induction growth for different samples.](image-url)
## Composition of solid precursors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition, %</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>P</td>
<td>11.6</td>
<td>44.9</td>
</tr>
<tr>
<td>S</td>
<td>39.5</td>
<td>34.5</td>
</tr>
<tr>
<td>C</td>
<td>4.9</td>
<td>54.3</td>
</tr>
<tr>
<td>M</td>
<td>0.1</td>
<td>59.5</td>
</tr>
</tbody>
</table>
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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