(A few aspects of) Geopolymer durability

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Geopolymers – aluminosilicates

Precursors
- Metakaolin
- Fly ash
- GGBS
- Silica fume, sediments, etc.

Activator (alkaline solution)
- Alkali hydroxide
- Alkali silicates
- Alkali carbonates
- etc.
Geopolymers – aluminosilicates

MK  Metakaolin
F.FA  Fly ash (class F)
C.FA  Fly ash (class C)
SF  Silica fume
GGBS  Ground gran. Blastf. slag
OPC  Ordinary Portland cement

- More calcium → towards hydraulicity
Geopolymers – aluminosilicates

- Quartz
- Calcite
- Anatase
- Kaolinite
- Mullite

Metakaolin
Geopolymer

Weakly bound water ➔ No hydrates

90% of water lost at 105°C

Pouhet, Cyr, Bucher, CBM 2019

Barbosa et al, 2000
Durability... a huge topic

- Geopolymers: not the same chemistry as Portland cement or alkali-activated slag (calcium-based systems)
  - Different (pore) structure
  - Effects on the durability

- Ageing
  - Stability of the material over time
  - How it will react with its environment

- Structure and composition
  - Amorphous → less stable than some crystalline phases
  - Alkalis → less bounded
  - Porous network → more or less connected
Durability... a huge topic

Weathering

Exposure classes
- Air (CO$_2$, UV...)
- Natural water (leaching...)
- Chemicals (acid, chlorides, sulfates, carbonates...)
- Frost

Sea water
CO$_2$
Natural water
Acid
Frost
Sulfates, carbonates
Durability... a huge topic

Concrete parameters influencing durability
- Porosity
- Permeability

Concrete deterioration
- Internal attacks (alkali–silica reaction (ASR), delayed ettringite formation (DEF))
- Aggressive chemical environments (sulphates, acid)
- Frost (freeze–thaw)
- Mechanical stress (abrasion)

Reinforced concrete deterioration
- Corrosion (carbonation, chlorides)

On pastes

**Porous network**

**H$_2$O/Na$_2$O**

<table>
<thead>
<tr>
<th>$\Phi_w$ (%) $T_{séchage}=105°C$</th>
<th>14.5</th>
<th>17</th>
<th>20</th>
<th>CEM I 52.5 ($w/c = 0.5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>49%</td>
<td>53%</td>
<td>56%</td>
<td>44%</td>
</tr>
</tbody>
</table>
Mass ratio **Water/Solid**

- Control of the porosity of the mixture

**Effect of water content**

Sharp decrease in performance with the addition of water, even worse than for portland cements

Cyr M., The Indian Concrete Journal, 94 (7) (2020) 5-13
Monomodal size distribution of pores?

Porous network

Pouhet, Cyr, Bucher, CBM 2019
SEM observations made on a section obtained by cutting with focused ion beam technique → see inside the material without degrading the porous network

- **Large** pores (200-500 nm macropores), formed by the dissolution of metakaolin during geopolymerization
- **Connected** (?) to each other by an interconnected monomodal fine pores network (10-40 nm mesopores)

Pouhet, Cyr, Bucher, CBM 2019
Porous network

- Consequences? (on pastes)
  - Drying
Consequences? (on pastes)

- Drying
- Leaching

Evolution of pH and composition of the extracted pore solution of geopolymer pastes after 28 days of ageing, and then after 1.5 months contact with deionized water (pH = 6.8)

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>GEO-28D-ENDO (No contact)</th>
<th>GEO-1.5M-W Deionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (mmol/L)</td>
<td>Concentration (mmol/L)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>415 ± 12</td>
<td>69 ± 5</td>
</tr>
<tr>
<td>K⁺</td>
<td>3.4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>27 ± 2</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>&lt; 0.1</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

Benavent, Lahalle, Patapy, Glid, Renaudin, Cyr
Stability of a sodium metakaolin-based geopolymer paste in neutral and CEM V basic environment
Porous network

- Consequences? (on pastes)
  - Drying
  - Leaching
  - Carbonation

Evolution of the pH pore solution in time

- After a year the pH in natural condition is lower: carbonation occurred
- The carbonation is fast and seems to begins from the second day in presence of CO₂
- But the pH remains “high” even after carbonation → less corrosion?
Consequences? (on pastes)

- Drying
- Leaching
- Carbonation (efflorescence)

After 7 days semi-immersed

1 photo every 5 minutes during 48 h

Pouhet, PhD, 2015
Porous network

• Consequences? (on pastes)
  ✓ Drying
  ✓ Leaching
  ✓ Carbonation

Could lead to scaling

Possible to decrease the leaching, for instance by adding small calcium sources (e.g. GGBS...)

Pouhet, PhD, 2015
Porous network

• Consequences? (on pastes)
  ✓ Drying
  ✓ Leaching
  ✓ Carbonation

• But
  ✓ Water permeability $K_{\text{water}}$ of $1.4 \times 10^{-18}$ m$^2$

  ✓ Air permeability (Cembureau) $K_{\text{gas}}$ of $10 \times 10^{-18}$ m$^2$

  Good durability, according to references on Portland cement

Cracking of the paste???
(effect of drying)
Accelerated testing?

• Tests developed for Portland cement
  ✓ Calcium-based cements
  ✓ Chemical equilibrium (with alkalis…)

  e.g. “Cure in water saturated with lime”

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Example of accelerated carbonation

Accelerated test

% CO₂

Natural conditions

Bernal et al. 2012
Accelerated testing?

• Tests developed for Portland cement
  ✓ Calcium-based cements
  ✓ Chemical equilibrium (with alkalis…)

Control solution

Accelerated tests
  - Different reaction products
  - Could lead to false conclusions regarding the risk of corrosion

depassivation of steel reinforcements
Accelerated testing?

- Tests proposed in the literature usually require a **preconditioning** of the specimens, especially a drying step at temperatures, ranging from:
  - 45°C (e.g. accelerated carbonation XP-P-18-458, 2008)
  - to 80°C (e.g. gas permeability XP-P-18-463, 2011)
  - or even to 105°C (e.g. porosity NF-P-18-459, 2010)

![Graph showing small increase in compressive strength (CS) with endogenous cure.](image)

62 MPa (28 days) vs. 68 MPa (63 days) with no drying.
• Tests proposed in the literature usually require a **preconditioning** of the specimens, especially a drying step at temperatures, ranging from:
  
  ✓ 45°C (e.g. accelerated carbonation XP-P-18-458, 2008)
  ✓ to 80°C (e.g. gas permeability XP-P-18-463, 2011)
  ✓ or even to 105°C (e.g. porosity NF-P-18-459, 2010)

No drying: **Endogenous**
Accelerated testing?

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No drying: **Endogenous**

40°C **Drying:**

No variation for $T = 40°C$
Accelerated testing?

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![Graph showing strength loss for T ≥ 50°C](Image)

Strength loss for T ≥ 50°C

<table>
<thead>
<tr>
<th>No drying:</th>
<th>Endogenous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying:</td>
<td></td>
</tr>
<tr>
<td>50°C</td>
<td></td>
</tr>
<tr>
<td>125°C</td>
<td>40°C</td>
</tr>
<tr>
<td>105°C</td>
<td>20°C-50%RH</td>
</tr>
<tr>
<td>80°C</td>
<td>20°C-vacuum</td>
</tr>
<tr>
<td>60°C</td>
<td>20°C-95%RH</td>
</tr>
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Accelerated testing?

• What was seen
  Trincal, ..., Cyr, CCR 2022
  - Drop in mechanical strength with oven drying at temperatures of 50°C to 125°C
  - Damages correlated with an increase in both MIP porosity and pore size
  - Drying at over 50°C → nano- to micro-cracking

• Recommendations
  Trincal, ..., Cyr, CCR 2022
  Oven drying at a temperature of 40°C appears to provide a good compromise between quite efficient drying and little resulting damage, even if not all free water is removed.
To conclude...

- Geopolymers are very different from Portland cements
- So they must not (always) be analysed the same way

Professor Zapinsky proved that Portland cement is more durable than geopolymers when tested under similar conditions...