The Role of Al$_2$O$_3$, SiO$_2$ and Na$_2$O on the Amorphous $\rightarrow$ Crystalline Phase Transformation in Geopolymer Systems

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Geopolymers - Chemistry

• Group of inorganic polymers

• **Synthesis**
  \[(\text{Al}_2\text{O}_3 + \text{SiO}_2) + \text{Alkaline activator} \rightarrow \text{geopolymers}\]

• **Mechanism**
  dissolution, orientation, polycondensation → polymeric network

• **Chemical formula**
  \[M_n[-(\text{SiO}_2)_z -\text{AlO}_2]_n \cdot w\text{H}_2\text{O}\]
  
  \[(Z = 1,2,3 \quad n= \text{degree of polymerisation})\]

  \[\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot3.8 \text{SiO}_2\cdot12 \text{H}_2\text{O} - (\text{cement composition})\]

• Amorphous or semi crystalline
Geopolymers & Zeolites

Zeolites – a class of aluminosilicate cpds

Similarities

• Raw materials
• Mechanism of reaction
  (dissolution, orientation, condensation
gel like -> crystalline)
• Chemical composition
Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O compositional diagram

- geopolymer
Na$_2$O.Al$_2$O$_3$.3.8 SiO$_2$.12 H$_2$O (cement composition)

- Zeolites

MK – Metakaolin
FA – Fly Ash
RHA – Rice husk ash
Geopolymers & Zeolites

Differences

• **Microstructure**
  - Geopolymers: amorphous or semi-crystalline
  - Zeolites: crystalline

• **Different properties → Different Applications**
  - (identified in Portland cement – radioactive waste encapsulation)

• Thermodynamically geopolymers are metastable
• Crystalline structures identified in geopolymer matrix
• Long term stability of geopolymer phase?
Geopolymers & Zeolites

Some differences in synthetic conditions

Factors Controlling synthesis

- Curing temperature
- Ageing time
- Reaction rate
- Concentration of Alkaline activator (Na$_2$O)
- Water content
- SiO$_2$ & Al$_2$O$_3$ content

The degree of crystallinity is largely determined by product formulation and synthesis conditions.

-very important in geopolymer product development
AIM

- Effect of SiO$_2$, Al$_2$O$_3$ & Alkali oxide on the stability of geopolymer phase with respect to crystallisation
- Low temperature curing regimes
- Long term stability & Impact on the physical properties
Materials & Experimental

- Metakaolin (complete reactivity)
- Sodium silicate / sodium hydroxide
- Curing temperature – 40°C
- Curing time - 7 months
- Compressive strength
- Phase development (XRD, SEM, EDAX)
Mix Formulations

Changing SiO₂ content
Mix 1, 2, 3 (Si38, Si30, Si25)

Changing Al₂O₃ content
Mix 4, 2, 5 (Al06, Al10, Al12)

Changing Na₂O content
Mix 6, 2, 7 (Na07, Na10, Na14)

(Y, X, A, P, S, HS)

Zeolite compositions

Geopolymers - metastable
## Mix Formulations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial composition</th>
<th>SiO₂ (moles)</th>
<th>Al₂O₃ (moles)</th>
<th>Na₂O (moles)</th>
<th>SiO₂/Al₂O₃ (molar ratio)</th>
<th>Al₂O₃/Na₂O (molar ratio)</th>
<th>SiO₂/Na₂O (molar ratio)</th>
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<tbody>
<tr>
<td>Si-38</td>
<td>1.0Na₂O.1.0Al₂O₃.3.8SiO₂.13.6H₂O</td>
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<td>Si-25</td>
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<td>1.00</td>
<td>2.50</td>
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<td>Al-06</td>
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<td>0.60</td>
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<td>Al-10</td>
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<td>1.00</td>
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<td>Al-12</td>
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<td>3.00</td>
<td>1.2</td>
<td>1.0</td>
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<td>1.20</td>
<td>3.00</td>
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<td>Na-07</td>
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<td>Na-10</td>
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<td>Na-14</td>
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<td>2.14</td>
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</table>

**SiO₂ series** – Si38, Si30, Si25  
**Na₂O series** – Na07, Na10, Na14  
**Al₂O₃ series** – Al06, Al10, Al12  
**H₂O - CONSTANT**
Compressive Strength Development

Si-38 > Si-30 > Si-25
Al-10 > Al-06 > Al-12.
Na-07 > Na-10 > Na-14

High strengths  Si38, Si30, Na07 (High SiO₂, Low Na₂O)
Low strengths  Si25, Al 12, Na14 (Low SiO₂, High Al₂O₃, High Na₂O)
Phase Development – XRD
(High Strength Category)

Amorphous phase throughout
(broad band around 28° 2-theta)
Similar pattern for Na-07 & Si-30

Mix Formulation – Si-38 High Strength Category
Microstructure - SEM
(High Strength Category)

Na-07, Si-38 and Si-30
Dense, homogeneous phases
Phase Development – XRD (Low Strength Category)

- Transition of amorphous to crystalline (mainly Zeolite A & Zeolite P)
- Associated with low strengths
Microstructure – SEM
(Low Strength Category)

Si 25
Porous microstructure

Higher magnification of Si 25
EDAX – Zeolite P
Conclusions

• Amorphous -> crystalline transformation occur in some mixtures

• High Al₂O₃ (SiO₂/Al₂O₃ = 2.5) and High Na₂O (Na₂O/SiO₂ = 1.4) favours amorphous → crystalline transformation

• Na₂O·Al₂O₃·3.8SiO₂·13H₂O – no tendency towards phase transformation

• Tentative relationship between development of crystalline phases and low strengths

• Initial mix formulation – key parameter

• findings can be relevant to the practical phase development of geopolymer systems under initial prolonged exposure to mild temperatures and high humidity levels.
THANK YOU