Phosphate-based Geopolymer

a review of recent literature

Joseph Davidovits
#8 Phosphate-based geopolymer

In acidic medium

phosphoric acid H₃PO₄
\[
\text{Al}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \implies 2\text{AlPO}_4 + 3\text{H}_2\text{O}
\]

\[
\text{(MK) Si}_2\text{O}_5\text{Al}_2\text{O}_2 + 2\text{H}_3\text{PO}_4 = \implies 2\text{AlPO}_4 + 2\text{SiO}_2 + 3\text{H}_2\text{O}
\]

**Geopolymer Book: Section 13.6 AlPO\textsubscript{4}-based geopolymers**

... AlPO\textsubscript{4} species: variscite AlPO\textsubscript{4}·2H\textsubscript{2}O, metavariscite AlPO\textsubscript{4}·2H\textsubscript{2}O and berlinite AlPO\textsubscript{4}. 100–300°C, variscite / metavariscite lose their water molecules to form \(\alpha\)-berlinite (trigonal AlPO\textsubscript{4}) stable phase up to 540°C, and > 550°C onwards tetragonal \(\beta\)-berlinite.

AlPO\textsubscript{4}-berlinite is **isostructural** with quartz SiO\textsubscript{2}, i.e. same molecular structure. Upon heating, same transitions as quartz, into tridymite and cristobalite equivalent molecular structures.

Transition from one form to the other is readily followed by X-Ray powder diffraction analysis.
Polymeric structures of AlPO₄-Geopolymers

⇒ Cross-linked (P-O-Al-O)n poly(alumino-phospho) chains

AlPO₄-berlinite (isostructural to quartz)

AlPO₄-tridymite/cristobalite
Synthesis and structure characterization of geopolymeric material based on metakaolin and phosphoric acid

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Abstract

A geopolymer material based on MK and phosphoric acid was synthesized from metakaolin at room temperature. The product of the geopolymerization has a polymeric Si-O-Al-O-P three-dimensional structure.

Material structure and geopolymerization mechanism were investigated using X-ray diffraction (XRD), infrared (FTIR) spectroscopy, and $^{29}$Si and $^{27}$Al magic angle spinning nuclear magnetic resonance (NMR). The XRD pattern of the obtained polymers is essentially amorphous.
Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials

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<table>
<thead>
<tr>
<th></th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>P/Al</th>
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<tbody>
<tr>
<td>MK / Na-PSS</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>MK / Phospho</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

Cast in sealed molds, kept at RT for 2 hours, 60°C for 24 hours. Removing the seals and kept at RT: Na-PSS demolded after 4 days, MK/Phospho after 14 days.
After Perera et al. (2008)

### Table 2 Physical and mechanical properties of the materials

<table>
<thead>
<tr>
<th></th>
<th>MKGP</th>
<th>MKSGP</th>
<th>MKP</th>
<th>MKSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD (g/cm³)</td>
<td>1.46</td>
<td>1.60</td>
<td>1.82</td>
<td>1.89</td>
</tr>
<tr>
<td>OP (%)</td>
<td>20</td>
<td>20</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CCS (MPa)</td>
<td>72 (5)</td>
<td>70 (6)</td>
<td>146 (17)</td>
<td>96 (10)</td>
</tr>
<tr>
<td>Shrinkage(^a) (%)</td>
<td>+0.7</td>
<td>+0.6</td>
<td>4.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

One standard deviation listed within brackets

\(^a\) Diametral shrinkage wet to dry on a wet basis, + indicates expansion
Note

Preparation of phosphoric acid-based porous geopolymers

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MK + H₃PO₄ 85% + Al powder for expansion and Al₂O₃ powder;
5 h at 80°C in sealed mold.

Excellent thermal stability up to 1400°C, porosity 85%, compressive strength ca. 7 MPa.
Phosphate-based geopolymers, with very low dielectric loss could be used as an insulated encapsulating material (for electronic devices): heat treatment at 300°C is lower than the usual temperatures for common packaging of ceramic materials.

The $2.4\text{H}_3\text{PO}_4\text{–Al}_2\text{O}_3\text{–}2\text{SiO}_2$ geopolymers are heat-resistant to approximately 1500°C. Therefore, the phosphoric acid geopolymers might serve as potential high-temperature packaging or encapsulating materials.
sealed container, 2 hours room t° before 60°C 24 hours, calcined clay + H₃PO₄ 85% with varying Si/P ratio. Best is Si/P = 2.25, equiv. to P/Al=1.
Phosphate-based geopolymer: Formation mechanism and thermal stability

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MK reaction with monoaluminum phosphate (MAP): Al(H\textsubscript{2}PO\textsubscript{4})\textsubscript{3}, powder in fact mixture of [Al(H\textsubscript{2}PO\textsubscript{4})\textsubscript{3}, AlPO\textsubscript{4}] and Al\textsubscript{2}(HPO\textsubscript{4})\textsubscript{3}. 
Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements

Hervé K. Tchakoute, Claus H. Rüscher, Elie Kamseu, Fernanda Andreola, Cristina Leonelli

24 hours room t° before 60°C 24 hours,
MK + H₃PO₄ of different concentration: molar 2 to 12 M good results, strength varying from 36 MPa to 93 MPa, whereas with 14 M = 0 MPa
Like Perera’s paper (2008), ageing 24 h at room $T^\circ$ and cure at 60°C, 24 h
- Na-poly(sialate) geopolymer: 63 MPa
- Phosphate-based geopolymer: 94 MPa
Polyimide fiber is not alkali resistant, yet acid-resistant. Good candidate for PH-based geopolymer composite.

Addition of 1.5% weight increase the Flexural strength from 10 MPa to 40 MPa.
Superhigh strength of geopolymer with the addition of polyphosphate

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Method to enhance the compressive strength of GP Na-poly(sialate) by addition of aluminum dihydrogen triphosphate (ATP).

Compressive strength reaches 160 MPa with an optimum 1.0 wt% ATP, i.e. 108% increase.

Fig. 1. Chemical structure of ATP.