The Geopolymer Route to High Tech Ceramics

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Outline

• Composition and starting materials
• Microstructure
• Processing route to ceramics
  – Oxides with tailorable CTE’s
  – Non-oxides nanocrystalline (SiC, Si₃N₄, SiAlON’s)

The term “geopolymer” was introduced by Joseph Davidovits to describe alkali aluminosilicate binders formed via the addition of aluminosilicate materials to alkaline silicate solution.

J. Davidovits, “Mineral Polymers and Methods of Making Them”
J. Davidovits, Geopolymer Chemistry and Applications, 4th Edition (2015), published by the Geopolymer Institute, St. Quentin, France

Terminology

Geopolymer Institute - www.geopolymer.org
Geopolymers (Polysialalates)

- Are a type of chemically bonded ceramics of chemical formula $M_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 11H_2O$

- Refractory inorganic polymers formed from both aluminum and silicon sources containing $AlO_4^-$ and $SiO_4$ tetrahedral units, under highly alkaline conditions ($NaOH$, $KOH$, $CsOH$) at room temperature

- They are a rigid, hydrated, alumino-silicate solid containing group I, charge-balancing cations

- They result in an amorphous, nano-particulate, nanoporous, impervious, acid-resistant, polymeric structure

- Metastable sodalite zeolite (when $Na$-based)
Geopolymer Composition

\[ 5\text{Si}^{+4}\text{O}_2 \]

\[ \text{M}^{+1}_2\text{O} \cdot \text{Al}^{+3}_2\text{O}_3 \cdot 4\text{Si}^{+4}\text{O}_2 \cdot 11\text{H}_2\text{O} \]

\[ \text{Al}^{+3}_2\text{O}_3 \cdot 2\text{Si}^{+4}\text{O}_2 \]

\[ \text{M}^{+1}_2\text{O} \cdot 2\text{Si}^{+4}\text{O}_2 \cdot 11\text{H}_2\text{O} \]

Metakaolin clay

“waterglass” or metasilicate solution
Alkali Activated Cements

KASH
(potassium aluminosilicate hydrate)

Stoichiometric geopolymer
**Geopolymers are a potential partial solution to global warming!**

- The manufacture of 1 ton of Portland cement liberates ~1 ton of CO₂
- Whereas the manufacture of 1 ton of geopolymers liberates ~0.25 tons of CO₂

### Comparison of OPC and Geopolymer (GPC) Composites

<table>
<thead>
<tr>
<th>Property</th>
<th>Portland Cement</th>
<th>Geopolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Flexure strength (MPa)</td>
<td>5-6</td>
<td>10-15</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Setting time (days)</td>
<td>28</td>
<td>1</td>
</tr>
</tbody>
</table>
Synthesis of Geopolymer
Raw Materials

- Slag (in the former USSR)
- Fly ash (Australia)
- Clays e.g. metakaolin (France, USA)
- Halloysite (New Zealand)
- Plasma incinerated utility waste (black glass) (UK)
- Recycled waste glass powder (cullet)
- Heated (1200 °C) basalt from volcanic tufts
- Calcined rice husks, bamboo leaves, elephant grass
How can a geopolymer form at RT?

Al(VI) in crystalline (Al₂O₃•2SiO₂•2H₂O)

Heat 750 °C/1h

Al(V) in amorphous Al₂O₃•2SiO₂ forms highly strained molecule

Dissolve at high pH

AlO₄⁻ tetrahedra and SiO₂•AlO₄⁻ oligomers in solution
How to make a geopolymer

The term “geopolymer” was introduced by Joseph Davidovits to describe alkali aluminosilicate binders formed via the addition of aluminosilicate materials to alkaline silicate solution.

Step 1
alkali silicate solution + Metakaolin clay

Step 2
Molar oxide ratio
- SiO$_2$ / Al$_2$O$_3$ 4.0
- K$_2$O / SiO$_2$ 0.25
- H$_2$O / K$_2$O 10
mix

Step 3
cast and seal

Step 4
store at RT or in an oven at low T
Geopolymers

PVA Mesh Used as Fiber Reinforcement (w/ added pigment)

Thick and Rigid

Thin and Flexible

Colored using common paint pigments and additives

2008/03/08 11:12
Geopolymers can be formed in plastic molds and colored
Microstructure
Typical GP XRD pattern shows a broad peak shift from metakaolin (a) to the resultant geopolymer (b), but says little about geopolymer structure other than it is amorphous

NMR gives great local information such as the coordination state of Al, which is predominantly 4-coordinated in geopolymers


Geopolymer Structure

- X-ray amorphous
- Al is integrated into a network of (IV) AlO$_4^-$ and SiO$_4$, such that the negative charge on AlO$_4^-$ is balanced by the alkali cation

Davidovits, J. Journal of Thermal Analysis 1991, 37, 1633
SEM micrograph of a fully reacted region of polysialate.
TEM of crushed Na-geopolymer
Microstructure of Precipitates

High resolution transmission electron microscopy (HRTEM) results for (a) NaGP, (b) KGP, and (c) CsGP.
High angle, annular dark field TEM (HAADF)
Nanoporosity in kaolin-based GP

Average logarithmic pore radius : 0.4362 nm
Average pore radius : 3.3711 nm
Porosity over weight : 0.3165 cm$^3$/g
Porosity over volume : 0.4106 cm$^3$/cm$^3$
Meso- and macro-pore surface over weight : 190.5778 m$^2$/g
Meso- and macro-pore surface over volume : 247.2794 m$^2$/cm$^3$
Total pore surface over weight : 274.6912 m$^2$/g
Total pore surface over volume : 356.4186 m$^2$/cm$^3$
Density of solid phase: 2.0481 g/cm$^3$

Nanoporosity in synthetic-based GP = 0.8 nm

Densities of single phase geopolymer using different Group I cations

<table>
<thead>
<tr>
<th>Alkali cation</th>
<th>Na</th>
<th>K</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Densities (g/cm$^3$)</td>
<td>1.51</td>
<td>1.47</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Porosity in geopolymers:

- $\text{H}_2\text{O}_2$ (45 µm)
- Canola oil (100’s µm)
- Kitty litter (bentonite)
- Alkoxy silanes (75 vol % at 1 µm pore size)*
- Excess $\text{H}_2\text{O}$ (reduces strength)

Calcination for Filtration

- Calcination (800 °C, 4h) to remove hydrophobic material under inert conditions
- Glassy structure shows substantial morphological change
  - Diffraction spectrum changes
  - Synchrotron data shows formation of cubic SiC

Premix peak at 24 2-Θ moves to 14 2-Θ Upon calcination. SiC is a trace phase

Noticeably increased porosity and slightly wider pores implies removal of film

No film is visible for even a 2.67 mol DIDE/mol GP sample after calcination
Pair Distribution Function (PDF) Work

- Novel materials are often disordered/complex on a local level
- PDF method – allow us to sit on an atom and look at our neighborhood
- PDF procedure:
  1. Collect total scattering data (X-ray or neutron) for material
  2. Subtract background and apply appropriate corrections to raw data
  3. This gives us the structure function, \( S(Q) \)
  4. Apply Fourier transform to get the PDF, \( G(r) \)

\[
S(Q) = \frac{I_{el,coh}(Q) + \left[ \langle f(Q) \rangle^2 - \langle f(Q)^2 \rangle \right]}{\langle f(Q) \rangle^2}
\]

\[
G(r) = \frac{2}{\pi} \int_0^\infty Q \left[ S(Q) - 1 \right] \sin(Qr) \, dQ
\]
Pollucite (CsSi$_2$AlO$_6$) Analysis and Modeling

PDFs for experimental GP samples heated to specified T, no soak

$\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ geopolymer

Long range order noticeable $> 1050 \, ^\circ\text{C}$
Pollockite (CsSi$_2$AlO$_6$) Analysis and Modeling

Subtraction of RT experimental geopolymer PDF from heated PDF patterns

Cs$_2$O•Al$_2$O$_3$•4SiO$_2$•11H$_2$O geopolymer

No T-O peak above RT GP
Na based geopolymer – Ordering in Na-GP

$x\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 11\text{H}_2\text{O}$ geopolymer, $x = 4$, 3, or 2

Graph showing the radial distribution function $G(r)$ for different Na-GP compositions:
- Red line: 4:1 NaGP
- Blue line: 3:1 NaGP
- Pink line: 2:1 NaGP

Presence of Zeolite A in 2:1 Na GP
Geopolymer – PDF as function of Alkali Choice

$2\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{X}_2\text{O}\cdot11\text{H}_2\text{O}$ geopolymer, $x = \text{Cs}, \text{K}, \text{or Na}$

Presence of Zeolite A in 2:1 Na GP

Relative Intensity

$r$ (Å)

$G(r)$ (Å$^{-2}$)
4SiO$_2$•Al$_2$O$_3$•K$_2$O•XH$_2$O geopolymer, $x = 14, 12, 11, 10, \text{or } 8$
Most of water evaporated below 250°C leading to a 5% shrinkage*

This includes free water at surface/pores, adsorbed water, and chemically bound water*

*TGA Results*

Water Dryout: RT – 350°C

Dehydration Cracking

• Geopolymers undergo shrinkage upon heating due to water loss\(^1\)
  - RT to 100\(^\circ\)C: Dehydration of physically bonded (free) water
  - 100 to 300\(^\circ\)C: Dehydration of chemically bonded (interstitial) water
  - >300\(^\circ\)C: Dehydroxylation of OH groups

• Dehydration shrinkage causes cracking of monolithic geopolymer

• Reinforcing or filler phases can be utilized to maintain structural integrity during shrinkage by crack-bridging and offering pathways for more graceful dehydration

\(^1\)J. Davidovits, Geopolymer Chemistry and Applications, 2008.
Reinforcements

- Chamotte/mullite particulates, granite, dolomite sediment
- Chopped fibers
  - Alumina (13 µm D x 100 µm long)
  - Basalt (50 µm D x ¼”, ½” long)
  - Carbon (7 µm D x 60 or 100 µm long)
- Alumina platelets (D = 50 µm)
- Woven fabric
  - Carbon fiber
  - Nextel 610 alumina, 720 mullite + alumina, 550 mullite
  - Basalt weaves and felts
- Mullite single crystal fibers (Moscow)
- Polymeric chopped fibers – polypropyline (½”, 1”, 2”)
- Biological fibers
  - Corn husk fiber bundles - Cordgrass (Illinois)
  - Jute (China, India) - Abaca (Manila hemp) and Hemp
  - Fique (Colombia) - Malva (Amazon)
  - Cork - Curaua (Amaon)
Alumina Platelets

- **Microgrit® WCA 50**
  - Manufactured by Micro Abrasives Corp., Westfield, Massachusetts, USA
  - Aspect ratio of 5:1

- **Diameter:**
  - 6% less than 16.12 µm
  - 50% between 42.81-52.50 µm
  - 3% greater than 102.00 µm

- **Miscellaneous**
  - Purity: 99.20% Al2O3
  - Density: 3.95 g/cm³
Residual Strength after Heat Treatment

- Competing effects on heating
  - Elevated diffusion promotes dehydration crack filling, densification
  - Differential thermal shrinkage creates new, larger cracks and residual strains
  - No apparent leucite transition weakening
Strength vs Temperature

- In-situ strength remained greater than 5MPa until over 1300°C
- Samples at 900°C deformed plastically
Strength by Fiber Weight Percent

• Composite strength increases rapidly with increasing fiber weight percent

• Modest strength increase for ½ inch long fibers compared to ¼ inch long fibers for the same weight percent

\[\text{Fiber Length (in)}\ |
\text{Fiber Weight (\%)}
\text{Average Strength (MPa)}
\text{Strength Increase ¼ to ½ in (\%)}
\hline
- & 0 & 2.2 & \\
¼ & 1 & 3.6$^1$ & 9.0 \\
½ & 1 & 3.9 & \\
½ & 2 & 7.3 & \\
¼ & 3 & 8.6$^1$ & \\
¼ & 5 & 13.5$^1$ & 24.1 \\
½ & 5 & 16.8 & \\
¼ & 7 & 16.5$^1$ & 46.9 \\
½ & 7 & 24.2 & \\
¼ & 10 & 19.5$^1$ & 38.8 \\
½ & 10 & 27.1 & \\
\hline

Thermal shock structural materials for VLO runway

Geopolymer composite pellets of 2 inches diameter, after thermal shock for several minutes with an oxy-acetylene torch
# BENCHMARK STRUCTURAL PROPERTIES of GP COMPOSITES

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexure strength (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGP-chamotte particulate</td>
<td>2.1 → 15.3 for 50 wt%</td>
<td>2.5 → 205</td>
</tr>
<tr>
<td>KGP-chopped basalt ¼” ϕ =13 μm</td>
<td>1.7 → 19.5 for 10 wt%</td>
<td>2.5 → 125</td>
</tr>
<tr>
<td>KGP-chopped basalt ½” ϕ=13 μm</td>
<td>2.2 → 27 for 10 wt%</td>
<td>1.2 → 38</td>
</tr>
<tr>
<td>Chopped Al₂O₃ fiber CsGP ϕ = 3 μm</td>
<td>10 → 20 for 20 wt%</td>
<td>0.25 → 117</td>
</tr>
<tr>
<td>Chopped C fiber 60 μm ϕ =7 μm</td>
<td>8.8 → 14.1 for max loading</td>
<td></td>
</tr>
<tr>
<td>Nextel 610 weave</td>
<td>8.7 → 50 for 33 vol%</td>
<td></td>
</tr>
<tr>
<td>Nextel 720 weave</td>
<td>8.7 → 40 for 27.3 vol %</td>
<td></td>
</tr>
<tr>
<td>Basalt plain weave</td>
<td>4.5 → 41.38 for 30 vol%</td>
<td></td>
</tr>
<tr>
<td>Nextel 610 weave in KGP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nextel 720 weave in KGP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain basalt weave in KGP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nextel 610/monazite in alumina</td>
<td></td>
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</tbody>
</table>
Processing route to ceramics
- Oxides with tailorable CTE’s
Geopolymers as a processing route to aluminosilicate oxides

Sodium geopolymer crystallizes into nepheline (NaAlSi$_2$O$_6$), on heating at 750°C

Potassium geopolymer crystallizes into leucite (KAlSi$_2$O$_6$), on heating at 950°C

Cesium geopolymer crystallizes into pollucite (CsAlSi$_2$O$_6$) on heating at 1100 °C.

Phase Diagrams: K

- **Leucite (KAlSi₂O₆)**
  - Refractory \(T_m \sim 1693^\circ C\)
  - High thermal expansion \(15.1 – 31 \times 10^{-6} \degree K^{-1}\)
  - High fracture toughness
  - Useful as a cermet due to high thermal expansion
  - Used widely in dentistry
  - Potential as a thermal barrier coating or ceramic matrix composite
  - Leucite crystals enhance the toughness of glass ceramics

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Phase Diagrams: Cs

- **Pollucite (CsAlSi$_2$O$_6$)**
  - Very refractory ($T_m \sim 1940^\circ$C)
  - Exceptional creep resistance comparable to YAG
  - Low thermal expansion (0.45% from 25 – 1000$^\circ$C) or (1.2 – 3.3 x 10$^{-6}$ oK$^{-1}$)
  - Relatively low density (2.9 g/cm$^3$)
  - High thermal shock resistance
  - Useful for ceramic matrix composites and thermal barrier coatings

“System Cs$_2$O-SiO$_2$-Al$_2$O$_3$. Calculated subsolidus at about 877$^\circ$C,”
Tailorable thermal expansion ceramics

- NaGP has CTE = 50 x 10^{-6} °C^{-1}
- KGP has CTE = 26 x 10^{-6} °C^{-1}
- Cs has CTE = 0.45 x 10^{-6} °C^{-1}
- Li, Rb and mixtures of Group I ions enable variation of CTE in crystallized geopolymer between 0.45 x 10^{-6} °C^{-1} to ~50 x 10^{-6} °C^{-1}
Processing route to ceramics – carbothermal reduction and carbothermal nitridization of geopolymers
Acheson Process to make SiC

1. Grind SiO₂ + C (coke)
2. 2,500 °C / (days)
3. Grind SiC (itself a grinding material)
4. (1,500 °C/ flowing Ar or N₂)
5. Grind geopolymers
6. Nano SiC, Si₃N₄ or SiAlON
Microstructure of Precipitates

High resolution transmission electron microscopy (HRTEM) results for (a) NaGP, (b) KGP, and (c) CsGP.
Hypothesis

It is well known that:
sodium geopolymer crystallizes into nepheline (NaAlSi$_2$O$_6$), on heating at 900-1100 °C,
potassium geopolymer crystallizes into leucite (KAISi$_2$O$_6$), on heating at 900-1200 °C,
cesium geopolymer crystallizes into pollucite (CsAlSi$_2$O$_6$) on heating at 900 °C.

So, one question arises:
Can we convert a geopolymer to its carbide and nitride analogues by carbothermal reduction using it a precursor?

This study investigated the feasibility of producing SiC, Si$_3$N$_4$ and SiAlON ceramics by *carbothermal reduction* under flowing Ar or *carbothermal nitridizationation* under flowing N$_2$ gas.
Experimental procedures

Route-1

MK+ (Na, K, and Cs)WG → (Na, K, and Cs) GP resin → Green compacts

GPs+18C powder → Ball milling with 18C/5h → Powdered GPs precursor → Grinding → Dried compact → Further drying 300 °C/1h → GPs
curing 50 °C/24h

As-treated compact

Microstructural characterization by XRD and SEM

*CTR: Carbothermal Reduction
**CTRN: Carbothermal Reduction and Nitridation
Results

X-ray diffraction patterns of NaGP+18C precursor after being carbothermally reacted between the temperature range of 1400°C-1600°C in argon.

Rietveld refinement results
3.2 Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under Ar

SEM micrographs of NaGP+18C precursor after being carbothermally reacted at between the temperature range of 1400°C-1600°C in argon.
Carbothermal reduction of NaGP under Ar producing globular or elongated grains
SiC Nano particles
Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction for 2h under Ar

Rietveld refinement results of products after being argon-fired in tube furnace.
Heat Treatment in $N_2$
• NaGP+18C heat at 1400-1600 °C in N₂
SEM micrographs of NaGP+18C precursor after being carbothermally reacted at between the temperature range of 1400°C-1600°C in nitrogen.
1: $\alpha$-Si$_3$N$_4$

2: hex-AlN
Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under N₂

SEM micrographs of KGP+18C precursor after being carbothermally reacted at between the temperature range of 1400°C-1600°C in nitrogen.
KGP-18C-N₂ – 1600°C

1: β-Si₃N₄, needles or globular
2: α-Si₃N₄, needles or globular
Coexistence of $\alpha$- and $\beta$-$\text{Si}_3\text{N}_4$ in needle, interfacial defects

The hardly observed $\beta$-$\text{Si}_3\text{N}_4$ in NaGP-18C-$\text{N}_2$-1600$^\circ$C may be a small region located near the well developed $\alpha$-$\text{Si}_3\text{N}_4$ needles.
Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under N₂

Rietveld refinement results of products from GP+18C after being nitrogen-fired in tube furnace.
3.2 XRD pattern and SEM micrograph of products made from GP+9C by carbothermal reduction and nitridation

X-ray diffraction patterns of NaGP+9C precursor after being carbothermally reacted between the temperature range of 1400°C-1600°C in nitrogen
SEM micrographs of NaGP+9C precursor after being carbothermally reacted between the temperature range of 1400°C-1600°C in nitrogen.
SEM micrographs of KGP+9C precursor after being carbothermally reacted between the temperature range of 1400°C-1600°C in nitrogen.
SEM micrographs of CsGP+9C precursor after being carbothermally reacted between the temperature range of 1400°C-1600°C in nitrogen.
3.4 Phase analysis and microstructural transformation of products made from GP+9C by carbothermal reduction under N₂

Rietveld refinement results of products from GP+9C after being nitrogen-fired in a tube furnace.
CONCLUSIONS OF CARBOThERMAL REDUCTION/NITRIDIZATION of GPs

• In this study, higher yield (over 95 %) of silicon carbide was synthesized from sodium precursor with 18C
• By carbothermal reduction, SiC, ($\alpha + \beta$) $\text{Si}_3\text{N}_4$ and SiAlON ceramic powders can be cost effectively synthesized from geopolymer precursors
• NaGP in both carbon compositions has an advantage over the KGP and CsGP in conversion of its carbide analogues as well as its low-cost
• By focusing on the NaGP and KGP precursors, useful structural ceramics and ceramic composites were made by an inexpensive geopolymer route
Summary of Topics Covered

• Composition and starting materials
• Microstructure
• Processing route to ceramics
  – Oxides with tailorable CTE’s
  – Non-oxides nanocrystalline (SiC, Si₃N₄, SiAlON’s)

Potential Applications of Geopolymers

• Low CO$_2$ producing cements and concretes
• Fire resistant coatings
• Low level radioactive waste encapsulation
• 3D printed rapid-prototyping molds
• Porous water purification filters
• Corrosion resistant coatings
• Coatings on wood, steel, other metals
• Refractory adhesives
• Porous insulators and refractories
• Alternative processing routes to isochemical ceramics
• High temperature resistant airplane runways (1200 °C) for VLOs
• Fuel cells alternative to PEMS devices
• Solar panel substrates
• Bush fire breaker panels
• Acoustic meta-materials
42nd International Conference and Expo on Advanced Ceramics and Composites (ICACC’18)

Symposium on Geopolymers
(17 conference proceedings to date)

January 21 – 26 (2018)
Daytona Beach, Fla. USA

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