Geopolymers: Recent Work and Future Directions

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Outline

I. Introduction
II. Geopolymers as Advanced Composites
III. Porosity Characterization
IV. Geopolymers as Adhesives
V. Synthetic Geopolymers
VI. Systematic Compression Testing Results
Geopolymers (Polysialates)

- Inorganic polymeric ceramics formed from both aluminum and silicon sources containing AlO$_4$ and SiO$_4$ tetrahedral units, under highly alkaline conditions (NaOH, KOH, CsOH) at ambient temperatures.

- They result in an amorphous, cross-linked, impervious, acid-resistant, 3-D structure.
Polysialate Building Blocks

Poly(sialate)
(-Si-O-Al-O-)

Poly(sialate-sialloxo)
(-Si-O-Al-O-Si-O-)

Poly(sialate-disialloxo)
(-Si-O-Al-O-Si-O-Si-O-)
Geopolymers as Advanced Composites

Geopolymer as Advanced Composites
- Processed at ambient temperatures
- Can be formed into complicated shapes
- Can be heated to form crystalline phases of specified properties

Current Advanced Composites
- Low end composites cost ~$1000/kg
- Fabrication techniques require high temperatures
- Parts are often limited to simple two-dimensional shapes
Geopolymers can be made in plastic molds and have a smooth surface finish.
C-fiber reinforced geopolymer
Geopolymers can be used for ceramic-to-metal joining (e.g. alumina to Al or to stainless steel) (cf. NiCrAlY bond layer)
Geopolymers as Advanced Composites

![Graph showing bending stress versus displacement](image)

- Before Reinforcement: WOF (0.05 kJ/m²)
- After Reinforcement: WOF (22 kJ/m²)
C.G. Papakonstantinou et al. demonstrated that carbon fiber reinforced Geopolymers retain 60% of their strength at 800°C!
Nanoporosity
Nanoporosity

Are Geopolymers Nanoporous?

- Previous TEM work indicates the presence of nanometer sized pores present (1 – 20nm)

- Mercury Intrusion Porosimetry (MIP) is limited to pore sizes of 10 nm

- Porotech LLC tested samples of K-Geopolymer derived from natural metakaolin
Nanoporosity

Integral pore volume distribution against pore radius

Pore radius, $r$ (nm)

Integral pore volume, $V_p$ (cm$^3$/g)
Nanoporosity

Differential distribution of surface against pore radius

![Graph showing the differential distribution of surface against pore radius. The x-axis represents pore radius in nm, ranging from 0 to 6. The y-axis represents specific surface area in cm²/g, ranging from 0 to 5.0E+02. The graph shows peaks in surface area at specific pore radii.]
Nanoporosity

Integral surface distribution against pore radius

m²/g

Pore radius, r (nm)
GP 10 at 200K
Nanoporosity

Summary of Properties

- Average logarithmic pore radius: 0.4362 nm
- Average pore radius: 3.3711 nm
- Porosity over weight: 0.3165 cm³/g
- Porosity over volume: 0.4106 cm³/cm³
- Meso- and macro-pore surface over weight: 190.5778 m²/g
- Meso- and macro-pore surface over volume: 247.2794 m²/cm³
- Total pore surface over weight: 274.6912 m²/g
- Total pore surface over volume: 356.4186 m²/cm³
- Density of solid phase: 2.0481 g/cm³

Could Geopolymers be used as filtering agents?
Geopolymers as an Adhesive
Geopolymers as an Adhesive

Use as an Adhesive

- Similar to dilute waterglass and silica sol based adhesives, but geopolymers have much lower water ratios.
- Has refractory advantages over organic adhesives.
- Typical refractory adhesives available require multiple high temperature curing steps.
- Geopolymers contain no organic carrier.
- Coefficients of thermal expansion can be tailored (more on that later…).
Test Performed

- ASTM D4562 pin and collar with tolerances ranging from 0.001”–0.003”

- Five sets of pin and collars were tested for:
  - 6061-T6 aluminum alloy
  - 625 nickel superalloy
  - aluminum oxide to aluminum oxide

- Additional (single) samples were heat treated (900°C/1hr) and tested
ASTM-D4562 Pin and Collar Test

1. Adhesive applied inside collar and around the pin

2. Pin and collar are assembled and cured at 60°C

3. Using a testing fixture pin through collar
Push Out Test
Push Out Test
ASTM-D4562 Pin and Collar Test
Push Out Test
Pushout Test Apparatus
Specimen after Pushout
# Geopolymers as an Adhesive

## Test Results - Average Steady-state Pushout Loads

<table>
<thead>
<tr>
<th>Pin / Collar Combination</th>
<th>Heat Treated?</th>
<th>Tolerance (10^{-3} in)</th>
<th>Shear Strength, $\tau_i$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al / Al</td>
<td>No</td>
<td>1</td>
<td>8.7 ± 1.3</td>
</tr>
<tr>
<td>Ni / Ni</td>
<td>No</td>
<td>1</td>
<td>8.8 ± 1.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$ / Al$_2$O$_3$</td>
<td>No</td>
<td>1</td>
<td>7.7 ± 2.9</td>
</tr>
<tr>
<td>Ni / Ni</td>
<td>Yes</td>
<td>1</td>
<td>14.2</td>
</tr>
<tr>
<td>Ni / Ni</td>
<td>Yes</td>
<td>2</td>
<td>12.5</td>
</tr>
<tr>
<td>Ni / Ni</td>
<td>Yes</td>
<td>3</td>
<td>19.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ / Ni</td>
<td>Yes</td>
<td>2</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Geopolymers as an Adhesive

SEM image of the Al$_2$O$_3$ / Geopolymer Join
Geopolymers as an Adhesive

Chemical mapping of the Al$_2$O$_3$ / Geopolymer Join

Counts

$\sim$38 $\mu$m
Synthetic Metakaolin
Synthetic Metakaolin

- Goal was to produce an aluminosilicate glass free from unwanted contaminants or crystalline phases.
- Would allow complete control of the Al$_2$O$_3$ to SiO$_2$ ratios
- Higher surface areas >100 m$^2$/g
PVA Method

50 w% solution Al(NO)₃•9H₂O

25 w% solution Colloidal Silica (Ludox SK)

5 w% solution PVA

Mix while heating

Heat until dry

Calcine at 800°C for 1 hr

Mill to achieve desired particle size
Synthetic Metakaolin (SEM)

(Natural) $\text{Al}_2\text{O}_3 \bullet 1.7 \text{SiO}_2$

(Synthetic) $\text{Al}_2\text{O}_3 \bullet 1.3 \text{SiO}_2$
Synthetic Metakaolin (SEM)

(Natural) $\text{Al}_2\text{O}_3 \bullet 1.7 \text{SiO}_2$

(Synthetic) $\text{Al}_2\text{O}_3 \bullet 1.3 \text{SiO}_2$
Synthetic Metakaolin (XRD)

Characteristics:
- **Natural** Al$_2$O$_3$ • 2.3 SiO$_2$
- **Synthetic** Al$_2$O$_3$ • 1.96 SiO$_2$
- **Synthetic** Al$_2$O$_3$ • 1.3 SiO$_2$

**Metakaolin “Hump”**
Synthetic K-Geopolymer (XRD)

Characteristic Peak Shift

0.7 K$_2$O • Al$_2$O$_3$ • 2.5 SiO$_2$

Al$_2$O$_3$ • 1.3 SiO$_2$
Synthetic K-Geopolymer (SEM)
Synthetic K-Geopolymer (SEM)
Synthetic K-Geopolymer (TEM)

TEM image

50 nm

Fourier Transform of the diffraction pattern
Synthetic K-Geopolymer (TEM)

TEM image

40 nm

Fourier Transform of the diffraction pattern
Synthetic K-Geopolymer (TEM)

TEM image

Fourier Transform of the diffraction pattern

40 nm
Cs Based Geopolymers

Goal of Cs Based Geopolymer Work

- Goal is synthesis and characterization of ultra-low thermal expansion matrix materials

- Pollucite (CsAlSi$_2$O$_6$) is a refractory silicate with a melting temperature at ~1940°C (Cs may limit to ~1500°C)

- Has very low creep resistance ~ similar to mullite or (YAG)

- Also has low thermal expansion coefficient (CTE) that can be adjusted according to stoichiometry and replacement of cesium with other alkalis
## Synthetic Cs-Geopolymer

### Coefficients of thermal expansion for pollucite compounds

<table>
<thead>
<tr>
<th>Composition</th>
<th>CTE (10^-6 / °C)</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_2O</td>
<td>Na_2O</td>
<td>K_2O</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>4.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>0.1</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Synthetic Cs-Geopolymer (XRD)

Characteristic Peak Shift

1.23 Cs$_2$O • Al$_2$O$_3$ • 3.95 SiO$_2$

Al$_2$O$_3$ • 1.96 SiO$_2$
Synthetic Cs-Geopolymer (XRD)

Synchrotron XRD

In-situ high temperature diffraction patterns of a Cs-Geopolymer mixed with platinum using synchrotron radiation showing the crystallization of pollucite.
Cs Based Geopolymers

DSC/TGA Results (heated/cooled at 5°C/min)

- Endotherm observed at approximately 1000°C, indicates the onset of crystallization of pollucite from the geopolymer glass
- The high mass loss below 250°C is due to the loss of free water
Synthetic Cs-Geopolymer (TGA/DSC)

DSC/TGA Results (heated/cooled at 5°C/min)

- A second endotherm resulted from volatilization of excess cesia from the pollucite that was formed. (loss of Cs was verified via EDS to be in the range of 1000°C-1400°C)
Synthetic Cs-Geopolymer (SEM)
Synthetic Cs-Geopolymer (SEM)
Synthetic Cs-Geopolymer (SEM)

Fracture surfaces
Systematic Compression Testing

Study done to determine

- Effect of alumina to silica ratio
- Effect of alkali mixtures of sodium and potassium
- Effect of aging (7-day strength compared to 28-day strength)

On the Geopolymers

- Compressive Strength
- Elastic Modulus
- Density
Systematic Compression Testing

Experimental Procedure

- Metakaolin was mixed with the alkali silicate solution in a high shear electric mixer for at least 15 min to form a geopolymer paste.
- The paste was poured into Teflon® tube molds sealed and cured at 40°C for 20 hrs.
- After demolding, samples were allowed to mature at room temperature for 7 and 90 days.
- 1” x 2” specimens were then cut, ground and tested in compression. Six samples for each composition.
Systematic Compression Testing

Experimental Difficulties

- Alkali silicate solutions with low concentrations of silica and high concentrations of sodium are unstable, causing precipitation of silica within hours.

- Samples lose large amounts of water at ambient temperature and pressure.

- Reintroduction of water to dehydrated samples results in severe internal and external cracking reducing the strength by greater than 50%.
# Systematic Compression Testing

## Starting Metakaolin

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin Balance</td>
<td></td>
</tr>
<tr>
<td>Quartz ($\text{SiO}_2$)</td>
<td>$&lt;2.0%$</td>
</tr>
<tr>
<td>Titanium Dioxide ($\text{TiO}_2$)</td>
<td>$&lt;2.0%$</td>
</tr>
<tr>
<td>Iron Oxide ($\text{Fe}_2\text{O}_3$)</td>
<td>$&lt;1.4%$</td>
</tr>
<tr>
<td>Potassium Oxide ($\text{K}_2\text{O}$)</td>
<td>$&lt;0.2%$</td>
</tr>
<tr>
<td>Magnesium Oxide ($\text{MgO}$)</td>
<td>$&lt;0.1%$</td>
</tr>
<tr>
<td>Calcium Oxide ($\text{CaO}$)</td>
<td>$&lt;0.1%$</td>
</tr>
<tr>
<td>Sodium Oxide ($\text{Na}_2\text{O}$)</td>
<td>$&lt;0.05%$</td>
</tr>
</tbody>
</table>
## 7-Day Compressive Strength

<table>
<thead>
<tr>
<th>SiO₂/Al₂O₃</th>
<th>2.3</th>
<th>2.8</th>
<th>3.3</th>
<th>3.8</th>
<th>4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Na</td>
<td>14.2</td>
<td>36.5</td>
<td>55.5</td>
<td>74.2</td>
<td>62.4</td>
</tr>
<tr>
<td>75% Na</td>
<td>10.1</td>
<td>45.8</td>
<td>71.3</td>
<td>85.0</td>
<td>59.1</td>
</tr>
<tr>
<td>50% Na</td>
<td>11.2</td>
<td>47.4</td>
<td>70.0</td>
<td>84.6</td>
<td>55.3</td>
</tr>
<tr>
<td>25% Na</td>
<td>6.8</td>
<td>45.5</td>
<td>68.2</td>
<td>72.4</td>
<td>67.7</td>
</tr>
<tr>
<td>100% K</td>
<td>7.1</td>
<td>43.9</td>
<td>60.3</td>
<td>75.3</td>
<td>56.6</td>
</tr>
</tbody>
</table>

### Strength (MPa)
- 0 - 30.0
- 30.1 - 45.0
- 45.1 - 60.0
- 60.1 - 75.0
- 75.1 - 90.0
## 7-Day Elastic Modulus

<table>
<thead>
<tr>
<th>%Na</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>2.3</th>
<th>2.8</th>
<th>3.3</th>
<th>3.8</th>
<th>4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% Na</td>
<td></td>
<td>1.6</td>
<td>3.7</td>
<td>5.1</td>
<td>5.9</td>
<td>5.5</td>
</tr>
<tr>
<td>50% Na</td>
<td></td>
<td>1.5</td>
<td>3.4</td>
<td>4.8</td>
<td>5.6</td>
<td>5.9</td>
</tr>
<tr>
<td>25% Na</td>
<td></td>
<td>1.2</td>
<td>3.4</td>
<td>4.8</td>
<td>5.7</td>
<td>5.3</td>
</tr>
<tr>
<td>100% K</td>
<td></td>
<td>1.3</td>
<td>3.4</td>
<td>4.7</td>
<td>5.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Modulus (GPa)</th>
<th>0 - 3.0</th>
<th>3.1 - 4.5</th>
<th>4.6 - 5.0</th>
<th>5.1 - 5.5</th>
<th>5.6 - 6.0</th>
</tr>
</thead>
</table>

- **SiO$_2$/Al$_2$O$_3$**
- **Modulus (GPa)**
# 7-Day Density

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>0 - 1.70</td>
</tr>
<tr>
<td>2.8</td>
<td>1.71 - 1.73</td>
</tr>
<tr>
<td>3.3</td>
<td>1.74 - 1.76</td>
</tr>
<tr>
<td>3.8</td>
<td>1.77 - 1.79</td>
</tr>
<tr>
<td>4.3</td>
<td>1.79 - 1.81</td>
</tr>
</tbody>
</table>

| 100% Na           | 1.68, 1.70, 1.72, 1.78, 1.80 |
| 75% Na            | 1.68, 1.70, 1.72, 1.80, 1.80 |
| 50% Na            | 1.71, 1.73, 1.76, 1.78, 1.80 |
| 25% Na            | 1.70, 1.73, 1.76, 1.79, 1.79 |
| 100% K            | 1.71, 1.74, 1.75, 1.78, 1.81 |
## 28-Day Compressive Strength

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>2.3</th>
<th>2.8</th>
<th>3.3</th>
<th>3.8</th>
<th>4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Na</td>
<td>12.7</td>
<td>30.8</td>
<td>66.7</td>
<td>71.6</td>
<td>52.5</td>
</tr>
<tr>
<td>75% Na</td>
<td>12.5</td>
<td>70.7</td>
<td>91.0</td>
<td>56.2</td>
<td>30.1</td>
</tr>
<tr>
<td>50% Na</td>
<td>6.4</td>
<td>42.2</td>
<td>71.3</td>
<td>84.2</td>
<td>81.1</td>
</tr>
<tr>
<td>25% Na</td>
<td>8.4</td>
<td>51.2</td>
<td>58.7</td>
<td>90.6</td>
<td>74.5</td>
</tr>
<tr>
<td>100% K</td>
<td>4.6</td>
<td>26.6</td>
<td>58.0</td>
<td>66.0</td>
<td>34.1</td>
</tr>
</tbody>
</table>

### Strength (MPa)

- 0 - 30.0
- 30.1 - 45.0
- 45.1 - 60.0
- 60.1 - 75.0
- 75.1 +
## 28-Day Elastic Modulus

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>2.3</th>
<th>2.8</th>
<th>3.3</th>
<th>3.8</th>
<th>4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Na</td>
<td>1.5</td>
<td>3.7</td>
<td>5.3</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>75% Na</td>
<td>1.3</td>
<td>5.4</td>
<td>5.9</td>
<td>5.9</td>
<td>4.1</td>
</tr>
<tr>
<td>50% Na</td>
<td>1.1</td>
<td>3.1</td>
<td>4.6</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>25% Na</td>
<td>1.0</td>
<td>3.6</td>
<td>4.5</td>
<td>5.4</td>
<td>6.2</td>
</tr>
<tr>
<td>100% K</td>
<td>0.9</td>
<td>2.4</td>
<td>4.2</td>
<td>4.5</td>
<td>3.7</td>
</tr>
</tbody>
</table>

| Modulus (GPa)     | 0 - 4.0 | 4.1 - 5.0 | 5.1 - 5.5 | 5.6 - 6.0 | 6.1 - 6.5 |
# 28-Day Density

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>2.3</th>
<th>2.8</th>
<th>3.3</th>
<th>3.8</th>
<th>4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Na</td>
<td>1.68</td>
<td>1.70</td>
<td>1.72</td>
<td>1.78</td>
<td>1.80</td>
</tr>
<tr>
<td>75% Na</td>
<td>1.68</td>
<td>1.7</td>
<td>1.74</td>
<td>1.8</td>
<td>1.80</td>
</tr>
<tr>
<td>50% Na</td>
<td>1.71</td>
<td>1.73</td>
<td>1.76</td>
<td>1.78</td>
<td>1.80</td>
</tr>
<tr>
<td>25% Na</td>
<td>1.70</td>
<td>1.73</td>
<td>1.76</td>
<td>1.79</td>
<td>1.79</td>
</tr>
<tr>
<td>100% K</td>
<td>1.71</td>
<td>1.74</td>
<td>1.75</td>
<td>1.78</td>
<td>1.81</td>
</tr>
</tbody>
</table>

| Density (g/cm$^3$) |  
|--------------------|-----|-----|-----|-----|-----|-----|-----|
|                    | 0 - 1.70 | 1.71 - 1.73 | 1.74 - 1.76 | 1.77 - 1.79 | 1.79 - 1.81 |
Systematic Compression Testing

Experimental Conclusions

- The density increases with silica content in a linear fashion at both 7 and 28 day curing time.

- A mixture of alkalis, yielded the best strengths.

- Over time, samples will dehydrate, reintroduction of water results in severe cracking.
Systematic Compression Testing

Experimental Conclusions
- Rm = 3.8 yielded the highest strengths
- Compressive strength (slightly) and tendency to crack (greatly) increase with aging time

Similar Results in Literature
- Showed a marked increase until Si/Al reached 3.0, at which strength dropped

Conclusions

• Polysialates are a promising class of alumino-silicate binder materials which can polymerize at ambient temperatures and incorporate a wide variety of chemical and physical components, to produce strong, useful, fireproof, acid-resistant and waste encapsulating, structural materials.

• They are fabricated at ambient T and P conditions, but only melt or crystallize above 1000-1400°C (e.g. forming kalsilite or pollucite), depending on the crosslinking alkali.
Conclusions (cont.)

• They have the potential to produce a wide variety of ceramic composites, as well as adhere to other ceramics or to metals.

• The average steady state, critical shear strengths of the bond layer between aluminum, nickel superalloy and Al₂O₃ were 8.7, 8.8, and 7.7 MPa, respectively.

• Maximum steady state, shear strengths were 10.9, 11.3, and 11.1 for the adhesive between aluminum, nickel and Al₂O₃ samples.

• Maximum initial debonding shear strengths up to 20 MPa were recorded.