#### **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, Si<sub>3</sub>N<sub>4</sub>, SiAlON's)

"Geopolymer-based Composites," W. M. Kriven, in Vol. 5, <u>Ceramics and Carbon</u> <u>Matrix Composites</u>, edited by Marina Ruggles-Wrenn. Part of an 8 volume set of books entitled <u>Comprehensive Composite Materials II</u>, Peter Beaumont and Carl Zweben, Co-editors-in-chief. Published by Elsevier, Oxford, UK, in press (2017)



### Terminology

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" U.S.Patent 4,349,386, September 14, (1982)
- J. Davidovits, "Geopolymer Chemistry and Properties"; pp.25-48 in Geopolymer'88 First European Conference on Soft Mineralogy, Vol.1 Edited by J. Davidovits and J. Orlinski. Geopolymer Institute and Technical University, Compiegne, France, (1988)
- J. Davidovits, "Geopolymers Inorganic Polymeric New Materials,"

J. Therm. Anal. 37 1633-56 (1991)

J. Davidovits, <u>Geopolymer Chemistry and Applications</u>, 4<sup>th</sup> Edition (2015), published by the Geopolymer Institute, St. Quentin, France

### Geopolymer Institute - <u>www.geopolymer.org</u>

# Geopolymers (Polysialates)

- Are a type of chemically bonded ceramics of chemical formula M<sub>2</sub>O•Al<sub>2</sub>O<sub>3</sub>•4SiO<sub>2</sub>•11H<sub>2</sub>O
- Refractory inorganic polymers formed from both aluminum and silicon sources containing AlO<sub>4</sub><sup>-</sup> and SiO<sub>4</sub> 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**

5Si<sup>+4</sup>O<sub>2</sub>

 $M_{2}^{+1}O \bullet Al_{2}^{+3}O_{3} \bullet 4Si^{+4}O_{2} \bullet 11H_{2}O_{3}$ 



### Metakaolin clay



 $M_{2}^{+1}O \bullet 2Si^{+4}O_{2} \bullet 11H_{2}O$ 

"waterglass" or metasilicate solution

## Alkali Activated Cements





#### Geopolymers are a potential partial solution to global warming!

- The manufacture of 1 ton of Portland cement liberates ~1 ton of CO<sub>2</sub>
- Whereas the manufacture of 1 ton of geopolymers liberates ~0.25 tons of CO<sub>2</sub>

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

<u>Property</u>	Portland Cement	<u>Geopolymers</u>
Compressive strength (MPa)	60	100
Flexure strength (MPa)	5-6	10-15
Density (g/cc)	2.7	1.4
Setting time (days)	28	1



## 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  $(Al_2O_3 \bullet 2SiO_2 \bullet 2H_2O)$  Al(V) in amorphous Al<sub>2</sub>O<sub>3</sub>•2SiO<sub>2</sub> forms highly strained molecule  $AIO_4^-$  tetrahedra and  $SiO_2$ . $AIO_4^-$  oligomers in solution

Dissolve at high pH



## 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



mix



#### Geopolymers can be formed in plastic molds and colored







### Microstructure



#### **XRD** Characteristic of Geopolymer



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

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

Davidovits, J., *Geopolymers - inorganic polymeric new materials.* Journal of Thermal Analysis, 1991. **37**(8): p. 1633-1656. M. Gordon, J. L. Bell and W. M. Kriven, "Comparison of naturally synthetically derived, potassium based geopolymers"; pp. 95-10-Ceramic Transactions, Vol. 165, (2004.)

#### Geopolymer Structure

- X-ray amorphous
- Al is integrated into a network of (IV) AlO<sub>4</sub><sup>-</sup> and SiO<sub>4</sub>, such that the negative charge on AlO<sub>4</sub><sup>-</sup> is balanced by the alkali cation



Davidovits, J. Journal of Thermal Analysis **1991**, *37*, 1633 Barbosa, V.F.F. and K.J.D. MacKenzie, Materials Research Bulletin, 2003. **38**(2): p. 319-331 Barbosa, V.F.F., K.J.D. MacKenzie, and C. Thaumaturgo, International Journal of Inorganic Materials, 2000. **2**(4): p. 319-331

#### 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 :  $0.3165 \text{ cm}^3/\text{g}$ 

Porosity over volume : 0.4106 cm<sup>3</sup>/cm<sup>3</sup>

Meso- and macro-pore surface over weight :  $190.5778 \text{ m}^2/\text{g}$ Meso- and macro-pore surface over volume :  $247.2794 \text{ m}^2/\text{cm}^3$ Total pore surface over weight :  $274.6912 \text{ m}^2/\text{g}$ Total pore surface over volume :  $356.4186 \text{ m}^2/\text{cm}^3$ Density of solid phase:  $2.0481 \text{ g/cm}^3$ 

### Nanoporosity in synthetic-based GP = 0.8 nm

Alkali cationNaKCsDensities  $(g/cm^3)$ 1.511.471.84

Densities of single phase geopolymer using different Group I cations

### Porosity in geopolymers:

- H<sub>2</sub>O<sub>2</sub> (45 μm)
- Canola oil (100's  $\mu$ m)
- Kitty litter (bentonite)
- Alkoxy silanes (75 vol % at 1  $\mu m$  pore size)\*
- Excess H<sub>2</sub>O (reduces strength)

\* "Geopolymer with Hydrogel Characteristics via Silane Coupling Agent Additives,"
 B. E. Glad and W. M. Kriven, J. Am. Cer. Soc., 97 [1] 295 - 304 (2014).



# **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- $\Theta$  moves to 14 2- $\Theta$ 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 mJ S E DIDE/mol GP sample after calcination 24 S E

### **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)

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

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$



### Pollucite (CsSi<sub>2</sub>AlO<sub>6</sub>) Analysis and Modeling



### Pollucite (CsSi<sub>2</sub>AlO<sub>6</sub>) Analysis and Modeling

Subtraction of RT experimental geopolymer PDF from heated PDF patterns



#### Na based geopolymer – Ordering in Na-GP



### Geopolymer – PDF as function of Alkali Choice



r (Å)



### Geopolymer – PDF as function of water for K-GP



#### WATER REMOVAL



<sup>\*</sup>Rahier, H., B. VanMele, and J. Wastiels, Low-temperature synthesized aluminosilicate glasses: Part II: Rheological transformations during low-temperature cure and high-temperature properties of a model compound. Journal of Materials Science, 1996. **31** 80-85, (1996)

M.SE

# **Dehydration Cracking**

- Geopolymers undergo shrinkage upon heating due to water loss<sup>1</sup>
  - RT to 100°C: Dehydration of physically bonded (free) water
  - 100 to 300°C: Dehydration of chemically bonded (interstitial) water
  - >300°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



# Reinforcements

- Chamotte/mullite particulates, granite, dolomite sediment
- Chopped fibers
  - Alumina (13  $\mu$ m D x 100  $\mu$ m long)
  - Basalt (50  $\mu$ m D x  $\frac{1}{4}$ ",  $\frac{1}{2}$ " long)
  - Carbon (7  $\mu$ m D x 60 or 100  $\mu$ m long)
- Alumina platelets (D = 50  $\mu$ m)
- Woven fabric
  - Carbon fiber
  - Nextel 610 alumina, 720 mullite + alumina, 550 mullite
  - Basalt weaves and felts
- Mullite single crystal fibers (Moscow)
- Polymeric chopped fibers polyproplyene (1/2", 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<sup>®</sup> WCA 50
  - Manufactured by Micro Abrasives Corp., Westfield, Massachusetts, USA
  - Aspect ratio of 5:1
- Diameter:
  - 6% less than 16.12  $\mu m$
  - 50% between 42.81-52.50  $\mu$ m
  - $\,$  3% greater than 102.00  $\mu m$
- Miscellaneous
  - Purity: 99.20% Al2O3
  - Density: 3.95 g/cm<sup>3</sup>
  - http://www.microgrit.com/microgrit%20wca.html





## **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







#### 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

#### <u>Material</u>

- KGP-chamotte particulate
- KGP-chopped basalt  $\frac{1}{2}$ "  $\phi = 13 \ \mu m$  $\frac{1}{2}$ "  $\phi = 13 \ \mu m$
- Chopped  $Al_2O_3$  fiber CsGP  $\phi$  = 3  $\mu$ m
- Chopped C fiber 60  $\mu$ m  $\phi$  =7  $\mu$ m
- Nextel 610 weave
- Nextel 720 weave
- Basalt plain weave
- Nextel 610 weave in KGP
- Nextel 720 weave in KGP
- Plain basalt weave in KGP
- Nextel 610/monazite in alumina

#### Flexure strength (MPa)

- 2.1 15.3 for 50 wt%
- 1.7 \_\_\_\_ 19.5 for 10 wt%
- 2.2 \_\_\_\_ 27 for 10 wt%
- 10 \_\_\_\_ 20 for 20 wt%
- 8.8 14.1 for max loading
- 8.7 50 for 33 vol%
- 8.7 \_\_\_\_ 40 for 27.3 vol %
- 4.5 41.38 for 30 vol%

#### Tensile strength (MPa)

- 2.5 \_\_\_\_ 205
- 2.5 → 125
- 1.2 ---- 38
- 0.25 → 117



# Processing route to ceramics - Oxides with tailorable CTE's



# Geopolymers as a processing route to aluminosilicate oxides

Sodium geopolymer crystallizes into nepheline (NaAlSi<sub>2</sub>O<sub>6</sub>), on heating at 750°C

Potassium geopolymer crystallizes into leucite (KAlSi<sub>2</sub>O<sub>6</sub>), on heating at 950°C

Cesium geopolymer crystallizes into pollucite (CsAlSi $_2O_6$ ) on heating at 1100 °C.



#### Phase Diagram: Na



"System Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>; isofracts," J. F. Schairer and N. L. Bowen, *Am. J. Sci.*, **254** [3] 129-195 (1956).



"System  $Na_2O-Al_2O_3$ -SiO<sub>2</sub>; composite," E. F. Osborn and A. Muan, revised and redrawn, "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.



## Phase Diagrams: K

- Leucite (KAlSi<sub>2</sub>O<sub>6</sub>)
  - Refractory ( $T_m \simeq 1693^{\circ}C$ )
  - High thermal expansion (15.1 31 x 10<sup>-6</sup> °K<sup>-1</sup>)
  - 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



"System  $K_2O-Al_2O_3$ -SiO<sub>2</sub>; composite," E. F. Osborn and A. Muan, revised and redrawn Phase Equilibrium Diagrams of Oxide Systems, Plate 5, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.



# Phase Diagrams: Cs

- Pollucite (CsAlSi<sub>2</sub>O<sub>6</sub>)
  - Very refractory ( $T_m \sim 1940^{\circ}C$ )
  - Exceptional creep resistance comparable to YAG
  - Low thermal expansion (0.45% from 25 1000°C) or (1.2 3.3 x 10<sup>-6</sup> °K<sup>-1</sup>)
  - Relatively low density (2.9 g/cm<sup>3</sup>)
  - High thermal shock resistance
  - Useful for ceramic matrix composites and thermal barrier coatings



"System  $Cs_2O-SiO_2-Al_2O_3$ . Calculated subsolidus at about 877°C," T. B. Lindemer, T. M. Besmann, and C. E. Johnson, *J. Nucl. Mater.*, **100** [1-3] 176-226 (1981).



### Tailorable thermal expansion ceramics

- NaGP has CTE = 50 x 10<sup>-6</sup> °C<sup>-1</sup>
- KGP has CTE = 26 x 10<sup>-6</sup> °C<sup>-1</sup>
- Cs has CTE =  $0.45 \times 10^{-6} \circ C^{-1}$
- Li, Rb and mixtures of Group I ions enable variation of CTE in crystallized geopolymer between 0.45 x 10 <sup>-6</sup> C<sup>-1</sup> to ~50 x 10<sup>-6</sup> C<sup>-1</sup>



Processing route to ceramics – carbothermal reduction and carbothermal nitridization of geopolymers



## Acheson Process to make SiC





### **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<sub>2</sub>O<sub>6</sub>), on heating at 900-1100 °C,

potassium geopolymer crystallizes into leucite (KAlSi<sub>2</sub>O<sub>6</sub>), on heating at 900-1200 °C,

cesium geopolymer crystallizes into pollucite (CsAlSi<sub>2</sub>O<sub>6</sub>) 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,  $Si_3N_4$ and SiAlON ceramics by *carbothermal reduction* under flowing Ar or *carbothermal nitridizationation* under flowing N<sub>2</sub> gas.



# Experimental procedures Route-1



#### Results

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







Mas E Illinois 3.2 Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under Ar



1600°C





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<sub>2</sub>



NaGP+18C heat at 1400-1600 °C in N<sub>2</sub>







1600°C



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<sub>3</sub>N<sub>4</sub>



#### 2: hex-AlN







Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under  $N_2$ 



1600°C





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



#### KGP-18C-N<sub>2</sub>-1600°C



1:  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, needles or globular 2:  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, needles or globular



 $\beta$ -Si<sub>3</sub>N<sub>4</sub>







Coexistence of  $\alpha$ - and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> in needle, interfacial defects





The hardly observed  $\beta$ -Si<sub>3</sub>N<sub>4</sub> in NaGP-18C-N<sub>2</sub>-1600°C may be a small region located near the well developed  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> needles



Phase analysis and microstructural transformation of products made from GP+18C by carbothermal reduction under  $N_2$ 



Rietveld refinement results of products from GP+18C after being nitrogen-fired in tube furnace.



#### 3.2 XRD pattern and SEM migrograph 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.









1600°C



1500°C



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  $N_2$ 



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,  $(\alpha + \beta)$  Si<sub>3</sub>N<sub>4</sub> 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, Si<sub>3</sub>N<sub>4</sub>, SiAlON's)

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#### Potential Applications of Geopolymers

- Low CO<sub>2</sub> 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

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