Alkali Leaching Properties of Waste Glass-Based Geopolymers

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Overview

• Project Motivation
• Goal and Research Questions
• Geopolymer Background
  ▫ Glass Motivation
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About Myself

• From Spring Valley, WI
• Bachelor’s Degree from UMD in Civil Engineering
  ▫ May 2016
• Master’s Degree from UMD in Civil Engineering
  ▫ December 2017?
• Presented research at American Concrete Institute (ACI) Convention in Detroit, MI
• Presenting at Transportation Research Board (TRB) Summer Workshop in Duluth, MN
• Will present research at ACI Convention in Anaheim, CA
Project Motivation

- Production of portland cement (PC) accounts for 6-7% of global anthropogenic carbon footprint [3]
- Looks like and performs similar to PC concrete
- Aluminosilicate source is generally an industry by-product or waste material
- Can possess unique properties
  - High heat resistance
  - Sulfate resistance
  - Chloride Resistance
Goal

Investigate the effect of chemical composition on the leaching properties of glass-based geopolymer mortars in order to improve the water stability
Research Questions

• What are the alkali leaching properties of glass-based geopolymers?

• What is the correlation between composition, stoichiometry, and leaching properties of glass-based geopolymers?

• Does lowering the alkali concentration or using a blend of activators improve the mechanical properties of glass-based geopolymers?

• Does the addition of an alumina source enhance the mechanical performance?
Geopolymers

An inorganic polymer binder created from the alkali activation of a finely divided aluminosilicate source
Geopolymerization

Chemical Attack → Dissolution → Gel 1

Growth ← Polymerization → Gel 2

[3]
Chemical Attack

Chemical Attack → Dissolution → Gel 1

Growth → Polymerization → Gel 2

Si, Al, O, Na, H

[3]
Chemical Attack

Legend
- = Al^{+3}
- = Si^{+4}
- = O^{2-}
- = OH^{-}
- = Na^{+}
- = H^{+}

NaOH

Aluminosilicate Source
Dissolution

Chemical Attack → Dissolution → Gel 1

Growth → Polymerization → Gel 2

[3]
Dissolution

Legend

- $\text{Al}^{3+}$
- $\text{Si}^{4+}$
- $\text{O}^{2-}$
- $\text{OH}^-$
- $\text{Na}^+$
- $\text{H}^+$

Geopolymer Background
Gelation

Chemical Attack → Dissolution → Gel 1

Growth → Polymerization → Gel 2

[3]
Gelation
Polymerization

Chemical Attack → Dissolution → Gel 1

Growth → Polymerization → Gel 2

[3]
Source Materials

- **Materials used in geopolymers**
  - Fly Ash (Class F and Class C)
  - Metakaolin
  - Slag
  - Glass

- **Composition is key**
Activator

• Roles of activator:
  ▫ Provides a medium for reactions to occur
  ▫ High pH for rapid dissolution
  ▫ Alkali cation balances charge of Al monomer
  ▫ Silica in the solution can accelerate geopolymerization

• Common Activators:
  ▫ Caustic alkalis (NaOH, Ca(OH)₂, or KOH)
  ▫ Nonsilicate weak acid salts (Na₂CO₃)
  ▫ Silicates (Na₂SiO₃) [3]
Stoichiometry

- $M^+ \rightarrow$ Either $Na^+$ or $K^+$
- $Al \rightarrow Al_2O_3$
- $Si \rightarrow SiO_2$
- $M^+/Al = 1$
- $Si/Al = 2-5$

<table>
<thead>
<tr>
<th>Researcher(s)</th>
<th>$M^+/Al$</th>
<th>$Si/Al$</th>
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</thead>
<tbody>
<tr>
<td>Davidovits 1979</td>
<td>0.8-1.2 (~1.0)</td>
<td>3.5-4.5 (~4.0)</td>
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<tr>
<td>Rowles and O'Connor 2003</td>
<td>1.3</td>
<td>3.0</td>
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<tr>
<td>Duxson et al. 2005; Fernández-Jiménez et al. 2006</td>
<td>1.0</td>
<td>1.8-2.0</td>
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<tr>
<td>Duxson et al. 2007</td>
<td>1.0</td>
<td>1.0-5.0</td>
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</table>
Waste Glass

- Rich in reactive silica
- Amorphous structure
- Recycled waste product
  - Municipal Solid Waste (MSW)

<table>
<thead>
<tr>
<th>Product Category</th>
<th>Generation (Thousand Tons)</th>
<th>Recycled (Thousand Tons)</th>
<th>(% of Generation)</th>
<th>Landfilled (Thousand Tons)</th>
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<tbody>
<tr>
<td>Durable Goods</td>
<td>2,280</td>
<td>Negligible</td>
<td>Negligible</td>
<td>2,050</td>
</tr>
<tr>
<td>Containers and Packaging</td>
<td>9,200</td>
<td>2,990</td>
<td>32.5</td>
<td>6,110</td>
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<tr>
<td><strong>Total Glass</strong></td>
<td><strong>11,480</strong></td>
<td><strong>2,990</strong></td>
<td><strong>26.0</strong></td>
<td><strong>8,390</strong></td>
</tr>
</tbody>
</table>

[10]
Glass Types

- Soda-lime
  - Container
  - Plate
- Borosilicate
- Glass Fibers
- Television (Tube)

<table>
<thead>
<tr>
<th></th>
<th>Container</th>
<th>Plate</th>
<th>Borosilicate</th>
<th>Glass Fibers</th>
<th>Television</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (% weight)</td>
<td>74.0</td>
<td>73.0</td>
<td>81.0</td>
<td>52.0-56.0</td>
<td>62.0</td>
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<tr>
<td>Al₂O₃ (% weight)</td>
<td>1.5</td>
<td>0.1</td>
<td>2.0</td>
<td>12.0-16.0</td>
<td>2.0</td>
</tr>
<tr>
<td>B₂O₃ (% weight)</td>
<td>0.0</td>
<td>0.0</td>
<td>13.0</td>
<td>5.0-10.0</td>
<td>0.0</td>
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<tr>
<td>CaO (% weight)</td>
<td>11.0</td>
<td>9.0</td>
<td>0.0</td>
<td>16.0-25.0</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>PbO (% weight)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0-2.0</td>
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<tr>
<td>Na₂O (% weight)</td>
<td>13.0</td>
<td>14.0</td>
<td>4.0</td>
<td>0.0-2.0</td>
<td>7.0</td>
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<tr>
<td>K₂O (% weight)</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>9.0</td>
</tr>
<tr>
<td>MgO (% weight)</td>
<td>0.2</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0-5.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Fe₂O₃ (% weight)</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0-0.8</td>
<td>0.0</td>
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</table>
Experimental Plan

- Phase I – 16 mortar mixtures each using a different glass and activated with 10M NaOH were designed to investigate the effects of stoichiometry on the leaching and mechanical properties.

- Phase II – Stoichiometric design-based mixtures using glass in combination with other varying aluminosilicate sources to provide supplementary Al and various chemical activators were designed to apply the concepts learned in Phase I.
Mixture Parameters

- **Mixture Design**
  - 0.5 water/solids ratio
  - 3:1 aggregate to aluminosilicate ratio
  - 2:1 aluminosilicate to activator ratio

- **Curing**
  - Placed in 80°C oven for 24 hours
  - Then:
    - 23°C, 95% Relative Humidity
    - Deionized (DI) water bath
Materials

- Aluminosilicate
  - Glass
- Activator Solution
  - 10M NaOH
- Silica sand
- Water
Glass Samples

- 16 glasses were collected and analyzed by x-ray fluorescence (XRF)
  - Eight different locations
  - Multiple waste streams
- Glasses were ground to desired particle size
  - d90 < 45 μm
  - d50 = 8-14 μm
  - d10 = 1.5-2.5 μm

<table>
<thead>
<tr>
<th>Glass ID</th>
<th>Origin Location</th>
<th>Waste Stream</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Utah</td>
<td>Consumer</td>
</tr>
<tr>
<td>B</td>
<td>New York</td>
<td>Consumer</td>
</tr>
<tr>
<td>C</td>
<td>Tennessee</td>
<td>Consumer</td>
</tr>
<tr>
<td>D</td>
<td>Tennessee</td>
<td>Industrial</td>
</tr>
<tr>
<td>E</td>
<td>Ohio</td>
<td>Consumer</td>
</tr>
<tr>
<td>G</td>
<td>Minnesota</td>
<td>Consumer</td>
</tr>
<tr>
<td>H</td>
<td>Indiana</td>
<td>Consumer</td>
</tr>
<tr>
<td>J</td>
<td>Missouri</td>
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<td>P</td>
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<tr>
<td>Q</td>
<td>Tennessee</td>
<td>Manufactured</td>
</tr>
<tr>
<td>R</td>
<td>Tennessee</td>
<td>Industrial</td>
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</tbody>
</table>
Scope

- 100% waste glass geopolymer mortars
- Leaching Properties
- Compressive Strength
- Solution Compositional Analysis
- Microstructural Characterization
Leaching Properties

- Containers filled with 250 mL DI water
- pH
- Conductivity
- Early data was collected (1, 3, and 7 days) and then every week until 56 days
- Solution samples collected (7, 28, and 56 days)
Compressive Strength

- ASTM C109
- Cubes stored in DI water (wet) and cubes cured ambiently (dry)
- 7, 28, and 56 days
Solution Compositional Analysis

- 0.5 mL sample collected
- Selective Ion Electrode
  - Na
- Spectrophotometry
  - Si
Microstructural Characterization

- Scanning electron microscope (SEM)
  - Secondary electron imaging (SEI)
  - Energy dispersive X-ray spectroscopy (EDS)
Phase I pH Results

The graph shows the pH levels over time for different samples labeled AN, BN, CN, etc., from days 0 to 56. The pH levels stabilize around 12.00 after an initial drop at day 0.
Phase I Conductivity

![Conductivity graph](image)

Conductivity (µS) vs Time (days) for different samples labeled with letters AN to RN.
Phase I Compressive Strength

JN  
Na/Al = 32.6

PN  
Na/Al = 3.8

Compressive Strength (psi) vs Time (days)

Dry
Wet

0 500 1000 1500 2000 2500 3000 3500 4000

7 28 56

Compressive Strength (psi) vs Time (days)

Dry
Wet

0 500 1000 1500 2000 2500 3000 3500 4000

7 28 56
Phase I Compressive Strength

Compressive Strength (psi)

Time (days)

DN

Na/Al = 2.0

Dry

Wet
Observations

- Glasses with a higher Na/Al ratio have shown more white precipitate on wet cured samples
- More liquid precipitate in dry cured samples
- All of the mortar mixtures have shown a large air void structure
Observations

• 100% glass mixtures should be amended to account for the following:
  ▫ Low compressive strength
  ▫ Strength loss
  ▫ Visible leaching of alkalis
Next Steps - Phase II

- New glass received from verified materials recycling facility (MRF)
- Explore other less caustic activators to increase compressive strength and decrease free sodium content
  - Ca(OH)$_2$
  - Na$_2$SiO$_3$
  - Na$_2$CO$_3$
Next Steps - Phase II

- Mix in additional alumina or calcium sources to obtain a Na/Al ~ 1-2
  - Metakaolin
  - Class F fly ash
Acknowledgments

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- American Engineering Testing – St. Paul, MN
- UMD Concrete Research Group
- Dr. Chanlan Chun
- Dr. Andrea Schokker
- Dr. Mary Christiansen

Thank You!


13. [University of Minnesota Duluth]. Retrieved July 9, 2017 from https://www.google.com/search?q=umd&client=safari&rls=en&source=lnms&tbm=isch&sa=X&ved=0ahUKEwijxfXrg_7UAhVFMyYKHZ3qAOsQ_AUIDCgD&biw=1440&bih=716#tbm=isch&q=university+of+minnesota+duluth&imgrc=1N50SpTjKtMfpM:
Questions?