Heavy Metals Leaching from Retro-Reflective Glass Beads Used in Road Markings

Dr. Bryan Boulanger
Dr. Aditya Raut-Desai
Zachry Department of Civil Engineering
Texas A&M University

ATSSA 41st Annual Convention and Traffic Expo in Phoenix, Arizona
14th February, 2011
PROJECT OVERVIEW

Determine heavy metal leaching from retro-reflective glass beads used in highway markings.

- What is the heavy metals content in retro-reflective glass beads?
- What is the potential for leaching?
- What is the effect of weathering factors on leaching?
OBJECTIVES

1. Determine heavy metal content in glass beads (particles loosely bound to surface of glass bead & bulk of glass bead)

2. Determine extent of heavy metal leaching from glass beads.
OBJECTIVE 1

Determine heavy metal content in glass beads

Task 1. XRF preliminary investigation
Task 2. Rinsing Study
Task 3. Surface Visualization and Bulk Composition
Task 4. KOH Fusion Digestion and ICP-MS analysis
Selection of Beads for Study

- Three types of beads were selected for this study
  - Varying heavy metal content
  - Designated as
    - Batch 1
    - Batch 2
    - Batch 3

- Supplied by American Glass Bead Manufacturing Association

- Source: manufactured in China
• Contaminants that **could be identified**
  – **Arsenic**
  – **Lead** (peak interference from titanium)
  – **Zinc**

• Contaminants that **could not be identified**
  – Mercury
  – Nickel
  – Copper
  – Chromium
  – Cadmium
Bead Rinsing Experiment

To determine the amount of leachable surface-bound particles.

**Method**

- **Apparatus:** total suspended solids (flow-through)
- 15g glass beads + 15mL DI water + vacuum (2 minutes)
- **Sample analysis:** Inductive Coupled Plasma Mass Spectroscopy (ICP-MS)

All experiments conducted in triplicates.
SURFACE VISUALIZATION AND BULK COMPOSITION

To identify and characterize loosely bound surface particles.

Method

– Scanning Electron Microscopy with Electron Dispersion Spectroscopy (SEM-EDS)

Results
KOH FUSION DIGESTION – ICP-MS ANALYSIS

To determine the total heavy metal content in glass beads.

Method

1. Crush glass beads (< 100 μm)
2. 0.25g crushed glass beads + 1.8g KOH + 0.2g KNO₃
3. Heat (500 – 750 °C) for 5 minutes
4. Dissolve in 100 mL DI water
5. Add 30mL HNO₃ + 0.3g oxalic acid to dissolve flocs
6. Dilute samples to 500 mL using DI water
Determine extent of heavy metal leaching from glass beads

Task 1. Flow-through Column Study
**FLOW-THROUGH COLUMN STUDY**

Method

- Test Duration: 48 hours
- Mass of Beads: 80 g
- Flow rate: 30 mL/hr

**Diagram:**

- DI Water Reservoir
- Peristaltic pump
- Glass wool plugs
- Glass beads
- O-Ring
- Sampling tube
- 30 mL/hr flux
### Summary of Results (pH 7)

Table 1. Mass of arsenic per mass of bead.

<table>
<thead>
<tr>
<th></th>
<th>KOH Fusion (Total) [µg/g glass bead]</th>
<th>Bead Rinse [µg/g glass bead]</th>
<th>Column Leaching [µg/g glass bead]</th>
<th>Fraction leached in initial 2 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>83 ± 2</td>
<td>0.032 ± 0.013</td>
<td>0.037 ± 0.010</td>
<td>86%</td>
</tr>
<tr>
<td>Batch 2</td>
<td>308 ± 24</td>
<td>0.644 ± 0.205</td>
<td>1.029 ± 0.082</td>
<td>63%</td>
</tr>
<tr>
<td>Batch 3</td>
<td>393 ± 7</td>
<td>0.468 ± 0.140</td>
<td>0.915 ± 0.111</td>
<td>51%</td>
</tr>
</tbody>
</table>

Table 2. Mass of total heavy metals per mass of bead.

<table>
<thead>
<tr>
<th></th>
<th>KOH Fusion (Total) [µg/g glass bead]</th>
<th>Bead Rinse [µg/g glass bead]</th>
<th>Column Leaching [µg/g glass bead]</th>
<th>Fraction leached in initial 2 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>169 ± 4</td>
<td>0.037 ± 0.016</td>
<td>0.084 ± 0.026</td>
<td>44%</td>
</tr>
<tr>
<td>Batch 2</td>
<td>470 ± 30</td>
<td>0.652 ± 0.202</td>
<td>0.989 ± 0.093</td>
<td>66%</td>
</tr>
<tr>
<td>Batch 3</td>
<td>515 ± 20</td>
<td>0.474 ± 0.136</td>
<td>1.125 ± 0.296</td>
<td>42%</td>
</tr>
</tbody>
</table>
Single-cycle experiments conducted in lab were inconclusive.

Multiple cycles would be more representative of real-life conditions.
EFFECT OF ABRASION - BATCH 1

![Graph showing the effect of abrasion on log As concentration over time.](image-url)

- Blue dots represent size < 149 microns.
- Red dots represent 149 microns < size < 250 microns.
- Green dots represent size > 250 microns.

The graph illustrates the decrease in As concentration over time for different particle size categories.
EFFECT OF ABRASION - BATCH 3
# Effect of Abrasion

Table 3. Effect of abrasion on total heavy metals leaching from glass beads.

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Bead Type: Level 1</th>
<th>Bead Type: Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size &lt; 149 microns [μg/g glass bead]</td>
<td>Batch 1: 1.36 ± 0.24 (17)</td>
<td>Batch 3: 2.46 ± 0.07 (6)</td>
</tr>
<tr>
<td>149 microns &lt; size &lt; 250 microns [μg/g glass bead]</td>
<td>Batch 1: 0.59 ± 0.25 (7.4 times)</td>
<td>Batch 3: 1.69 ± 0.55</td>
</tr>
<tr>
<td>Size &gt; 250 microns [μg/g glass bead]</td>
<td>Batch 1: 0.08 ± 0.03</td>
<td>Batch 3: 1.33 ± 0.30</td>
</tr>
</tbody>
</table>

**Graphs:**
- **Bead Type: Level 1**
  - Size < 149 microns
  - 149 microns < size < 250 microns
  - size > 250 microns

- **Bead Type: Level 3**
  - 149 microns > size
  - 250 microns > size > 149 microns
  - size > 250 microns
Summary of Results

- Composition of beads (Arsenic is major component)
- Leaching
  - Significant portion of leaching observed in first two minutes.
  - Leaching observed from bulk of glass beads
  - Correlation between amount leached and total metal content.
  - Arsenic: a major component of leachate.
- Effect of environmental factors
  - Leaching observed in water having pH typical of rainwater.
  - pH, Temperature, UV exposure effects were inconclusive.
  - Abrasion: increased amount of leaching observed with decreasing particle size.
- Similarities between our and NJIT study
ACKNOWLEDGEMENTS

• American Glass Beads Manufacturing Association

• Dr. Paul Carlson, Division head
  Principal Investigator
  Transportation Operations Group
  Texas Transportation Institute, TAMUS

• Dr. William James, Manager
  (ICP-MS & XRF Analyses)
  Elemental Analysis Laboratory
  Department of Chemistry, TAMU

• Mr. Tom Stephens, Asst. Research Scientist
  (SEM-EDS Analyses)
  Microscopy and Imaging Center, TAMU
THANK YOU