LABORATORY-SCALE RADIOACTIVE GLASS TESTING

E. V. Morrey
M. L. Elliott
J. M. Tingey

Nuclear Waste Technical Review Board
May 11, 1992

PNL HWVP Technology Development Project
Battelle-Pacific Northwest Laboratory
Outline

- Primary Objectives of Testing
- Broad Approach to Waste Simulant and Models Validation
- Detailed Approach to Radioactive Laboratory-Scale Testing
- Waste Slurry Data Comparisons
- Glass Property Data Comparisons
- Plans for Future Work
- Conclusions
Primary Objectives of Testing

- Confirm that waste simulants accurately represent HWVP glass and process stream properties.

- Provide radioactive glass composition and properties data for use in models validation and product quality.
Waste Simulant and Glass Property Models Validation

Approach
Test Data/Property Models Correlation

Property Models
- Glass Envelope Studies
- Laboratory Simulant Slurry Studies

HWVP Process
- Laboratory-Scale
  - Radioactive
  - Simulant
- Bench-Scale
  - Radioactive
  - Simulant
- Pilot-Scale
  - Simulant

Validated Models for HWVP
- Design
- Feed Processability
- Operations
- Permitting
- Safety
- Waste Form Qualification
CHARACTERIZATION OF RADIOACTIVE NCAW SAMPLES

LABORATORY SAMPLING

EXTRUDE 2 SEGMENTS

PHYSICALLY CHARACTERIZE THE TWO SEGMENTS OF WASTE

COMBINE THE TWO SEGMENTS

CHARACTERIZE THE PHYSICAL PROPERTIES; MEASURE THE VISCOSITY OF THE SUPERNATE

ANALYZE CHEMICAL AND RADIOCHEMICAL PROPERTIES OF THE SOLIDS AND SUPERNATE

ARCHIVE 50 ml OF THE COMPOSITE OF THE TWO SEGMENTS
RADIOACTIVE PROCESS LABORATORY TESTING

B PLANT PRETREATMENT

ADD FERRIC NITRATE, AGITATE, ALLOW SOLIDS TO SETTLE

ADD 3:1 VOLUME RATIO WATER, AGITATE, ALLOW SOLIDS TO SETTLE, DECANT WATER WASH

ADD 3:1 VOLUME RATIO WATER, AGITATE, ALLOW SOLIDS TO SETTLE, DECANT WATER WASH

ADD SODIUM HYDROXIDE AND SODIUM NITRITE

CHARACTERIZE THE PHYSICAL, RHEOLOGICAL, CHEMICAL AND RADIOCHEMICAL PROPERTIES

HWVP FEED PROCESSING AND VITRIFICATION

CONCENTRATE AND REACT THE WASHED SOLIDS WITH FORMIC ACID

CHARACTERIZE THE PHYSICAL, RHEOLOGICAL, AND CHEMICAL PROPERTIES

ADD GLASS FRIT

CHARACTERIZE THE PHYSICAL, RHEOLOGICAL, CHEMICAL AND RADIOCHEMICAL PROPERTIES

VITRIFY MELTER FEED
Radioactive NCAW Glass, DST 101-AZ, Core Sample #2
RADIOACTIVE PRODUCT LABORATORY TESTING

DURABILITY TESTING

MONOLITHIC 28-DAY LEACH TEST

- CUT MONOLITH SAMPLES
- WASH LEACH CONTAINERS AND GLASS SAMPLES
- PERFORM MCC-1 LEACH TEST
- ANALYZE LEACHATE, CHEMICAL AND RADIOCHEMICAL

CRUSHED GLASS 7-DAY LEACH TEST

- CRUSH GLASS SAMPLES
- WASH LEACH CONTAINERS AND GLASS SAMPLES
- PERFORM PCT LEACH TEST
- ANALYZE LEACHATE, CHEMICAL AND RADIOCHEMICAL

GLASS CHARACTERIZATION

- MEASURE GLASS DENSITY
- CRUSH AND ANALYZE GLASS, CHEMICAL AND RADIOCHEMICAL
Radioactive NCAW Glass, DST 101-AZ, Core Sample #1
MCC-1 Leach Test Samples
Waste Slurry Data Comparisons

- Waste Slurries Compared (NCAW)
  - Radioactive (101-AZ, Core 1 & 2)
  - Simulant
  - Independent Simulant Data Base

- Properties Compared (abbreviated list)
  - Wt % Solids
  - Wt % Oxides
  - Density
  - Particle Size Distribution
  - Settling Behavior
  - Rheology
  - Chemical

- Based on preliminary results, behavior of simulant waste appears consistent with radioactive waste.
Comparison of Simulant Database to Radioactive Density Data

\[ y = 0.9961 + 0.0049x + 0.0001x^2 \]

Solids Concentration - wt%

\( \odot \) = Actual Radioactive Waste

Formated NCAW Slurry
SYNTHETIC vs. ACTUAL FORMATED HWVP FEED
APPARENT VISCOSITY AND YIELD STRESS

![Graph showing apparent viscosity vs. shear rate for different wt% values: 31.9 Wt% DB Sim, 28.4 Wt% DB Sim, 17.4 Wt% Sim #3, 19.1 Wt% DB Sim, 15.9 Wt% Rad, and 12.2 Wt% Rad.](image-url)
Glass Properties Data Comparison

- Glass Compared
  - Radioactive (101-AZ, Core 1 & 2)
  - Simulant
  - Model

- Properties Compared
  - Durability (MCC-1 & PCT)
  - Density
  - Crystallinity & Phase Separation
  - Redox State
## Preliminary Results of 101-AZ Core #1
### Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Radioactive Glass 101-AZ Core #1 (wt% oxides)</th>
<th>Calculated Glass Composition (wt% oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.2</td>
<td>5.1</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.7</td>
<td>9.8</td>
</tr>
<tr>
<td>CaO</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10.2</td>
<td>11.3</td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>9.8</td>
<td>10.7</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>52.0</td>
<td>50.3</td>
</tr>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Others</td>
<td>5.8</td>
<td>5.2</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Waste Loading</td>
<td>30%</td>
<td>30%</td>
</tr>
</tbody>
</table>
Comparison of Simulants and Model to Radioactive MCC-1 Durability

Normalized Boron Release in grams/m²/28 days

- Out-of-Cell Testing
- In-Cell Testing
- Model Prediction
- HWVP Limit

- Simulant 3
- ATM-10
- Core 1
- Core 2

Pacific Northwest Laboratory
S9202037.9
MCC-1 Normalized Release Rates of Radionuclides from 101-AZ Core 2

- Sr-90
- Sb-125
- Cs-137
- Pu-239 & 240
- Pu-238
- Np-237

Boron Normalized Release Rate

grams/m²/28days
Comparison of Simulant and Model to Radioactive Glass Redox State

Model:
Moles formic acid = 3X moles nitrate + 2X moles nitrite

Fe(II)/Fe(III) Ratio

Simulant 3  0.005
101-AZ Core 1  0.026
101-AZ Core 2  0.085
Acceptable Range  0.005 to 0.3
Future Plans for Core Sample Testing

- Core samples from follow-on waste types with sludge wash pretreatment will be vitrified and tested. An estimated 12-15 core samples are needed for model validation.

- Testing of the third NCAW core sample will include off-gas measurements during formatting (e.g. H$_2$, NO, NO$_2$, N$_2$O, CO$_2$, C-14, I-129, volatile organics).

- Future testing may be expanded to include off-gas measurements during calcining and vitrification and viscosity and electrical conductivity measurements on molten glass.
Summary

- On a laboratory-scale actual NCAW waste can be pretreated, formated, mixed with glass frit to form a glass with a predictable chemical composition, durability, crystallinity, and redox state.

- Comparisons to preliminary radioactive data indicate that simulants and models are representative of actual radioactive process slurries and glass.

- Additional data/evaluation and model development are needed for improved model validation.