Performance Modeling Applied to the Treatment and Disposal of a Mixed Waste at the SRS

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PERFORMANCE MODELING APPLIED TO THE TREATMENT AND DISPOSAL OF A MIXED WASTE AT THE SAVANNAH RIVER SITE (U)

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ABSTRACT
Performance modeling for Low Level Mixed Waste disposal was conducted using the measured leach rates from a number of vitrified waste formulations. The objective of the study was to determine if the improved durability of a vitrified mixed waste would allow trench disposal at the Savannah River Site (SRS).

Leaching data were compiled from twenty-nine diverse reference glasses, encompassing a wide range of exposed glass surface area to leachant volume ratios (SA/V), and various leachant solutions; all of which had been leached at 90°C, using the MCC-1 or PCT procedures (ASTM Procedures C1220-92 and C1285-94, respectively). The normalized leach rates were scaled to the ambient disposal temperature of 25°C, and compared to the allowable leach rate of uranium - which would meet the performance assessment requirements. The results indicated that a glass of above average durability (vs. the reference glasses) would meet the uranium leaching concentration for direct SRS trench disposal.

INTRODUCTION
Vitrification, the conversion of source materials into a solid amorphous glass matrix, has emerged as a viable treatment technology for the immobilization of Low-Level Radioactive Waste (LLW) and mixed waste (LLW/hazardous waste). Vitrification has been selected for the High Level Radioactive Waste (HLW) stored at the Department of Energy (DOE) West Valley, NY; Savannah River Site, SC; and Hanford Site, WA sites. The U.S. Environmental Protection Agency (EPA) has declared vitrification to be the "Best Developed Available Technology" for the treatment of the DOE HLW/mixed wastes [1]. The advantages of vitrification include immobilization of radioactive and hazardous constituents, substantial volume reduction, and a final wasteform with high chemical/physical durability.
Over the past two decades, substantial research has been conducted to vitrify the legacy of High Level Radioactive (HLW) waste remaining from the United States weapons production programs. More recently, vitrification has been proposed for the treatment of Low Level Radioactive (LLW) and mixed (radioactive/hazardous) wastes. Vitrification has been selected by the DOE to treat the low level fraction of the high level wastes stored at the Hanford reservation, to treat some of the mixed wastes stored at the Idaho National Engineering Laboratory site, and a mixed waste at Savannah River Site (SRS).

Final disposal of the vitrified wastes will depend on whether the final wasteform remains a hazardous waste by the EPA hazardous waste management Resource Conservation and Recovery Act (RCRA) regulations, or whether the waste can be de-characterized or "delisted" as hazardous. The SRS waste being vitrified is a RCRA listed F-006 wastewater treatment sludge from electroplating operations. The sludge was generated during the production of depleted uranium "targets" in the SRS "M-Area", for the eventual production of plutonium-239. The treated waste will remain a "listed" F-006 waste after treatment, and would therefore have to be disposed to a RCRA Subtitle C disposal facility. Disposal of the vitrified waste at the SRS is the preferred option, but the SRS low level waste disposal facilities are not permitted Subtitle C facilities, and no such facilities are anticipated at the SRS. Therefore, the SRS has submitted a "Delisting Petition" to the Region IV EPA for the vitrified M-Area sludge [2].

In order for low-level radioactive wastes to be disposed at DOE sites, the DOE Order 5820.2A mandates that a site-specific radiological Performance Assessment (PA) must be conducted. The final waste and disposal facility must comply with the performance objectives of the order. The time period for which compliance is required is not specified in the order, but it is generally assumed that the performance objectives be met for a minimum of 10,000 years. [3] The key performance objectives for the SRS E-Area disposal are:

- Protect public health and safety in accordance with other applicable DOE orders (other than 5820.2A),
- Radioactive dose to public is less than 25 mrem/yr; all pathways,
- Prevent dose to inadvertent intruder to:
  - less than 100 mrem/yr for continuous exposure, or
  - less than 500 mrem for a single acute exposure, and
- Protect groundwater resources consistent with federal, state, and local requirements - usually assumed to be less than 4 mrem/yr from radionuclides or the Maximum Contaminant Limits (MCLs) for chemical constituents from water ingestion.

The performance assessment assumes that the integrity of the wasteform, the wasteform container, and/or the vault structure itself will degrade within the 10,000 year period. Therefore, only naturally occurring geologic phenomena are used to calculate the affect on the environment or potential human uses (or intrusion) from the disposed materials.
For example, the affect of a disposed waste on the groundwater, and its potential use as a human drinking water supply, is a function of the chemical mobility of the waste in the natural environment, and the distance and attenuation of the waste in the soil column between the waste and the water table. In the case of the M-Area plating line sludge, the final vitrified waste form will contain quantities of uranium isotopes which would exceed the SRS E-vault or trench Performance Assessment disposal limits. However, as stated above, the durability of the vitrified wasteform is not included in the performance assessment. The retention of the constituents in the glass matrix will inhibit the migration of the radioactive materials to the drinking water supply. If the durability of the glass were included in the performance assessment calculations, the authors believe that the final M-Area product could meet the performance objectives.

The objective of this presentation is to demonstrate that current laboratory leaching procedures can be used to "predict" the long-term leaching performance of vitrified wastes, and that specifically, the vitrified M-Area waste should meet the performance criteria with respect to groundwater protection for the SRS low level radioactive trench disposal. The Curies of the various uranium isotopes present in the M-Area sludge are shown in Table I.

Table I Curies of Uranium Isotopes In M-Area Sludge

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Ci</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-234</td>
<td>4.23</td>
</tr>
<tr>
<td>U-235</td>
<td>0.19</td>
</tr>
<tr>
<td>U-236</td>
<td>0.13</td>
</tr>
<tr>
<td>U-238</td>
<td>9.55</td>
</tr>
</tbody>
</table>

SRS PERFORMANCE ASSESSMENT GROUNDWATER MODELING

Previous performance assessments for the SRS have shown that the limiting pathway for public exposure is via transport to a drinking water well and subsequent ingestion [3]. The modeling of the M-Area waste considered both the radiological and chemical toxicity of uranium. The limits used were:

- radiological toxicity, 4 mrem/yr from uranium (equivalent to 45 µg/m/L),
- chemical toxicity, a maximum proposed drinking water limit of 20 µg/m/L (20 ppb) uranium, due to heavy metal (kidney) toxicity [4].

The groundwater modeling code used for the SRS EAV performance assessment [3] and the 1987 SRS Groundwater Protection Environmental Impact Statement [5,6,7] is the "PATHRAE" code. This code was designed and accepted by the EPA for modeling the land disposal of LLW waste [8]. The PATHRAE code is designed on one-dimensional advection through the unsaturated soil zone, and is primarily affected by water infiltration rate, fraction of saturation, porosity, soil density, and contaminant sorption coefficients. Saturated zone transport is a one-dimensional advection and 2 dimensional dispersion as a primary function of groundwater velocity, dispersion coefficients, aquifer porosity and soil density and contaminant sorption coefficients. The rate of infiltration to groundwater is
assumed constant over the entire period, in this case 10,000 years. The leach rate
from the inventory is assumed constant, except for radiological decay and
solubility influences. The modeling conducted in this presentation for the
disposal of the vitrified M-Area waste at the SRS E-Area Low Level Waste
disposal utilized the following waste and site specific parameters and disposal
site assumptions. It was assumed that the waste would be distributed over the
entire area of the waste trenches, to minimize a localized uranium concentration.

Table II. Parameters for PATHRAE Modeling of SRS E-Area Disposal Site

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source (Ref. #)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trench Dimensions (m)</td>
<td>200 x 48</td>
<td>EAV-PA (3)</td>
</tr>
<tr>
<td>Downgradient Drinking Well Distance (m)</td>
<td>100</td>
<td>EAV-PA (3)</td>
</tr>
<tr>
<td>Annual Rainfall Infiltration (cm/yr)</td>
<td>40</td>
<td>EAV-PA (3)</td>
</tr>
<tr>
<td>Unsaturated Zone Depth (m)</td>
<td>9</td>
<td>EAV-PA (3)</td>
</tr>
<tr>
<td>Uranium Solubility (moles U/L)</td>
<td>2.0x10^-6</td>
<td>EAV-PA (3)</td>
</tr>
<tr>
<td>Drinking Water Uptake (L/yr)</td>
<td>730</td>
<td>EPA (4)</td>
</tr>
<tr>
<td>Uranium K_d (ml/g)</td>
<td>35</td>
<td>Sheppard (10)</td>
</tr>
<tr>
<td>Volume of Wasteform (m^3)</td>
<td>380</td>
<td>Pickett (2)</td>
</tr>
<tr>
<td>Density of Wasteform (kg/m^3)</td>
<td>2600</td>
<td>Pickett (2)</td>
</tr>
<tr>
<td>SRS Specific Hydrogeologic Factors</td>
<td>-</td>
<td>EAV(3) and Ryan (9)</td>
</tr>
</tbody>
</table>

The PATHRAE code calculates contaminant leaching, and subsequent
groundwater concentration at the drinking water well, based on a constant
fractional leach rate \( \alpha_L \) (yr^-1). This \( \alpha_L \) is multiplied by the initial inventory of
each isotope \( I_0 \) (Ci) to obtain a preliminary value for the annual activity release
in Ci/yr. The preliminary value is corrected for isotopic radioactive decay and
solubility limitations, and corrected to human dose equivalents in millirem/year
(mrem/yr). The significant decay products for the M-Area uranium inventory, in
a 10,000 year period, are U-238 and U-234. At a fractional release rate of
6.0 x 10^-6/yr, U-238 causes 2.5 mrem/yr dose, U-234 causes a 1.25 mrem/yr, and
all other radionuclides provide a dose of 0.25 mrem/yr, for a total of 4.0
mrem/year. Since the major isotope present is U-238 (Table I), this translates to a
concentration of 45 \( \mu \)g U/L (45 ppb). The fractional release \( \alpha_L \) resulting in a
uranium concentration of 20 \( \mu \)g/L (20 ppb) is 2.65 x 10^-6/yr. This fractional
release from the E-Area trenches, of 2.65% of the uranium inventory over 10,000
years, is the release rate which would meet the health based drinking water goal.

GLASS CORROSION
Corrosion Mechanisms And Glass Dissolution

Waste glass corrosion involves a series of complex processes which are
highly dependent on environmental conditions and initial glass composition. The
model most widely accepted at present involves three primary mechanisms (11):

- diffusion controlled ion-exchange (diffusion of water into the glass, and
  exchange of hydrogen for soluble cations),
- dissolution of the glass matrix, (complete breakdown of the glass structure
  via hydrolysis reactions), and
formation of thermodynamically stable products from the glass constituents (crystalline phases on the glass surface, or precipitation of amorphous phases).

The diffusion controlled ion-exchange dominates the early stages of glass dissolution, while glass matrix dissolution dominates the latter stages (12). The surface layers may reduce leaching by forming a protective barrier [13], or could cause leaching to increase by altering the solution chemistry [11,14].

While these three corrosion mechanisms control the mechanism by which glass dissolves, solubility considerations determine the dissolution rate. The dissolution rate is highest initially, when the chemical potential gradient between the glass and the solution is the greatest [15]. As soluble constituents are released, the driving concentration gradient is decreased, and the corrosion rate declines. In most leaching environments, highly soluble elements such as sodium, lithium, and boron are almost completely released into solution. Components such as silicon, aluminum, and iron become supersaturated as leachant chemistry changes, and can be re-precipitated as surface layers. If the vitrified wasteform is subjected to limited infiltration of groundwater over long time periods, then the contacting solution may experience saturation with respect to all but the most soluble components. Solution saturation, especially with respect to the primary glass former, silicon, causes the dissolution rate to decline dramatically [11,16].

Most long-term leaching data suggest that the overall glass corrosion rate should decrease with time[12]. Test conducted with high Surface Area (SA) to Volume (V) ratios, at durations long enough to reach silicon saturation, generally show that dissolution rates approach a low, steady-state value [17].

Glass Leach Rate Calculations

An analytical model that reliably predicts contaminant leaching from glass in a disposal environment has yet to be developed. However, a substantial amount of empirical leaching data has been generated in the last two decades, during the development of durable glass wasteforms for the stabilization of radioactive and mixed wastes. Standard leaching test protocols report the concentration of the elemental glass components (i.e., silicon, boron, sodium) observed in the leaching solution, at various times. The leach solution concentration is normalized to based on the concentration of each component in the initial glass. The Normalized Concentration $NC_i$ is defined as:

$$ NC_i = \frac{C_i}{F_i} \text{ where,} $$

$NC_i = \text{normalized concentration of the element } i \text{ in the leachant (g/m}^3, \text{ or ppm)},$

$C_i = \text{concentration of element } i \text{ in leachant (g/m}^3), \text{ and}$

$F_i = \text{mass fraction of element } i \text{ in glass (g/g } \text{glass}).$

If leaching data exist for two different times, at otherwise identical conditions, an approximation of the Normalized Leach Rate (NLR), at average time, can be calculated.
\[ NLR_i = \frac{(NC_i)_n - (NC_i)_{n-1}}{(SA/V) (t_n - t_{n-1})} \]  

where;

- \( NLR_i \) = normalized leach rate for element \( i \) (g/m²·day)
- \( SA \) = exposed glass surface (m²), and
- \( V \) = leachant volume (m³)
- \( t_n - t_{n-1} \) = delta time (days)

This approximation is poor during the early stages of glass dissolution, when the rate is affected strongly by the large differences in glass vs. solution concentrations. However, over long time periods (months to years), and in situations where the surface area is large compared to the volume of leachant, the \( NLR_i \) will remain relatively constant. High \( SA/V \) conditions are expected in disposal sites where groundwater infiltration is limited due to climatic or geological conditions, and the surface area of the waste is significant.

Boron has been selected as a good indicator of the overall leach rate of a glass, since it is a key component of boro-silicate glasses, is among the most soluble of glass constituents, and does not tend to saturate the solution or form secondary precipitation products. \( NLR_i \) can be approximated as \( NLR_{boron} \).

If both the \( NLR_i \) and the effective surface area are assumed to be relatively constant over a delta period of time \( t_n \) to \( t_{n-1} \), then the total mass release (\( M_{Total} \)) can be calculated by:

\[ M_{Total} = (NLR_{boron}) \text{ g/m}^2\cdot\text{day} \times (SA) \text{ m}^2 \times (\text{delta time}) \text{ days} \]  \hspace{1cm} (3)

The mass release of less soluble glass components, such as uranium, will be a fraction of the boron release. A conservative assumption for these calculations is \( NLR_{uranium} = NLR_{boron} \). Therefore, the total mass release of uranium at time \( t \) can be found as:

\[ M_{Total \text{ uranium release}} = (NLR_{boron}) \text{ g/m}^2\cdot\text{day} \times (SA) \text{ m}^2 \times (\text{delta time}) \text{ days} \]  \hspace{1cm} (4)

then the fractional release = \[ \frac{M_T}{M_{initial}} = \frac{(NLR_{boron}) \text{ g/m}^2\cdot\text{day} \times (SA) \text{ m}^2 \times (\text{days})}{M_{initial \ g}} \]  \hspace{1cm} (5)

**PATHRAE vs. GLASS LEACH RATE MODELING**

PATHRAE's use of a constant fractional leach rate \( \beta_L \) is therefore similar to the constant approximation of glass leaching based on boron release and surface area to volume of leachant ratio. I. e. the PATHRAE fractional release is:

\[ \beta_L \ (\text{yr}^{-1}), \text{ fractional release/year} = \frac{M_T \ g \text{ released by time } t}{M_{initial \ g}} \]  \hspace{1cm} (6)
Substituting the average fractional release from the leaching model; Eq. 5, gives

$$AE_L(\text{yr}^{-1}) = \frac{(NLR_{\text{boron}} \text{ g/m}^2\cdot\text{day}) \cdot (SA, \text{ m}^2) \cdot (\text{delta time, days})}{\text{Mass initial g}} \times \text{years}$$  \hspace{1cm} (7)

This equation assumes that the Normalized Release Rate for the vitrified M-Area waste remains relatively constant over the 10,000 year time frame. This is reasonable, considering that in order to meet the performance assessment, the glass must release no more than 2.65% of the uranium in the 10,000 year time frame.

In the specific case of the modeling of the release of uranium from a vitrified waste in an E-Area trench, the PATHRAE $AE_L$ can be related to the approximate glass leaching. The final volume of vitrified waste is assumed to be ~100,000 gallons, or 380 m$^3$. Since the density of the final glass is ~2.6 x 10$^6$ g/m$^3$, then the final mass will be ~9.9 x 10$^8$ g.

The glass will be prepared as small glass ovoids, approximately 13 mm in diameter. The volume (V) of a single ovoid = $2/3 \pi r^3 = 5.75 \times 10^{-7}$ m$^3$. The surface area of a single ovoid = $3 \pi r^2 = 3.98 \times 10^{-4}$ m$^2$. The number of ovoids can be estimated by dividing the total volume V by the volume per ovoid = 380 m$^3$ / 5.75 $\times$ 10$^{-7}$ m$^3$. $\approx$ 6.6 x 10$^8$ ovoids. The surface area (SA) of the vitrified waste will be ~6.6 x 10$^8$ x 3.98 x 10$^{-4}$ m$^2$.

To relate $AE_L$ to the leach rate calculations for this case, substitute the M-Area parameters in equation 7;

$$AE_L(\text{yr}^{-1}) = \frac{(NLR_{\text{boron}} \text{ g/m}^2\cdot\text{day}) \cdot (SA, \text{ m}^2) \cdot (\text{delta time, days})}{\text{Mass initial g}} \times \text{years}$$  \hspace{1cm} (7)

or, rearranging,

$$NLR_{\text{boron}} \text{ g/m}^2\cdot\text{yr} = \frac{AE_L \text{ yr}^{-1} \cdot (\text{Mass initial g})}{(SA, \text{ m}^2)}$$  \hspace{1cm} (8)

NLR$\text{boron}$ = Average bulk corrosion rate, g/m$^2$$\cdot$yr
SA = initial effective area = 2.6 x 10$^5$ m$^2$,
M$\text{glass}$ = initial mass of glass = 9.9 x 10$^8$ g

$$NLR_{\text{boron}} \text{ g/m}^2\cdot\text{yr} = \frac{AE_L \text{ yr}^{-1} \cdot (9.9 \times 10^8 \text{ g})}{(2.6 \times 10^5 \text{ m}^2)} = AE_L \text{ yr}^{-1} \cdot 3.8 \times 10^3 \text{ g/m}^2$$  \hspace{1cm} (9)

Assuming $NLR_{\text{uranium}} = NLR_{\text{boron}}$, then

$$NLR_{\text{uranium}} = \approx 3800 \ AE_L \text{ yr}^{-1} \text{g/m}^2$$  \hspace{1cm} (10)
This is a direct relationship between the leaching of the M-Area glass beads and the PATHRAE fractional leach rate parameter. The PATHRAE code was used previously to calculate a fractional release rate \(\dot{E}_L = 2.65 \times 10^{-6}\text{ yr}^{-1}\), giving a drinking water concentration of 20 ppb. Substituting this into equation 10 gives:

\[
NLR_u = (3800 \text{ g/m}^2)(2.65 \times 10^{-6}\text{ yr}^{-1}) = 0.010 \text{ g/m}^2\text{-yr} = 2.7 \times 10^{-5} \text{ g/m}^2\text{-day (11)}
\]

Therefore, the normalized average bulk glass uranium release rate \(NLR_{\text{uranium}}\) that would meet the 20 ppb drinking water standard is \(\sim 2.7 \times 10^{-5} \text{ g/m}^2\text{-day}\).

**ACCEPTABILITY OF M-AREA GLASS LEACH RATE**

Now that a normalized uranium leach rate has been calculated for the vitrified M-Area waste, it can be determined whether the actual waste will meet this level. Three methods can be used:

1) comparison to natural glasses such as obsidian and tektites,
2) comparison to other glasses using standard leaching procedures, and
3) long term leaching studies with actual M-Area glasses.

**Natural Glasses**

The first method is appropriate to obtain a rough estimate of whether the M-Area waste glass can meet the \(2.7 \times 10^{-5} \text{ g/m}^2\text{-day}\) leach rate, under ambient conditions. Jantzen has compared the durability of natural glasses (10^5 to 10^6 years) to ancient man-made glasses (10^3 years)[18] and found that these glasses bounded the expected durability of nuclear waste glasses. Advanced waste glasses should approach 10^6 years in a repository environment. Since the PATHRAE code calculations indicated that a release of 2.65% per 10,000 years would meet the 20 ppb drinking water limit, a total release would occur in \(3.8 \times 10^5\) years. This is consistent with the durability of nuclear waste glasses.

**Standard Leaching Test Results**

A number of long term static leach test results were collected from the literature. Twenty-nine studies, from seven different references, were utilized to form a reference database [20-26]. All the tests were conducted at 90°C, with a variety of leachants and SA/V ratios. The times ranged from 84 to 920 days, at a minimum SA/V of 340 m^-1. An average long term normalized leach rate for boron was determined from each of the 29 studies. Using the Arrhenius equation, the \(NLR_{\text{boron}} 90^\circ C\) data was then corrected to an ambient temperature of 25°C. An activation energy of 75 kJ/mole for the Arrhenius calculation was selected from the average of the range activation energies of 60-90 kJ presented in Reference 19. The temperature corrected leaching data ranged from \(1.0 \times 10^{-6}\) to \(1.6 \times 10^{-4} \text{ g/m}^2\text{-day}\). A lognormal probability plot (Figure 1) showed that seventy % of the glasses from the 29 different reference glasses would satisfy the
calculated leach rate of $2.7 \times 10^{-5}$ g/m²-day needed to meet the 20 ppb groundwater concentration.

CONCLUSION
The allowable leach rate needed to meet the drinking water standard for uranium at a groundwater well downgradient of an E-Vault trench is well within the durability attained by modern nuclear waste glass formulations. Empirical leaching studies to confirm that actual M-Area glasses will meet this standard are now underway.

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Lognormal probability plot for long-term leach rates with allowable leach rates from performance assessment calculations.
REFERENCES


