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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

MEMORANDUM

TO: J. F. ORTALDO
FROM: S. L. GORE*, G. G. WICKS, R. M. WALLACE

DATE: October 1, 1982

FILE

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INTRODUCTION AND SUMMARY

Over the past two years, the leaching behavior of Savannah River Plant (SRP) waste glass has been extensively studied in order to predict the long term stability of the glass. Recently, Wicks and Wallace developed a physical and mathematical model of the leaching process, based on simple concepts of glass corrosion and protective layer formation which accurately describes the three stage corrosion behavior of waste glass. Emphasis is now being placed on confirming the model by more detailed studies of glass corrosion. The effects of pH, SA/V ratio, surface finish, protective layers formed, time and temperature are being studied in detail, and the model is being extended by applying it to other waste glass systems.

In this study the effects of time and temperature on the leaching of SRP waste glass are examined. Data obtained in previous studies on both lab scale and full scale, TNX-continuous melted glasses are used. Based on these data we conclude that:

- The time dependence of normalized leach rates (based on Si) correspond relatively well with the behavior predicted by the SRL Leachability Model.

* Co-op from Mississippi State University.
Over the temperature range 40-150°C, leachants which are less aggressive to waste glass have higher activation energies for leaching, representing a higher barrier to glass dissolution.

The aggressiveness of the leachants evaluated in the present study is in the order: pH3 buffer > pH 11 buffer > deionized water > MCC silicate water > MCC brine > pH 7 buffer. The pH 3 buffer is 40X more aggressive than the pH 7 buffer.

Arrhenius plots of Cs and U leachability in three different leachants indicate differences in the leaching behavior of these elements compared to Si occur at elevated temperatures. These differences may result from changes in corrosion mechanisms or changes in oxidation state as in the case of uranium.

**DISCUSSION**

**Time Dependence**

The normalized elemental mass loss ($NL_i$), Table 1, has been related to the time of leaching in unsaturated systems by the SRL Leachability Model\(^2\) as follows:

$$NL + B(NL)^2 = K_r t$$

or $NL$ at (for Stage 2 leaching – network dissolution)

and $NL$ at $t^{1/2}$ (for Stage 3 leaching – layer formation and diffusion controlled dissolution)

Plots of $NL_i$ versus both $t$ and $t^{1/2}$ for times of 3, 7, 14 and 28 days are shown in Figure 1 and summarized in Table 1. As noted in the figure, both curves fit the data relatively well. However, the correlation coefficient for $t^{1/2}$ is slightly better. In addition, these curves must go through zero at time = 0 which suggests that there are different mechanisms or transient effects evoked for very short term leaching. These potential effects would be very large for the larger $y$-intercept assuming linear time dependence but less dominant for $t^{1/2}$ dependence.

For time periods less than 3 days, where most standard leaching tests only begin, glass leaching behavior may be quite different. Work is currently in progress investigating the very early stages of glass corrosion as a function of parameters such as surface finish, temperature and flow rate. These data will allow us to better understand short term leaching behavior.

**Temperature Dependence**

A direct correlation between leaching behavior and activation energy has been observed. The activation energy ($Q$) and leach-
ability \( L \) are related by 

\[ L = k \exp(-Q/RT) \]

where \( T \) is the absolute temperature, \( k \) is constant and \( R \) is the gas constant. Therefore, from the slope of a plot of \( \log L \) versus \( 1/T \) the activation energy can be obtained. For glasses previously leached in buffered solutions of pH 3 and pH 11, the leachability based on Si was relatively high and the activation energies calculated were relatively low, about 5.5 kcal/mole (Table 2). The lowest leachabilities observed occurred after leaching in a pH 7 solution with a relatively high activation energy of 14.2 kcal/mole. In the intermediate case of deionized water, the leach rates based on Si were between these extremes corresponding to about 11 kcal/mole. Similar correlations were observed for brine and silicate leachants as summarized in Figure 2. Also noted in this graph is the 90°C data for the full scale CM glass leached in deionized water which falls on the sample curve for laboratory-produced glass also leached in the same medium. The activation energy cannot be precisely interpreted at this time due to the complex and varied leaching processes involved. However, in an oversimplified interpretation, the activation energy represents the low barrier to glass dissolution.

A relatively linear representation was obtained by plotting \( \log \) of leachability of Cs versus \( T^{-1} \) for the three temperatures studied (Figure 3). At lower temperatures, deionized water was the most aggressive leachant corresponding to the highest leachability and lowest activation energy, followed by silicate water and finally brine. However, at approximately 110°C, the three curves intersect and the relative aggressiveness of the leachants reverse. The reasons for this behavior are not presently understood but may be related to changes in the dissolution rate and subsequent sorption characteristics of Cs as a function of temperature, or possible insoluble compound formation at higher temperatures.

A plot of \( \log \) of leachability of uranium (Figure 4) with \( T^{-1} \) shows a sharp decrease in slope at higher temperatures. In addition, this plot is clearly not as linear as observed for other elements and as predicted by simple glass corrosion theory. This change in slope may be attributed to several factors including possible compound formation as well as changes in oxidation state of the uranium. Higher temperatures favor a lower oxidation state of the uranium and improved performance.

SLG, GGW, RMW: pmc
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### TABLE 1

**TIME DEPENDENCE OF LEACHING OF SRP WASTE GLASS***

<table>
<thead>
<tr>
<th>TNX Premixed Waste Glass</th>
<th>May 1982</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>t</strong></td>
<td><strong>NL(Si)</strong></td>
</tr>
<tr>
<td>3</td>
<td>8.82</td>
</tr>
<tr>
<td>7</td>
<td>13.51</td>
</tr>
<tr>
<td>14</td>
<td>16.24</td>
</tr>
<tr>
<td>28</td>
<td>20.72</td>
</tr>
<tr>
<td><strong>STD DEV.</strong></td>
<td>+0.75</td>
</tr>
</tbody>
</table>

\[
NL(Si) = 3.22 t^{1/2} + 4.03
\]

\[
CORR. COEFF. = 0.989
\]

<table>
<thead>
<tr>
<th><strong>131/TDS Lab Scale Waste Glass</strong></th>
<th>Sept 1981</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>t</strong></td>
<td><strong>NL(Si)</strong></td>
</tr>
<tr>
<td>3</td>
<td>12.69</td>
</tr>
<tr>
<td>7</td>
<td>14.98</td>
</tr>
<tr>
<td>14</td>
<td>21.70</td>
</tr>
<tr>
<td>28</td>
<td>26.88</td>
</tr>
<tr>
<td><strong>STD DEV.</strong></td>
<td>+0.92</td>
</tr>
</tbody>
</table>

\[
NL(Si) = 4.18 t^{1/2} + 5.06
\]

\[
CORR. COEFF. = 0.990
\]

* MCC-1 Static Leach Tests, 90°C, Deionized Water Leachant.
<table>
<thead>
<tr>
<th></th>
<th>pH 3</th>
<th>pH 11</th>
<th>D.I. H₂O</th>
<th>Silicate</th>
<th>Brine</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C (Lab)</td>
<td>0.53</td>
<td>0.45</td>
<td>0.05</td>
<td>0.04</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>90°C (Lab) (TNX-CM)</td>
<td>2.32</td>
<td>1.40</td>
<td>0.96</td>
<td>0.56</td>
<td>0.32</td>
<td>0.060</td>
</tr>
<tr>
<td>150°C (Lab)</td>
<td>4.96</td>
<td>4.66</td>
<td>4.28</td>
<td>2.96</td>
<td>1.41</td>
<td>1.53</td>
</tr>
</tbody>
</table>

\[ Q \quad \text{(kcal/mole)} \]

5.55 5.80 11.05 10.69 12.29 14.22

Based on MCC-1, 28 day static leach tests, Sept. 1981.°

Disc 7
NORMALIZED LEACH RATES BASED ON STAGE 2 & STAGE 3 LEACHING BEHAVIOR FOR TNX GLASS MCC-1 TESTS, 90°C, DEIONIZED WATER

\[ NL + \frac{B(NL)^2}{2} = K_f t \text{ (Unsat)} \]

- \( NL \propto t \) (Stage 2)
- \( NL \propto t^{1/2} \) (Stage 3)
ACTIVATION ENERGIES BASED ON SILICON EXTRACTION MCC-1 TESTS, 28 DAYS
ACTIVATION ENERGIES BASED ON CESIUM EXTRACTION

MCC-1 TESTS, 28 DAYS

Δ Deionized H₂O
● Silicate H₂O
□ Brine

Δ Deionized H₂O
● Silicate H₂O
□ Brine

Δ Deionized H₂O
● Silicate H₂O
□ Brine

1/L (g/cm²-day)

1/T °K

0.0028

0.0032

0.0024

0.0020
ACTIVATION ENERGIES BASED ON URANIUM EXTRACTION
MCC-1 TESTS, 28 DAYS

Note: Linear approximation is a poor fit.