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MEMORANDUM FOR: F. Robert Cook
High-Level Waste Licensing
Management Branch
Division of Waste Management

FROM: Everett A. Wick
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SUBJECT: TRIP REPORT - MATERIALS RESEARCH SOCIETY 1982 ANNUAL
MEETING, NOVEMBER 1-4, 1982, BOSTON, MASSACHUSETTS

Attached is the subject trip report.

Original Signed By:

Everett A. Wick
High-Level Waste Licensing
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As stated

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TRIP REPORT - MATERIALS RESEARCH SOCIETY 1982 ANNUAL
MEETING, NOVEMBER 1-3, 1982, BOSTON, MASSACHUSETTS

Introduction

I attended the first 3 days of the Sixth International Symposium on the Scientific Basis for Nuclear Waste Management in Boston, Mass., November 1-3, 1983. During this period papers were presented on waste forms, mostly borosilicate glass.

Summary

1. Two accelerated test methods were suggested as viable means for demonstrating long term leach rates for borosilicate waste glasses. One method, suggested by McVay of PNL, is to vary the ratio of the glass surface to solution volume to accelerate leaching. The second, suggested by Bates of ANL, is to simulate the aging of glass by hydrating it with water vapor and then subjecting the "aged" glass to leach tests.
2. Spent fuel waste forms were not addressed at this meeting.
3. There was disagreement among the authors on whether layers formed on waste glass by reaction with a leachant protect the glass by reducing the rate of subsequent leaching. Wicks and Wallace of SRL concluded that at a pH of 7 a protective surface layer forms on the glass. Lutze and Malow (Hahn-Meitner Institute) reported that leaching of borosilicate glass in water at 165° C and 200° C resulted in formation of a layer of crystals and that subsequent leaching was reduced by about 95%. Bates and Steindler of ANL

concluded that surface layers do not protect the glass from leaching by a fresh leachate.

There also was divergence in opinion concerning the solubility theory of leaching.

4. McVay reported that additions of silicic acid to the leachant reduced the leach rate and concluded that the leach rate of a constituent in the glass decreases as its concentration in the leachant increases. However, the Swedes (Christensen and Hermansson) and Clark of the University of Florida reported much higher initial leach rates in silicate groundwater and in sodium chloride solutions than in distilled water.

Discussion

The papers judged most interesting during the three days I attended the Symposium are presented below. These were:

D.4.1 NWTS Waste Package Design and Materials Testing Status FY82, J. F. Kircher and D. J. Bradley, Office of Nuclear Waste Isolation.

Conceptual designs were completed in FY82 and detailed designs for each repository media are now underway. These designs emphasize safe handling, retrieval, long term containment "for hundreds of years to 1000 years" and slow release (for "many thousands of years").

Borosilicate glass is the reference waste form for defense waste and is also being considered for commercial high level waste.

The waste form for spent fuel was not discussed at this meeting but the spent fuel package configuration was mentioned briefly in a slide. A

spent fuel waste package shown in a slide contained rods from 3 pressurized water reactor fuel assemblies (1.45 MTHM) or from 7 boiling water reactor fuel assemblies (1.3 MTHM).

Carbon steel is a leading container material candidate but Kircher emphasized that work on titanium is still going forward. An additional corrosion resistant barrier may be required.

Some corrosion data were presented for cast ferrous materials. In Hanford basaltic groundwater under oxic conditions, 7 month data at 150° C shows a rate of ¼ mil per year or ¼ inch per 1000 years. In salt, the corrosion rate in deaerated brine is in the range of 3-6 mils/year for test periods up to 5 months.

The above tests will be repeated in the gamma pool to observe the effects of radiation, which, in general, increases corrosion rates. In basaltic groundwater, gamma radiation (2×10^6 rads/hr) increased the reaction layer thickness by about a factor of 10.

The presence of iron in the three types of repository groundwaters was found to enhance leaching (as determined by boron concentration in the leachant) of borosilicate glass, but it is not a drastic increase in leach rate.

Demonstration of the waste package will be done at the site at depth over a period of 30 to 40 years. Design of emplacement equipment is getting started.

Paper D1.5 Leaching Chemistry of Defense Borosilicate Glass, R. M. Wallace and C. G. Wicks (SRL).

The speaker began by presenting the processes which, in the authors' view, are important in waste glass corrosion: interdiffusion (ion exchange), matrix dissolution, and surface layer formation. Based on the MCC-1 tests at 90° C (presumably on SRP glass), the speaker reported that the pH stabilized within the first three days and that the ratios of elements in the leachates were independent of time. The authors reached the following conclusions from the results of their tests:

- The interdiffusion process reaches a steady state in three days.
- Glass corrosion is congruent
- Only part of some constituents end up in the leachate
- The remainder form an insoluble surface layer
- The final pH of the leachate is controlled by borate and silicate buffering.

According to the speaker, the surface of the unaltered glass is coated with a gel layer which, in turn, is coated with a precipitate layer. A model of the dissolution process is based on the assumption that the interdiffusion process is at steady state, that the interface between the bulk glass and the precipitate layer is initially amorphous silica, that the silica dissolves, and that the thickness of the layer is proportional to the amount of silica dissolved. The dissolution in two different pH regimes was described. At a pH of 3 the authors find rapid congruent leaching (five times as fast as at pH 7), and no surface layer formation. At a pH of 7 the authors find partially congruent leaching with formation of a protective surface layer. The speaker concluded that mathematical models can be developed to describe long term leaching of waste glass at 90° C but that such models are not easy to develop for short term leaching.

Paper D1.7 Morphology and Chemical Composition of a Surface Layer Formed Upon Leaching of Nuclear Waste Glass, W. Lutze and G. Malow (Hahn-Meitner Institute) and T. J. Headley (SNL).

As a result of the leaching of borosilicate glass in water (exact composition not given) at 165 and 200° C, the outer layer of the leached surface was covered with a layer of crystals about 1- μ thick. A 30- μ thick layer of crystals was formed after about 30 days. The leach rate decreases from its initial three-day value of 1.86 to $0.08 \times 10^3 \text{ g cm}^{-2} \text{ d}^{-1}$. New phases still appeared at the surface even after one year in NaCl solution.

A question was asked by J. Bates (who presented paper D2.9 discussed below), on whether the glass covered with the layer of crystals had been done in a closed system.) Unfortunately, the speaker seemed to have a problem with English and answered that surface kinetics seem to be independent of solution concentration. When asked if the crystalline phase forms below 100° C, it was stated that no such experiments were done, but the crystal formation does take longer at the lower temperature (165° C).

See the discussion of Paper D2.9, below.

Paper D.1.8 Glass Surface Area to Solution Volume Ratio and Its Implications to Accelerated Leach Testing, C. Q. Buckwalter and G. L. McVay, PNL.

This was presented by McVay at the Gaithersburg meeting in May 1982, but it is a key paper. The increase of surface area to solution ratio may be a viable method of increasing the rate of weatherization as it pertains to solution concentration. This may be used to model long term behavior of leaching.

McVay reached the following conclusions:

- The leach rate is a function of the solution concentration
- Adding ductile iron increases the leach rate
- SA/V ratio can strongly influence leach rate, or have no effect if enough water is presented
- Silicic acid addition reduced rate of leaching of all glass components
- Leaching depths of all solution components were similar, with none greater than silica
- Accelerated leach testing using SA/V ratios to simulate long term leaching is possible

Paper D.2.4 Effects of Solution Chemistry and Atmosphere on Leaching of Alkali-Borosilicate Glass, H. P. Hermansson, H. Christensen (Studsvik Energitechnik AB, Sweden) and D. E. Clark (University of Florida).

Simulated alkali-borosilicate waste glass displayed much higher initial leach rates in silicate groundwater and in sodium chloride solutions than in distilled water.

McVay asked why the silicate water leaches faster than distilled water (this result disagrees with his findings presented in paper D.1.8 discussed above). An unidentified member of the audience commented that the silicate phase in solution can accelerate the leach rate by scavenging dissolved species, but silicate phases on the surface may retard leach rates. Thus, where the silicate phases form is critical.

Paper D.2.5 Basic Leaching Processes in Silicate Glass: The Effect of Solution pH and Ions in Solution on Gel Layers, B. C. Bunker, E. K. Beauchamp and G. W. Arnold (SNL).

It is commonly assumed that the leaching mechanism consists of two phases:

Stage No. 1: Parabolic kinetics, i.e., leach rate is proportional to the square root of time, during which H_3O^+ diffuses into the glass and Na^+ out of the glass.

Stage No. 2: Linear kinetics, i.e., leach rate is proportional to time, during which the leached layer becomes a diffusion barrier.

The Sandia experiments were conducted at fixed pH by a pH-stat titration arrangement. Although the pH is fixed, the two stages are observed. In this case, however, the authors claim that the observation is not consistent with the above models. The controlling feature was not diffusion in bulk glass, but diffusion through a hydrosilicate layer. The pH in this gel layer controls the rate of leaching, i.e., the gel pH may not be the same as the solution pH. At pHs exceeding 2, the silicate gel at the surface has a negative charge so that positively charged colloids tend to be absorbed onto the surface. Also Fe^{+3} in solution scavenges leach products and thus accelerates leaching by decreasing the solution concentration (note similarity to McVay's observation of increased leaching due to the presence of metallic iron in solution in paper D.1.8 above).

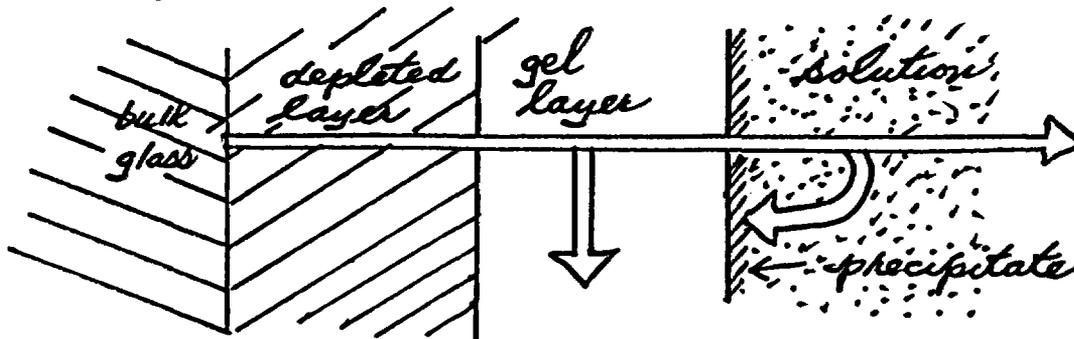
The following conclusions were drawn:

1. Hydrolysis product diagrams can be used to predict adsorption.
2. Colloidal particles in solution can affect leaching.
3. pH and ions can lead to changes in leach rate.
4. SA/V effects (see paper D.1.8) can be explained using the adsorption effects.

Paper D2.9 Extended Leach Studies of Actinide Doped SRL 131 Glass,

J. K. Bates, D. J. Lam and M. J. Steindler (ANL).

Eighteen-month tests were conducted using MCC-1 conditions with dionized water at 90° in order to correlate leachate analysis and surface analysis. The pathways of the material from the bulk of the glass may be diagrammed as follows:



The following conclusions were reached:

1. Saturation is attained for all elements in one year for the MCC-1 tests.
2. Solution and layer composition are influenced by small changes in minor element composition.
3. Surface layers do not protect the glass from leaching by fresh leachate.

The third conclusion is the most significant. Considering the emphasis on the formation of protective layers on waste glass exposed to leaching solutions (e.g., Papers D1.5, D1.7, D2.4 audience discussion) the sensitivity of this layer to fresh leachate is crucial in a repository environment with a potential flow of groundwater through the waste package.

Paper D.10.5 Alteration of Nuclear Waste Glass by Aging, Bates and Steindler, ANL.

The reaction between waste glass and water vapor may be possible in a repository until resaturation conditions have been reached.

The layer thickness can be used to measure the degree of hydration that has occurred.

Leaching of hydrated glass indicates whether hydration is a serious aging phenomenon that will affect long term waste storage.

SRL 131 glass with actinides and fission product radiotracers was hydrated (80, 120, 162, 202 and 240C) for up to 2.5 years. The mechanism of hydration is the same at all temperatures.

Conclusions

1. Hydration by water vapor offers an exact way of simulating aging that may occur in a repository.
2. Leaching of hydrated glass may yield different results than leaching of fresh glass.

3. Dating of natural glasses must take careful account of several variables.



E. A. Wick