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# COMPARISON OF PROPERTIES OF BOROSILICATE GLASS AND CRYSTALLINE CERAMIC FORMS FOR IMMOBILIZATION OF SAVANNAH RIVER PLANT WASTE

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## ABSTRACT

Properties of borosilicate glass and the crystalline ceramic Synroc-D waste forms for immobilization of Savannah River Plant (SRP) defense high-level waste are compared. Waste loading, leach resistance, thermal stability, mechanical stability, and radiation stability are the properties compared. Leaching data are from comparative tests performed independently at the Savannah River Laboratory (SRL) and at the Materials Characterization Center, supplemented by data on borosilicate glass from SRL and data on Synroc-D from Lawrence Livermore National Laboratory (LLNL). Mechanical stability data are from comparative impact tests at Argonne National Laboratory. Data on other properties are primarily from tests at SRL and LLNL. The comparison shows that borosilicate glass is superior in some properties, and Synroc-D is superior in others, with neither material showing a clear advantage. Based on product properties alone, either material would be acceptable for SRP waste. Potential improvements in the quality of both waste forms are discussed.

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# COMPARISON OF PROPERTIES OF BOROSILICATE GLASS AND CRYSTALLINE CERAMIC FORMS FOR IMMOBILIZATION OF SAVANNAH RIVER PLANT WASTE

## INTRODUCTION

Borosilicate glass and crystalline ceramic are candidate waste forms for immobilization of Savannah River Plant (SRP) defense high-level nuclear waste.[1] The waste form will be manufactured in the Defense Waste Processing Facility (DWPF) at SRP. Eventually, waste forms will be emplaced in a federal underground repository for permanent disposal.[2,3]

Since 1977, borosilicate glass has been the reference waste form for Du Pont development and design studies for the DWPF. In 1979, the Department of Energy (DOE) initiated a program to evaluate a number of alternative waste forms, including other glasses, ceramics, concretes, cermets, metals, and composite materials.[4]

After a two-year, multi-laboratory development program on seven of these waste forms, including borosilicate glass, a detailed assessment of the forms was made based on product performance properties and process feasibility.[1] From this assessment, the crystalline ceramic "Synroc-D" and the reference borosilicate glass forms were chosen for final consideration in selecting the DWPF waste form in 1982. Synroc-D is being developed by Lawrence Livermore National Laboratory (LLNL),[5,6] from the original concept developed by Professor A. E. Ringwood at the Australian National University.[7] Borosilicate glass is being developed for SRP waste by the Savannah River Laboratory (SRL).[8-10] Either form would be acceptable for SRP waste, based on product properties alone. Final selection of a waste form for the DWPF will involve a number of factors, including product performance, processability, system costs, safety, and risk to future generations.

The purpose of this report is to review and compare the available data on product properties of borosilicate glass and crystalline ceramic waste forms. DWPF production processes for the two forms are described and compared in Reference 11. Large-scale waste forms have been made with borosilicate glass, but not with Synroc-D. The properties discussed were measured with small-scale laboratory specimens.

Basic features of the two materials will be described, followed by detailed comparisons of their important properties.

Leach resistance is the waste-form property considered most essential to adequate performance of each material.[12] The sizable body of leaching data is summarized, and, where possible, direct comparisons between borosilicate glass and the Synroc-D crystalline ceramic are made. Physical properties, including thermal and mechanical stabilities, are compared, followed by a discussion of the relative radiation stability of the two materials. Finally, improvements in each waste form that might result from optimization studies are discussed.

## SUMMARY

Borosilicate glass is a vitreous material that can accommodate wide variations in waste composition, and thus is an attractive host for immobilization of SRP defense high-level waste. Crystalline ceramic waste forms, such as Synroc-D, are also viable candidates. The ceramic materials are dense, mineral-like phase assemblages that can be tailored to create durable host phases for the waste elements. The properties of borosilicate glass and Synroc-D are compared in this report. Waste loading, leach resistance, thermal stability, mechanical stability, and radiation stability are the properties compared. Results of the comparison are summarized in Table 1.

Waste loading of the current reference borosilicate glass waste form is 28 wt % as oxides. On an equivalent basis, the waste loading of Synroc-D for blended waste is about 52 wt %. Densities of the glass and ceramic forms are about 2.8 g/cm$^3$ and 4.0 g/cm$^3$, respectively.

Extensive data are presented on comparative leaching properties of borosilicate glass and Synroc-D. The waste forms are compared by leach rate for cesium, strontium, uranium, and eight other elements, under a variety of test conditions. The effects of waste composition, leachant composition, temperature, and flow rate are evaluated. Comparative leaching data are available only for MCC tests up to 28 days duration.

Neither borosilicate glass nor Synroc-D is superior in leach resistance for all of the principal radwaste elements. However, on the average, Synroc-D is slightly better for the elements studied. Synroc-D is significantly better than borosilicate glass for uranium retention, but borosilicate glass is much better for strontium. Differences between the two for cesium retention are small and depend on waste composition.

The effects of waste composition and leachant composition on leaching are in general relatively small over the expected range of variation. The effect of temperature on leaching between 40 and 150°C ranges from a factor of 4 increase to a factor of 150 increase, depending on the element and leachant. Leachant flow rate effects are variable, depending on the element leached, but are relatively small at low flow rates. For other factors, such as pH, Eh, ratio of solid surface area to volume of leachant (SA/V), pressure, and surface condition, the data exist mainly for borosilicate glass, with little comparative leaching data for Synroc-D.

Physical properties relating to thermal and mechanical stability of the waste forms are interrelated and are considered together. Cracking of the waste form during large-scale production is a known phenomenon for borosilicate glass, and a probable one

## TABLE 1

### Summary of Properties of Borosilicate Glass and Synroc-D Waste Forms

| Property | Borosilicate Glass | Synroc-D Ceramic |
|---|---|---|
| Waste Loading,[a] wt % | 28 | ~50[b] |
| Density, g/cm$^3$ | 2.75 | 4.0 |
| Relative Radionuclide Content | 1 | ~3 |
| Leach Rate,[c] g/(m$^2$)(day) | | |
| Cesium | ~1 | ~1 |
| Strontium | $<10^{-3}$ | $\sim10^{-1}$ |
| Uranium | $\sim10^{-1}$ | $\sim10^{-4}$ |
| Impact Response,[d] wt % fines | 0.14-0.18 | 0.16 |
| Radiation Stability | Very Good | Undetermined |

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a. Nominal loading of waste oxides, calculated with aluminum removal.

b. For blended waste; small-scale specimens with different simulated wastes had loadings from 13 to 52 wt %.

c. Average leach rates from 28-day MCC-1 Static Leach Tests at 90°C.

d. Fines less than 10 micrometers, measured in impact tests with 10 J/cm$^3$ energy density.

for Synroc-D. Bulk fracture and surface cracking can be controlled to some extent with both forms. The impact resistances of borosilicate glass and Synroc-D are almost identical under a variety of conditions. The principal thermal effect of interest for borosilicate glass is devitrification, which can be controlled; there is no analogous thermal effect with crystalline ceramic.

Radiation stability studies have been performed for borosilicate glass. For Synroc-D, radiation properties are inferred from studies of natural mineral analogs. There is no evidence of significantly detrimental effects of radiation on either waste form.

Improvements in product quality may be possible from optimization of either waste form. Borosilicate glass may benefit from frit reformulation, from increased waste loading, and from measures to decrease thermal fracturing. For Synroc-D ceramic, potential improvements may be possible by developing more durable phases and by process changes that could ensure consistent product quality without stringent process control.

## DESCRIPTION OF BOROSILICATE GLASS

Glasses are amorphous, vitreous materials formed by melting together the oxides of various elements. Because of the amorphous structure, glasses can accommodate wide variations in composition. This property makes glass an attractive host for nuclear waste, which may contain more than 40 elements in variable amounts.

Silica is the principle glass former in most glasses. With increasing silica content, glasses exhibit the following changes: (1) durability increases, which is desirable for nuclear waste forms, but (2) the melting temperature increases, which makes the glasses more difficult to produce and increases the volatility of radionuclides such as cesium. A practical melting temperature for preparing nuclear waste glasses without significant cesium volatility is 1150°C.

Borosilicate glasses are a generic family of glass compositions, many of which melt in the 1050-1250°C range, have relatively good durability, and are compatible with SRP high-level waste.[8] Borosilicate glasses are rich in soda, silica, and boron. Extensive studies[9,10,13] have shown that borosilicate glass is a suitable material for immobilization of SRP high-level waste. The desirable properties coupled with the well-developed processing technology, led to a choice of borosilicate glass as the reference waste form for the DWPF.[14]

The SRP borosilicate glass waste form typically contains about 28 wt % as oxides of SRP high-level waste sludge (after aluminum removal). Compositions of some typical simulated sludges are given in Table 2, expressed relative to $Fe_2O_3$ content in the sludge. A composite simulated sludge has been defined which contains a weighted average of major elements found in SRP waste tanks.[15,16] High-aluminum and high-iron simulated sludges represent extreme compositions that were found in individual tanks.

About 75% of the aluminum in SRP sludge is removed before the sludge is incorporated into borosilicate glass. Removal of inert $Al_2O_3$ has two beneficial effects: (1) the amount of high-level waste to be solidified is reduced substantially; (2) the viscosity of the molten glass at 1150°C is lowered. Table 2 shows that the sludge compositions expressed as the weight ratio of a component to $Fe_2O_3$ are invariant to removal or addition of another component. This is illustrated for $Al_2O_3$; sludges with and without aluminum removal have identical ratios to $Fe_2O_3$ for all components except $Al_2O_3$.

Borosilicate waste glasses are formed by melting a mixture of glass-forming components and waste slurry. In practice, the glass-forming additives are premelted to give a material called "frit" that is easy to handle and, when remelted, rapidly incorporates the waste. In addition to silica, soda, and boron, frits generally contain several other elements that impart desirable properties to the product. The current reference frit for the SRP borosilicate glass waste form is designated Frit 131, with the composition given in Table 3. Other frit compositions[17] also give suitable borosilicate glass waste forms. Improvement of the frit composition is an ongoing program to optimize leach resistance, waste solubility in the melt, viscosity of the melt, and resistance to devitrification.

Typical overall compositions of borosilicate glasses containing simulated SRP high-level wastes are shown in Table 4. The $SiO_2$ and $Na_2O$ contents arise primarily from the frit, but with small contributions from the waste. In studies with simulated waste, $Ce_2O_3$, $Nd_2O_3$, SrO, and $Cs_2O$ were added to represent numerous minor elements in the waste. The amounts of SrO and $Cs_2O$ shown in Table 4 are five to ten times greater than in actual waste. Preparation of borosilicate glass containing actual SRP waste has been demonstrated.[18,19]

The process for making large-scale borosilicate glass waste forms centers around a slurry-fed, joule-heated, continuous glass melter from which molten glass is poured into canisters of 0.61 m (2 ft.) diameter and 3.0 m (9 ft., 10 in.) height. Cesium enters the frit-sludge slurry from a separate stream. The sludge is pretreated to remove mercury and part of the aluminum.[11] The glass density is typically 2.75 g/cm$^3$ at ambient temperature.

## TABLE 2

Composition of Typical Simulated SRP Sludges

| | Wt Ratio to $Fe_2O_3$ | | |
|---|---|---|---|
| | Composite | High-Aluminum | High-Iron |
| $Fe_2O_3$ | 1.000 | 1.000 | 1.000 |
| $Al_2O_3$[a] | 0.196<br>(0.782) | 3.428<br>(14.295) | 0.023<br>(0.092) |
| $MnO_2$ | 0.275 | 0.821 | 0.067 |
| $U_3O_8$ | 0.090 | 0.241 | 0.232 |
| CaO | 0.075 | 0.066 | 0.068 |
| NiO | 0.124 | 0.147 | 0.171 |
| $SiO_2$ | 0.024 | 0.106 | 0.007 |
| $Na_2O$ | 0.141 | 0.258 | 0.085 |
| $Na_2SO_4$ | 0.026 | 0.033 | 0.009 |
| $Ce_2O_3$ | 0.021 | 0.067 | 0.018 |
| $Nd_2O_3$ | 0.021 | 0.067 | 0.018 |
| SrO | 0.011 | 0.033 | 0.009 |

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a. $Al_2O_3$ content after aluminum removal (before aluminum removal in parentheses). All other components have the same weight ratio after aluminum removal as before.

## TABLE 3

Composition of Frit 131, wt %

| | |
|---|---|
| $SiO_2$ | 57.9 |
| $Na_2O$ | 17.7 |
| $B_2O_3$ | 14.7 |
| $Li_2O$ | 5.7 |
| MgO | 2.0 |
| $TiO_2$ | 1.0 |
| $ZrO_2$ | 0.5 |
| $La_2O_3$ | 0.5 |

## TABLE 4

### Composition of Typical Borosilicate Glasses Incorporating Simulated SRP High-Level Waste, wt %

| | Composite | High-Aluminum | High-Iron |
|---|---|---|---|
| Frit Components: | | | |
| $SiO_2$[a] | 42.1 | 42.7 | 42.1 |
| $Na_2O$[a] | 14.9 | 14.1 | 14.2 |
| $B_2O_3$ | 10.6 | 10.7 | 10.7 |
| $Li_2O$ | 4.1 | 4.2 | 4.1 |
| MgO | 1.4 | 1.5 | 1.5 |
| $TiO_2$ | 0.7 | 0.7 | 0.7 |
| $ZrO_2$ | 0.4 | 0.4 | 0.4 |
| $La_2O_3$ | 0.4 | 0.4 | 0.4 |
| Waste Components: | | | |
| $Fe_2O_3$ | 13.8 | 4.3 | 16.0 |
| $Al_2O_3$[b] | 2.7 | 14.7 | 0.4 |
| $MnO_2$ | 3.8 | 3.5 | 1.1 |
| $U_3O_8$ | 1.2 | 1.0 | 3.7 |
| CaO | 1.0 | 0.3 | 1.1 |
| NiO | 1.7 | 0.6 | 2.7 |
| $SO_3$ | 0.2 | 0.1 | 0.1 |
| Fission Product Simulants: | | | |
| $Ce_2O_3$ | 0.29 | 0.29 | 0.28 |
| $Nd_2O_3$ | 0.29 | 0.29 | 0.28 |
| SrO | 0.15 | 0.14 | 0.14 |
| $Cs_2O$ | 0.21 | 0.21 | 0.21 |

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a. Includes minor contribution from waste.
b. With aluminum removal.

Glasses are generally subject to several phenomena that could affect their performance as a waste form. These effects are: (1) devitrification; (2) fracture; (3) rapid hydrothermal reactions. Conditions of waste-form manufacture and isolation are to be chosen to minimize any adverse effects of these phenomena.

Devitrification refers to unintentional crystallization in glass, which can occur if the glass experiences temperatures of 500 to 900°C for a long period of time. Devitrification usually decreases durability of the glass.[13]

Fracture or cracking may be caused by impact or by thermal stresses as the waste form cools from the melt.[20] The effect of fracture is to increase the surface area of the waste form.

Hydrothermal reactions occur when glass is exposed to water at elevated temperatures and pressures, as for example 300°C and 300 atm. Under these conditions, the glass can alter completely to mineral-like crystalline phases which may or may not retain the waste radionuclides well.[21] Because of the low heat content of SRP borosilicate glass waste forms (about 400 watts per canister), hydrothermal reactions will not occur under anticipated repository conditions of less than 100°C and 70 atm.

Important properties of the borosilicate glass waste form include leachability, thermal and mechanical stability, and radiation stability. These properties are discussed in following sections of this report, where they are compared with the properties of the crystalline ceramic waste form.

## DESCRIPTION OF CRYSTALLINE CERAMIC

Crystalline ceramics are dense, fine-grained assemblages of compatible chemical phases. Stable oxide phases, such as titanates, silicates, or aluminates can be fabricated into durable mineral-like ceramics. Certain oxide phases can incorporate specific nuclear waste elements into the oxide crystal structure. Thus, the concept of creating a highly durable ceramic waste form involves "tailoring" nuclear waste with additives that promote the formation of desired host phases.

Several different crystalline phase assemblages have been suggested for defense waste. The first such proposal was the silicate-based "Supercalcine" ceramic,[22] which later evolved into the aluminate-based "Tailored Ceramic" developed by Rockwell.[23] Another approach, first proposed by A. E. Ringwood at the Australian National University, uses phases that are similar to natural minerals that have survived over geologic time and may have contained radioactive elements;[24] a titanate-based ceramic designated "Synroc" has such properties. "Synroc-D", developed by Lawrence Livermore National Laboratory, is a variant of this concept suitable for SRP defense waste.[6,25] Because Synroc-D has very good durability and is the best developed of the crystalline ceramic waste forms, it was selected as the reference alternative waste form for SRP high-level waste.[1]

The reference Synroc-D waste form contains about 65 wt % as oxides of SRP high-level waste sludge without aluminum removal (about 50 wt % on an aluminum removal basis).[26] Simulated sludges similar to those in Table 2 have been incorporated into Synroc-D waste forms. Because aluminum may be a desirable component of waste ceramics, the sludge pretreatment process does not include an aluminum dissolution step, and Synroc-D is tailored to the waste composition "without aluminum removal."

Chemical additives are mixed with the waste before ceramic fabrication to ensure that the proper crystalline phases form in the product. Titania is added to form the mineral-like titanate phases that are the basis for Synroc-D. Other components, such as calcium oxide, zirconia, and silica also are required to make the durable phases. The additives are tailored to the composition of the waste so that sufficient amounts of the required phases will be formed to accommodate all of the radioactive elements. Many of the nonradioactive elements in the waste, such as iron and aluminum, tend to form durable phases even without tailoring.

Typical overall compositions of Synroc-D ceramic waste forms containing simulated SRP high-level wastes are given in Table 5. The CaO and $SiO_2$ contents arise primarily from the additives, but with small contributions from the waste. Fission product simulants were added in the same manner as for borosilicate glass. With these compositions, the waste loadings (without aluminum removal) are 62.7 wt % with composite sludge, 39.8 wt % with high-aluminum sludge, and 53.7 wt % with high-iron sludge. The corresponding loadings for comparison with borosilicate glass would be 48.8, 12.8, and 51.6 wt %, respectively, when aluminum removal is accounted for. Synroc-D has been prepared only with simulated, not actual, SRP waste.

The crystalline phases[5] nominally present in Synroc-D are listed in Table 6. In addition, a glassy phase generally is present. The spinel phase contains most of the iron and aluminum, and in principle should contain very few atoms of the radioactive waste elements.[5] Perovskite is the principal host for strontium, lanthanides, and trivalent actinides. Zirconolite will contain uranium and other tetravalent actinides. Nepheline will accommodate most of the sodium in the waste and is the host for cesium. Some cesium also may enter the glassy phase. Each crystalline phase can contain a wide range of chemical contents and ionic

## TABLE 5

Composition of Typical Synroc-D Ceramics Incorporating Simulated SRP High-Level Waste, wt %

| | Composite | High-Aluminum | High-Iron |
|---|---|---|---|
| Synroc Additives: | | | |
| $TiO_2$ | 18.8 | 16.8 | 18.4 |
| $ZrO_2$ | 6.6 | 5.1 | 10.6 |
| $CaO$[a] | 7.1 | 5.0 | 7.7 |
| $SiO_2$[a] | 7.2 | 1.2 | 6.7 |
| $Fe_2O_3$[a] | -- | 34.9 | -- |
| $Al_2O_3$[a] | -- | -- | 8.0 |
| Waste Components: | | | |
| $Fe_2O_3$ | 23.8 | -- | 30.2 |
| $Al_2O_3$[b] | 18.6 | 33.8 | -- |
| $MnO_2$ | 7.4 | 1.5 | 2.3 |
| $U_3O_8$ | 2.1 | 0.5 | 7.0 |
| $NiO$ | 3.0 | 0.3 | 4.7 |
| $Na_2O$ | 3.3 | 0.5 | 2.6 |
| $Na_2SO_4$ | 0.6 | 0.05 | 0.6 |
| Fission Product Simulants: | | | |
| $Ce_2O_3$ | 0.50 | 0.13 | 0.3 |
| $Nd_2O_3$ | 0.50 | 0.15 | 0.3 |
| $SrO$ | 0.25 | 0.05 | 0.3 |
| $Cs_2O$ | 0.25 | 0.05 | 0.3 |

---

a. Includes minor contribution from waste.
b. Without aluminum removal.

## TABLE 6

## Phase Composition of Synroc-D Ceramic[a]

| Crystalline Phase | Approximate Abundance, wt % | Normal Form | Waste Elements[b] |
|---|---|---|---|
| Spinel | 48 | $FeAl_2O_4$-$Fe_2TiO_4$ | Al, Fe, Mn, Ni |
| Perovskite | 15 | $CaTiO_3$ | $\underline{\text{Sr}}$, $\underline{\text{Ce}}$, $\underline{\text{Nd}}$, Ca |
| Zirconolite | 19 | $CaZrTi_2O_7$ | Ca, $\underline{\text{U}}$ |
| Nepheline and Glassy Phase | 18 | $NaAlSiO_4$ | Na, $\underline{\text{Cs}}$, Al, Si |

---

a. With composite sludge; from Reference 5.
b. Radioactive elements are underlined.

radii, without losing durability. Such versatility is necessary for the ceramic to accommodate expected variations in waste composition.

The conceptual process for making crystalline ceramic waste forms centers around a hot isostatic press that consolidates an intimately mixed calcine of waste and additives into canistered forms with 0.56 m (22 in.) diameter and 0.91 m (36 in.) height.[11,26] The ceramic is formed at 1050 to 1150°C under pressures of up to 170 MPa. During this treatment, pores in the solid collapse, and the crystalline phases develop. The crystallites or grains in the monolith are on the order of a micrometer in size. Other major process steps are ball milling and calcination. Crystalline ceramic waste forms have not been produced with large-scale process equipment, and thus no data are available on the effect of full-scale processing on product performance.

Synroc-D density is typically 4.0 g/cm$^3$ at ambient temperature. The Synroc-D waste form is more dense than borosilicate glass and can have a higher waste loading. Because of these factors, Synroc-D could immobilize up to three times more radioactive waste per unit volume (in terms of Ci/cm$^3$) than borosilicate glass. Higher waste loading also implies higher waste-form temperatures.

Ceramics are generally subject to several phenomena that could affect their performance as a waste form. These effects are: (1) metamictization; (2) fracture; (3) thermodynamic instability. Rapid hydrothermal reactions are not a major concern for Synroc-D.[27]

Metamictization is a radiation damage effect that causes a crystalline phase to become disordered or amorphous at some threshold radiation dose. The metamict phase might be less durable than the crystalline phase. Natural zirconolite and perovskite minerals occur that have become metamict over geologic time. However, their leach rates have remained very low.[28,29]

Fracture may be caused by impact or by thermal stresses as a ceramic waste form cools after hot isostatic pressing. The fine-grained structure of a ceramic tends to resist propagation of cracks. On the other hand, the formation of a glassy phase at grain boundaries could make the ceramic more susceptible to fracture. The effect of fracture is to increase the surface area of the waste form.

One of the principal phases of Synroc-D, perovskite, is an example of a phase that is thermodynamically unstable in the presence of common silicate minerals or natural groundwaters.[30] Fortunately, perovskite has considerable kinetic stability, and the reactions are slow. The reaction products are new mineral phases which may or may not retain the waste radionuclides well. The importance of thermodynamic stability in crystalline ceramic waste forms has not yet been fully assessed.

Important properties of the Synroc-D ceramic form include leachability, thermal and mechanical stability, and radiation stability. These properties are discussed in the following sections of this report, where they are compared with the properties of the borosilicate glass waste form.

## LEACHING PROPERTIES

Leachability has been identified by a DOE Interface Working Group as the most important property of waste forms.[12] Resistance to leaching in aqueous media is a measure of the chemical durability of a waste form, and thus of its ability to retain radionuclides. In a multibarrier geologic waste repository, interaction of the waste form with groundwater leachants is the most plausible of processes or events that could transfer significant amounts of radioactive materials to the biosphere. Because the waste form is an important barrier against such transfer, low leach rates are desirable properties.

Under expected repository conditions, waste elements should be released at a lower rate than is typical of any waste form by itself. Laboratory leach tests do not simulate all of the interactions of waste forms, rock media, and groundwater. Experimental data indicate that waste release from the neighborhood of a waste form may be much slower than the release rates estimated from simple leach tests on both Synroc-D and borosilicate glass.[13,31-34]

Over geologic time periods, the release of waste elements from the repository will be governed by the waste form, by the engineered barriers, and by the natural environment and chemistry of the rock formation. Much of the geochemistry of potential repository sites is known, and this knowledge can be used to predict the future behavior of the disposed waste. Waste migration will be retarded by the groundwater chemistry, the solubility of waste elements, and interactions between the waste form, other engineered barriers, and the rock.

A variety of laboratory leaching data are available for the borosilicate glass and Synroc-D waste forms for SRP defense high-level waste. Materials for studying the leaching properties most often have contained simulated wastes, although borosilicate glass also has been tested with actual SRP waste. A portion of the large body of data is suitable for direct comparison of borosilicate glass and Synroc-D. Four laboratories participated in comparative leach tests on the two waste forms.

These sources of data will be described, followed by an extensive tabulation and discussion of the results of comparative leach tests on borosilicate glass and Synroc-D. The waste forms can be compared on the basis of leach rates for cesium, strontium, uranium, and eight other elements. From the data, the effects of experimental variables such as waste composition, leachant composition, temperature, and flow rate can be evaluated.

Major conclusions from the comparative leach tests are:

- Neither borosilicate glass nor Synroc-D is superior in leach resistance for all of the principal radwaste elements; however, Synroc-D is slightly better for most of the elements studied.
- Cesium is retained better by borosilicate glass under some conditions, and by Synroc-D under others.
- Strontium is retained significantly better by borosilicate glass under all conditions tested except high flows.
- Uranium is retained significantly better by Synroc-D under all conditions tested except high flows.
- Borosilicate glass is better for calcium leaching, while Synroc-D is better for sodium, aluminum, iron, silicon, and manganese.
- The effects of waste composition and leachant composition on leaching are relatively small; changes in leach rates from these effects are typically less than a factor of 5.
- The effect of temperature on leaching can be described by activation energies from 3.4 to 12.1 kcal/mole.
- The effect of flow rate is variable and ranges from almost no effect to causing major changes in waste-form behavior; however, at the lowest flow rate studied, which corresponds more closely to possible groundwater flows near a repository, leach rates are about the same as from static leach tests.
- Both borosilicate glass and Synroc-D leach incongruently, with different leach rates for different elements.

**Sources of Comparative Data**

Data for comparison of the leaching properties of the borosilicate glass and Synroc-D ceramic waste forms come from four principal sources:

- The SRL Comparative Leach Test Program (CLTP)
- Materials Characterization Center (MCC) comparative tests
- Tests on borosilicate glass by SRL
- Tests on Synroc-D by LLNL

Each of these sources of information is described below. Materials, tests, leachants, conditions, and analyses are discussed briefly. The sources of data available for comparison under various experimental conditions are summarized in Table 7.

### SRL Comparative Leach Test Program

The SRL Comparative Leach Test Program[35] studied the leaching properties of several candidate forms for SRP high-level waste, including borosilicate glass and Synroc-D. Waste-form developers prepared state-of-the-art materials for evaluation at SRL. The waste forms incorporated simulated SRP waste sludges (Table 2) and cesium. The simulated sludges were either supplied by SRL or made by the developers according to SRL formulations.

Special batches of borosilicate glass were prepared for the Comparative Leach Test Program by the Chemical Technology Division of SRL. The glasses contained composite, high-aluminum, and high-iron sludges, and had the compositions given in Table 4.

LLNL prepared several batches of Synroc-D for the Comparative Leach Test Program. The particular batches considered in this report are designated S-29 with composite sludge, S-30 with high-iron sludge, and S-31 with high-aluminum sludge.[6] In each of these materials, the cesium host phase was formed in situ during fabrication of the Synroc-D samples. The resulting Synroc-D compositions are given in Table 5.

Only the MCC-1 Static Leach Test[36] was employed in the SRL Comparative Leach Test Program. MCC-1 is one of a group of proposed standard leaching tests that span wide ranges of conditions.[37] MCC-1 is a provisionally approved standard test for use within the DOE waste management complex. The test requires individual solid samples for each leach period. Samples are exposed to specified aqueous leachants in closed Teflon® vessels. Test vessels are maintained at constant temperature in an oven. Conditions are carefully specified in the test procedure.[36]

The MCC-1 test uses three leachants: deionized (DI) water, silicate water, and brine. Tests with DI water provide baseline data on leaching in pure water; silicate water and brine are

## TABLE 7

### Summary of Comparative Leaching Data Sources[a]

| | 40°C | | | 90°C | | | 150°C | | |
|---|---|---|---|---|---|---|---|---|---|
| | DI | Silicate | Brine | DI | Silicate | Brine | DI | Silicate | Brine |
| **MCC-1, 2** | | | | | | | | | |
| 3,7,14 days | | | | | | | | | |
| Composite: | | | | | | | | | |
| Glass | 1 | 2[b,c] | c | 1,2,3 | 2[b,c] 3[d] | 2[b,c] 3[d] | 2 | c | c |
| Ceramic | 2[b] | 2[b,c] | c | 1,2,4 | c | c | 2 | 2[b,c] | 2[b,c] |
| High-Al: | | | | | | | | | |
| Glass | 1 | c | c | 1 | c | c | | c | c |
| Ceramic | 1 | c | c | 1 | c | c | | c | c |
| High-Fe: | | | | | | | | | |
| Glass | 1 | c | c | 1 | c | c | | c | c |
| Ceramic | 1 | c | c | 1 | c | c | | c | c |
| 28 days | | | | | | | | | |
| Composite: | | | | | | | | | |
| Glass | 1,3 | 3 | 3 | 1,2,3 | 1,2,3 | 1,2,3 | 2,3 | 2,3 | 2,3 |
| Ceramic | 4 | 4 | 4 | 1,2,4 | 1,2,4 | 1,2,4 | 2,4 | 4 | 2,4 |
| High-Al: | | | | | | | | | |
| Glass | 1 | | | 1 | 1 | 1 | | | |
| Ceramic | 1 | | | 1,4 | 1,4 | 1,4 | | | |
| High-Fe: | | | | | | | | | |
| Glass | 1 | | | 1 | 1 | 1 | | | |
| Ceramic | 1 | | | 1,4 | 1,4 | 1,4 | | | |
| **MCC-3** | | | | | | | | | |
| 14 days[c] | | | | | | | | | |
| Composite: | | | | | | | | | |
| Glass | c | c | c | 2[c] | c | c | c | c | c |
| Ceramic | c | c | c | 2[c] 4 | c | c | c | c | c |
| **MCC-4** | | | | | | | | | |
| 28 days | | | | | | | | | |
| Composite: | | | | | | | | | |
| Glass | | | | 2 | | | c | c | c |
| Ceramic | | | | 2 | | | c | c | c |

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a. Key:
1. SRL Comparative Leach Test Program
2. Materials Characterization Center comparative tests
3. Savannah River Laboratory tests on borosilicate glass
4. Lawrence Livermore National Laboratory tests on Synroc-D

b. 14-day test only.

c. Conditions not required by standard tests.

d. 7-day test only.

generic simulants of natural waters that might be expected in the vicinity of proposed geologic repositories. MCC-1 silicate water contains 0.058 g/L $SiO_2$ and 0.179 g/L $NaHCO_3$. MCC-1 brine contains 90.0 g/L NaCl, 48.2 g/L KCl, and 116.0 g/L $MgCl_2$.

Test conditions of temperatures, times, and ratio of sample surface area to leachant volume (SA/V) are specified in the MCC-1 procedure. The principal temperature is 90°C, with optional tests at 40 and 70°C. Tests are run for 3, 7, 14, and 28 days with DI water, with longer times optional; tests with silicate water and brine are for 28 days, with longer times optional. Tests at 3, 7, and 14 days are single determinations, while those at 28 days are triplicate. The standard value of SA/V is 0.01 $mm^{-1}$. In the SRL Comparative Leach Test Program, the required tests up to 28 days were run at 90°C with all three standard leachants, and at 40°C with DI water only.

Samples for the Comparative Leach Test Program were neutron-activated prior to leaching.[38-40] Cs, Ce, Fe, and Zr were determined by low-background gamma-ray spectroscopy on evaporated, pelletized leachates.[41] U, Na, and Al were determined by rapid reirradiation of leachate pellets in a special neutron-activation analysis facility.[42] Sr was not determined.

In the neutron activation method, the fraction of each radionuclide leached was measured by comparing the radioactivity of the leachate with that of the solid leach sample. The leach rate was then calculated from the product of the fraction leached and the weight of the sample, divided by the surface area and the total time leached.

Leach rates were calculated differently for the reirradiation analyses (and also for chemical analysis methods used by other laboratories), where only the mass of an element in the leachate was measured. This mass, divided by the fraction of the element in the solid, the surface area, and the leach time, gave the leach rate.

### Materials Characterization Center

The MCC performed tests on a number of candidate waste forms, at the request of the High-Level Waste Technology Program Office at Savannah River.[1,43] Two of the materials studied were borosilicate glass and Synroc-D ceramic (S-29), from the same batches of waste-form material used in the SRL Comparative Leach Test Program. The MCC tested only waste forms that contained composite sludge.

Numerous MCC-1 tests were run by the MCC. The test matrix through 28 days at 90°C was run with all three standard leachants. Some data were obtained at 40°C in 14-day tests with DI and silicate waters only. Cs was determined by atomic absorption spectroscopy, and some 17 other elements were determined by inductively coupled plasma (ICP) emission spectroscopy. Elements obtained by ICP included Al, B, Ca, Ce, Fe, Li, Mg, Mn, Na, Nd, Ni, Pb, Si, Sr, Ti, U, and Zr.

In addition to MCC-1 data, the MCC obtained limited data from MCC-2, MCC-3, and MCC-4 leach tests. MCC-2 is a high-temperature, static test. MCC-3 is an agitated powder test designed to determine ultimate solubilities. MCC-4 is a low-flow-rate dynamic test.

MCC-2 also is a provisionally approved standard test[36] and is virtually identical to MCC-1 except for the use of Teflon®-lined steel pressure vessels capable of withstanding temperatures above 100°C. The principal test temperature is 150°C, with optional tests at 110 and 190°C. The comparative tests were run at 150°C with all three standard leachants for up to 28 days. Leachates were analyzed by the same methods as for MCC-1.

The MCC-3 test, still under development,[44] is similar to MCC-1 and MCC-2, except that the system is agitated rather than static and uses powdered samples so that the SA/V value is much higher. In an MCC-3 type test, the MCC obtained 14-day data for uranium at 90°C with DI water.

The MCC-4 test, also still under development,[44] has features that are similar to MCC-1, such as the same standard temperatures, times, and leachants. However, the leachant flows past the sample and is collected, so that a single sample is used for multiple time points. Three standard flow rates, 0.1, 0.01, and 0.001 mL/min, are specified. Duplicate tests are run for each set of conditions. In an MCC-4 type test, the MCC obtained data at 90°C with DI water for times up to 28 days, for both borosilicate glass and Synroc-D, with composite sludge. Leachates were analyzed by the same methods as for MCC-1.

### Savannah River Laboratory

The SRL Chemical Technology Division, as primary developer of the borosilicate glass waste form for SRP high-level waste, performed a series of standard leach tests on borosilicate glass.[13] These tests were completely independent of those in the SRL Comparative Leach Test Program. The tests on borosilicate glass were part of a data matrix provided to the High-Level Waste Technology Program Office by waste-form developers.[1]

The SRL developer leach tests were only with borosilicate glass containing composite sludge. The material had the same formulation (Table 4) but was from a different batch than the material used by the Comparative Leach Test Program or the MCC.

SRL employed both the MCC-1 and the MCC-2 tests with all three standard leachants. The required tests up to 28 days were run at 90°C. At 40 and 150°C, only 28-day tests in triplicate were run. Leachate analyses were by atomic absorption for Cs and by ICP for Sr, Na, Si, B, U, Ce, and Nd. Additional analyses for U were by neutron activation.

These SRL leach tests on borosilicate glass are suitable for direct comparison with tests on Synroc-D from the other data sources. However, the SRL data represent but a small part of a very large data base on borosilicate glass.[13] These additional data are from a series of studies which address the effects of many of the important leaching factors on borosilicate glass durability. These factors include: duration of exposure to leachant (more than 3 years); glass frit composition; waste composition, including actual waste as well as simulated waste; leachant composition and pH; leachant flow rate; and temperature.

### Lawrence Livermore National Laboratory

LLNL, as the primary developer of the Synroc-D ceramic waste form for SRP high-level waste, performed a variety of standard leach tests on Synroc-D.[5] These tests were also part of the data matrix provided by waste-form developers to the High-Level Waste Technology Program Office.[1]

LLNL tested Synroc-D materials containing composite (S-29), high-iron (S-30), and high-aluminum (S-31) sludges, from the same batches as supplied to the SRL Comparative Leach Test Program. Material from the S-29 batch also was supplied for testing by the MCC.

Both MCC-1 and MCC-2 tests with all three standard leachants were employed. Samples with composite sludge were tested at 40, 90, and 150°C, while those with high-aluminum and high-iron sludges were tested only at 90°C. The required tests through 28 days were run at 90°C, and tests at 28 days only were run at 40°C and 150°C. Leachates were analyzed for the same elements as reported by the MCC.

LLNL has made a large number of additional leaching measurements on Synroc-D, particularly with MCC-3 and MCC-4 type tests.[5] As in the case of borosilicate glass, only those data from which a direct comparison can be made are considered in this report.

## Elemental Leach Rates

Leaching data for a variety of elements are available and suitable for comparing borosilicate glass and Synroc-D ceramic. The most important elements leached from forms containing simulated waste are cesium, strontium, and uranium. These elements represent the principal hazardous radionuclides in actual high-level waste.

$^{90}$Sr and $^{137}$Cs are fission products, both with half-lives of about 30 years, that dominate the radioactivity of the waste for the first several hundred years of isolation. After these fission products decay, the only hazards remaining in the waste are the relatively minor amounts of long-lived radionuclides, principally actinides, that will persist for thousands of years. Uranium, in addition to being a constituent of the waste, is a stand-in for other long-lived actinides such as $^{237}$Np, $^{238}$Pu, and $^{239}$Pu. The degree to which uranium actually simulates leaching of the other actinides must be confirmed in future experiments.

Other elements for which comparative leaching data are available are cerium, sodium, aluminum, iron, zirconium, silicon, calcium, and manganese. Cerium is representative of rare-earth fission products in the waste. The remaining elements are from nonradioactive bulk chemicals in SRP waste and/or from the waste-form additives. Leaching of the nonradioactive elements is a measure of the durability of the waste-form matrix.

Comparison of data from different laboratories reveals uncertainties that are caused by systematic differences in test procedures between laboratories. A round-robin test[45] of the MCC-1 procedure was performed by 16 laboratories to assist in defining the precision and accuracy of MCC-1. Variance between laboratories was much greater than the intra-laboratory variance. Thus, intra-laboratory comparisons of waste forms from leaching data are considered more reliable than inter-laboratory comparisons. Tables of leaching data in the following sections highlight intra-laboratory comparisons when they occur. Precision measures on individual data points are standard deviations calculated from triplicate test results.

In the following discussions of leach rate data, the comparison between borosilicate glass and Synroc-D is stated in terms of a simple ratio of the leach rates under identical conditions. The ratio is less than unity when borosilicate glass has the lower (better) leach rate, and greater than unity when Synroc-D has the lower (better) leach rate. For each set of conditions, the ratio is given for each intra-laboratory comparison and for the averages of the inter-laboratory data. Thus, the ratio of averages incorporates all of the data (and all of the associated uncertainties) for that set of conditions.

Time dependent leaching data for the static tests are presented as log-log plots of leach rate versus time. Each data point is an integrated, rather than an incremental, leach rate. The data are expected to approach a line with -1 slope at longer times when the amount leached becomes constant. In the following Figures of leaching data, lines drawn to connect points from one laboratory do not represent a theoretical fit of the data.

## Cesium

More cesium leach rate data are available than for any of the other elements. The data show generally good agreement among the laboratories; variances are much less than the expected factor of 10, and typically are no worse than a factor of 3.

The comparison of cesium leaching properties of borosilicate glass and Synroc-D is summarized in Table 8, which gives the ratios of data averages for 28-day MCC-1 and MCC-2 tests under a variety of conditions. There is clearly an effect of waste type: Synroc-D is better with high-iron sludge, borosilicate glass is better with high-aluminum sludge, but the forms are virtually indistinguishable with composite sludge. Table 8 also shows that the cesium leaching ratio has a small trend with temperature for forms with composite sludge leached in silicate water.

Data on the time dependence of cesium leaching between 3 and 28 days are available. Also, the effect of flow rate on cesium leaching has been determined in MCC-4 tests. Results from MCC-1 tests at 40 and 90°C will be discussed, followed by results from MCC-2 tests at 150°C, and then by the MCC-4 tests.

The early time dependence of cesium leach rates at 40°C in DI water is shown for borosilicate glass and Synroc-D in Figures 1 and 2. The forms containing high-aluminum sludge are compared in Figure 1. The data decrease monotonically with time, as expected, and show a large difference between the two forms. With high-aluminum sludge, the borosilicate glass leach rate is 500 to 1400 times lower. The forms containing high-iron sludge are compared in Figure 2. Again, the data decrease monotonically with time, but in this case the Synroc-D leach rate is 2 to 6 times lower. With composite sludge, no data are available on Synroc-D at 40°C and early times.

Cesium leach rates from 28-day tests at 40°C are accumulated in Table 9, which shows that the data are sparse. With composite sludge, in any of the three leachants, the comparison of borosilicate glass and Synroc-D is indeterminate.

## TABLE 8

### Summary of Comparisons of Cesium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | Ratio of Cesium Leach Rates[a,b]<br>Composite | High-Al | High-Fe |
|---|---|---|---|---|
| 40°C | Deionized Water | 0.26 | 0.002 | 6.3 |
| | Silicate Water | 0.4 | - | - |
| | Brine | >0.4 | - | - |
| 90°C | Deionized Water | 1.4 | 0.14 | 3.8 |
| | Silicate Water | 1.9 | 0.068 | 3.3 |
| | Brine | >1.1 | 0.041 | 3.9 |
| 150°C | Deionized Water | 0.94 | - | - |
| | Silicate Water | 3.1 | - | - |
| | Brine | 1.8 | - | - |

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a. MCC-1 and MCC-2 static leach tests.

b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

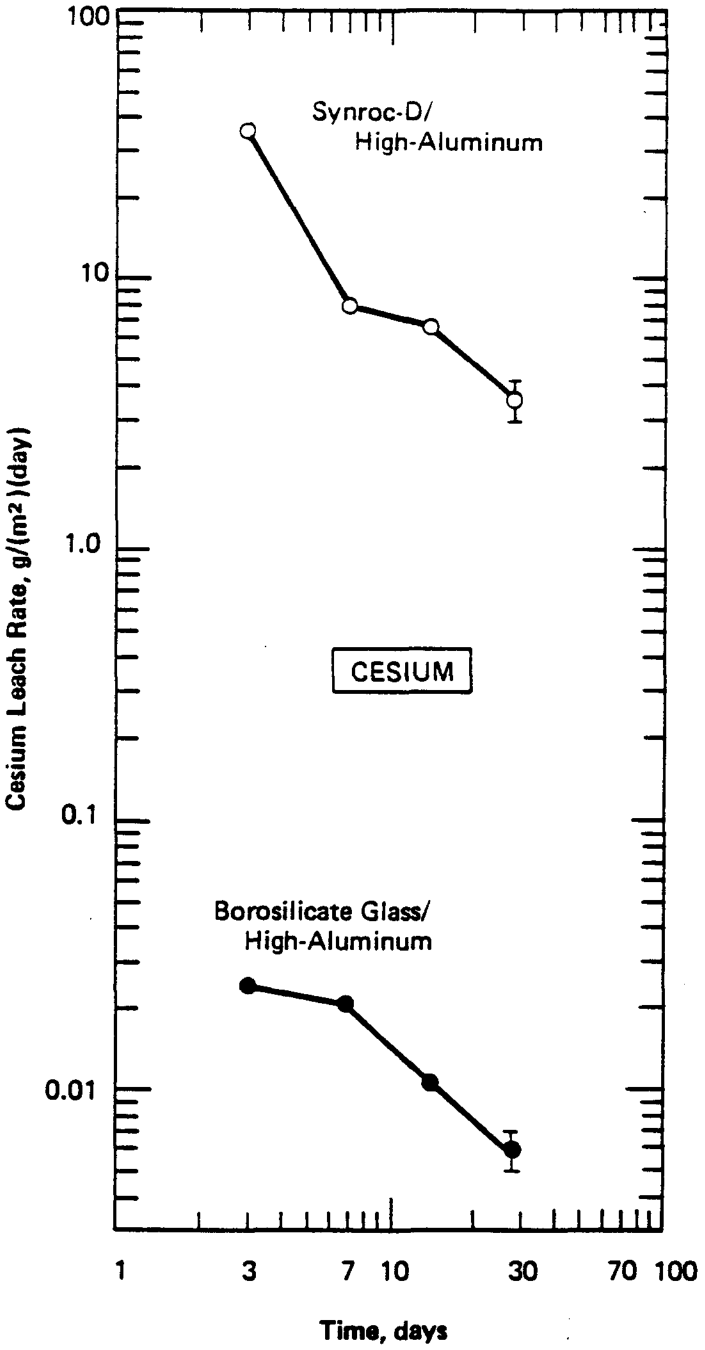

**FIGURE 1.** Cesium Leach Rates with High-Aluminum Sludge in Deionized Water at 40°C

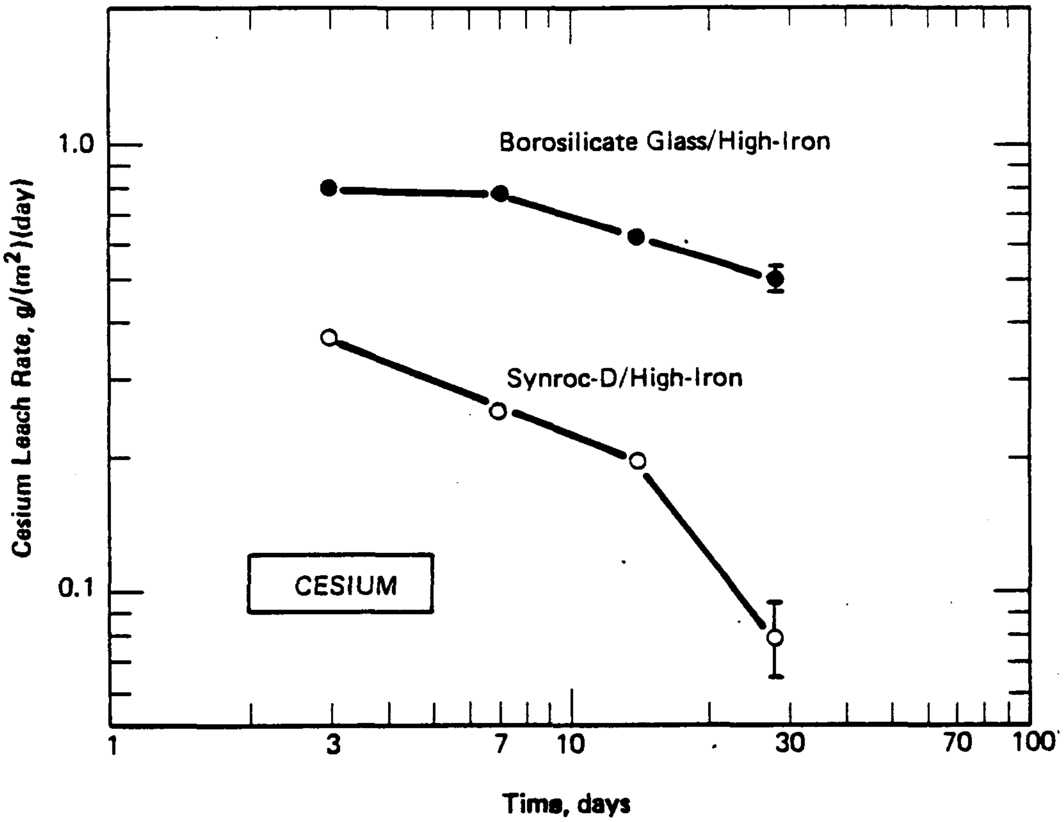

FIGURE 2. Cesium Leach Rates with High-Iron Sludge in Deionized Water at 40°C

## TABLE 9

### Comparison of Cesium Leach Rates from 28-day MCC-1 Tests at 40°C

| Leachant | Sludge Type | Ref. | Cesium Leach Rate, $g/(m^2)(day)$ Borosilicate Glass | Synroc-D Ceramic | RATIO |
|---|---|---|---|---|---|
| Deionized Water | Composite | a | 0.055 ±0.003 | - | - |
| | | b | 0.14 ±0.06 | - | - |
| | | c | - | 0.37 | - |
| | | d | 0.098 | 0.37 | 0.26 |
| | **High-Al** | **a** | **0.006 ±0.001** | **3.56 ±0.58** | **0.002**[e] |
| | **High-Fe** | **a** | **0.501 ±0.025** | **0.079 ±0.015** | **6.3** |
| Silicate Water | Composite | b | 0.08 ±0.09 | - | - |
| | | c | - | 0.18 | - |
| | | d | 0.08 | 0.18 | 0.4 |
| Brine | Composite | b | 0.04 ±0.05 | - | - |
| | | c | - | <0.1 | - |
| | | d | 0.04 | <0.1 | >0.4 |

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a. From SRL Comparative Leach Test Program.
b. Reference 13.
c. Reference 5.
d. Average of inter-laboratory data.
e. Bold data designate an intra-laboratory comparison.

At 90°C, the time dependence in DI water is shown in Figures 3, 4, and 5. Data between 3 and 28 days for borosilicate glass and Synroc-D with composite sludge are shown in Figure 3. Two problems are apparent when the data from all sources are displayed. First, the effect of inter-laboratory variance is easily seen in Figure 3. Second, a few of the nonreplicated points at early times appear to be outliers, not confirmed by similar points from other laboratories. With these uncertainties, the cesium leach rates of the two forms with composite sludge at 90°C in DI water are indistinguishable.

The time dependence of forms with high-aluminum sludge, at 90°C in DI water, is shown in Figure 4. The Synroc-D data are not monotonic, but the 3-day point may be an outlier. Excepting this point, the borosilicate glass leach rate is 7 to 30 times lower. The forms containing high-iron sludge are compared in Figure 5. The data are well behaved and show that the Synroc-D leach rate is 4 to 5 times lower.

Cesium leach rates from 28-day tests at 90°C are given in Table 10. Considerable data are available for this case. With composite sludge in silicate water, Synroc-D may possibly have the advantage. Otherwise, the results in silicate water and brine parallel those in DI water.

MCC-2 tests at 150°C have been run with borosilicate glass and Synroc-D containing composite sludge. Figure 6 shows the time dependence in DI water. The cesium leach rate of Synroc-D is lower, by factors of 1.4 to 2.5. This is not a large difference, given the uncertainties in the measurements. Results of 28-day tests at 150°C are given in Table 11. In DI water, the comparison is indeterminate, but in silicate water and brine, Synroc-D appears to have a slight advantage.

MCC-4 tests were run by the MCC at 90°C in DI water on borosilicate glass and Synroc-D containing composite sludge. Table 12 gives selected incremental leach rates for cesium at three flow rates. The leach rates increase with flow rate, as expected, and tend to level out after about 10 days. Figure 7 shows the ratio of incremental leach rates as a function of time. The cesium leach rates of borosilicate glass and Synroc-D are indistinguishable at any of the flow rates. The points at 28 days agree well with the results of static tests, which give average leach rates.

### Strontium

Somewhat fewer leaching data on strontium are available than for cesium. Data are available for borosilicate glass and Synroc-D with composite sludge, but not with high-aluminum or high-iron

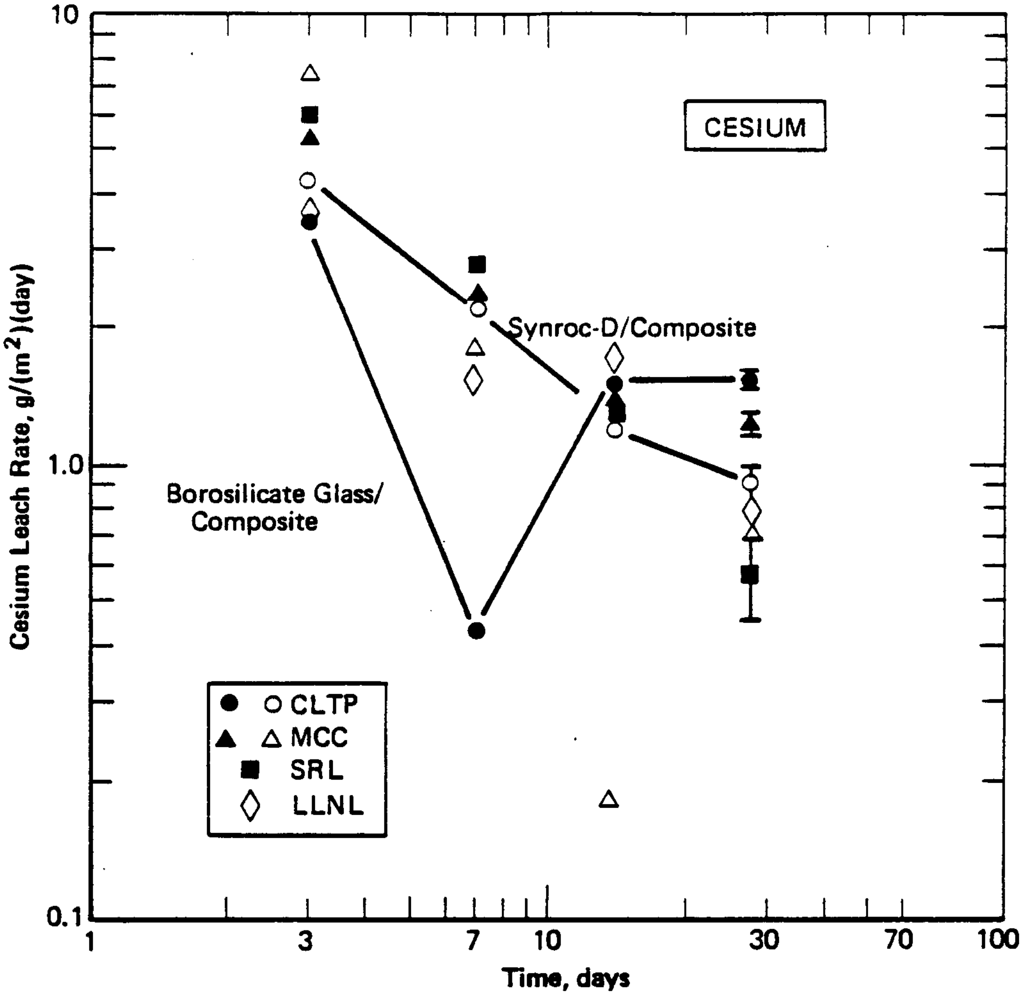

FIGURE 3. Cesium Leach Rates with Composite Sludge in Deionized Water at 90°C

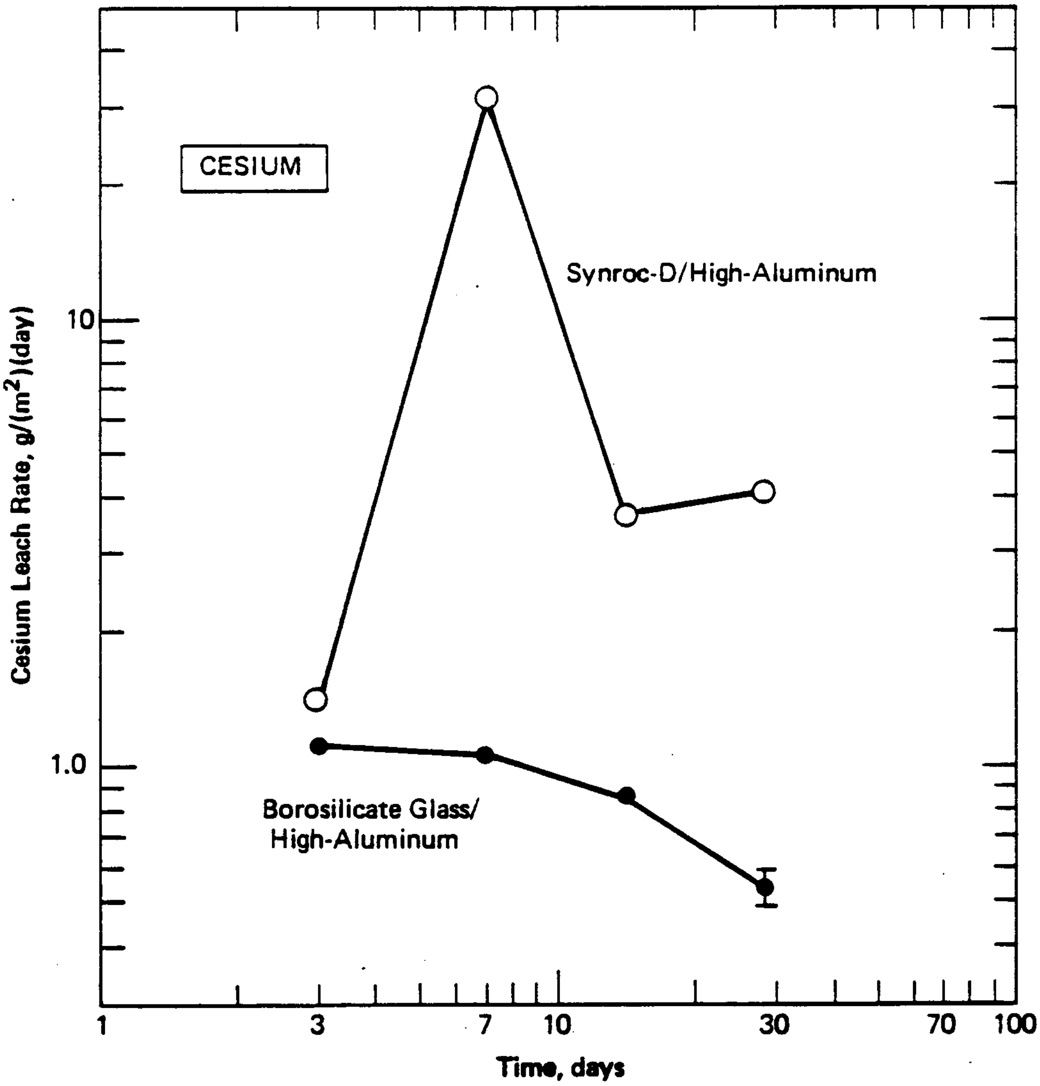

FIGURE 4. Cesium Leach Rates with High-Aluminum Sludge in Deionized Water at 90°C

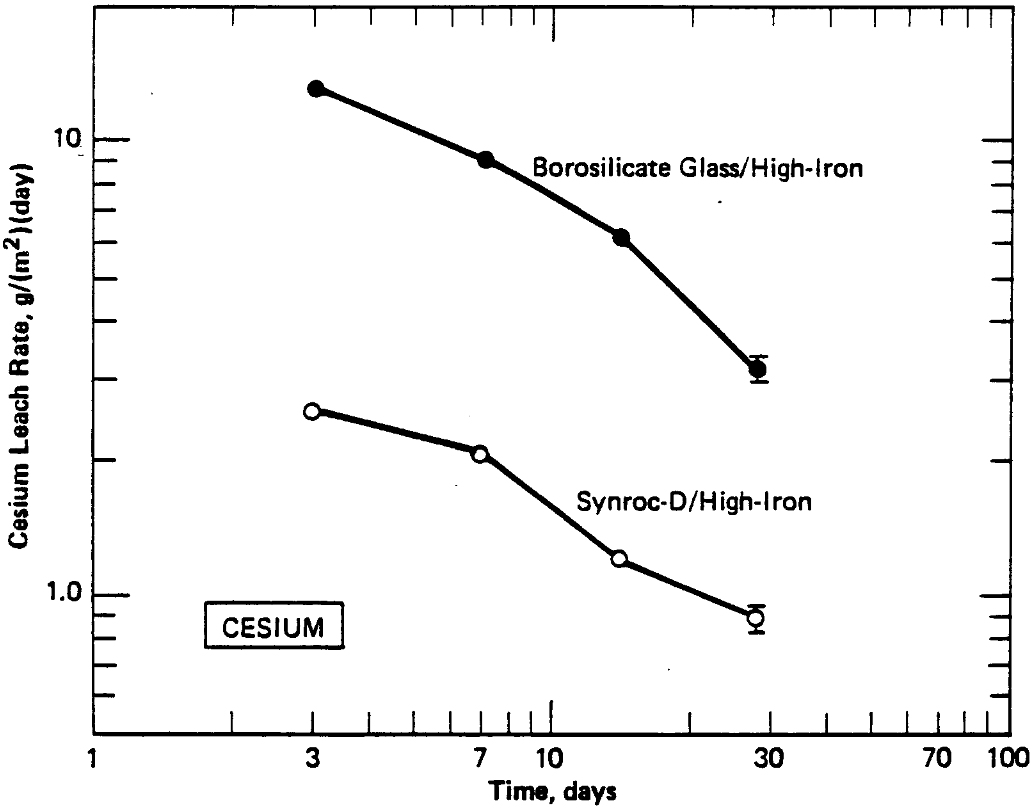

**FIGURE 5.** **Cesium Leach Rates with High-Iron Sludge in Deionized Water at 90°C**

## TABLE 10

Comparison of Cesium Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Cesium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | Composite | a | **1.54 ±0.03** | **0.91 ±0.07** | **1.7**[b] |
| | | c | **1.23 ±0.07** | **0.71 ±0.07** | **1.7** |
| | | d | 0.58 ±0.03 | - | - |
| | | e | - | 0.79 | - |
| | | f | 1.12 | 0.80 | 1.4 |
| | High-Al | a | **0.54 ±0.06** | **4.1 ±4.8** | **0.13** |
| | | e | - | 3.86 | - |
| | | f | 0.54 | 4.0 | 0.14 |
| | High-Fe | a | **3.24 ±0.25** | **0.90 ±0.06** | **3.6** |
| | | e | - | 0.80 | - |
| | | f | 3.24 | 0.85 | 3.8 |
| Silicate Water | Composite | a | **0.76 ±0.04** | **0.37 ±0.02** | **2.1** |
| | | c | **0.94 ±0.01** | **0.22** | **4.3** |
| | | d | 0.49 ±0.03 | - | - |
| | | e | - | 0.54 | - |
| | | f | 0.73 | 0.38 | 1.9 |
| | High-Al | a | **0.27 ±0.01** | **4.95 ±0.75** | **0.055** |
| | | e | - | 2.95 | - |
| | | f | 0.27 | 3.95 | 0.068 |
| | High-Fe | a | **1.08 ±0.08** | **0.45 ±0.05** | **2.4** |
| | | e | - | 0.20 | - |
| | | f | 1.08 | 0.33 | 3.3 |
| Brine | Composite | a | **0.44 ±0.03** | **0.56 ±0.30** | **0.79** |
| | | c | <1.3 | <0.1 | - |
| | | d | 0.35 ±0.07 | - | - |
| | | e | - | 0.45 | - |
| | | f | 0.40 | <0.37 | >1.1 |
| | High-Al | a | **0.13 ±0.01** | **4.8 ±2.4** | **0.027** |
| | | e | - | 1.50 | - |
| | | f | 0.13 | 3.2 | 0.041 |
| | High-Fe | a | **1.05 ±0.10** | **0.37 ±0.04** | **2.8** |
| | | e | - | 0.17 | - |
| | | f | 1.05 | 0.27 | 3.9 |

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a. From SRL Comparative Leach Test Program.

b. Bold data designate an intra-laboratory comparison.

c. From tests performed by MCC, Reference 43.

d. Reference 13.

e. Reference 5.

f. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

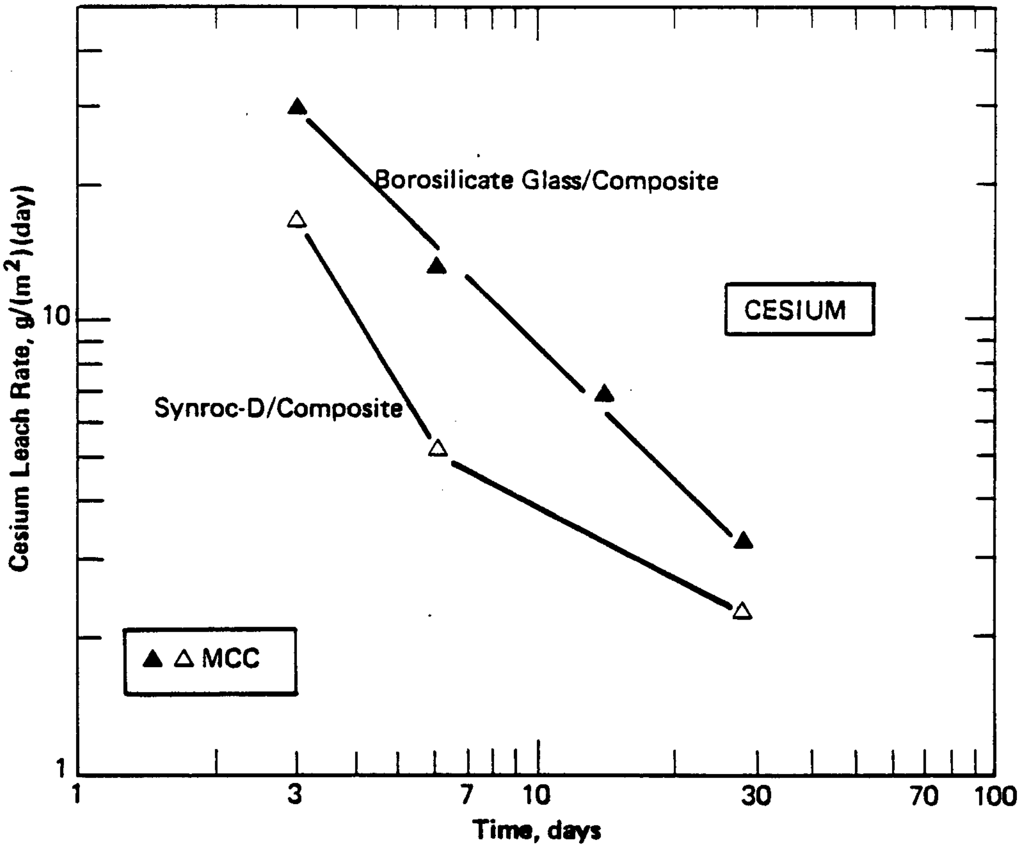

FIGURE 6. Cesium Leach Rates with Composite Sludge in Deionized Water at 150°C

TABLE 11

Comparison of Cesium Leach Rates
from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Cesium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | **3.28** | 2.33 ±0.11 | 1.4[b] |
| | c | 1.30 ±0.02 | - | - |
| | d | - | 2.53 | - |
| | e | 2.29 | 2.43 | 0.94 |
| Silicate Water | a | 2.86 ±0.15 | - | - |
| | c | 1.71 ±0.05 | - | - |
| | d | - | 0.74 | - |
| | e | 2.29 | 0.74 | 3.1 |
| Brine | a | **1.90 ±0.10** | **0.58 ±0.21** | **3.3** |
| | c | 2.65 ±0.49 | - | - |
| | d | - | 1.96 | - |
| | e | 2.28 | 1.27 | 1.8 |

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a. From tests performed by MCC, Reference 43.
b. Bold data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average of inter-laboratory data.

TABLE 12

Cesium Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Cesium Incremental Leach Rate, g/($m^2$)(day) | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.22 | 0.20 | 3.42 | 1.58 | 7.91 | 5.28 |
| 10 | 1.17 | 0.68 | 3.21 | 3.18 | 4.53 | 3.98 |
| 17 | 0.81 | 0.50 | 3.02 | 3.83 | 5.08 | 4.84 |
| 24 | 0.60 | 0.72 | 3.27 | 2.58 | 4.32 | 3.50 |
| 28 | 0.95 | 0.68 | 2.75 | 2.26 | 4.51 | 3.47 |

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a. Tests performed by MCC, Reference 43.
b. Flow rate of deionized water at 90°C.

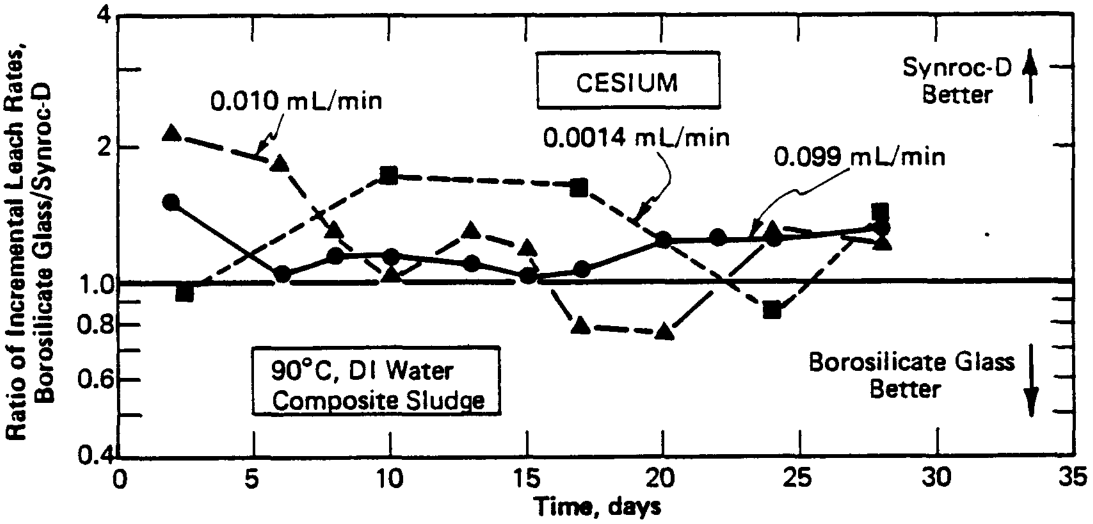

FIGURE 7. Cesium Leaching in MCC-4 Low-Flow-Rate Tests

sludges. The comparison of strontium leaching properties from 28-day MCC-1 and MCC-2 tests is summarized in Table 13. Borosilicate glass is significantly better under all of the conditions tested. In addition, the effect of flow rate on strontium leaching has been determined in MCC-4 tests. Results from the MCC-1 tests at 40 and 90°C will be discussed, followed by results from MCC-2 tests at 150°C, and then by the MCC-4 tests.

The limited data on strontium leach rates at 40°C are given in Table 14. Data are available for 28 days, but not for earlier times. Strontium leach rates are small, particularly for borosilicate glass, and in many cases are less than detection limits. At 40°C, the strontium leach rate of borosilicate glass in DI water is more than 100 times lower than for Synroc-D, and in silicate water is more than 30 times lower. No comparison can be made from the brine data.

At 90°C, the time dependence between 3 and 28 days in DI water is shown in Figure 8. Although most of the data for borosilicate glass are less than detection limits, a clear distinction in strontium leaching behavior is apparent. The borosilicate glass leach rate is 7 to more than 900 times lower.

Strontium leach rates from 28-day tests at 90°C are given in Table 15. Again, borosilicate glass leach rates are all less than detection limits. In DI water, the leach rate of borosilicate glass is more than 300 times lower than for Synroc-D, and in silicate water it is more than 100 times lower. No comparison can be made from the brine data.

Results of 28-day MCC-2 tests at 150°C are given in Table 16. Even at this high temperature, most of the strontium data for borosilicate glass are still less than detection limits. In DI water, the leach rate of borosilicate glass is more than 500 times lower, and in silicate water it is more than 100 times lower. With brine, the data values for borosilicate glass from two laboratories are inconsistent; thus, the comparison with Synroc-D in brine is indeterminate. Between 3 and 28 days, in DI water, borosilicate glass leach rates range from more than 60 to more than 120 times lower.

MCC-4 tests were run by the MCC at 90°C in DI water. Table 17 gives selected values of incremental leach rates for strontium at three flow rates. The leach rates increase with flow rate, with those of borosilicate glass increasing more severely than those of Synroc-D. Figure 9 shows the ratio of incremental leach rates as a function of time. The ratio is strongly affected by flow rate, ranging from <0.003 under static conditions to near unity at the relatively high flow rate of 0.099 mL/min (about 100 m/yr groundwater velocity in the vicinity of a repository). At a more

## TABLE 13

### Summary of Comparisons of Strontium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | RATIO[a] |
|---|---|---|
| 40°C | Deionized Water | <0.001 |
|  | Silicate Water | <0.03 |
| 90°C | Deionized Water | <0.003 |
|  | Silicate Water | <0.01 |
| 150°C | Deionized Water | <0.002 |
|  | Silicate Water | <0.01 |
|  | Brine | <0.96 |

---

a. Ratio of averages of borosilicate glass to Synroc-D leach rates, both with composite sludge, from MCC-1 and MCC-2 static leach tests.

## TABLE 14

### Comparison of Strontium Leach Rates from 28-day MCC-1 Tests with Composite Sludge at 40°C

| Leachant | Ref. | Strontium Leach Rate, g/(m$^2$)(day)<br>Borosilicate Glass | <br>Synroc-D Ceramic | RATIO |
|---|---|---|---|---|
| Deionized Water | a | <0.001 | - | - |
| | b | - | 0.087 | - |
| | c | <0.001 | 0.087 | <0.01 |
| Silicate Water | a | <0.001 | - | - |
| | b | - | 0.033 | - |
| | c | <0.001 | 0.033 | <0.03 |
| Brine | a | <0.001 | - | - |
| | b | - | <0.004 | - |
| | c | <0.001 | <0.004 | - |

---

a. Reference 13.
b. Reference 5.
c. Average of inter-laboratory data.

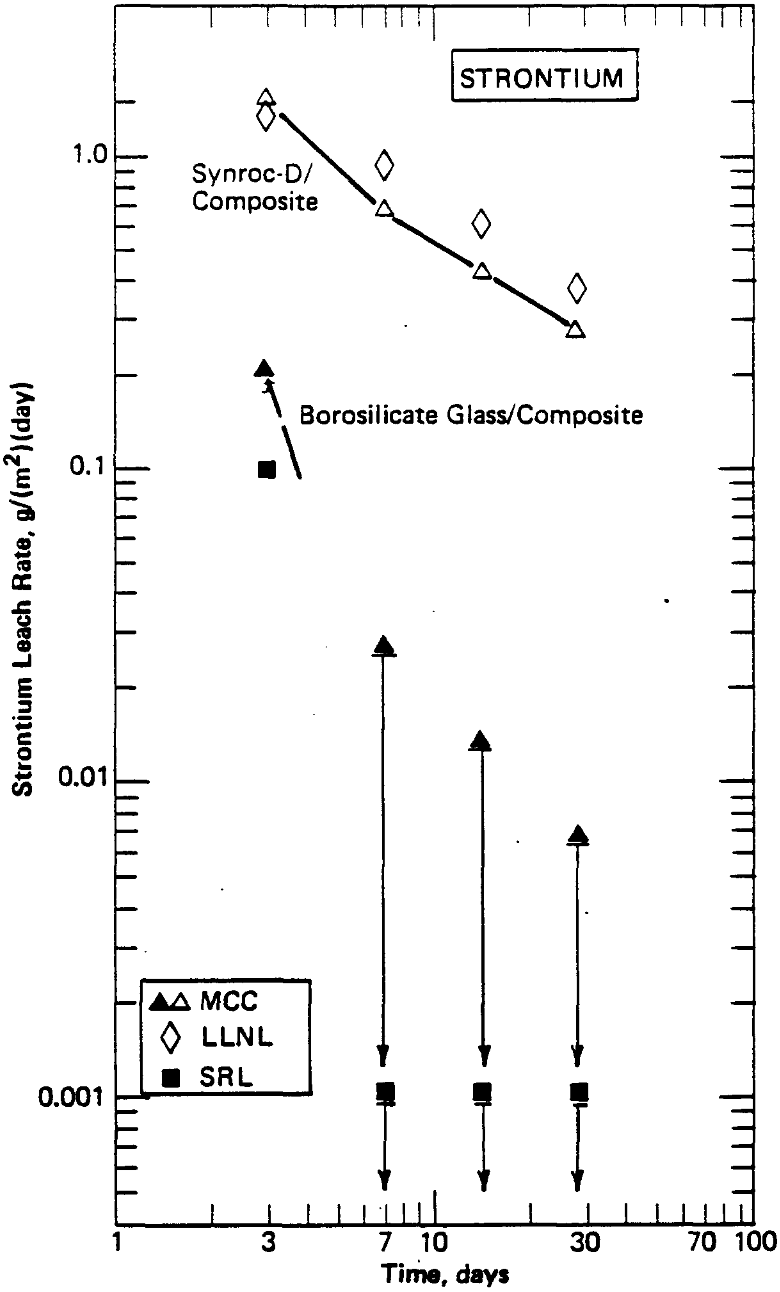

FIGURE 8. Strontium Leach Rates with Composite Sludge in Deionized Water at 90°C

## TABLE 15

## Comparison of Strontium Leach Rates from 28-day MCC-1 Tests with Composite Sludge at 90°C

| Leachant | Ref. | Strontium Leach Rate, g/(m$^2$)(day) | | RATIO |
|---|---|---|---|---|
| | | Borosilicate Glass | Synroc-D Ceramic | |
| Deionized Water | a | **<0.0065** | **0.28** | **<0.023**[b] |
| | c | <0.001 | - | - |
| | d | - | 0.38 | - |
| | e | <0.001 | 0.33 | <0.003 |
| Silicate Water | a | **<0.0066** | **0.079** | **<0.08** |
| | c | <0.001 | - | - |
| | d | - | 0.099 | - |
| | e | <0.001 | 0.089 | <0.01 |
| Brine | a | <0.33 | <0.2 | - |
| | c | <0.001 | - | - |
| | d | - | <0.1 | - |
| | e | <0.001 | <0.1 | - |

---

a. From tests performed by MCC, Reference 43.
b. Bold data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average or lowest detection limit of inter-laboratory data.

## TABLE 16

### Comparison of Strontium Leach Rates from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Strontium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | <0.01 | **0.60 ±0.02** | **<0.02**[b] |
| | c | <0.002 | - | - |
| | d | - | 1.82 | - |
| | e | <0.002 | 1.21 | <0.002 |
| Silicate Water | a | <0.006 | - | - |
| | c | 0.006 ±0.004 | - | - |
| | d | - | 0.493 | - |
| | e | <0.006 | 0.493 | <0.01 |
| Brine | a | **<0.006** | **1.18 ±0.28** | **<0.005** |
| | c | 2.61 ±0.06 | - | - |
| | d | - | 1.53 | - |
| | e | <1.31 | 1.36 | <0.96 |

---

a. From tests performed by MCC, Reference 43.
b. Bold data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

## TABLE 17

Strontium Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| Time, days | Strontium Incremental Leach Rate, $g/(m^2)(day)$<br>0.0014[b] mL/min<br>Borosilicate Glass | <br>0.0014[b] mL/min<br>Synroc-D Ceramic | <br>0.010[b] mL/min<br>Borosilicate Glass | <br>0.010[b] mL/min<br>Synroc-D Ceramic | <br>0.099[b] mL/min<br>Borosilicate Glass | <br>0.099[b] mL/min<br>Synroc-D Ceramic |
|---|---|---|---|---|---|---|
| 2 | 0.005 | 0.117 | 0.48 | 0.70 | 3.22 | 2.83 |
| 10 | 0.006 | 0.265 | 0.06 | 1.12 | 2.39 | 2.14 |
| 17 | - | 0.231 | 0.06 | 1.04 | 2.08 | 1.85 |
| 24 | 0.005 | 0.296 | - | 1.02 | 1.90 | 1.48 |
| 28 | - | 0.289 | 0.07 | 0.95 | 2.10 | 1.46 |

---

a. Tests performed by MCC, Reference 43.

b. Flow rate of deionized water at 90°C.

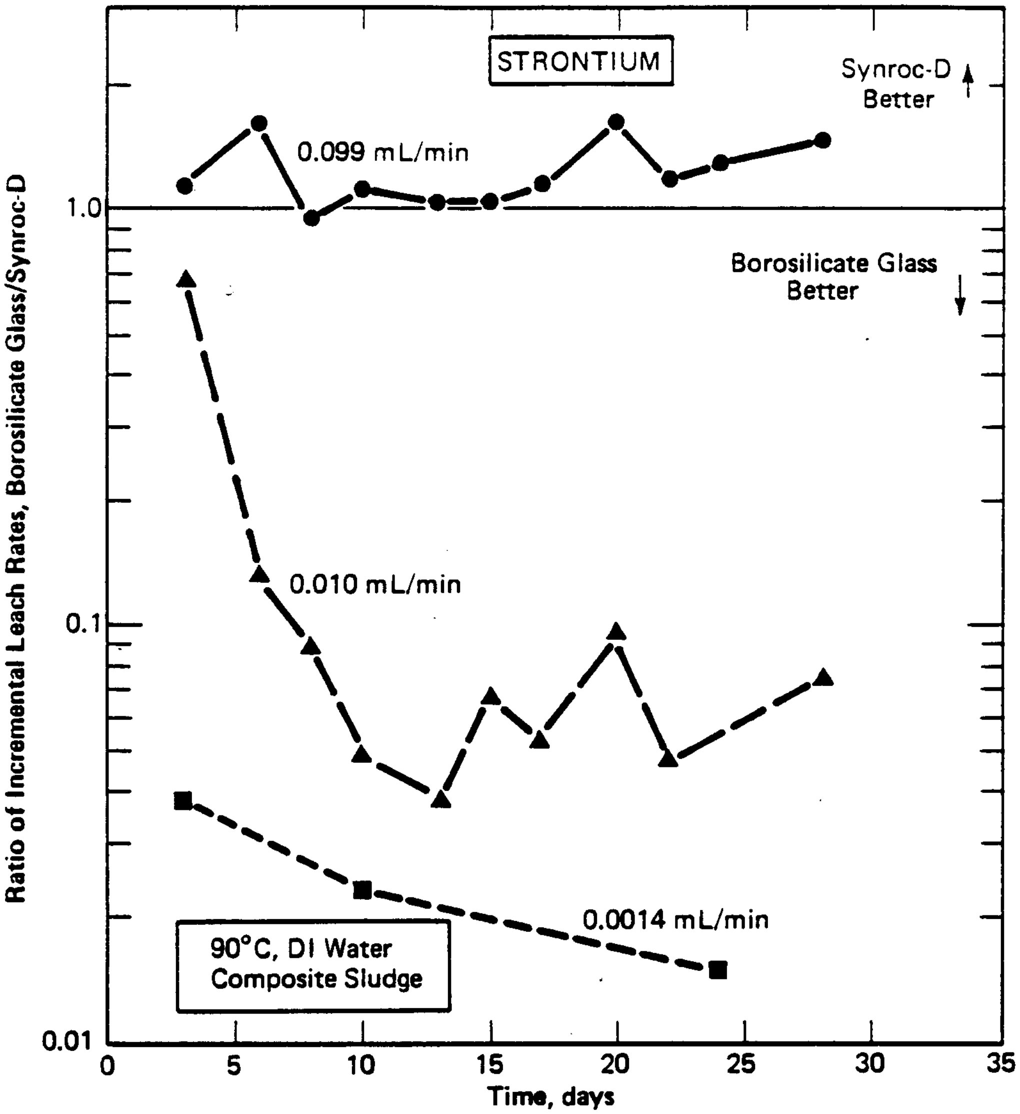

FIGURE 9. Strontium Leaching in MCC-4 Low-Flow-Rate Tests

realistic velocity of 1 m/yr (approximated by the tests at 0.0014 mL/min), the strontium leach rate for borosilicate glass is about 70 times lower than that of Synroc-D.

### Uranium

A substantial amount of uranium leach data is available. The comparison of uranium leaching properties of borosilicate glass and Synroc-D is summarized in Table 18 for 28-day MCC-1 and MCC-2 tests. Synroc-D is significantly better under all of the conditions tested. In addition, data from MCC-3 agitated powder tests and MCC-4 low-flow-rate tests are available. Results from MCC-1 tests at 40 and 90°C will be discussed, followed by results from MCC-2 tests at 150°C, and then by the MCC-3 and MCC-4 tests.

Data on the time dependence of uranium leaching between 3 and 28 days are available at 40°C with high-aluminum and high-iron sludges. The tests were in DI water. With both sludges, the uranium leach rates for Synroc-D were less than detection limits. With high-aluminum sludge, the borosilicate glass data values overlap the Synroc-D detection limits, so that no comparison is possible. However, with high-iron sludge, the Synroc-D leach rate is more than 10 to more than 50 times lower. With composite sludge, no data are available on Synroc-D at 40°C and early times.

Uranium leach rates from 28-day tests at 40°C are given in Table 19. With composite sludge, the uranium leach rate of Synroc-D in silicate water is 400 times lower than that of borosilicate glass. Insufficient data are available for a comparison in brine.

At 90°C, the time dependence in DI water is shown in Figures 10 and 11. Data between 3 and 28 days for borosilicate glass and Synroc-D with composite sludge are shown in Figure 10. Although inter-laboratory variance is substantial, a clear distinction in uranium leaching behavior is apparent. The Synroc-D leach rate is 6 to 2650 times lower. The forms containing high-iron sludge are compared in Figure 11, which shows that between 3 and 28 days, the Synroc-D leach rate is 7 to more than 460 times lower. The time dependence of forms with high-aluminum sludge, not shown, gives Synroc-D leach rates that are more than 2 to more than 9 times lower than those of borosilicate glass.

Uranium leach rates from 28-day tests at 90°C are given in Table 20. Considerable data are available for this case. Many of the Synroc-D leach rates are less than detection limits. In silicate water, the results parallel those in DI water, with Synroc-D leach rates up to 1000 times lower. In brine, the only comparison that can be made from the data is with composite

## TABLE 18

### Summary of Comparisons of Uranium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| | | Ratio of Uranium Leach Rates[a,b] | | |
|---|---|---|---|---|
| Temperature | Leachant | Composite | High-Al | High-Fe |
| 40°C | Deionized Water | - | >0.2 | >57 |
| | Silicate Water | 400 | - | - |
| 90°C | Deionized Water | 1200 | >8 | >420 |
| | Silicate Water | 1000 | >70 | 600 |
| | Brine | 22 | - | - |
| 150°C | Deionized Water | 2800 | - | - |
| | Silicate Water | >44 | - | - |
| | Brine | 190 | - | - |

---

a. MCC-1 and MCC-2 static leach tests.

b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

## TABLE 19

### Comparison of Uranium Leach Rates from 28-day MCC-1 Tests at 40°C

| Leachant | Sludge Type | Ref. | Uranium Leach Rate, $g/(m^2)(day)$ | | RATIO |
|---|---|---|---|---|---|
| | | | Borosilicate Glass | Synroc-D Ceramic | |
| Deionized Water | Composite | a | 0.011 ±0.005 | - | - |
| | | b | 0.018 ±0.002 | - | - |
| | | c | 0.015 | - | - |
| | High-Al | a | **0.001 ±0.00** | **<0.005** | **>0.2**[d] |
| | High-Fe | a | **0.017 ±0.00** | **<0.0003** | **>57** |
| Silicate Water | Composite | b | 0.036 ±0.006 | - | - |
| | | e | - | 0.00009 | - |
| | | c | 0.036 | 0.00009 | 400 |
| Brine | Composite | b | <0.71 | - | - |

---

a. From SRL Comparative Leach Test Program.
b. Reference 13.
c. Average of inter-laboratory data.
d. Bold data designate an intra-laboratory comparison.
e. Reference 5.

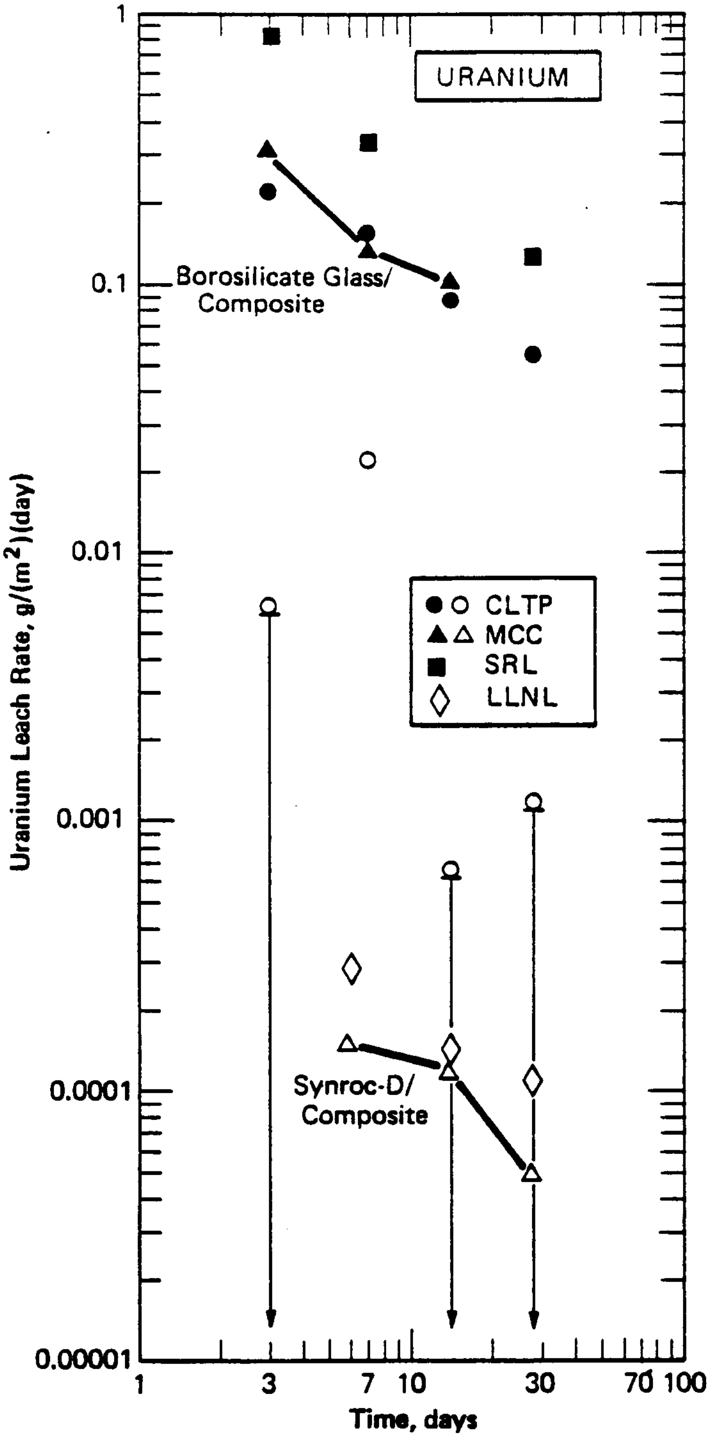

FIGURE 10. Uranium Leach Rates with Composite Sludge in Deionized Water at 90°C

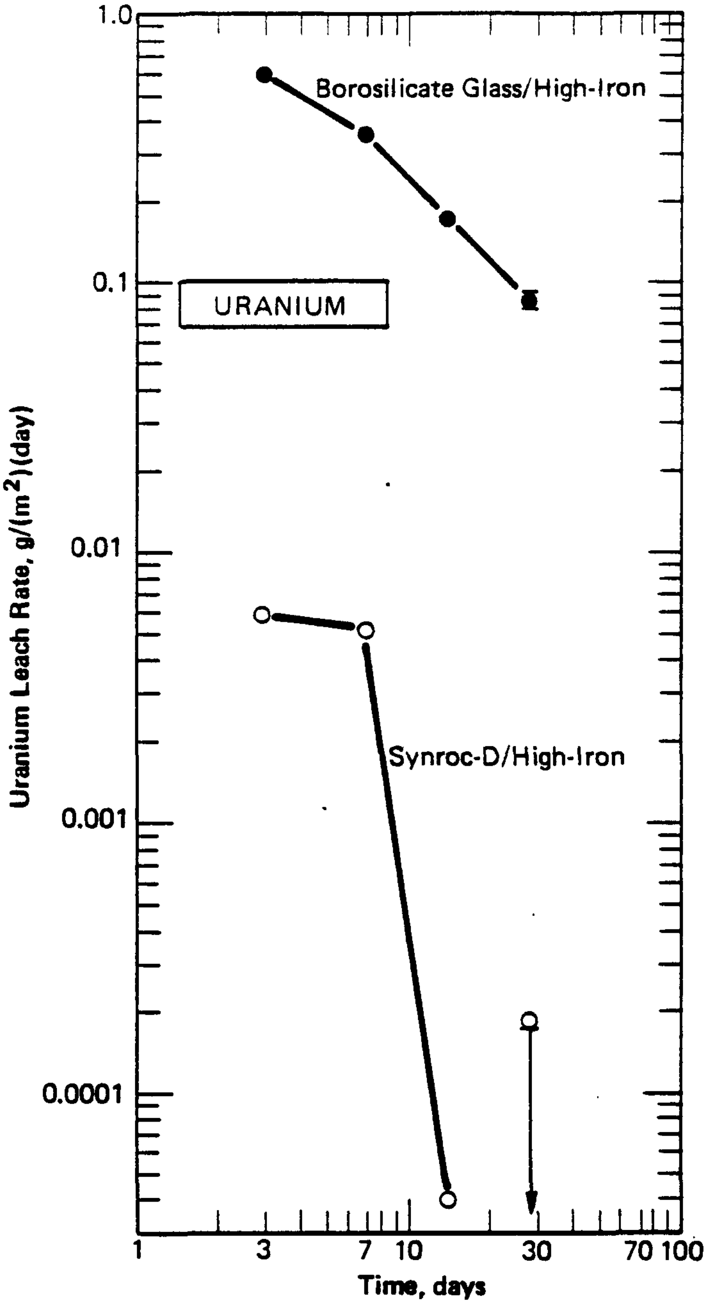

FIGURE 11. Uranium Leach Rates with High-Iron Sludge in Deionized Water at 90°C

TABLE 20

Comparison of Uranium Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Uranium Leach Rate, $g/(m^2)(day)$ | | | | |
|---|---|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | | Synroc-D Ceramic | | RATIO |
| Deionized Water | Composite | a | **0.055** | **±0.003** | **<0.001** | | **>55**[b] |
| | | c | | - | 0.000049 | ±0.000006 | - |
| | | d | 0.13 | | | - | - |
| | | e | | - | 0.00011 | | - |
| | | f | 0.093 | | 0.000080 | | 1200 |
| | High-Al | a | **0.040** | **±0.005** | **<0.005** | | **>8** |
| | | e | | - | <0.07 | | - |
| | | f | 0.040 | | <0.005 | | >8 |
| | High-Fe | a | **0.084** | **±0.003** | **<0.0002** | | **>420** |
| | | e | | - | <0.005 | | - |
| | | f | 0.084 | | <0.0002 | | >420 |
| Silicate Water | Composite | a | **0.236** | **±0.002** | **<0.001** | | **>230** |
| | | c | **0.18** | **±0.006** | **0.00021** | **±0.00002** | **860** |
| | | d | 0.44 | ±0.12 | | - | - |
| | | e | | - | 0.00034 | | - |
| | | f | 0.29 | | 0.00028 | | 1000 |
| | High-Al | a | **0.274** | **±0.002** | **<0.004** | | **>70** |
| | | e | | - | <0.07 | | - |
| | | f | 0.274 | | <0.004 | | >70 |
| | High-Fe | a | **0.169** | **±0.012** | **0.0003** | **±0.0002** | **600** |
| | | e | | - | <0.005 | | - |
| | | f | 0.169 | | 0.0003 | | 600 |
| Brine | Composite | a | <0.019 | | <0.014 | | - |
| | | c | **0.011** | **±0.001** | **0.00050** | **±0.00002** | **22** |
| | | d | <0.71 | | | - | - |
| | | f | 0.011 | | 0.00050 | | 22 |
| | High-Al | a | <0.029 | | <0.082 | | - |
| | | e | | - | <0.07 | | - |
| | | f | <0.029 | | <0.07 | | - |
| | High-Fe | a | <0.006 | | <0.066 | | - |
| | | e | | - | <0.005 | | - |
| | | f | <0.006 | | <0.005 | | - |

---

a. From SRL Comparative Leach Test Program.

b. Bold data designate an intra-laboratory comparison.

c. From tests performed by MCC, Reference 43.

d. Reference 13.

e. Reference 5.

f. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

sludge, for which the Synroc-D leach rate is 22 times lower than that of borosilicate glass.

The time dependence of uranium leaching from MCC-2 tests at 150°C in DI water with composite sludge are shown in Figure 12. The leach rate of Synroc-D is 500 to 4500 times lower. Results of 28-day tests at 150°C are given in Table 21. The uranium leach rate of Synroc-D is much less than that of borosilicate glass, in all three leachants.

In an MCC-3 agitated powder test, the uranium concentration was 0.0066M from borosilicate glass and 0.00087M from Synroc-D, after 14 days. Thus, the uranium concentration from Synroc-D is 7.6 times lower.

MCC-4 tests were run at 90°C in DI water with samples containing composite sludge. Table 22 gives selected incremental leach rates for uranium at three flow rates. The leach rates increase with flow rates; the leach rates of borosilicate glass level out, but those of Synroc-D appear to increase with time. Figure 13 shows the ratio of incremental leach rates as a function of time. The points are severely scattered, probably due entirely to uncertainties in the data. However, at early times at all three flow rates, the uranium leach rate of Synroc-D is consistently two to three orders of magnitude lower. At 28 days and 0.099 mL/min, the leach rate of Synroc-D is only 6 times lower, but at a more realistic flow rate of 0.0014 mL/min there is no evidence that Synroc-D would lose its large advantage.

### Other Elements

Comparative leaching data are available for eight additional elements: cerium, sodium, aluminum, iron, zirconium, silicon, calcium, and manganese. Data for these elements are relatively sparse, except for sodium and aluminum. Many of the comparisons are indeterminate, including all those for cerium and zirconium. Where comparisons are possible, borosilicate glass is better for calcium, while Synroc-D is better for sodium, aluminum, iron, silicon, and manganese. The data are displayed in Tables 23-45 and Figures 14-35, and are discussed briefly below. Table 23 gives comparative 28-day leach rates at 40°C in DI water for five elements.

Cerium leaching comparisons between borosilicate glass and Synroc-D are summarized in Table 24, for 28-day MCC-1 tests. The data are given at 40°C in Table 23 and at 90°C in Table 25. For both forms, the cerium leach rates are very small, and most are less than detection limits. All of the comparisons are indeterminate.

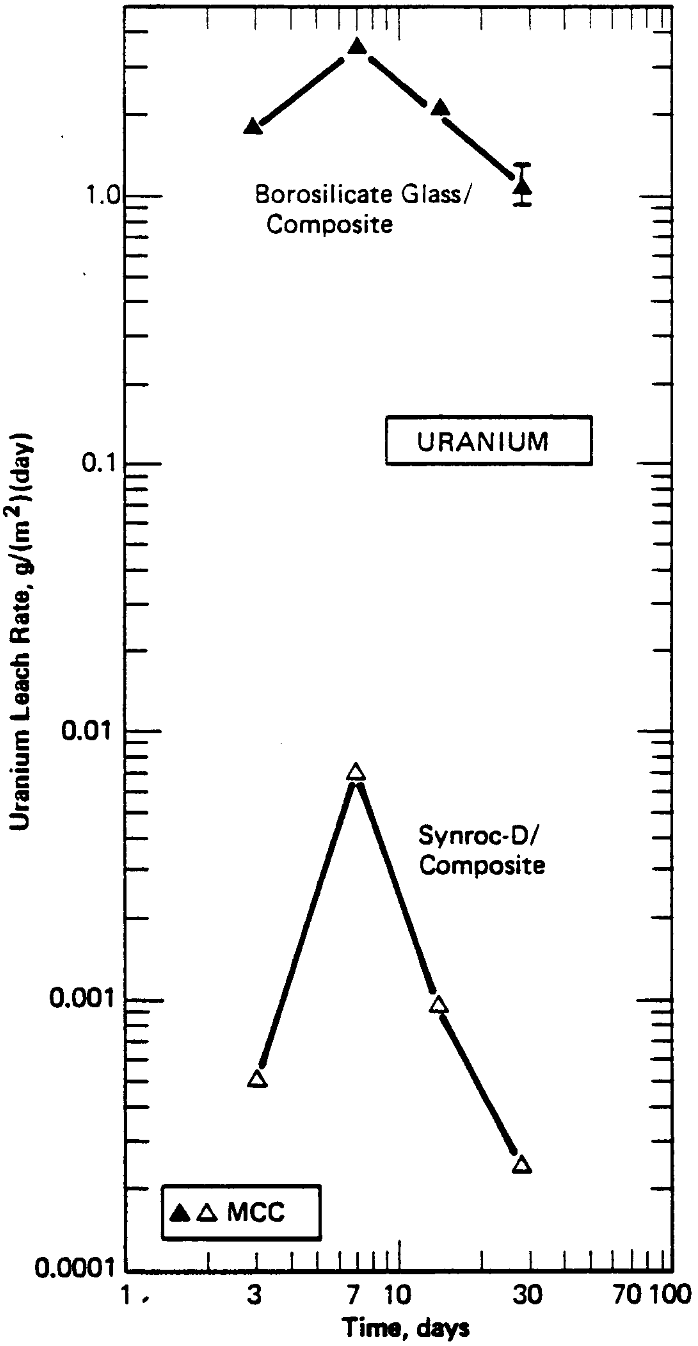

**FIGURE 12.** Uranium Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 21

### Comparison of Uranium Leach Rates from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Uranium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | **1.09 ±0.19** | **0.000243 ±0.000003** | **4500**[b] |
| | c | 0.24 | - | - |
| | d | - | <0.017 | - |
| | e | 0.67 | 0.000243 | 2800 |
| Silicate Water | a | 1.10 ±0.13 | - | - |
| | c | 0.38 | - | - |
| | d | - | <0.017 | - |
| | e | 0.74 | <0.017 | >44 |
| Brine | a | **0.28 ±0.04** | **0.0015 ±0.0009** | **190** |
| | c | <0.71 | - | - |
| | e | 0.28 | 0.0015 | 190 |

---

a. From tests performed by MCC, Reference 43.
b. Bold data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

### TABLE 22

### Uranium Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Uranium Incremental Leach Rate, g/($m^2$)(day) | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.0032 | - | 0.146 | 0.0001 | 0.352 | 0.0018 |
| 10 | 0.0507 | 0.00004 | 0.174 | 0.0001 | 0.353 | 0.0007 |
| 17 | 0.0295 | 0.00021 | 0.055 | 0.0003 | 0.235 | 0.0002 |
| 24 | 0.0281 | 0.00002 | 0.047 | 0.0002 | 0.295 | 0.001 |
| 28 | - | - | 0.062 | 0.0051 | 0.322 | 0.054 |

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a. Tests performed by MCC, Reference 43.
b. Flow rate of deionized water at 90°C.

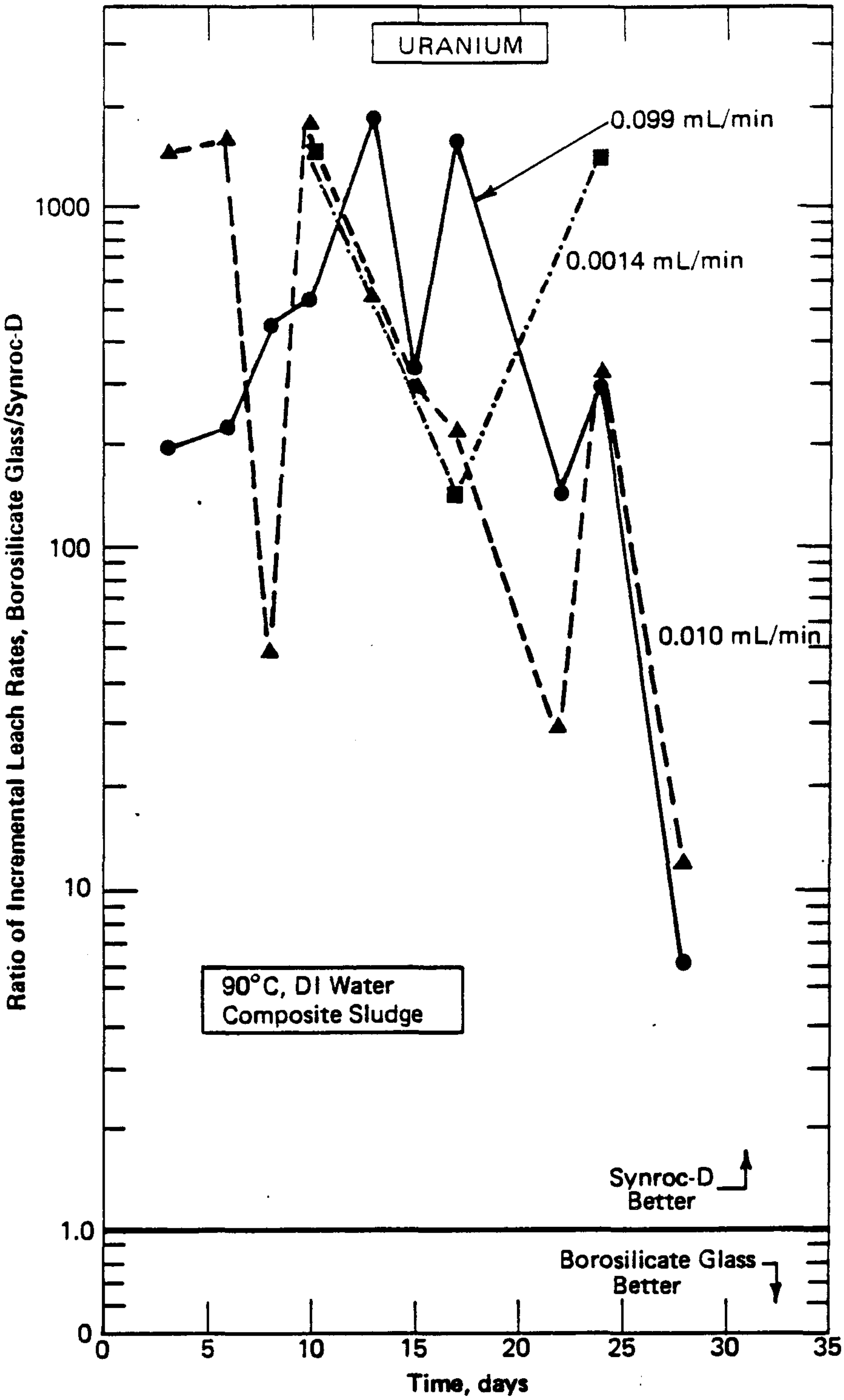

FIGURE 13. Uranium Leaching in MCC-4 Low-Flow-Rate Tests

## TABLE 23

### Comparison of Leach Rates at 40°C from 28-day MCC-1 Tests with Deionized Water

| | | | Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|---|
| Element | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Cerium | Composite | a | <0.001 | - | - |
| | | b | <0.36 | - | - |
| | | c | <0.001 | - | - |
| | High-Al | a | **0.003 ±0.001** | **<0.005** | **>0.6**[d] |
| | High-Fe | a | <0.022 | 0.005 ±0.004 | <4.4 |
| Sodium | Composite | a | 0.039 ±0.004 | - | - |
| | | b | 0.070 ±0.028 | - | - |
| | | c | 0.055 | - | - |
| | High-Al | a | **0.012 ±0.002** | **<1.07** | **>0.011** |
| | High-Fe | a | **0.542 ±0.030** | **0.098 ±0.026** | **5.5** |
| Aluminum | Composite | a | 0.122 ±0.110 | - | - |
| | | e | - | 0.009 | - |
| | | c | 0.122 | 0.009 | 14 |
| | High-Al | a | **0.012 ±0.001** | **0.014 ±0.004** | **0.86** |
| | High-Fe | a | **0.635 ±0.014** | **0.080 ±0.018** | **7.9** |
| Iron | Composite | a | <0.0005 | - | - |
| | High-Al | a | <0.010 | <0.001 | - |
| | High-Fe | a | <0.019 | <0.0005 | - |
| Zirconium | Composite | a | <0.003 | - | - |
| | High-Al | a | <0.004 | <0.003 | - |
| | High-Fe | a | <0.013 | <0.0003 | - |

---

a. From SRL Comparative Leach Test Program.
b. Reference 13.
c. Average or lowest detection limit of inter-laboratory data.
d. Bold data designate an intra-laboratory comparison.
e. Reference 5.

## TABLE 24

## Summary of Comparisons of Cerium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | Ratio of Cerium Leach Rates[a,b] | | |
|---|---|---|---|---|
| | | Composite | High-Al | High-Fe |
| 40°C | Deionized Water | - | >0.6 | <4.4 |
| 90°C | Deionized Water | <2.5 | >93 | <8.2 |
| | Silicate Water | >3 | - | <18 |
| | Brine | - | - | <5 |

---

a. MCC-1 static leach tests.

b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

TABLE 25

Comparison of Cerium Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Cerium Leach Rate, $g/(m^2)(day)$ | | | | |
|---|---|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | | Synroc-D Ceramic | | RATIO |
| Deionized Water | Composite | a | **<0.004** | | **0.0016** | **±0.0004** | **<2.5**[b] |
| | | c | <0.055 | | | - | - |
| | | d | <0.36 | | | - | - |
| | | e | | - | <0.11 | | - |
| | | f | <0.004 | | 0.0016 | | <2.5 |
| | High-Al | a | **0.56** | **±0.71** | **<0.006** | | **>93** |
| | High-Fe | a | **<0.041** | | **0.005** | **±0.004** | **<8.2** |
| Silicate Water | Composite | a | **0.003** | **±0.001** | **<0.001** | | **>3** |
| | | c | <0.05 | | <0.043 | | - |
| | | d | <0.36 | | | - | - |
| | | f | 0.003 | | <0.001 | | >3 |
| | High-Al | a | <0.020 | | <0.008 | | - |
| | High-Fe | a | **<0.027** | | **0.0015** | **±0.0003** | **<18** |
| Brine | Composite | a | <0.029 | | <0.034 | | - |
| | | c | <2.7 | | <2.0 | | - |
| | | d | <0.36 | | | - | - |
| | | f | <0.029 | | <0.034 | | - |
| | High-Al | a | <0.11 | | <0.042 | | - |
| | High-Fe | a | **<0.154** | | **0.031** | **±0.006** | **<5.0** |

---

a. From SRL Comparative Leach Test Program.
b. **Bold** data designate an intra-laboratory comparison.
c. From tests performed by MCC, Reference 43.
d. Reference 13.
e. Reference 5.
f. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

Sodium has extensive leaching data in DI and silicate waters, but none in brine. The comparison of sodium leaching properties of borosilicate glass and Synroc-D is summarized in Table 26 for 28-day MCC-1 and MCC-2 tests. With composite and high-iron sludges, the leach rate of Synroc-D is 2 to 60 times lower; with high-aluminum sludge, the comparisons are indeterminate. The data at 40°C are shown in Figures 14 and 15, and in Table 23. Similarly, the data at 90°C are shown in Figures 16, 17, and 18, and in Table 27. The data at 150°C are shown in Figure 19 and Table 28. Results of MCC-4 tests are given in Table 29 and Figure 20. In these flow tests, Synroc-D generally had the lower leach rate, but the difference declined from a factor of about 6 at the lowest flow to about 1.5 at the highest flow. Overall, the leaching behavior of sodium resembles that of cesium.

Aluminum also has extensive leaching data in DI and silicate waters, but very little data in brine. The comparison of aluminum leaching properties of borosilicate glass and Synroc-D is summarized in Table 30 for 28-day MCC-1 and MCC-2 tests. For nearly all of the comparisons, the Synroc-D leach rate is 2 to 14 times lower; in two exceptional cases, the comparison is either indeterminate or unsubstantiated. The data at 40°C are shown in Figures 21 and 22, and in Table 23. At 90°C, the data are shown in Figures 23, 24, and 25, and in Table 31. The data at 150°C are shown in Figure 26 and Table 32. Results of MCC-4 flow tests are given in Table 33 and Figure 27. In these tests, Synroc-D always had the lower leach rate; the lower flows had similar effects on the ratios of leach rates, which approach unity at 28 days. However, at the highest flow, the ratio increases with time, and at 24 days the aluminum leach rate of Synroc-D is about 20 times lower than that of borosilicate glass.

Iron leaching comparisons between borosilicate glass and Synroc-D are summarized in Table 34, for 28-day MCC-1 and MCC-2 tests. The data are given at 40°C in Table 23, at 90°C in Table 35, and at 150°C in Table 36. Most of the data at 40 and 90°C are less than detection limits. For both forms, the iron leach rates are very small, except for Synroc-D in brine at 150°C. In the few comparisons that are possible, the leach rate of Synroc-D is about 2 times lower.

Zirconium leaching data are nearly all less than detection limits, as shown at 40°C in Table 23 and at 90°C in Table 37. All of the zirconium leach rates are very small. From the data, only one comparison between borosilicate glass and Synroc-D is possible, but it is indeterminate.

Silicon has no data with high-aluminum or high-iron sludges, and at 40°C there are no data from Synroc-D for comparison. The comparison of silicon leaching properties of borosilicate glass

TABLE 26

Summary of Comparisons of
Sodium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | Ratio of Sodium Leach Rates[a,b] Composite | High-Al | High-Fe |
|---|---|---|---|---|
| 40°C | Deionized Water | - | >0.011 | 5.5 |
| 90°C | Deionized Water | 3.7 | >0.2 | >7.0 |
| | Silicate Water | 2.1 | 0.32 | 62 |
| 150°C | Deionized Water | 4.4 | - | - |
| | Silicate Water | 60 | - | - |

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a. MCC-1 and MCC-2 static leach tests.
b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

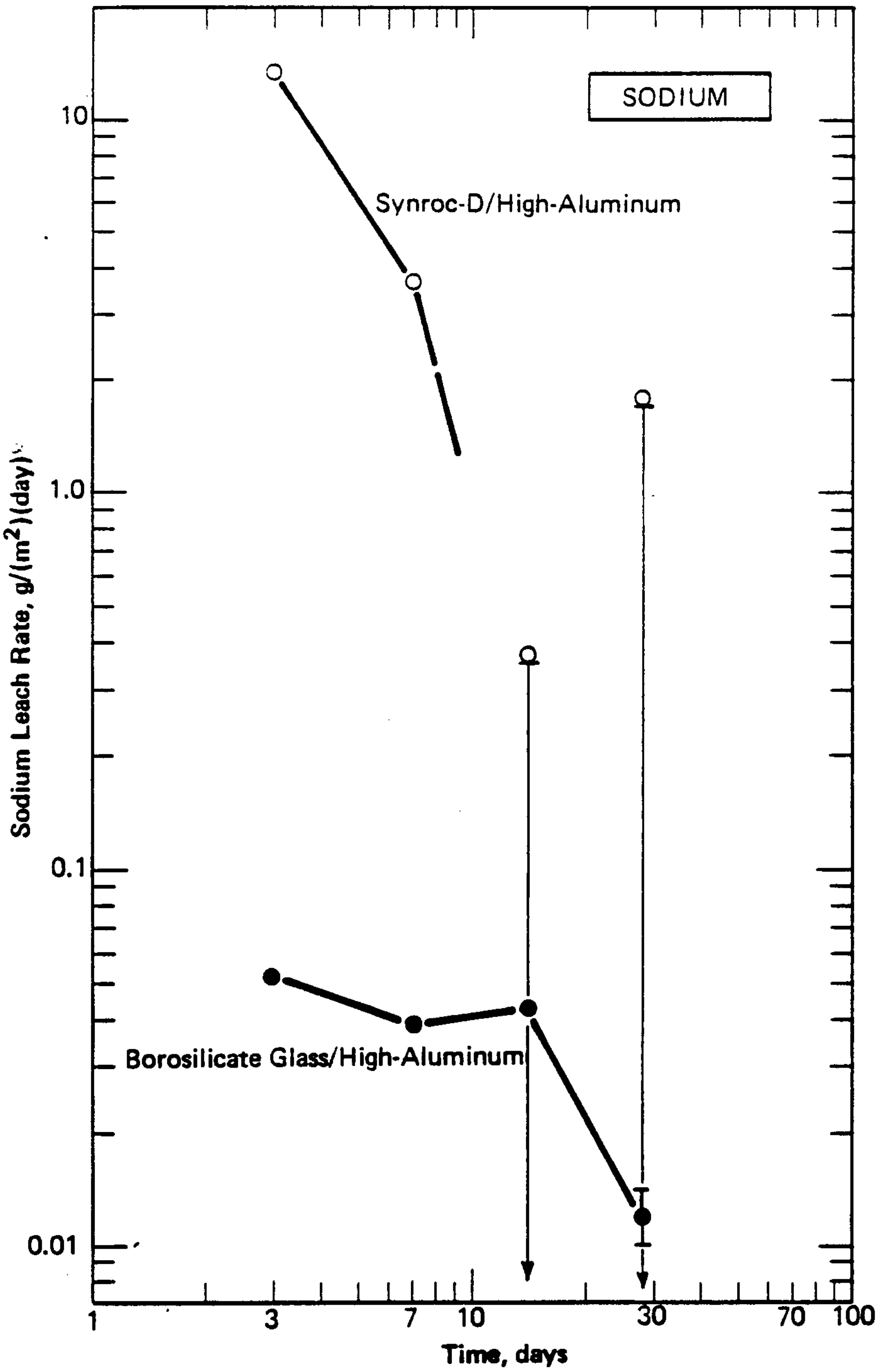

FIGURE 14. Sodium Leach Rates with High-Aluminum Sludge in Deionized Water at 40°C

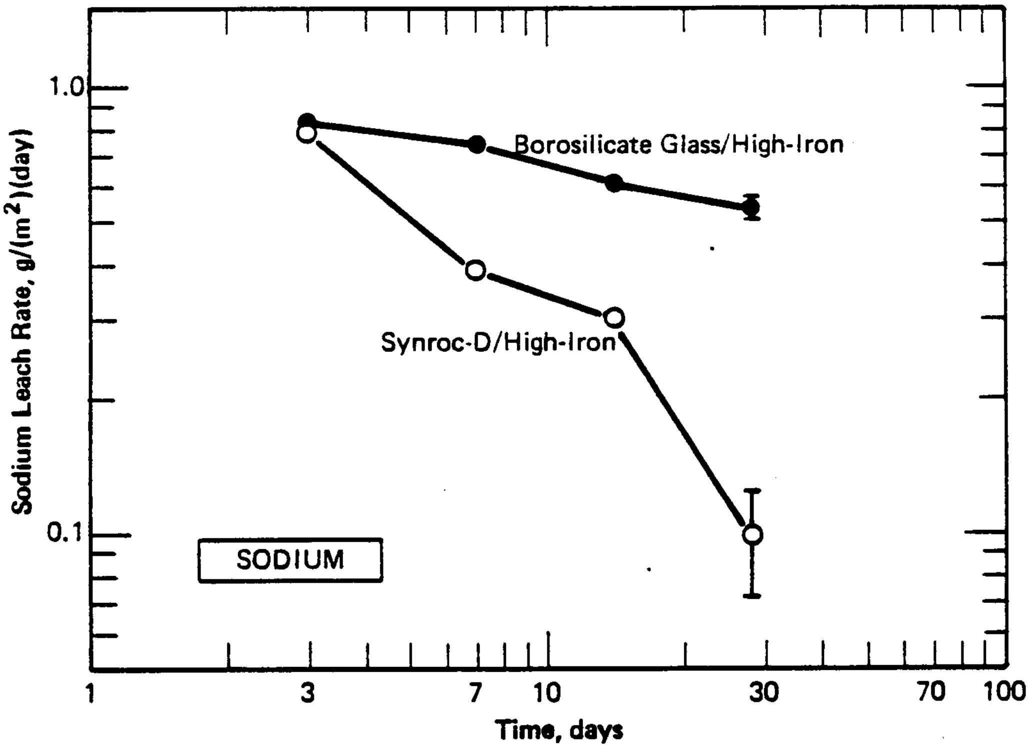

FIGURE 15. **Sodium Leach Rates with High-Iron Sludge in Deionized Water at 40°C**

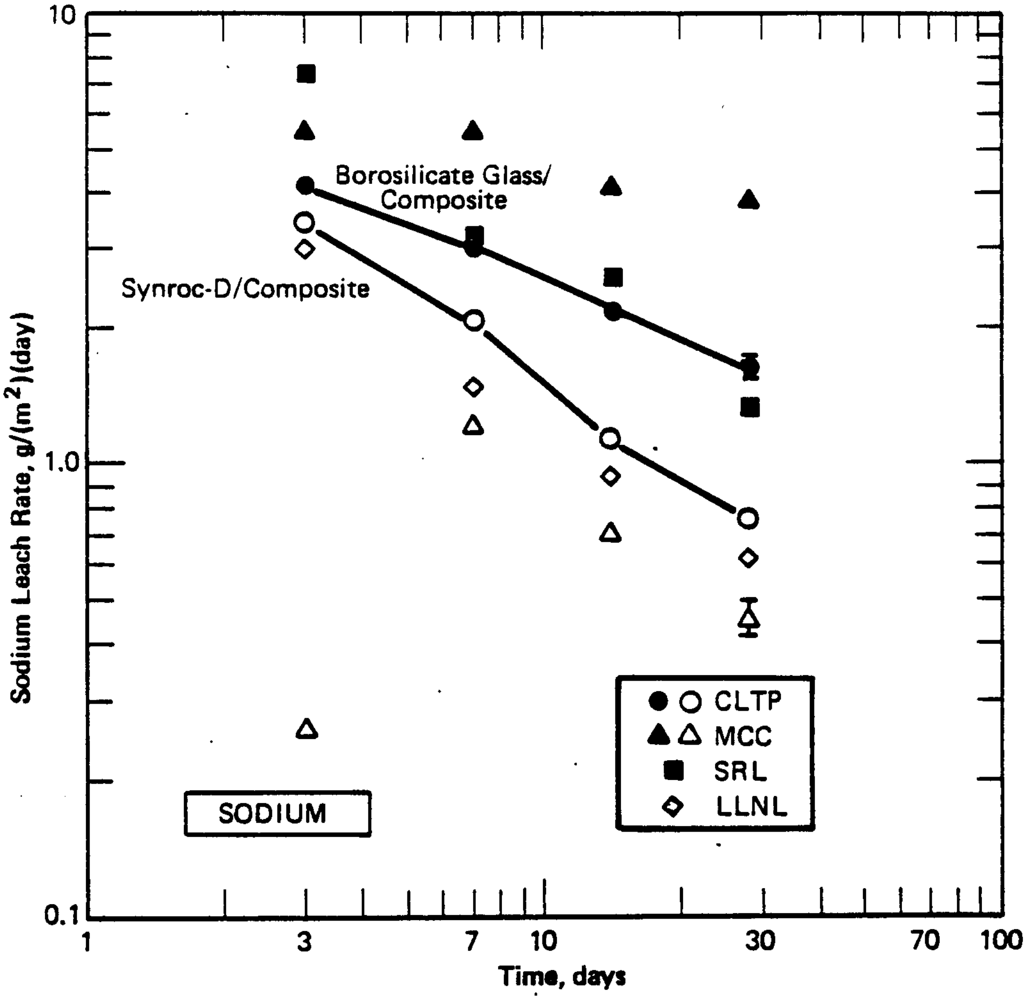

FIGURE 16. Sodium Leach Rates with Composite Sludge in Deionized Water at 90°C

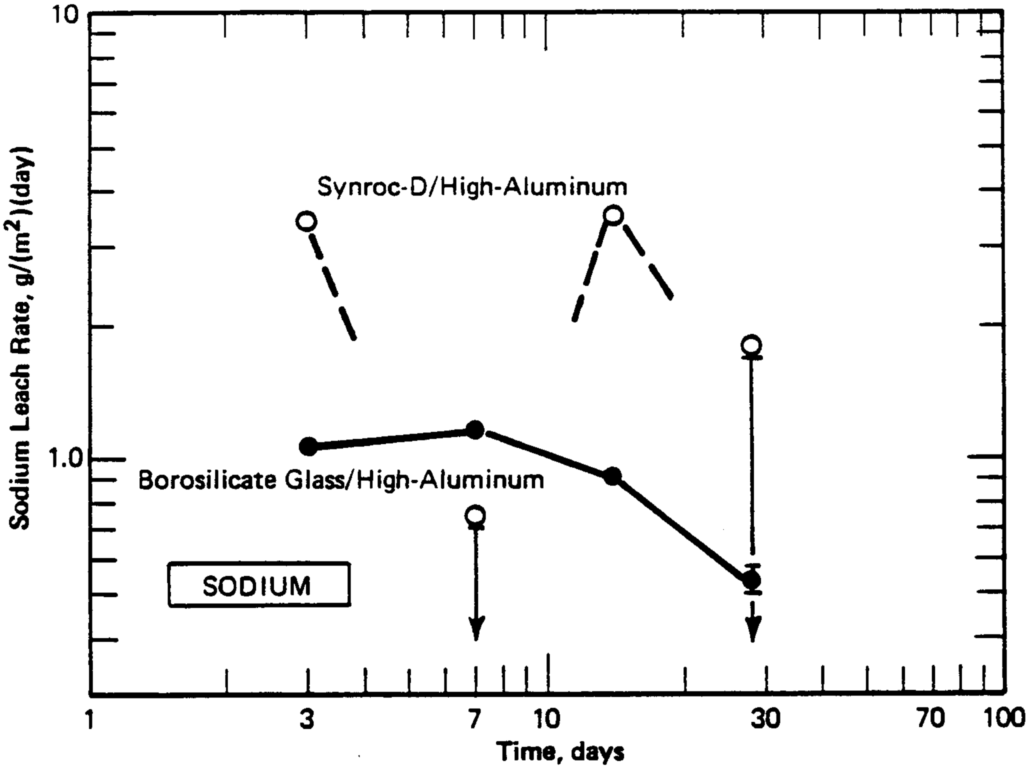

FIGURE 17. Sodium Leach Rates with High-Aluminum Sludge in Deionized Water at 90°C

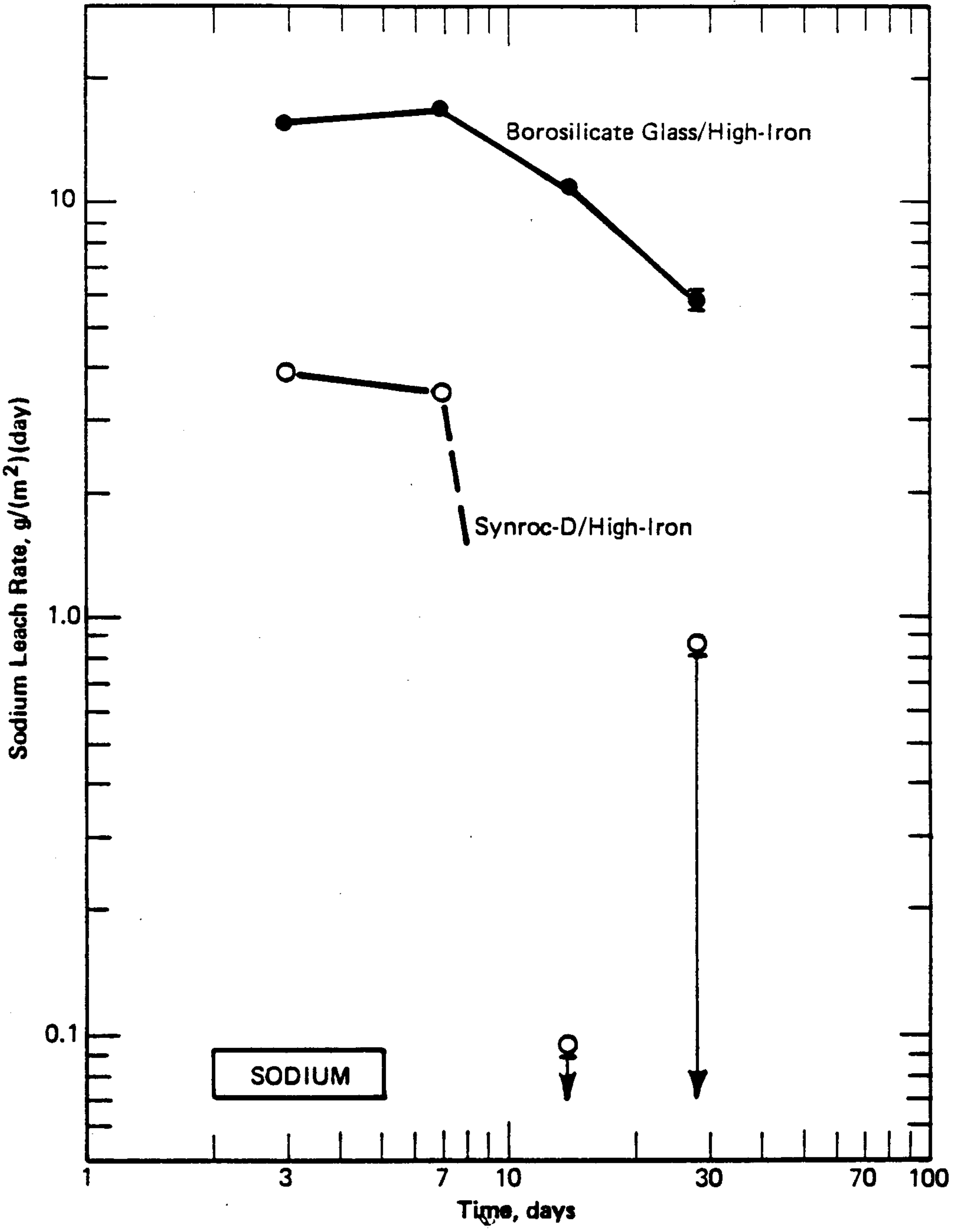

**FIGURE 18.** **Sodium Leach Rates with High-Iron Sludge in Deionized Water at 90°C**

## TABLE 27

## Comparison of Sodium Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Sodium Leach Rate, g/(m$^2$)(day) | | |
|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | Composite | a | 1.64 ±0.06 | 0.76 ±0.04 | 2.2[b] |
| | | c | **3.83 ±0.11** | **0.46 ±0.04** | **8.3** |
| | | d | 1.34 ±0.07 | - | - |
| | | e | - | 0.62 | - |
| | | f | 2.27 | 0.61 | 3.7 |
| | High-Al | a | **0.54 ±0.05** | **<1.76** | **>0.3** |
| | | e | - | 3.46 | - |
| | | f | 0.54 | <2.61 | >0.2 |
| | High-Fe | a | **5.84 ±0.07** | **<0.82** | **>7.1** |
| | | e | - | 0.84 | - |
| | | f | 5.84 | <0.83 | >7.0 |
| Silicate Water | Composite | a | **1.09 ±0.07** | **1.42 ±0.05** | **0.77** |
| | | c | **2.04 ±0.03** | **0.36 ±0.08** | **5.7** |
| | | d | 1.32 ±0.35 | - | - |
| | | e | - | 0.33 | - |
| | | f | 1.48 | 0.70 | 2.1 |
| | High-Al | a | **0.40 ±0.11** | **<3.25** | **>0.12** |
| | | e | - | 1.24 | - |
| | | f | 0.40 | 1.24 | 0.32 |
| | High-Fe | a | **4.32 ±0.11** | **<0.70** | **>6.2** |
| | | e | - | 0.07 | - |
| | | f | 4.32 | 0.07 | 62 |

---

a. From SRL Comparative Leach Test Program.
b. **Bold** data designate an intra-laboratory comparison.
c. From tests performed by MCC, Reference 43.
d. Reference 13.
e. Reference 5.
f. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).

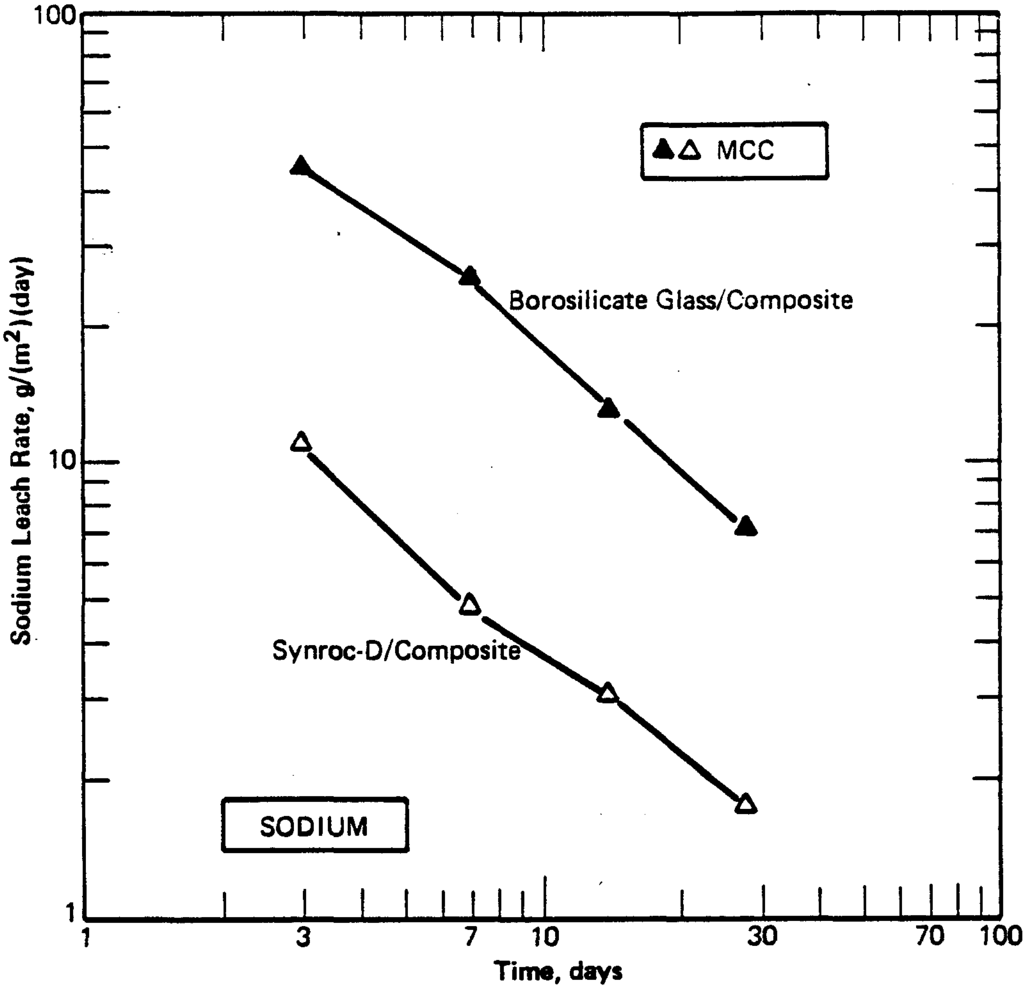

FIGURE 19. Sodium Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 28

### Comparison of Sodium Leach Rates from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Sodium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | **7.18 ±0.22** | **1.47 ±0.04** | 4.9[b] |
| | c | 8.19 ±0.15 | - | - |
| | d | - | 1.99 | - |
| | e | 7.69 | 1.73 | 4.4 |
| Silicate Water | a | 4.88 ±0.81 | - | - |
| | c | 4.77 ±1.11 | - | - |
| | d | - | 0.081 | - |
| | e | 4.83 | 0.081 | 60 |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average of inter-laboratory data.

## TABLE 29

## Sodium Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Sodium Incremental Leach Rate, g/($m^2$)(day) | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.06 | 0.19 | 2.67 | 1.15 | 7.89 | 4.19 |
| 10 | 1.51 | 0.44 | 3.39 | 1.76 | 6.10 | 3.94 |
| 17 | 2.43 | 0.38 | 3.26 | 1.72 | 5.40 | 3.28 |
| 24 | 2.65 | 0.47 | 3.61 | 1.83 | 5.39 | 2.84 |
| 28 | 2.95 | 0.50 | 3.24 | 1.41 | 4.80 | 1.55 |

---

a. Tests performed by MCC, Reference 43.
b. Flow rate of deionized water at 90°C.

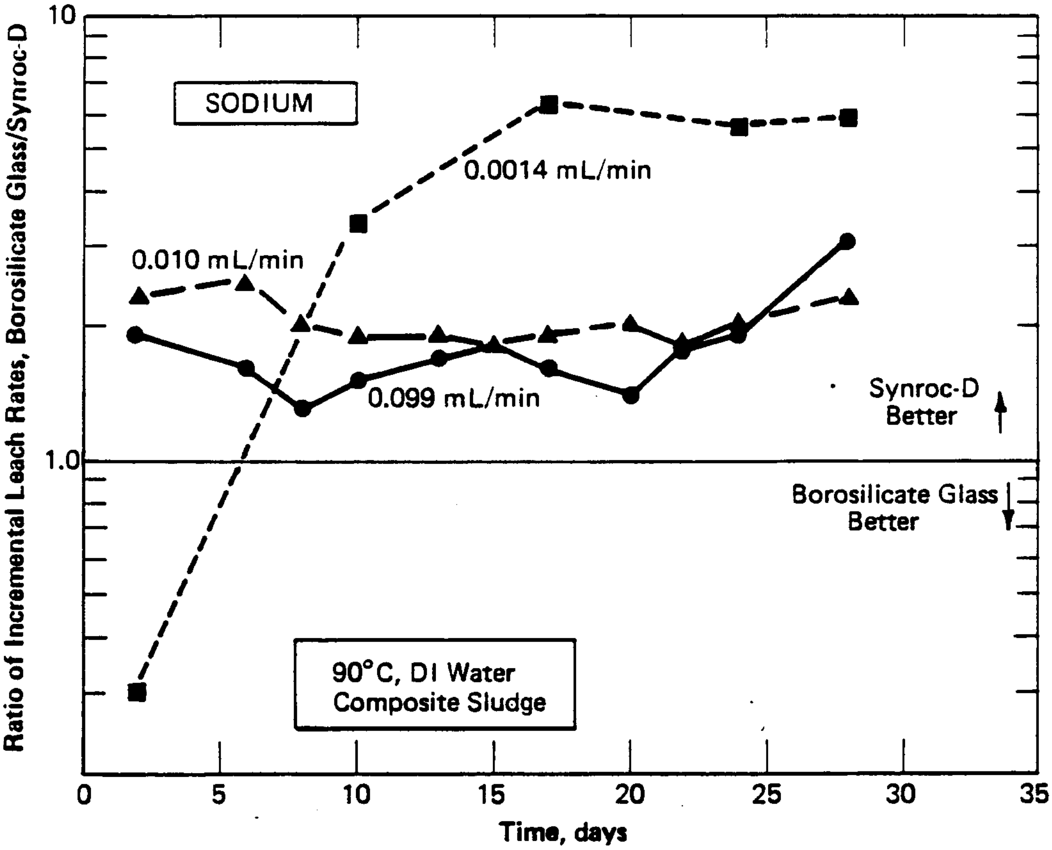

FIGURE 20. Sodium Leaching in MCC-4 Low-Flow-Rate Tests

TABLE 30

Summary of Comparisons of
Aluminum Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | Ratio of Aluminum Leach Rates[a,b] Composite | High-Al | High-Fe |
|---|---|---|---|---|
| 40°C | Deionized Water | 14 | 0.86 | 7.9 |
| 90°C | Deionized Water | 1.8 | 12 | 3.0 |
| | Silicate Water | 2.6 | 7.1 | 2.3 |
| 150°C | Deionized Water | 2.5 | - | - |
| | Silicate Water | 5.6 | - | - |
| | Brine | >1700 | - | - |

---

a. MCC-1 and MCC-2 static leach tests.
b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

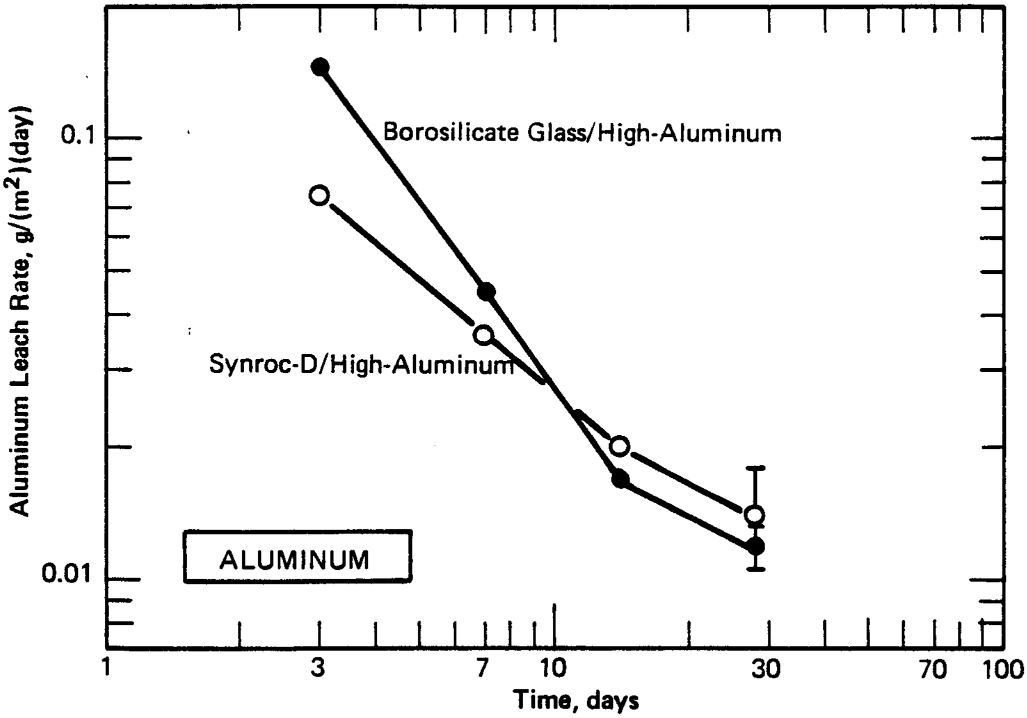

FIGURE 21. Aluminum Leach Rates with High-Aluminum Sludge in Deionized Water at 40°C

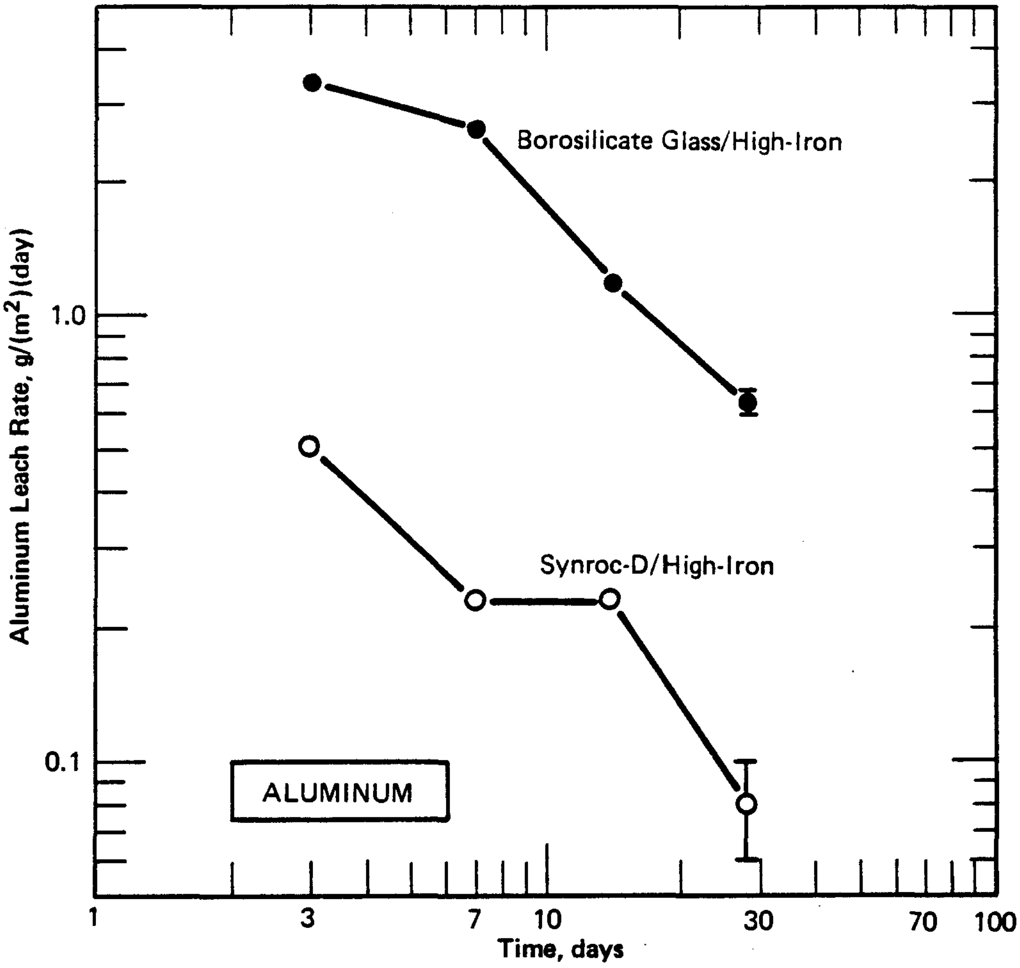

FIGURE 22. Aluminum Leach Rates with High-Iron Sludge in Deionized Water at 40°C

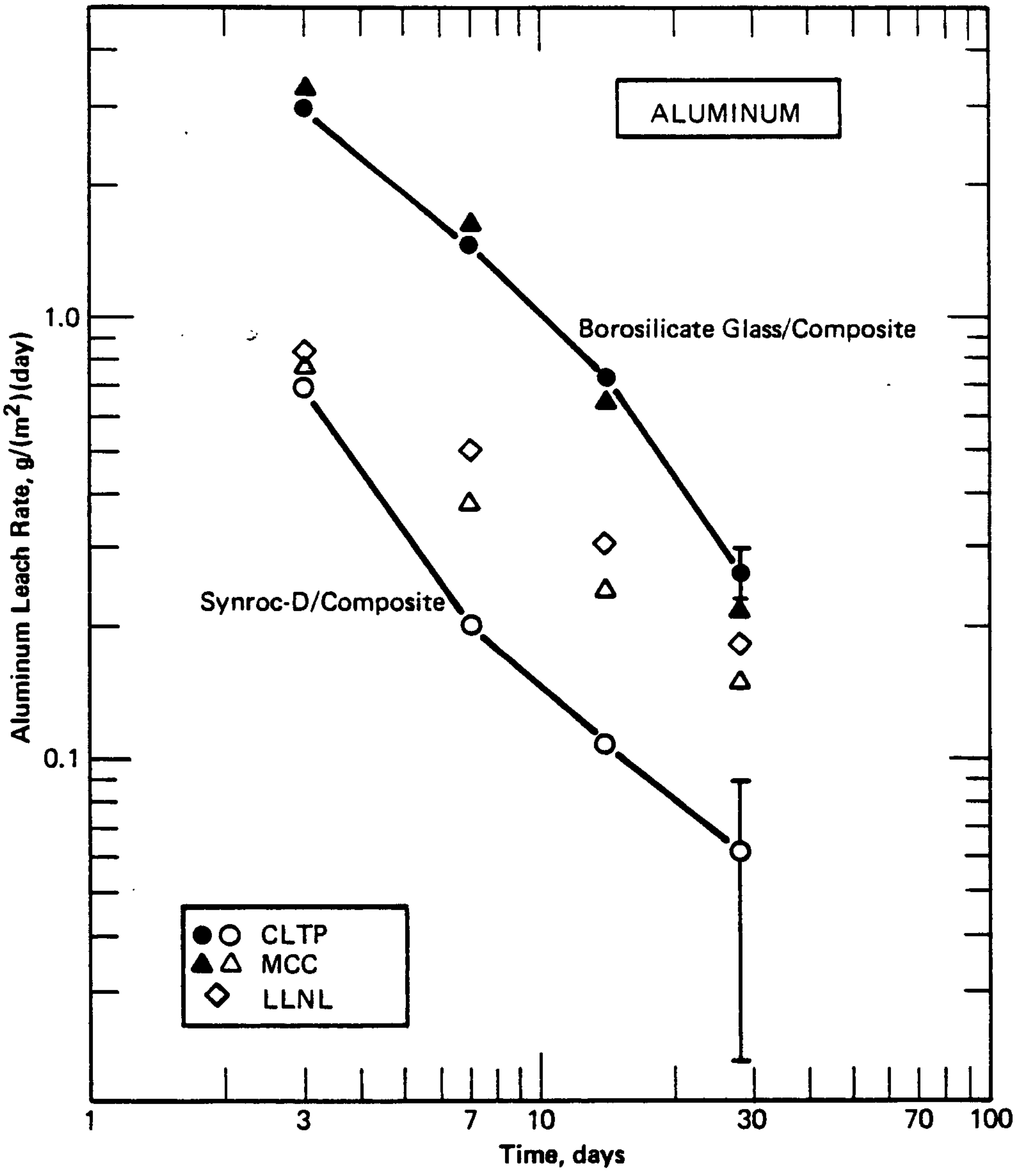

FIGURE 23. Aluminum Leach Rates with Composite Sludge in Deionized Water at 90°C

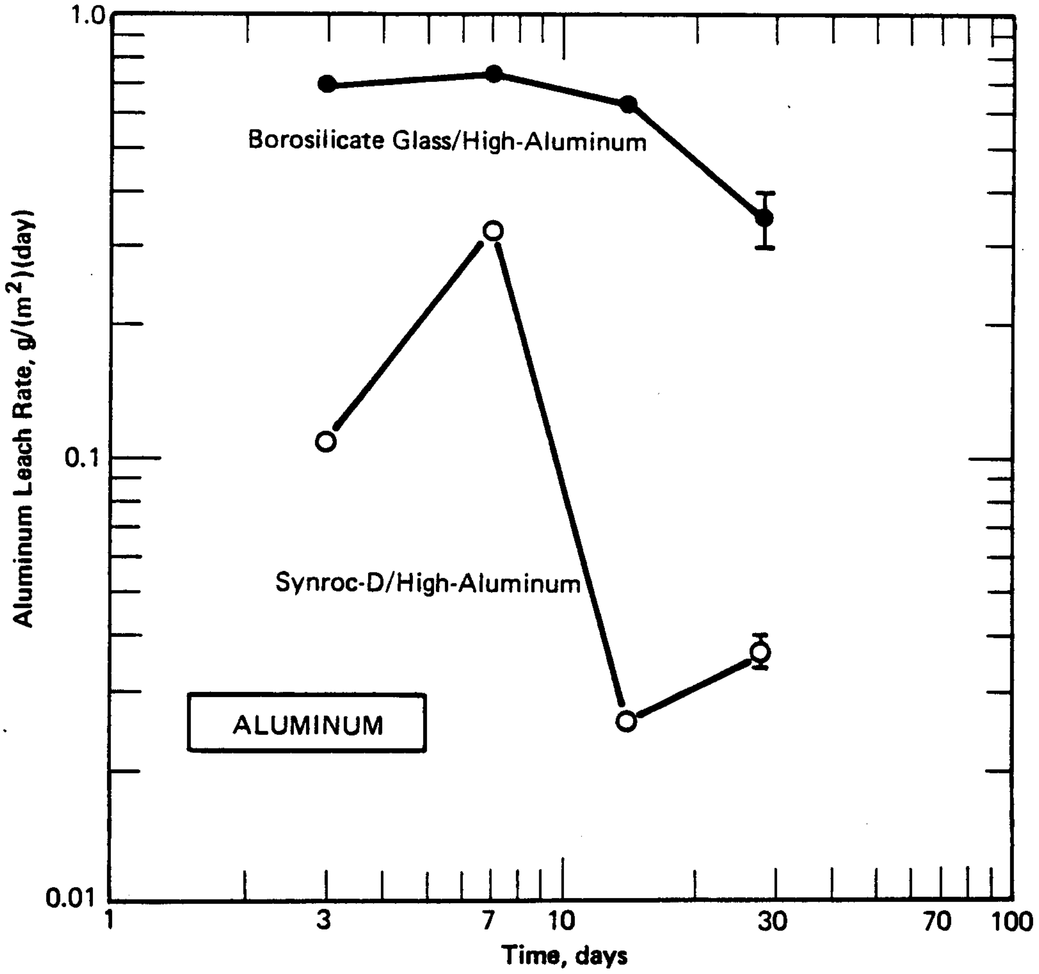

**FIGURE 24.** Aluminum Leach Rates with High-Aluminum Sludge in Deionized Water at 90°C

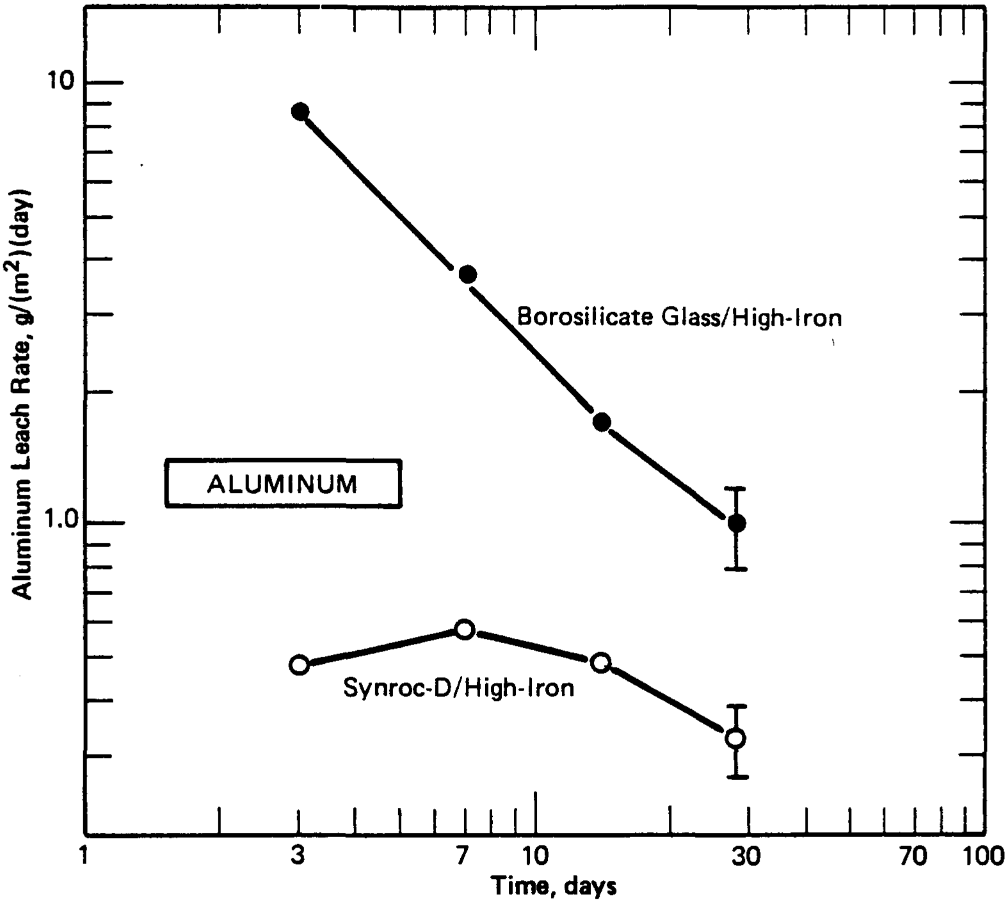

FIGURE 25. Aluminum Leach Rates with High-Iron Sludge in Deionized Water at 90°C

## TABLE 31

## Comparison of Aluminum Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Aluminum Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | Composite | a | **0.265 ±0.035** | **0.056 ±0.034** | **4.7**[b] |
| | | c | **0.22 ±0.01** | **0.15 ±0.01** | **1.5** |
| | | d | - | 0.18 | - |
| | | e | 0.24 | 0.13 | 1.8 |
| | High-Al | a | **0.346 ±0.055** | **0.037 ±0.029** | **9.4** |
| | | d | - | 0.022 | - |
| | | e | 0.346 | 0.030 | 12 |
| | High-Fe | a | **0.999 ±0.202** | **0.326 ±0.061** | **3.1** |
| | | d | - | 0.33 | - |
| | | e | 0.999 | 0.33 | 3.0 |
| Silicate Water | Composite | a | **0.216 ±0.021** | **0.110 ±0.013** | **2.0** |
| | | c | **0.18 ±0.01** | **0.054 ±0.002** | **3.3** |
| | | d | - | 0.070 | - |
| | | e | 0.20 | 0.078 | 2.6 |
| | High-Al | a | **0.213 ±0.003** | **0.038 ±0.002** | **5.6** |
| | | d | - | 0.021 | - |
| | | e | 0.213 | 0.030 | 7.1 |
| | High-Fe | a | **0.476 ±0.027** | **0.341 ±0.026** | **1.4** |
| | | d | - | 0.08 | - |
| | | e | 0.476 | 0.21 | 2.3 |

---

a. From SRL Comparative Leach Test Program.

b. **Bold** data designate an intra-laboratory comparison.

c. From tests performed by MCC, Reference 43.

d. Reference 5.

e. Average of inter-laboratory data.

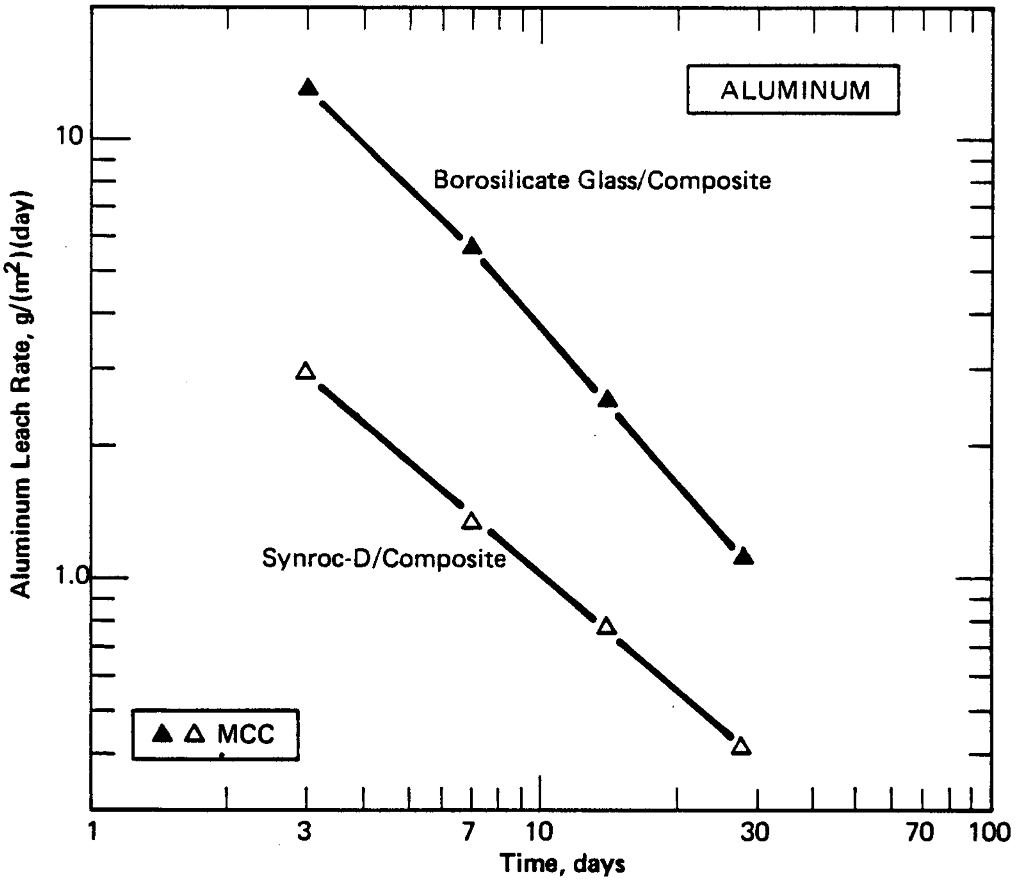

FIGURE 26. Aluminum Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 32

## Comparison of Aluminum Leach Rates from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Aluminum Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | **1.13 ±0.03** | **0.427 ±0.002** | **2.6**[b] |
| | c | - | 0.475 | - |
| | d | 1.13 | 0.451 | 2.5 |
| Silicate Water | a | 1.09 ±0.11 | - | - |
| | c | - | 0.194 | - |
| | d | 1.09 | 0.194 | 5.6 |
| Brine | a | 1.70 ±0.11 | - | - |
| | c | - | <0.001 | - |
| | d | 1.70 | <0.001 | >1700 |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 5.
d. Average of inter-laboratory data.

## TABLE 33

## Aluminum Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Aluminum Incremental Leach Rate, g/($m^2$)(day) | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.04 | 0.03 | 2.17 | 0.41 | 7.72 | 1.12 |
| 10 | 0.61 | 0.15 | 1.60 | 0.80 | 5.73 | 0.57 |
| 17 | 0.31 | 0.16 | 1.31 | 0.86 | 5.84 | 0.41 |
| 24 | 0.19 | 0.16 | 1.12 | 0.80 | 4.98 | 0.23 |
| 28 | 0.13 | 0.13 | 0.82 | 0.70 | 4.80 | - |

---

a. Tests performed by MCC, Reference 43.

b. Flow rate of deionized water at 90°C.

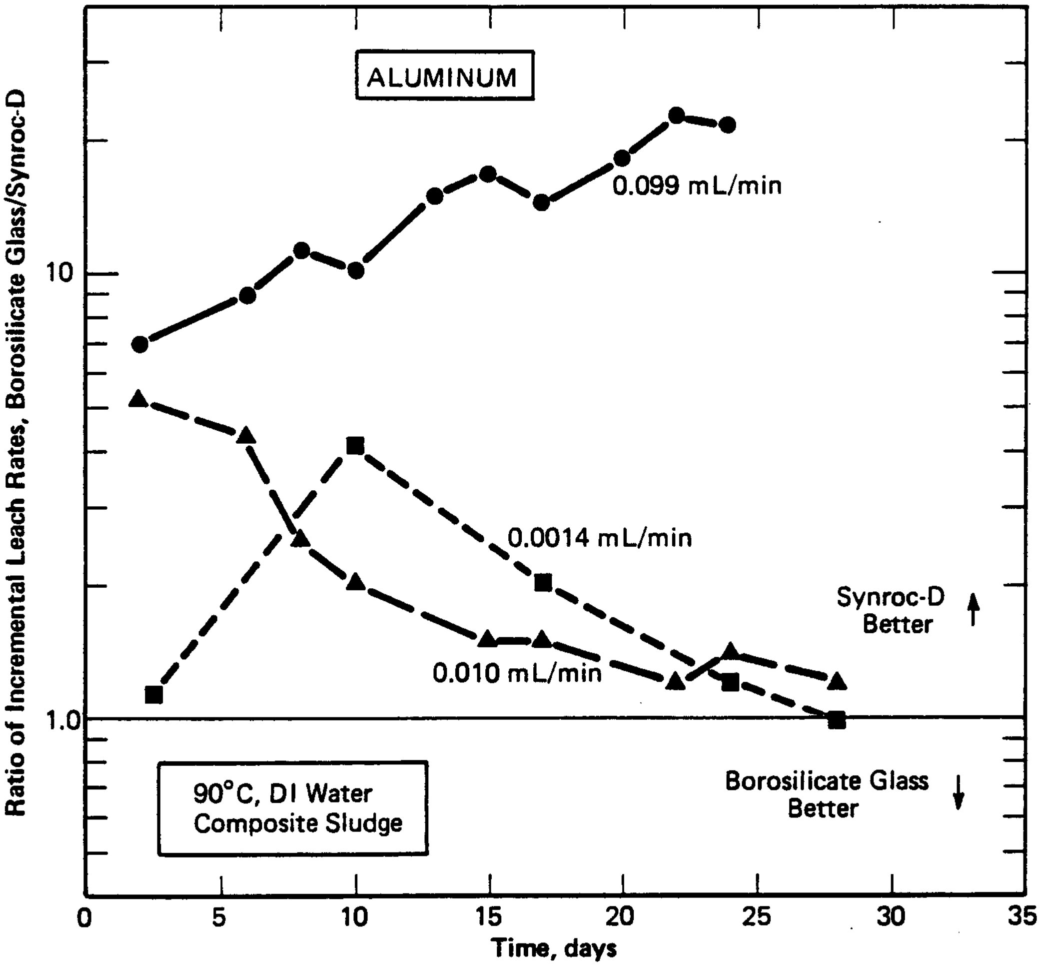

FIGURE 27. Aluminum Leaching in MCC-4 Low-Flow-Rate Tests

## TABLE 34

### Summary of Comparisons of Iron Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| | | Ratio of Iron Leach Rates[a,b] | |
|---|---|---|---|
| Temperature | Leachant | Composite | High-Al |
| 90°C | Deionized Water | - | <31 |
| | Silicate Water | >2.3 | - |
| 150°C | Deionized Water | 2.5 | - |
| | Silicate Water | 2 | - |

---

a. MCC-1 and MCC-2 static leach tests.

b. Ratio of averages of borosilicate glass to Synroc-D leach rates.

TABLE 35

Comparison of Iron Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Iron Leach Rate, g/(m$^2$)(day) | | |
|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | Composite | a | <0.001 | <0.001 | - |
| | | b | <0.00019 | <0.00028 | - |
| | | c | - | 0.00034 | - |
| | | d | <0.00019 | <0.00031 | - |
| | High-Al | a | **<0.093** | **0.0030** | <31[e] |
| | High-Fe | a | <0.041 | <0.002 | - |
| Silicate Water | Composite | a | <0.001 | <0.001 | - |
| | | b | **0.00061** | **<0.00012** | **>5.1** |
| | | c | - | 0.000429 | - |
| | | d | 0.00061 | <0.00027 | >2.3 |
| | High-Al | a | <0.034 | <0.002 | - |
| | High-Fe | a | <0.021 | <0.001 | - |
| Brine | Composite | a | <0.025 | <0.017 | - |
| | | b | - | <0.0060 | - |
| | | d | <0.025 | <0.006 | - |
| | High-Al | a | <0.025 | <0.007 | - |
| | High-Fe | a | <0.151 | <0.007 | - |

---

a. From SRL Comparative Leach Test Program.
b. From tests performed by MCC, Reference 43.
c. Reference 5.
d. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).
e. **Bold** data designate an intra-laboratory comparison.

## TABLE 36

## Comparison of Iron Leach Rates
## from 28-day MCC-2 Tests with Composite Sludge at 150°C

| | | Iron Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|
| Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | a | **0.008 ±0.001** | **0.00073 ±0.00016** | **11**[b] |
| | c | - | 0.0057 | - |
| | d | 0.008 | 0.0032 | 2.5 |
| Silicate Water | a | 0.010 ±0.001 | - | - |
| | c | - | 0.005 | - |
| | d | 0.010 | 0.005 | 2 |
| Brine | a | - | 0.147 ±0.084 | - |
| | c | - | 0.211 | - |
| | d | - | 0.179 | - |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 5.
d. Average of inter-laboratory data.

TABLE 37

Comparison of Zirconium Leach Rates from 28-day MCC-1 Tests at 90°C

| | | | Zirconium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|---|
| Leachant | Sludge Type | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| Deionized Water | Composite | a | <0.008 | <0.002 | - |
| | | b | <0.033 | - | - |
| | | c | - | <0.0004 | - |
| | | d | <0.008 | <0.0004 | - |
| | High-Al | a | <0.019 | <0.006 | - |
| | High-Fe | a | <0.025 | <0.001 | - |
| Silicate Water | Composite | a | <0.005 | <0.001 | - |
| | | b | - | 0.00060 | - |
| | | c | - | <0.0004 | - |
| | | d | <0.005 | <0.0005 | - |
| | High-Al | a | <0.058 | <0.006 | - |
| | High-Fe | a | **<0.013** | **0.0018** | **<7.2**[e] |
| Brine | Composite | a | <0.056 | <0.015 | - |
| | | b | - | <0.03 | - |
| | | c | - | <0.0079 | - |
| | | d | <0.056 | <0.0079 | - |
| | High-Al | a | <0.113 | <0.029 | - |
| | High-Fe | a | <0.069 | <0.004 | - |

---

a. From SRL Comparative Leach Test Program.
b. From tests performed by MCC, Reference 43.
c. Reference 5.
d. Average of inter-laboratory data (with appropriate treatment of data reported as detection limits).
e. **Bold** data designate an intra-laboratory comparison.

and Synroc-D, with composite sludge only, is summarized in Table 38 for 28-day MCC-1 and MCC-2 tests. In DI and silicate waters, the leach rate of Synroc-D is 2 to 4 times lower; in brine the comparisons are indeterminate. The data are shown in Figures 28 and 29, and in Table 39. Results of MCC-4 tests are given in Table 40 and Figure 30. In these tests, Synroc-D generally had the lower leach rate, but the difference declined slightly, from a factor of about 2.5 at the lowest flow to about 1.5 at the highest flow.

Calcium has no comparative data at 40°C, or with high-aluminum and high-iron sludges, or with brine. The few available comparisons are summarized in Table 41 for 28-day MCC-1 and MCC-2 tests. At 90°C, the leach rate of borosilicate glass with composite sludge is more than 30 times lower in DI water and more than 9 times lower in silicate water. At 150°C, in DI water, the leach rate of borosilicate glass is 15 times lower; the comparison in brine is indeterminate. The data are shown in Figures 31 and 32, and in Table 42. Results of MCC-4 tests are given in Table 43 and Figure 33. In these tests, the calcium leach rate of borosilicate glass changed from about 3 times lower at the intermediate flow, to about 4 times higher than that of Synroc-D at the highest flow. Overall, the leaching behavior of calcium closely resembles that of strontium.

Manganese also has no comparative data at 40°C, or with high-aluminum and high-iron sludges. The comparison of manganese leaching properties of borosilicate glass and Synroc-D, with composite sludge only, is summarized in Table 44 for 28-day MCC-1 and MCC-2 tests. In DI water, the comparisons are indeterminate, but in silicate water and brine, the leach rate of Synroc-D is 5 to more than 27 times lower. The data are shown in Figures 34 and 35, and in Table 45.

## Effects of Leaching Conditions

The comparative leaching tests described in the preceding sections were run by explicitly varying the simulated waste composition, the leachant composition, and the temperature. The effects of these diverse conditions on the leach rates of borosilicate glass and Synroc-D, as derived from the data, will be discussed. The effect of flow rate from the MCC-4 type tests also will be summarized. A number of other variables were not studied in the comparative tests. These include pH, Eh, SA/V, pressure, radiation dose, and surface condition. However, various individual studies on borosilicate glass or Synroc-D have addressed many of these effects.

## TABLE 38

### Summary of Comparisons of Silicon Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | RATIO[a] |
|---|---|---|
| 90°C | Deionized Water | 2.5 |
| | Silicate Water | 4.2 |
| | Brine | >1.3 |
| 150°C | Deionized Water | 2.0 |
| | Silicate Water | 3.2 |
| | Brine | 0.52 |

---

[a] Ratio of averages of borosilicate glass to Synroc-D leach rates, both with composite sludge, from MCC-1 and MCC-2 static leach tests.

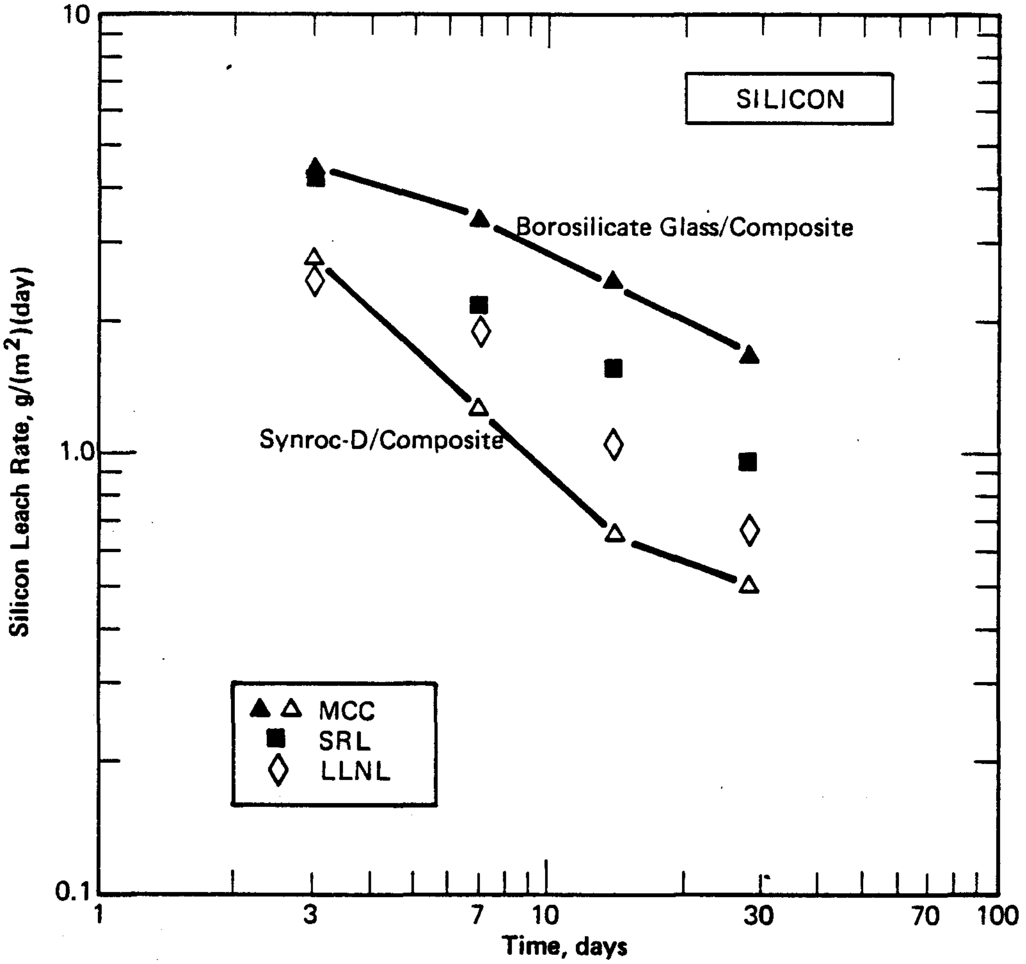

FIGURE 28. Silicon Leach Rates with Composite Sludge in Deionized Water at 90°C

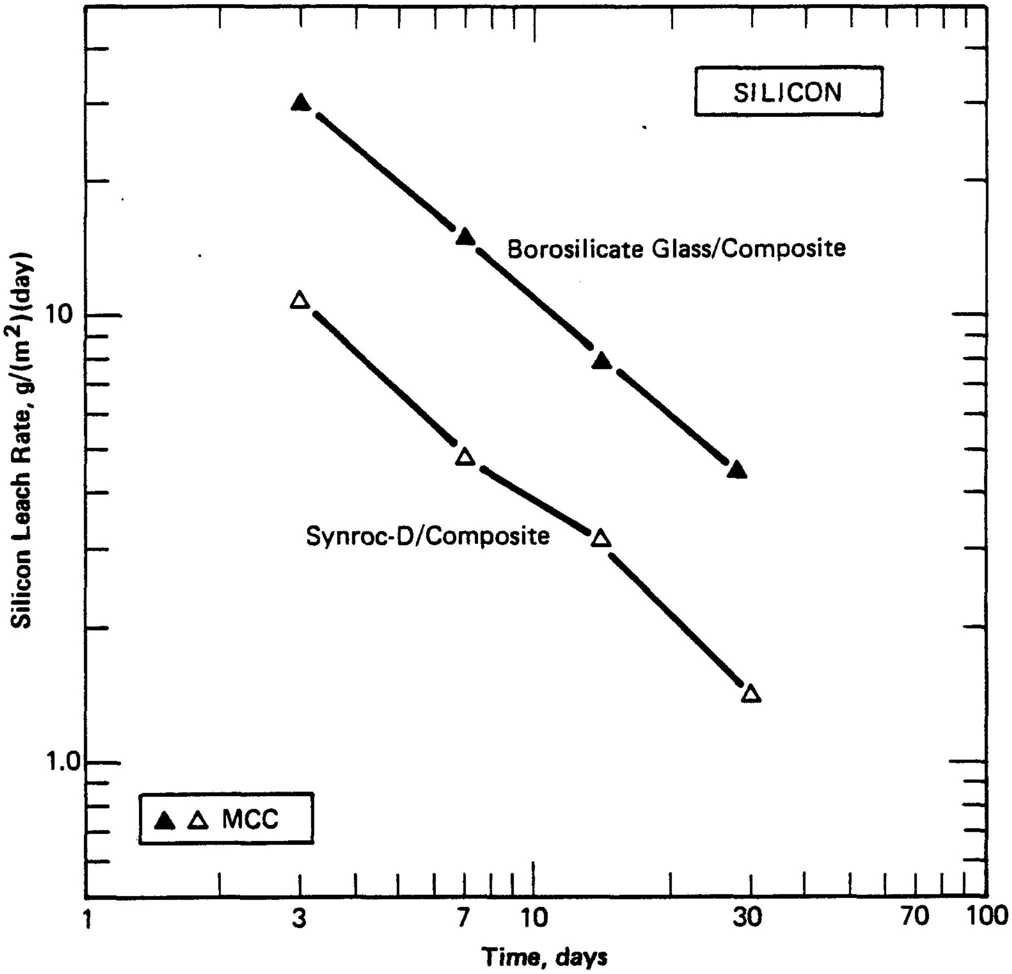

FIGURE 29. Silicon Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 39

### Comparison of Silicon Leach Rates from 28-day MCC-1 and MCC-2 Tests with Composite Sludge

| Temperature | Leachant | Ref. | Silicon Leach Rate, $g/(m^2)(day)$ Borosilicate Glass | Silicon Leach Rate, $g/(m^2)(day)$ Synroc-D Ceramic | RATIO |
|---|---|---|---|---|---|
| 90°C | Deionized Water | a | **1.66 ±0.02** | **0.50 ±0.02** | **3.3**[b] |
| | | c | 0.96 ±0.02 | - | - |
| | | d | - | 0.54 | - |
| | | e | 1.31 | 0.52 | 2.5 |
| | Silicate Water | a | **0.77 ±0.02** | **0.13 ±0.05** | 5.9 |
| | | c | 0.56 ±0.02 | - | - |
| | | d | - | 0.19 | - |
| | | e | 0.67 | 0.16 | 4.2 |
| | Brine | a | **0.083±0.009** | **<0.08** | >1.0 |
| | | c | 0.32 ±0.03 | - | - |
| | | d | - | 0.22 | - |
| | | e | 0.20 | <0.15 | >1.3 |
| 150°C | Deionized Water | a | **4.48 ±0.06** | **1.42 ±0.03** | **3.2** |
| | | c | 4.28 ±0.06 | - | - |
| | | d | - | 2.87 | - |
| | | e | 4.38 | 2.15 | 2.0 |
| | Silicate Water | a | 3.18 ±0.32 | - | - |
| | | c | 2.96 ±0.21 | - | - |
| | | d | - | 0.954 | - |
| | | e | 3.07 | 0.954 | 3.2 |
| | Brine | a | **0.65 ±0.04** | **1.26 ±0.33** | **0.52** |
| | | c | 1.41 ±0.02 | - | - |
| | | d | - | 2.68 | - |
| | | e | 1.03 | 1.97 | 0.52 |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 13.
d. Reference 5.
e. Average of inter-laboratory data.

## TABLE 40

## Silicon Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Silicon Incremental Leach Rate, g/(m$^2$)(day) | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.04 | 0.12 | 2.12 | 1.33 | 6.65 | 4.61 |
| 10 | 1.00 | 0.53 | 2.60 | 2.10 | 5.50 | 4.35 |
| 17 | 1.14 | 0.47 | 2.52 | 2.12 | 4.85 | 3.33 |
| 24 | 1.10 | 0.56 | 2.56 | 2.16 | 4.92 | 3.58 |
| 28 | 1.18 | 0.51 | 2.37 | 1.92 | 4.66 | 2.65 |

---

a. Tests performed by MCC, Reference 43.
b. Flow rate of deionized water at 90°C.

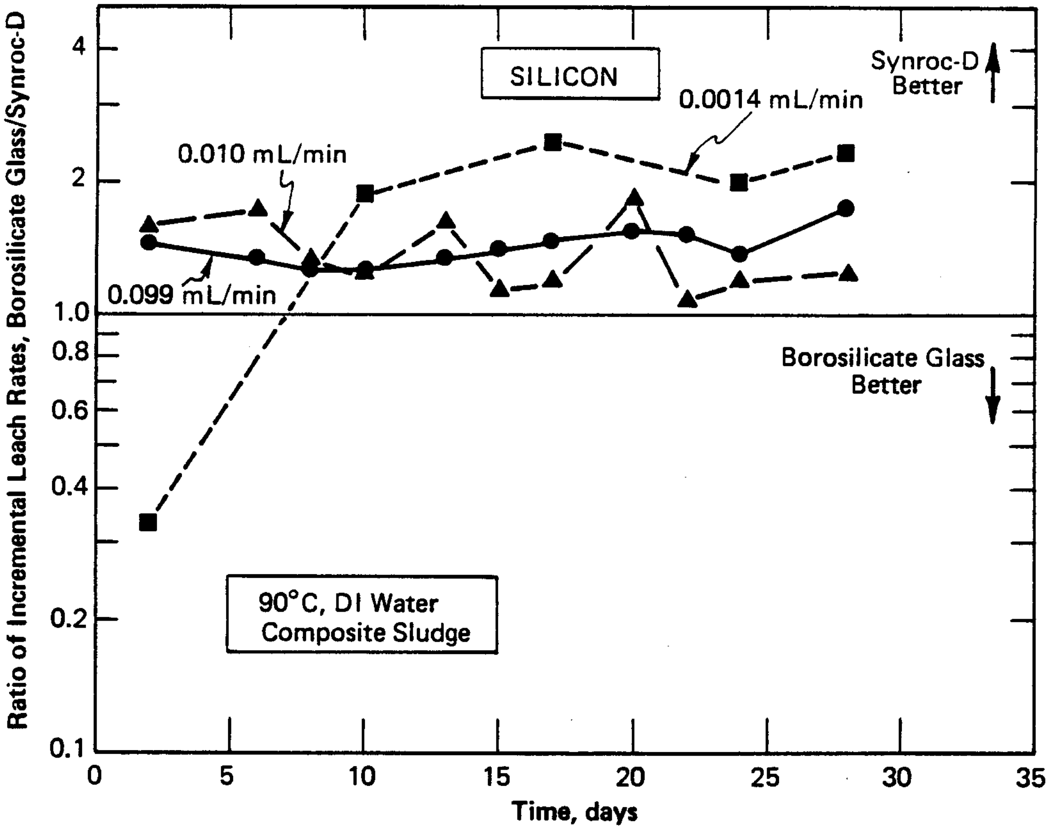

FIGURE 30. Silicon Leaching in MCC-4 Low-Flow-Rate Tests

# TABLE 41

## Summary of Comparisons of Calcium Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | RATIO[a] |
|---|---|---|
| 90°C | Deionized Water | <0.035 |
| | Silicate Water | <0.11 |
| 150°C | Deionized Water | 0.067 |
| | Silicate Water | <1.3 |

---

[a] Ratio of averages of borosilicate glass to Synroc-D leach rates, both with composite sludge, from MCC-1 and MCC-2 static leach tests.

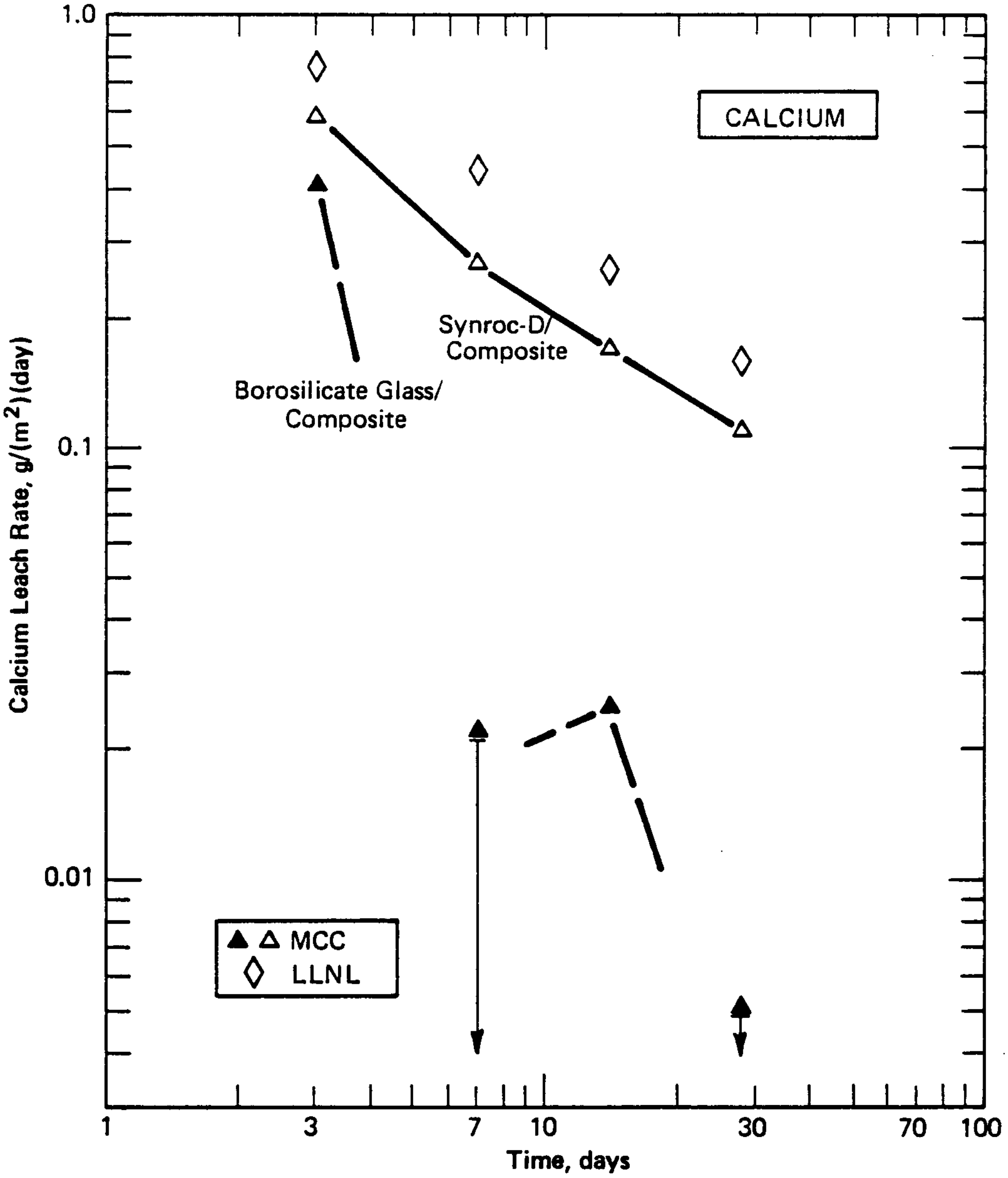

FIGURE 31. Calcium Leach Rates with Composite Sludge in Deionized Water at 90°C

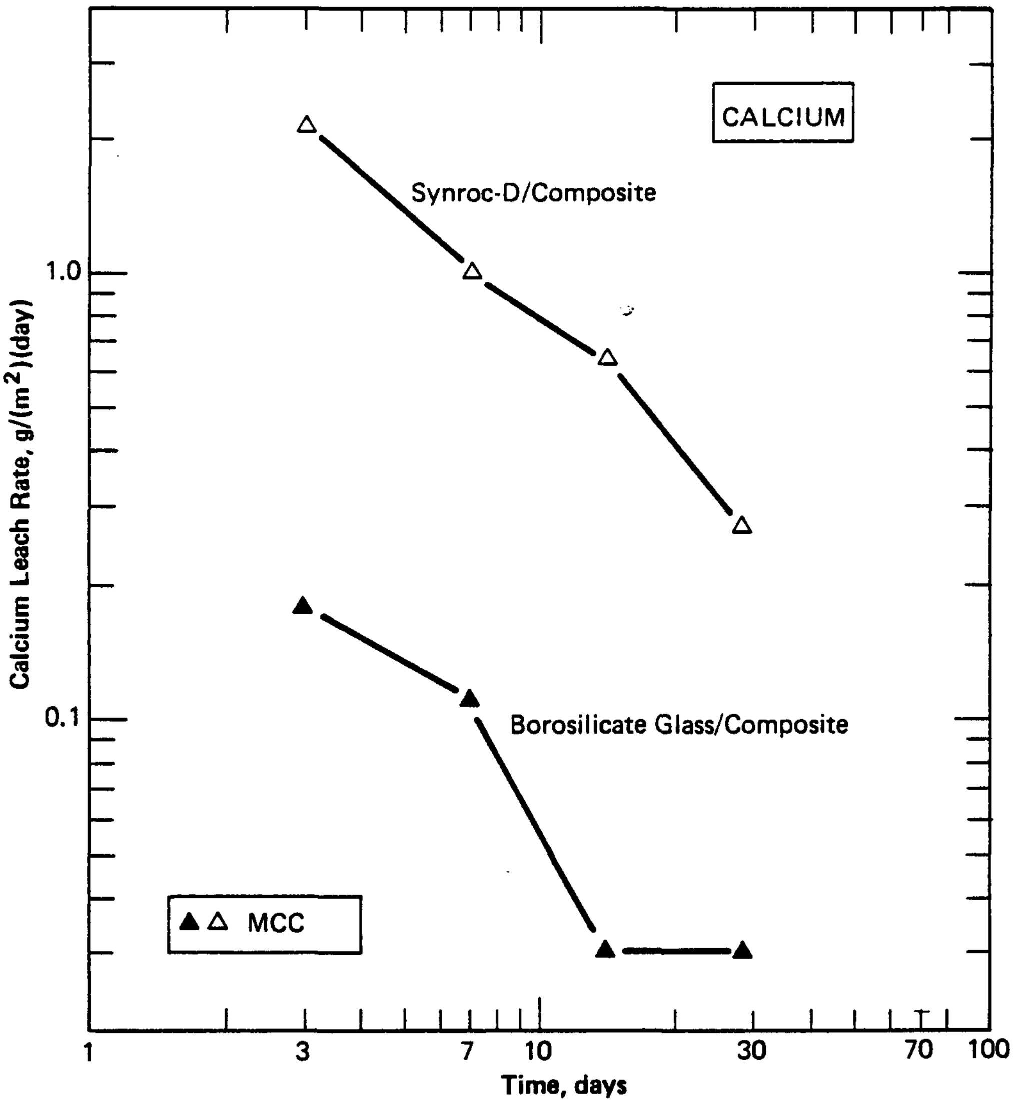

FIGURE 32. Calcium Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 42

### Comparison of Calcium Leach Rates from 28-day MCC-1 and MCC-2 Tests with Composite Sludge

| | | | Calcium Leach Rate, $g/(m^2)(day)$ | | |
|---|---|---|---|---|---|
| Temperature | Leachant | Ref. | Borosilicate Glass | Synroc-D Ceramic | RATIO |
| 90°C | Deionized Water | a | **<0.0049** | **0.11 ±0.006** | **<0.045**[b] |
| | | c | - | 0.16 | - |
| | | d | <0.0049 | 0.14 | <0.035 |
| | Silicate Water | a | **<0.005** | **0.030 ±0.0006** | **<0.17** |
| | | c | - | 0.061 | - |
| | | d | <0.005 | 0.046 | <0.11 |
| | Brine | a | - | <0.04 | - |
| 150°C | Deionized Water | a | **0.03** | **0.271 ±0.010** | **0.11** |
| | | c | - | 0.628 | - |
| | | d | 0.03 | 0.45 | 0.067 |
| | Silicate Water | a | <0.25 | - | - |
| | | c | - | 0.186 | - |
| | | d | <0.25 | 0.186 | <1.3 |
| | Brine | c | - | 0.516 | - |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 5.
d. Average of inter-laboratory data.

## TABLE 43

## Calcium Leach Rates from MCC-4 Low-Flow-Rate Tests[a]

| | Calcium Incremental Leach Rate, $g/(m^2)(day)$ | | | | | |
|---|---|---|---|---|---|---|
| | 0.0014[b] mL/min | | 0.010[b] mL/min | | 0.099[b] mL/min | |
| Time, days | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic | Borosilicate Glass | Synroc-D Ceramic |
| 2 | 0.02 | 0.03 | 0.48 | 0.26 | 3.16 | 1.01 |
| 10 | - | 0.10 | 0.18 | 0.41 | 2.91 | 0.87 |
| 17 | - | 0.08 | 0.16 | 0.41 | 3.61 | 0.73 |
| 24 | - | 0.11 | 0.14 | 0.45 | 3.21 | 0.76 |
| 28 | - | 0.10 | - | 0.37 | 2.40 | 0.50 |

---

[a] Tests performed by MCC, Reference 43.

[b] Flow rate of deionized water at 90°C.

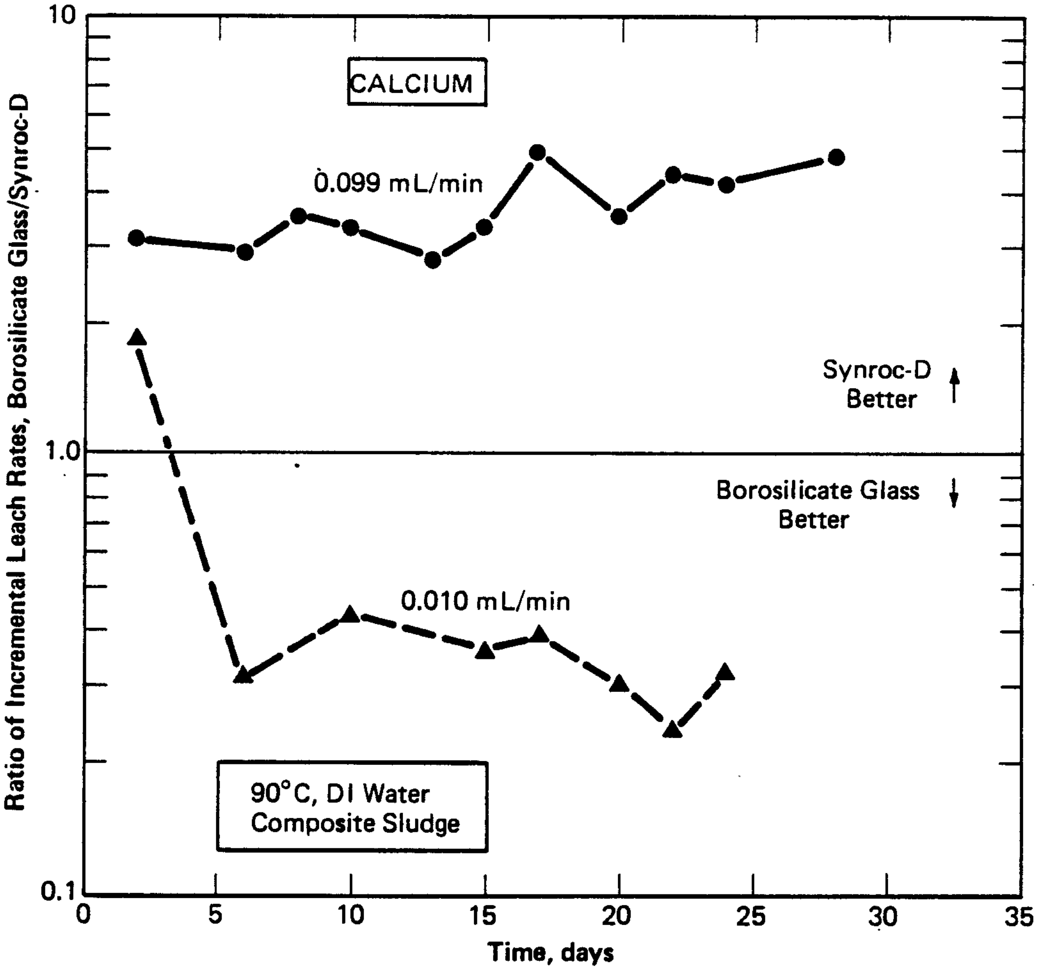

FIGURE 33. Calcium Leaching in MCC-4 Low-Flow-Rate Tests

## TABLE 44

### Summary of Comparisons of Manganese Leach Rates of Borosilicate Glass and Synroc-D Ceramic

| Temperature | Leachant | RATIO[a] |
|---|---|---|
| 90°C | Deionized Water | 0.34 |
| | Silicate Water | >13 |
| | Brine | >27 |
| 150°C | Deionized Water | 0.3 |
| | Brine | 5.1 |

---

[a] Ratio of averages of borosilicate glass to Synroc-D leach rates, both with composite sludge, from MCC-1 and MCC-2 static leach tests.

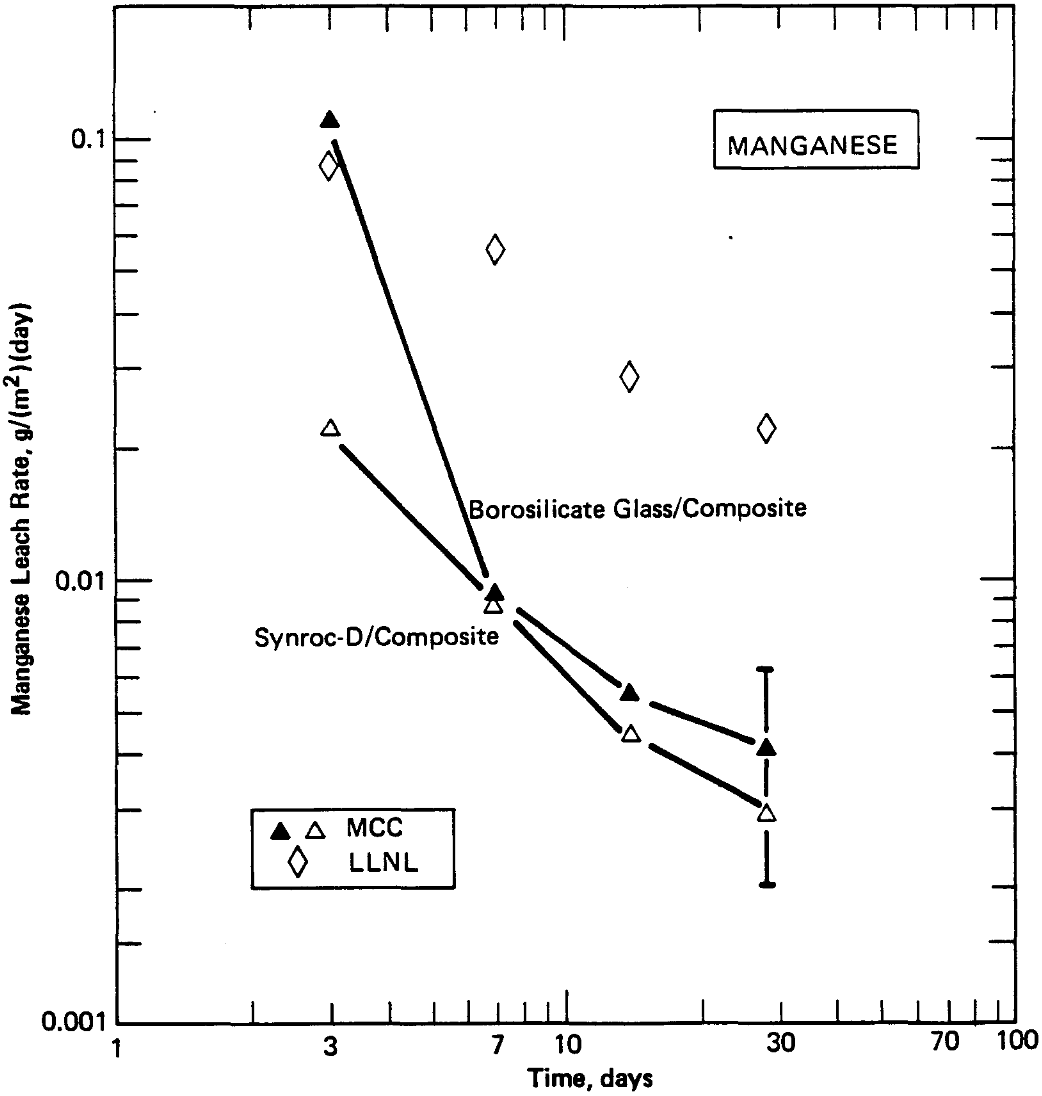

FIGURE 34. Manganese Leach Rates with Composite Sludge in Deionized Water at 90°C

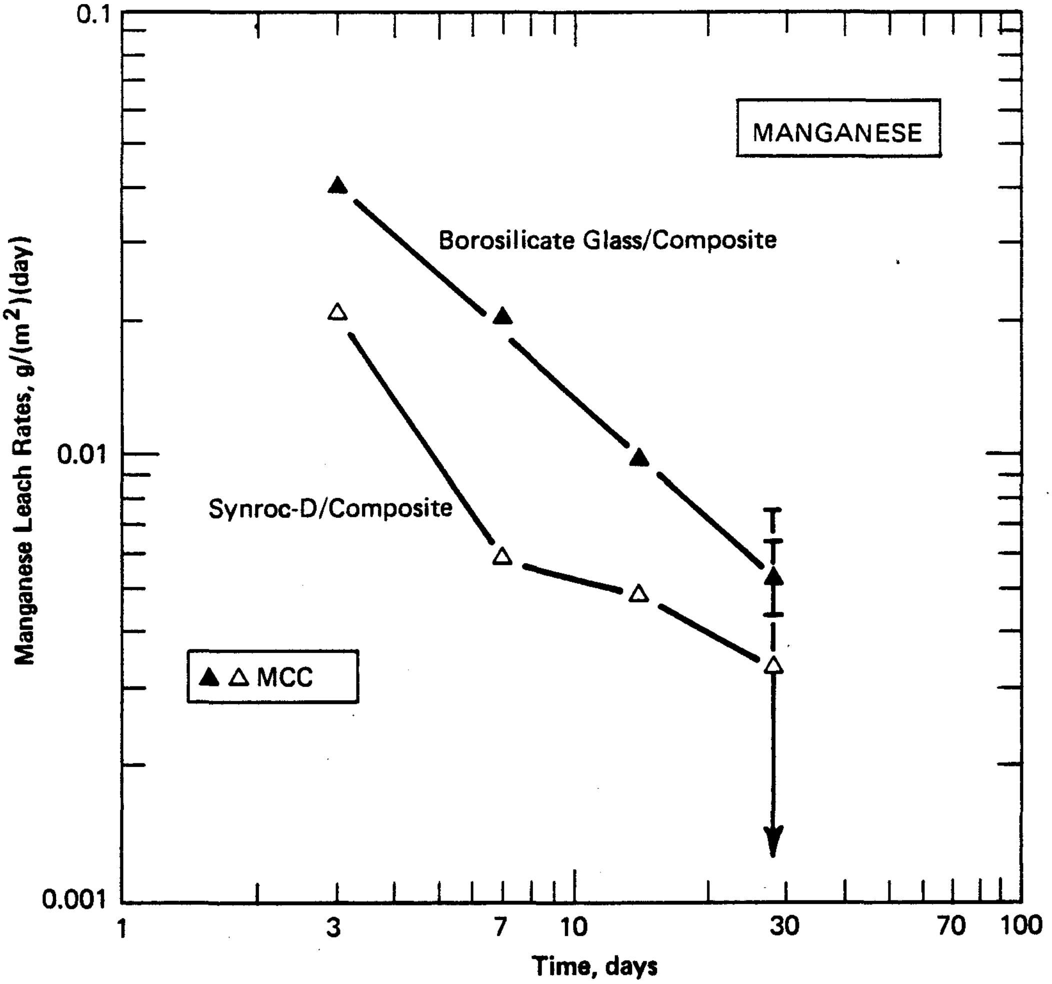

FIGURE 35. Manganese Leach Rates with Composite Sludge in Deionized Water at 150°C

## TABLE 45

### Comparison of Manganese Leach Rates from 28-day MCC-1 and MCC-2 Tests with Composite Sludge

| | | | Manganese Leach Rate, $g/(m^2)(day)$ | | | | |
|---|---|---|---|---|---|---|---|
| Temperature | Leachant | Ref. | Borosilicate Glass | | Synroc-D Ceramic | | RATIO |
| 90°C | Deionized Water | a | **0.0041** | **±0.0021** | **0.0029** | | **1.4**[b] |
| | | c | | - | 0.022 | | - |
| | | d | 0.0041 | | 0.012 | | 0.34 |
| | Silicate Water | a | **0.013** | **±0.006** | **<0.00015** | | **>87** |
| | | c | | - | 0.0020 | | - |
| | | d | 0.013 | | <0.001 | | >13 |
| | Brine | a | **0.19** | **±0.02** | **<0.0070** | | **>27** |
| 150°C | Deionized Water | a | **0.005** | **±0.001** | **0.0033** | **±0.0041** | **1.5** |
| | | c | | - | 0.034 | | - |
| | | d | 0.005 | | 0.019 | | 0.3 |
| | Silicate Water | c | | - | 0.005 | | - |
| | Brine | a | **1.49** | **±0.12** | **0.151** | **±0.038** | **9.9** |
| | | c | | - | 0.429 | | - |
| | | d | 1.49 | | 0.290 | | 5.1 |

---

a. From tests performed by MCC, Reference 43.
b. **Bold** data designate an intra-laboratory comparison.
c. Reference 5.
d. Average of inter-laboratory data.

## Waste Composition

The data show that waste composition (sludge type) generally did not have a large effect on leach rates in the comparative tests. Leach-rate differences between sludge types were typically a factor of 3 to 5, and were less in many cases. The relative behavior of borosilicate glass and Synroc-D, with respect to leach rates of waste forms containing the three simulated sludges, could be determined only for cesium and aluminum, which had opposite effects with Synroc-D.

For most combinations of element leached, waste form, temperature, and leachant, the 28-day leach rates with the different sludge types were in the following order, from best (lowest leach rates) to worst (highest leach rates):

High-Aluminum < Composite < High-Iron

In some cases, forms containing high-aluminum and composite sludges have about the same leach rates. Major exceptions to the above ordering are:

1. for cesium leaching from Synroc-D, the order is reversed;

2. for uranium leaching from borosilicate glass in silicate water, the order is reversed, but the effect is small;

3. for silicon leaching from Synroc-D, high aluminum sludge is slightly worse than the other two sludges.

Cesium leach rates showed the largest effect of sludge type, and also displayed the reversal of order between borosilicate glass and Synroc-D. With borosilicate glass, cesium leach rates with high-aluminum sludge were 3 to 9 times lower than with composite sludge, which in turn were 2 to 9 times lower than with high-iron sludge. With Synroc-D, the leach rates with high-iron sludge were lowest, 1 to 5 times less than with composite sludge, which had rates 4 to 10 times lower than with high-aluminum sludge.

Data on forms with high-aluminum and high-iron sludges were not available for all conditions. Those conditions for which the effect of sludge type could be determined are:

| | | | |
|---|---|---|---|
| ● 40°C, | Borosilicate Glass, | DI Water only: | Cs, U, Na, Al |
| | Synroc-D, | DI Water only: | Cs, Al |
| ● 90°C, | Borosilicate Glass, | all 3 leachants: | Cs |
| | | DI, Silicate Water: | U, Na, Al |
| | Synroc-D | all 3 leachants: | Cs, Al, Si |
| | | DI, Silicate Water: | Ca |
| | | DI Water only: | Sr |

### Leachant Composition

The data in preceding sections also show that leachant composition (among the three MCC-defined generic leachants) did not have a large effect in the comparative tests. Typically, the differences in leach rate between leachants were only a factor of 2 to 4. Generally, the relative effects of changes in leachant composition were the same for borosilicate glass and Synroc-D.

Data for DI water and silicate water are abundant, with somewhat less data available for brine. For most combinations of element leached, waste form, temperature, and sludge type, the 28-day leach rates with the different leachants were in the following order, from best to worst:

$$\text{(Silicate Water or Brine)} < \text{DI Water}$$

The following exceptions are noted:

1. For uranium: DI water is better (leaches less) than silicate water, with both waste forms; brine is best with borosilicate glass, but worst with Synroc-D.

2. For iron: DI water is better than silicate water, with borosilicate glass only; brine is worst (by a factor of 30), with Synroc-D.

3. For manganese: DI water is better than silicate water, which is much better than brine, with borosilicate glass; brine is worst with Synroc-D.

### Temperature

The effect of temperature on leach rates over the limited range from 40 to 150°C can be described by the Arrhenius equation,

$$L = k \exp(-E_a/RT)$$

where $E_a$ is the activation energy. From the 28-day leach rates tabulated in the preceding sections, activation energies from 3.4 to 12.1 kcal/mole were calculated. The relative behavior of borosilicate glass and Synroc-D with respect to temperature could be determined only for cesium and aluminum, for which the effects were opposite.

$E_a$ values were calculated from the slope of a line through the inter-laboratory data points plotted as log L vs 1/T(°K). The best line through the data was obtained by linear regression. Cases were considered only if data were available at all three temperatures (40, 90, and 150°C). Results are given in Table 46 for waste forms with composite sludge. An $E_a$ of 5.5 kcal/mole corresponds to a ten-fold increase in leach rate from 40 to 150°C, while 11 kcal/mole corresponds to a hundred-fold increase.

For cesium, the activation energies for borosilicate glass are larger than those for Synroc-D. However, for aluminum, the opposite trend occurs, and the activation energies for Synroc-D are larger than those of borosilicate glass.

For borosilicate glass, sodium and silicon leach rates are most sensitive to temperature, while aluminum leach rates are the least; cesium and uranium have intermediate temperature sensitivities. For Synroc-D, aluminum leach rates are most sensitive to temperature, while cesium, strontium, and calcium are the least.

Table 46 shows that the effect of leachant composition on $E_a$ is relatively small. For each waste form and element leached, DI and silicate waters give about the same activation energy. In most cases, there are insufficient data to calculate $E_a$ for brine leaching.

### Flow Rate

Data from comparative low-flow-rate leach tests performed at the MCC were outlined in the Elemental Leach Rates section. MCC-4 type tests were run at 90°C in DI water with waste forms containing composite sludge. Elements studied for both forms were cesium, strontium, uranium, sodium, aluminum, silicon, and calcium.

A variety of behavior with flow rate was observed. A few generalizations can be made. First, leach rates at the lowest flow studied (0.0014 mL/min) usually were indistinguishable from results of static tests (flow rate 0 mL/min). Second, leach rates increased monotonically with flow (but not necessarily linearly). Third, the increase in leach rate with flow was relatively small, but with some key exceptions. For most of the cases, a 70-fold increase in flow rate increased 28-day leach rates by only a factor of 2 to 5.

The following exceptions are severe enough to prevent extrapolating the observed effects of flow rate to other cases:

1. For strontium: with borosilicate glass the leach rate increased by a factor of 400, which caused borosilicate glass to lose its superiority in this property.

### TABLE 46

### Leach Rate Activation Energies,[a] kcal/mole

| | Borosilicate Glass[b] | | Synroc-D[b] | |
|---|---|---|---|---|
| | Deionized Water | Silicate Water | Deionized Water | Silicate Water |
| Cesium | 7.7 | 7.6 | 4.7 | 3.4 |
| Strontium | - | - | 5.9 | 6.4 |
| Uranium | 8.6 | 6.6 | - | - |
| Sodium | 12.1 | - | - | - |
| Aluminum | 5.3 | - | 9.0 | 10.1 |
| Silicon[c] | 10.2 | 10.1 | - | - |
| Calcium | - | - | 5.0 | 5.2 |

---

a. From 28-day MCC-1 and MCC-2 tests at 40, 90, and 150°C.

b. With composite sludge.

c. For borosilicate glass in brine, $E_a$ = 11.5 kcal/mole.

2. For uranium: with borosilicate glass the leach rate increased by a factor of 10, but with Synroc-D the increase was a factor of 1000, which greatly diminished the superiority of Synroc-D in this property.

3. For aluminum: with borosilicate glass the leach rate increased by a factor of 40, which greatly enhanced the superiority of Synroc-D in this property. Also, with Synroc-D the aluminum leach rate was greater at the intermediate flow than at the highest flow.

4. For calcium: with borosilicate glass the overall change was not measured, but from the intermediate to the highest flow, the leach rate increased by a factor of 20, which caused borosilicate glass to lose its superiority in this property.

### Other Factors

Variables such as pH, Eh, SA/V, pressure, radiation dose, and surface condition have not been studied in comparative leach tests. The general influence of such factors on waste-form leaching has been discussed.[46,47] A brief indication of the state of knowledge of these factors is given below.

The effect of pH on leaching is known for borosilicate glass.[13] Leach rates are lowest in the neutral range (pH 5 to 9), but increase by factors of 10 or more at both high and low pH. For Synroc-D, less is known about the pH dependence of leaching. Ceramic phases in general are more leachable at low pH than in the neutral range.

The effect of Eh on leaching of borosilicate glass and Synroc-D is unknown. Most leaching experiments have been done under ambient oxidizing conditions. In general, elements such as uranium and other actinides would be expected to be less leachable under reducing conditions. Groundwaters in all potential repository systems contain little dissolved oxygen,[48] and thus would present a reducing environment for leaching.

The ratio of solid surface area to leachant volume (SA/V) can affect the apparent leach rates of materials because of concentration phenomena.[49] Some measurements with variable SA/V have been made with borosilicate glass.[13,50] With Synroc-D, effects of SA/V have been studied in MCC-1 and MCC-3 type tests[5] that are not strictly comparable to the tests with borosilicate glass. However, in all cases, the leach rates decrease with increasing SA/V.

The effect of pressures up to 1500 psi on the leach rate of borosilicate glass has been studied.[50] Pressure has little effect. Similar experiments have not been done with Synroc-D.

As discussed in a later section on Radiation Stability, radiation effects may increase leach rates by disrupting the solid or by radiolysis of the leachant. Experimental evidence to date suggests that radiation effects have only minor influence on leach rates. Extensive measurements have been made with borosilicate glass.[13] Fewer data are available with Synroc-D.[28]

The condition of the surface of the solid being leached can have an effect on leach rates. Polished samples generally have lower leach rates than unpolished samples, for both borosilicate glass[13] and Synroc-D.[28] Film formation on the surface has a profound effect on leaching of borosilicate glass.[50] Very little is known about the presence or absence of protective films during leaching of Synroc-D.

## PHYSICAL PROPERTIES

The mechanical and thermal properties of borosilicate glass and Synroc-D can affect the quality of the waste form product. Once the waste form is emplaced in the repository, it must only withstand relatively mild temperatures and moderate pressures. The integrity of the form, however, is more severely threatened by the conditions it experiences before final emplacement. The waste form must be able to withstand expected and potential conditions in the processing facility, in interim storage, during shipment to the repository, and for operations within the repository itself, without significantly impairing its future performance or releasing radionuclides during these operations. Release from accidents could be caused by leaching or by dispersion of the waste.

Mechanical properties are important to a waste form's long-term performance. Whenever fractures occur, additional surface area is formed. This increased surface area could be attacked by groundwater in a repository, resulting in more waste elements being released.

A suitable waste form must also be able to withstand impacts from rare, but possible, accidents during transportation or handling. If small particles are produced in an accident, these particles could be dispersed if the waste form container is breached.

Thermal properties could affect waste form performance if they result in undesirable phase changes or lead to greater mechanical stresses than the form can withstand. Other thermally related properties associated with unwanted chemical reactions, volatilization, or decomposition of parts of the waste form must also be considered in the context of the waste form's environment.

Borosilicate glass and Synroc-D are similar in many of their mechanical and thermal properties, as shown in Tables 47 and 48, respectively.[5,13] During simulations of the impact from a hypothetical transportation accident, the forms also show similar behavior.

These physical properties are discussed below in the context of their effects on performance of the waste form.

## Mechanical Behavior

Borosilicate glass and Synroc-D both belong to the broad category of ceramic materials. Ceramics generally are noted for their high strengths, especially in compression. However, ceramics and glasses tend to be less ductile than other materials, such as metals, and more susceptible to cracking.

The structural support and integrity of the waste form is provided by the canister during all normal handling operations associated with production, interim storage, transportation to the repository, and emplacement in the repository. The strength (Table 47) and impact resistance (discussed below) of both borosilicate glass and Synroc-D should be sufficient to prevent any significant deterioration in quality of the two waste forms during these operations.

## Cracking During Production

Except possibly for accidents, the greatest stresses either waste form would experience are due to temperature changes during production. For this period, mechanical and thermal properties of the waste form are interrelated and must be considered together.

The crystalline ceramic and borosilicate glass products are formed or cast at high temperatures (about 1150°C) and subsequently cooled to much lower temperatures at which filled canisters can be handled. Thermal gradients occur because the center of a large waste form will cool more slowly than its surface. Stresses caused by these thermal gradients can be large enough to fracture the waste form. Also, the surrounding canister can impose stresses on the form if the two materials contract at different rates upon cooling. These effects can lead to two types of fracture: bulk cracks and surface cracks, respectively.

## TABLE 47

### Mechanical Properties of Borosilicate Glass and Synroc-D Ceramic[a]

| Property | Borosilicate Glass | Synroc-D[b] |
|---|---|---|
| Tensile Strength (MPa)[c] | 62.1 | 75.9[d] |
| Compressive Strength (MPa) | 550 | 280 |
| Young's Modulus[e] (GPa) | 66.9 | 139 |
| Poisson's Ratio[f] | 0.18 | 0.28 |
| Density (g/cm$^3$) | 2.75 | 4.00 |

---

a. From References 5 and 13.

b. Prepared at LLNL with 69 wt % loading of SRL composite sludge without aluminum removal.

c. 1 MPa = 145.0 psi.

d. For Synroc-C, Synroc formulation for simulated commercial power-reactor waste.

e. Young's Modulus, or the modulus of elasticity, measures the stiffness of the material.

f. Poisson's ratio is the ratio of equatorial to axial strain under an applied axial stress, multiplied by -1.

TABLE 48

Thermal Properties of Borosilicate Glass and Synroc-D Ceramic[a]

| Property | Borosilicate Glass | Synroc-D |
|---|---|---|
| Thermal Conductivity (W/m•K) | 0.95 (100°C) | 1.85 (20°C)<br>1.91 (200°C) |
| Heat Capacity (J/g•K) | 0.83 (25°C) | 0.74 (20°C)[b] |
| Thermal Diffusivity[c] ($m^2/s$) | $3.8 \times 10^{-7}$ | $6.5 \times 10^{-7}$ |
| Linear Thermal Expansion Coefficient ($°C^{-1}$) | $10.9 \times 10^{-6}$ | $11 \times 10^{-6}$ [d] |
| Softening Point (°C) | 502 | -- |
| Solidus Temperature (°C) | -- | 1270 |

---

a. From References 5 and 13.
b. For Synroc-B, "basic" Synroc formulation.
c. Calculated from other properties.
d. For 22-950°C.

The thermal gradients are important only because of the large size of the waste forms that would be produced in the DWPF. In smaller laboratory-scale specimens, few cracks or fractures are observed. Most of the data on cracking of borosilicate glass were obtained from full-size forms, 0.61 m in diameter. While Synroc-D has not been produced with full-scale equipment, its performance can be estimated by comparing the properties of the ceramic to those of glass.

Both types of cracking, bulk and surface, have been observed in full-size borosilicate glass castings.[20] Cracking in hot-isostatically-pressed Synroc-D forms also is expected, but might not be as extensive.

### Bulk Fracture

Radial and axial cracking due to thermal shock can occur for both borosilicate glass and Synroc-D. The cracking is observed[20] in borosilicate glass as it cools quickly from 500 to 450°C. The cracks extend radially from the center of the glass cylinder to the surface, and are expected to increase the total glass surface area by 4X or more during normal cooling. At sufficiently slow cooling rates, bulk fracture can be avoided. However, this critical cooling rate may be as low as 2°C/hr for full-size canisters.

Fast cooling also could cause fracturing in Synroc-D monoliths. Although the ceramic has a higher thermal conductivity than borosilicate glass (Table 48), consideration of its greater stiffness (measured by Young's Modulus, Table 47) would predict a critical cooling rate about 28% lower than for glass. However, the micron-size grains of the Synroc-D microstructure might impede crack formation and make the form more resistant to thermal shock, although this effect might be offset by the presence of the intergranular glassy phase. Commercial heat-resistant glasses and glass-ceramics contain small solid inclusions, which can interfere with the propagation of cracks.

Residual stresses have been observed in Synroc-D.[5] Hot-pressed samples, 0.15 m in diameter by 0.025 m high, were annealed at 950°C, cooled to 600°C at 50°C/min, then at 15°C/min down to 300°C. These samples showed residual stresses. The stresses were not observed in Synroc-B material (without waste), which does not contain nepheline or glassy phases. Therefore, internal strains probably existed in the amorphous material in Synroc-D. The thermal gradients expected from such a cooling schedule are equivalent to those of a 0.56 m diameter monolith, cooling at less than 5°C/hr.

Another phenomenon occurs during the cooling of borosilicate glass, which may make it more susceptible to bulk fracturing than the crystalline ceramic. The glass is molten at higher temperatures than about 500°C, but becomes rigid as the "glass transition temperature" is reached. The hotter, molten core of the glass cools and shrinks after the surface has stiffened; this places the glass core in tension. Radial cracking, shrinkage voids, and pores can develop when the core contracts as it cools.[20]

### Surface Cracking

Another type of fracture has occurred in large glass forms, due to physical interaction with the contracting canister during cooling. Fine circumferential cracks form near the surface when the rigid glass shears,[20] at about 350°C. Simple, effective measures would probably be used in DWPF forms preparation to reduce or eliminate this cracking.

The reference canister material for borosilicate glass production is type 304L stainless steel, which has a 50% larger thermal expansion coefficient than does glass. The metal thus shrinks faster upon cooling, compressing the glass. Glass bonds to the steel, and the canister can "drag" the glass surface along the canister axis because the glass is cooler at the bottom than near the top and, therefore, contracts less upon cooling. Shearing due to this thermal expansion mismatch causes cracking.

The fine cracking is of concern because it occurs at the surface, where leaching waters would first be encountered. If the crack surfaces are not widely separated, however, mass transport of leachant and dissolved waste elements would be slow in the crack, and the internal surface would not yield a large increase in waste form dissolution. If the canister is breached but maintains its structural integrity, the cracks would probably remain virtually closed.

Surface fracture can be significantly reduced or eliminated by using canister materials that match the thermal expansion of glass, such as carbon steel, other types of stainless steel, or possibly a ceramic liner. Canister liners could be chosen to match the properties of glass. Lubricants such as graphite, which can prevent the glass from bonding to the metal, have also proven effective.[20] One of these methods would probably be used in a borosilicate glass-based DWPF.

Synroc-D should not experience similar surface cracking. Carbon steel was chosen as the container for hot isostatic pressing,[11] partly due to the experiences with full-scale glass canisters. Carbon steel and Synroc-D have similar thermal expansion properties. Also, the temperature would be the same throughout the waste form during consolidation. The initial temperature gradients and the axial stresses caused by the filling of a glass canister would not occur.

### Impact Resistance

Data from impact tests indicate how well the waste forms would perform under the worst conditions of handling, transportation, and storage, including possible accidents. During an accident, the waste form could shatter into smaller pieces, yielding small particles (fines) which could be dispersed if the container were breached. The usual measure of impact behavior is the fraction of the particles that are small enough to be dispersed in the air and inhaled. This "respirable" size is commonly defined as less than 10 micrometers in diameter.

Samples of borosilicate glass and Synroc-D show almost identical behavior in impact tests. The results[51] of impact tests performed by Argonne National Laboratory (ANL) are summarized in Table 49. These results for small-scale forms do not directly predict the behavior of large monoliths, but are valid for comparing the properties of the different materials.

The ANL test method was similar to the proposed standard impact test[44] for waste forms, MCC-10. The procedure was developed for use on brittle waste forms, and simulates a single impact of 10 J/cm$^3$ energy density. Two samples of SRL borosilicate glass yielded 0.14 and 0.18 wt % respirable fines, while Synroc-D generated 0.16 wt % fines. Another borosilicate glass, PNL 76-68 for simulated commercial high-level waste, exhibited identical behavior, as did several other types of Synroc ("Synroc-B" and "Synroc-C") formed with different production techniques.

Tests at a much higher energy density, 140 J/cm$^3$, were also performed with Synroc-B, Synroc-C, and several types of borosilicate glass.[51,52] Again, the results for Synroc and borosilicate glass were essentially the same.

### Thermal Effects

Synroc-D is formed as a crystalline solid at about 1150°C. No degradation of its properties or changes in its phase compositions would be expected, even after long periods at elevated temperatures. Borosilicate glass could crystallize ("devitrify") under extreme conditions. However, with normal processing and handling, and for probable abnormal conditions, devitrification should not be a problem.

### TABLE 49

### Results of MCC-10 Type Impact Tests[a]

| Waste Form | Wt % Respirable Fines (<10 μm diameter) |
|---|---|
| Borosilicate Glass | |
| SRL-131 | 0.14 ±0.02[b] |
| SRL-131 | 0.18 ±0.05 |
| PNL 76-68[c] | 0.17 ±0.04 |
| Crystalline Ceramic | |
| Synroc-D (LLNL) | 0.16 ±0.02 |
| Synroc-B (LLNL)[d] | 0.15 ±0.02 |
| Synroc-C (ANL)[e] | 0.15 ±0.03 |
| Synroc-C (ANL) | 0.13 ±0.03 |

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a. Single impact of 10 J/cm$^3$ energy density; from Reference 51.
b. Standard deviation.
c. Reference glass for commercial power-reactor wastes.
d. Basic Synroc formulation; contains no simulated waste.
e. Synroc formulation for simulated commercial wastes.

## Devitrification of Glass

In early tests with full-scale canisters, small crystallites of spinel ($NiFe_2O_4$) or acmite ($NaFeSi_2O_6$) were formed and grew, especially near the bottom of canisters. These crystallites could nucleate small cracks or increase the leachability of the waste form.[13,53]

Devitrification occurred with imperfectly-mixed feed, or when the glass was held above 500°C for long periods. However, these tests were performed using older melting concepts: in-can melting, where glass frit and calcined waste were melted together in the canister itself; and calcine-fed melting, where calcine and frit were combined in a continuous melter, and molten material cast into the canister.

In the current reference process, liquid waste and glass frit are slurried into a continuous melter. For these well-mixed feeds and convective cooling of full-scale canisters, no appreciable devitrification occurs.[13]

An extensive laboratory study[13] assessed the likelihood and effect of devitrification for SRP glasses. The study concluded that extensive devitrification is unlikely during normal cooling of waste-glass canisters after manufacture or during storage. Devitrification could occur during an extended accidental fire. Long annealing treatments in the production facility, which could eliminate small cracks, could also promote crystal growth. These tests also showed that, even if the glass form was extensively devitrified, its leach rates rarely increased by more than 10X. Therefore, devitrification should not greatly affect the durability of an average glass waste form.

After emplacement of the glass in a repository, no crystal growth should occur. Even at 200°C, calculations show that no significant devitrification would occur during billions of years.[54]

## Other Thermal Effects

Volatility of borosilicate glass was measured at 900°C. Only 19 mg/hr of volatiles were evolved.[13] Therefore, unlikely high-temperature excursions, as might occur in a transportation fire, would not impact product safety. No similar tests have been performed on Synroc-D, but volatility should be no greater than for glass.

Expansion of either waste form during a temperature excursion would be too small to affect the integrity of the container. After a long-term temperature excursion, cooling stresses could arise in the waste forms, as discussed above.

## RADIATION STABILITY

Another important consideration in selecting a solid form for immobilizing high-level waste is the form's stability to the effects of radiation generated in the decay of radioactive elements in the waste over long isolation periods ($10^3$ to $10^6$ years). Radiation could produce changes in physical properties and leachability, and thus affect the performance of the waste form in the repository. Characterization of these effects is relatively well advanced for the borosilicate glass form, but is at a relatively early stage for ceramic forms, including Synroc.

The general conclusion from studies of radiation effects on borosilicate glass is that the form's performance in a repository should not be significantly diminished by self-irradiation for periods of $10^6$ years or longer. Preliminary indications for Synroc-D are inconclusive, but suggest that there should be no major deterioration in its ability to retain waste elements.

The mechanisms for radiation damage and the measured and/or projected effects for SRP high-level waste are discussed below for borosilicate glass and Synroc-D waste forms.

### Sources of Radiation Effects

The major sources of radiation damage in high-level waste forms are alpha decay of actinide elements (uranium, neptunium, plutonium, and americium) and beta decay of the fission products (primarily $^{137}$Cs and $^{90}$Sr), including the accompanying gamma radiation. Maximum radiation doses to SRP high-level waste glass during $10^6$ years of storage are estimated to be $4 \times 10^{10}$ rads of beta radiation, $7 \times 10^9$ rads of gamma radiation, and $3 \times 10^{24}$ particles/$m^3$ from alpha and alpha-recoil radiation.[55] For the Synroc-D form with its higher concentration of radionuclides, the comparable doses would be about a factor of three greater than those for the glass form.[26]

Four principal mechanisms of interaction between the internally generated radiation and the waste form material could affect the form's long-term performance in a repository.[47,56,57]. These are:

1. Displacement of atoms from their lattice sites through collisions with alpha particles and by recoil from alpha decay.

2. Accumulation of helium atoms from alpha particles produced during decay of actinides.

3. Chemical transmutations, primarily from the beta decay of $^{137}Cs$ to $^{137}Ba$, and $^{90}Sr$ to $^{90}Zr$ (via $^{90}Y$).

4. Ionization in the waste form and leachant, produced by interaction of beta and alpha particles and gamma rays with electrons.

The combination of these mechanisms could produce, to varying degrees depending on the nature of the material, structural changes (such as volume changes, metamictization in crystalline materials, and microcracking), changes in leachability and mechanical properties, and an accumulation of stored energy.[57,58] Metamictization is the term used to describe the radiation-induced change of an ordered crystalline phase to an amorphous phase.

**Sources of Data**

It is generally accepted that displacement damage produced by alpha decay is the primary cause of radiation effects expected in waste forms.[58] Thus, most waste-form irradiation experiments have emphasized alpha-decay effects. The generally accepted method for evaluating alpha-decay effects is by doping the waste form with the short-lived actinides $^{244}Cm$ or $^{238}Pu$, to accelerate the accumulation of damage by self-irradiation.[36,59]

Most of the data from actinide doping experiments, as well as from other types of irradiation experiments, are for glass waste forms, primarily borosilicate glass.[47] External irradiations of glass forms have been performed using beta/gamma sources to evaluate ionization effects. Irradiations with charged particles and neutrons have been employed to simulate alpha-displacement effects. As yet, no definitive experiment has been completed to determine the effects of transmutation. However, the concentration of transmuted elements in the SRP waste forms will be so small as to make a strong influence of transmutation on the overall waste-form properties highly unlikely.

Effects of radiation on borosilicate glass forms with SRP waste have been studied by actinide doping, external gamma irradiation, and charged particle irradiation.[55,60] No comparable experiments have been performed for Synroc-D. At present, the irradiation behavior of Synroc-D can only be inferred from studies of radiation damage in natural mineral analogs[29,61] and from irradiation experiments on zirconolite and perovskite.[5,28]

## Structural Effects

Potential structural effects of interest include volume increases (swelling) and cracking in both forms, and metamictization in the ceramic form. Swelling and associated cracking in the waste form could lead to an increase in exposed surface area for leaching. (Breaching of the canister from waste form swelling should not be a problem for periods well beyond the expected canister lifetime of 100-1000 years).

Structural effects in SRP borosilicate glass induced by alpha decay have been observed to be very small. Tests[55,60] with borosilicate glass samples doped with $^{244}$Cm and $^{238}$Pu indicate that internal alpha irradiation to a dose corresponding to approximately $10^6$ years of storage causes the glass to expand by only approximately 1%. Volume expansion of glass as a function of alpha exposure is shown in Figure 36. Some microcracking in the glass samples was observed for exposures $>5 \times 10^{23}$ alphas/m$^3$ of glass; however, the microcracks appeared to have no detectable effect on leach rates.[60] No effects of helium accumulation in Cm- and Pu-doped samples were observed. Irradiation of borosilicate glass samples with $^{60}$Co gamma radiation to $8.5 \times 10^{10}$ rad (which represents more than $10^6$ years of accumulated beta-gamma dose) resulted in essentially no volume change.[55]

An understanding of similar structural effects in the Synroc-D waste form is hampered by the unavailability of direct data for multiphase Synroc forms. Instead, the radiation effects must be inferred primarily from studies of natural mineral analogs and limited laboratory tests on single phases. Alpha-induced displacement effects in Synroc would likely occur in the zirconolite and perovskite phases, which would contain the actinides. Data on swelling and metamictization in naturally occuring zirconolite and perovskite minerals containing uranium and thorium, and in neutron-irradiated samples of these mineral phases, have been compiled and analyzed by Van Konynenberg and Guinan.[28] From the data compiled, zirconolite and perovskite would be expected to become x-ray metamict and to swell about 2-3% for an alpha exposure equivalent to $10^6$ years storage of a Synroc-D form with SRP waste.[5] Differential expansion of the phases within Synroc would probably cause microcracking and possibly some reduction in strength; however, the magnitude of these effects can not be predicted from existing data.

## Effects on Leaching

Radiation can affect the leaching behavior of a waste form by increasing the exposed surface area through cracking, as discussed above, and by increasing the form's inherent leachability. (Radiolysis effects on the leachant would be negligible after

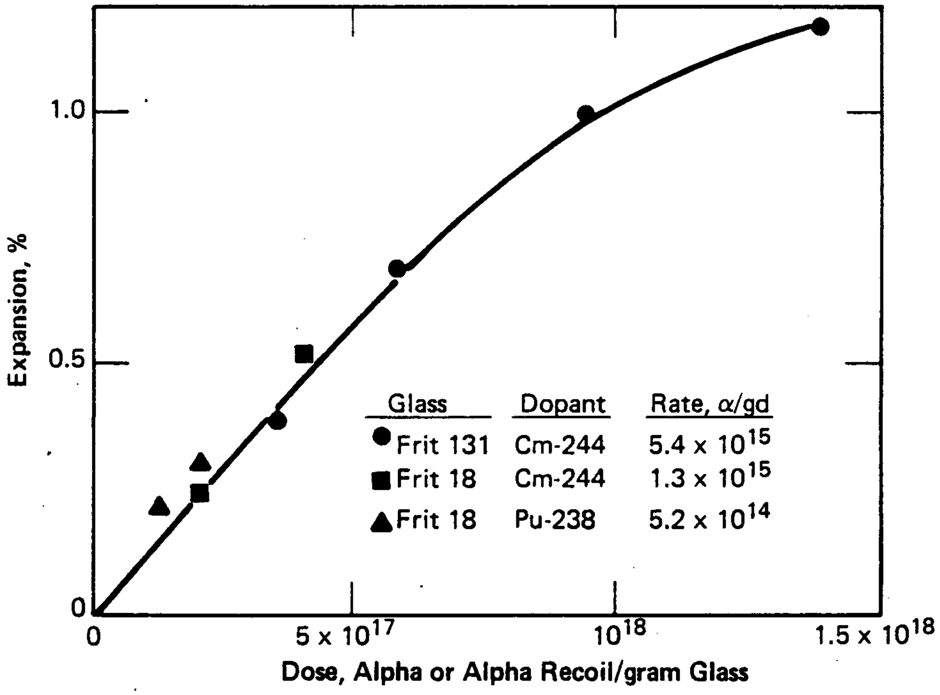

FIGURE 36. Expansion of SRP Borosilicate Glass Due to Alpha and Alpha-Recoil Irradiation (from Reference 55)

1000 years, and thus would not be important in the long term performance of the waste form in a repository.)

Effects of radiation on leachability of borosilicate glass are very small.[8,55,60] Leachability of a $^{244}$Cm-doped borosilicate glass has been measured in deionized water at 23°C by modified IAEA tests.[55] A similar series of tests was performed for a $^{239}$Pu-doped glass with an alpha dose $2.3 \times 10^4$ times lower than the Cm-doped samples. Leach rates for the two sample types ranged from about 0.1 g/(m$^2$)(day) initially to about $10^{-3}$ g/(m$^2$)(day) at 200 days. Very little difference in leach rates was observed between the "damaged" and "undamaged" samples, as shown in Figure 37. The alpha dose in the $^{244}$Cm-doped glass after 150 days corresponded to about $10^6$ years exposure in an actual SRP glass waste form. Even for alpha exposures well beyond the $10^6$ year level, the leach rate of the Cm-doped glass was still decreasing with time.

Current knowledge about the effects of radiation on Synroc leachability has been primarily derived from natural mineral studies. Leach tests with natural minerals containing uranium indicate that both perovskite and zirconolite have low leach rates after extensive alpha damage, based on uranium at 200°C in deionized water.[29] Leach rates varied from about $4 \times 10^{-4}$ g/(m$^2$)(day) to $2 \times 10^{-3}$ g/(m$^2$)(day) for estimated alpha doses of approximately $4 \times 10^{24}$ alphas/m$^3$ and $3 \times 10^{26}$ alphas/m$^3$, respectively. These rates were comparable to uranium leach rates measured in Synroc forms made with simulated commercial waste. Uranium and calcium leach rates for natural perovskite and zirconolite,[5] measured in a modified IAEA test, are shown in Figure 38. These rates are within an order of magnitude of leach rates measured in synthetic Synroc.[29] Although these data are very limited and subject to interpretation, they do suggest that the Synroc-D form for SRP waste should remain a durable host for radionuclides for at least $10^6$ years.

## POTENTIAL IMPROVEMENTS FROM WASTE FORM OPTIMIZATION

Improvements in waste form quality are expected for both borosilicate glass and Synroc-D. Because of its higher level of development and its simpler product characteristics, the requirements for improving the borosilicate glass waste form are better understood. The potential for improvement of Synroc-D is less certain because this product has been produced only with laboratory-scale equipment and simulated waste.

Glass forms produced in the DWPF could benefit from new frit compositions, from higher waste loadings, and from steps to decrease fracture. Ceramic forms could be improved by minimizing the amorphous phase, increasing the fraction of the cesium and

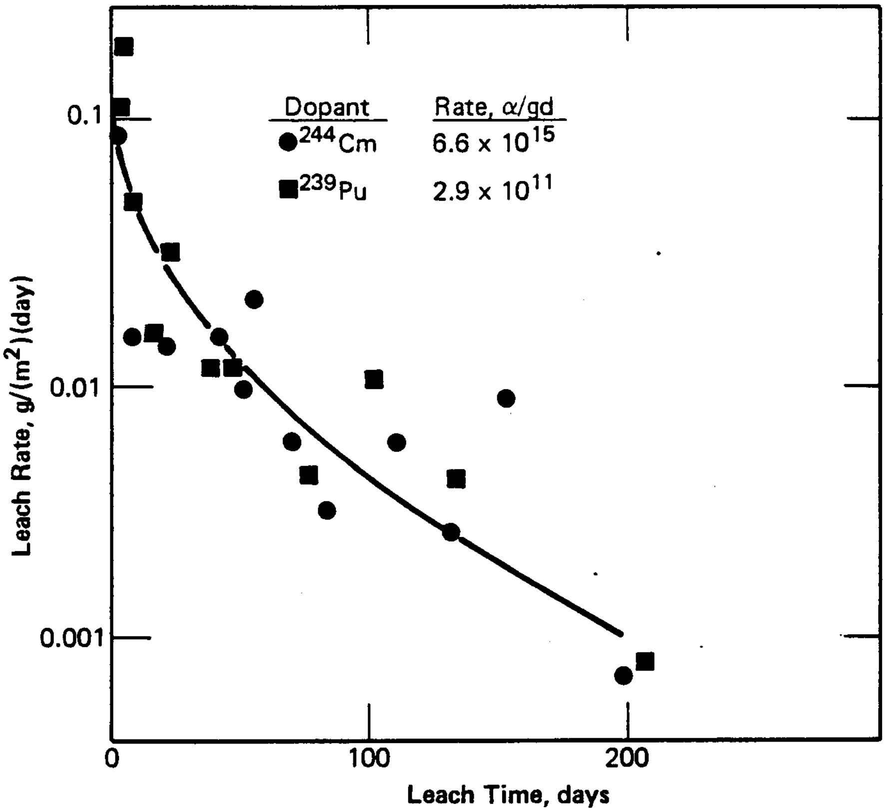

FIGURE 37. Leach Rate for SRP Borosilicate Glass Based on $^{244}$Cm or $^{239}$Pu, from Modified IAEA Test in Deionized Water at 23°C (from Reference 55)

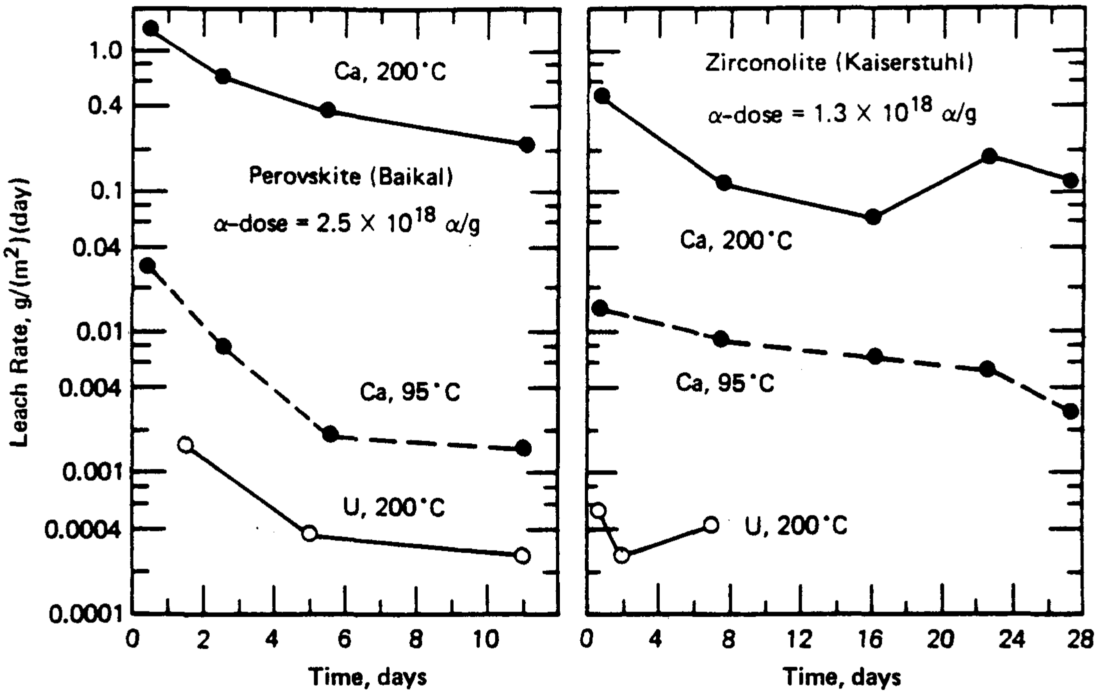

FIGURE 38. Leach Rates Based on Calcium and Uranium for Some Natural Synroc Mineral Analogs (from Reference 5)

strontium that enters durable phases, and decreasing the dependence of product quality on processing procedures.

## Potential Improvements in Borosilicate Glass

The leachability of borosilicate glass is expected to improve because of changes in the chemical composition. Two major improvements have been identified: new frit compositions, and higher waste loadings.

### Frit Optimization

New frit compositions have been developed which increase the durability of borosilicate glass containing simulated SRP waste.[13] Leach rates that are up to 6 times lower have been observed for these frits.

The new frit compositions include more silica than does Frit 131, the current reference frit. Frit 131 was developed for use in a calcine-fed ceramic melter. The glass-forming process now involves a slurry-fed melter, which can process a more viscous melt. A higher-viscosity glass containing more silica, which produces a more durable product, can thus be accommodated.

### Increased Waste Loading

High concentrations of SRP waste (up to about 50 wt %) have been shown to improve the leach resistance of the glass product.[13] Waste elements, primarily iron and aluminum, are beneficial to product quality. An increase of the reference waste loading from 28 wt % to 35 wt % has decreased leach rates by 30% in laboratory tests.[13]

For glasses containing Frit 131, melt viscosity is lowest between 20 and 37 wt % waste content.[13] An increase to 35 wt % would cause no more processing difficulties, although the effects of waste loading for new frits must be tested. Laboratory-scale tests show that up to 50 wt % waste oxides might be incorporated into the glass without causing a decrease in product durability.[13]

### Decrease in Thermal Fracturing

As mentioned in the Physical Properties section of this report, the extent of fracture in full-scale glass monoliths can be improved by thermal treatments, canister liners, or a closer match between the thermal expansion coefficients of glass and the canister.

## Potential Improvements in Synroc-D Ceramic

The expected quality of Synroc-D waste forms could be improved by two methods. First, fundamental changes in the waste form composition could provide more durable product phases. Second, process studies could ensure that consistent product quality would be achieved without stringent process control.

### Ceramic Phase Improvements

The quality of the crystalline ceramic waste form is determined by the durabilities of its individual phases. The nepheline and amorphous phases, which are more prone to leaching than the titanates and spinels, would be primary targets for waste form improvement.

Early laboratory tests were based on a simplified simulated waste composition, which did not include minor components of the sludge. Initial tests with simulated waste containing many of these minor components indicate the Synroc properties should not be degraded significantly. In fact, when $Na_3PO_4$ was added at the level expected in SRP waste (0.70 wt %), cesium leach rates were decreased by up to a factor of four.* Sodium release was also lowered. Apparently, phosphate stabilized the glassy phase and made it more durable.

Phosphate could be a beneficial additive, even in excess of the amount in the sludge. If more phosphate is added than is needed to stabilize the glass, the excess would be expected to combine with other elements in the waste form. Small amounts of monazite-type phases, which are durable radionuclide hosts,[62,63] may form. In addition, it has been proposed** that phosphates could combine with other Synroc-D elements to form a more durable host for cesium, analogous to carnotite, $Cs_2(UO_2)_2P_2O_8$.

If strontium could be stabilized in a low-temperature perovskite before silicon is added in the process, less strontium would enter the leachable glassy phase. In LLNL tests in which silicon was added after calcination, the strontium leach rates were lowered by more then an order of magnitude.† This effect may not be achievable with actual waste, which will contain much more silicon than was present in the simulated sludge used by LLNL.

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* A. B. Harker (Rockwell Science Center), private communication.

** C. C. Herrick (Los Alamos National Laboratory), private communication.

† J. H. Campbell (Lawrence Livermore National Laboratory), "Recent Developments in Synroc-D at LLNL," private communication.

Cesium leach rates could also be decreased by altering the DWPF Stage 2 (cesium removal) feed to Stage 1 (solidification). By preconsolidating cesium in hollandite and blending the hollandite and calcine before pressing, LLNL achieved a factor of 8 to 10 lower cesium release rate than for Synroc-D in which cesium was contained in nepheline.[6] This technique, however, would greatly increase process complexity. A more cost-effective method may be to introduce cesium adsorbed on zeolite, which is the reference ceramic process studied in the recent Processability Analysis.[11] When heated, Cs-loaded zeolite transforms to pollucite ($CsAlSi_2O_6$) and feldspar ($CsAlSi_3O_8$), both of which are more durable than nepheline.[64]

Finally, if it is possible to treat high-aluminum waste separately from the other extremes of waste composition, the sodium could be fixed in magnetoplumbite.[65] Nepheline would not be required to stabilize sodium and, in theory, cesium leach rates could be reduced.

### Process Flexibility

The choice of fabrication steps for a waste form does not necessarily affect expected improvements in that waste form. However, the proposed process for Synroc-D is much more complex than the process for making borosilicate glass.[11] In a complex process, product quality may suffer if process steps are not carefully controlled. Recent experiments[66] show that Synroc-D may be much more tolerant of variations in waste feed composition and in process control steps than had previously been assumed. Areas where the ceramic may be relatively insensitive to the process include: particle sizes, oxidation/reduction (redox) control, and additive compositions.

Synroc-D was originally based on Synroc-C, a proposed ceramic waste form for commercial high-level waste, and Synroc-B, a form containing Synroc-C phases but no waste.[29] Many of the process concerns for Synroc-D were based on experience with the commercial waste form.

Synroc-B requires very fine particle sizes both for its waste feed and for its mineral additives.[67] Micrometer-size particles are necessary because the solid phases are formed "sub-solidus;" that is, no liquid is present during forming. In Synroc-D for SRP waste, however, silicon and sodium are always present. These elements form a small amount of liquid during hot isostatic pressing. In Synroc-D, the speed at which chemical elements can arrange themselves into the proper phases is greatly increased, and larger particle sizes might be accommodated.

Tests with simulated waste feeds having larger particle sizes than those in actual SRP waste show that careful control of particle sizes, by extensive ball milling, may not be necessary.[66]

Exact control of oxidizing/reducing ("redox") conditions may also not be necessary. Synroc-C required very reducing conditions to force cesium into the hollandite phase.[29] Hollandite is not a phase in Synroc-D. Somewhat reducing conditions are still required to ensure uranium is present as $U^{4+}$, rather than $U^{6+}$; phases containing hexavalent uranium are more leachable than zirconolite and perovskite.[68] Tests at LLNL[66] and Rockwell Science Center,* however, show that Synroc-D has similar leach rates if it is produced under redox conditions ranging from "moderately oxidizing" to "very reducing." In hot pressing tests at SRL, no undesirable phases were formed in Synroc-D, even though no attempt was made to control redox conditions.

Control of the composition of mineral additives may also be less stringent than previously thought. Up to 100% variation in major waste elements might be accommodated by the same composition of additives.[66]

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* A. B. Harker (Rockwell Science Center), private communication.

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