CHARACTERIZATION OF SAVANNAH RIVER PLANT WASTE GLASS

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ABSTRACT

The objective of the glass characterization programs at the Savannah River Laboratory (SRL) is to ensure that glass containing Savannah River Plant high-level waste can be permanently stored in a federal repository, in an environmentally acceptable manner. To accomplish this objective, SRL is carrying out several experimental programs, including

- Fundamental studies of the reactions between waste glass and water, particularly repository groundwater.
- Experiments in which candidate repository environments are simulated as accurately as possible.
- Burial tests of simulated waste glass in candidate repository geologies.
- Large-scale tests of glass durability.
- Determination of the effects of process conditions on glass quality.

In this paper, the strategy and current status of each of these programs is discussed. The results indicate that waste packages containing SRP waste glass will satisfy emerging regulatory criteria.

INTRODUCTION

The Savannah River Laboratory is carrying out an intensive program to quantify the long-term performance of SRP waste glass in a federal geologic repository. This includes:

- Fundamental studies leading to a defensible model of glass performance.
- Extensive testing of glass performance under actual repository conditions to verify such a model and its predictions.

In this report, the results and status of SRL's programs in each of these areas are presented.

VITRIFICATION PROCESS

At the Savannah River Plant (SRP), construction of the world's largest solidification facility for nuclear waste has been underway for over a year. In this plant, the Defense Waste Processing Facility (DWPF), the nearly 30 million gallons of alkaline high-level liquid waste now stored in carbon steel tanks will be converted to a durable borosilicate glass.

This conversion process is shown schematically in Fig. 1. In the SRP tank farm, the insoluble portion of the waste (called "sludge") will be treated with caustic to reduce the volume of material to be vitrified. The sludge contains virtually all of the long-lived radionuclides ($t_{1/2} > 30$ yrs). The soluble portion of the high-level waste will be treated with sodium tetraphenylborate (to remove radioactive cesium), and with sodium titanate (to remove the small amounts of residual strontium and plutonium in the soluble waste). The tetraphenylborate salts and the titanate will then be transferred to the DWPF, reacted with formic acid to remove organics, and mixed with the sludge.

Glass-forming chemicals in the form of a premelted glass frit will then be added to the waste. The resultant slurry will be fed to a joule-heated glass melter, and converted to a borosilicate glass at 1150°C. The glass will be poured into a stainless steel canister, which will be welded closed, decontaminated, and then stored (1). Important attributes of the waste glass and canister immediately after pouring are shown in Fig. 2. It must be emphasized that these values are estimates of the maximum values expected; average values are likely to be a factor of 2-3 lower.

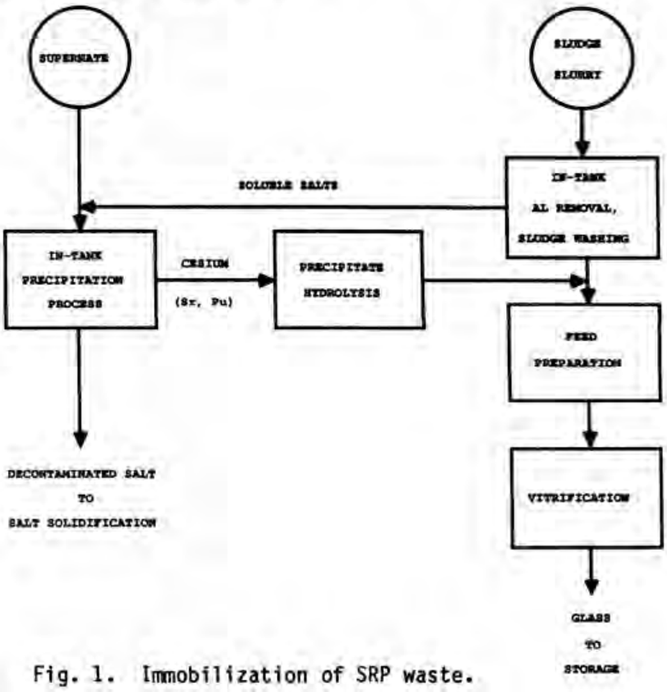

Fig. 1. Immobilization of SRP waste.

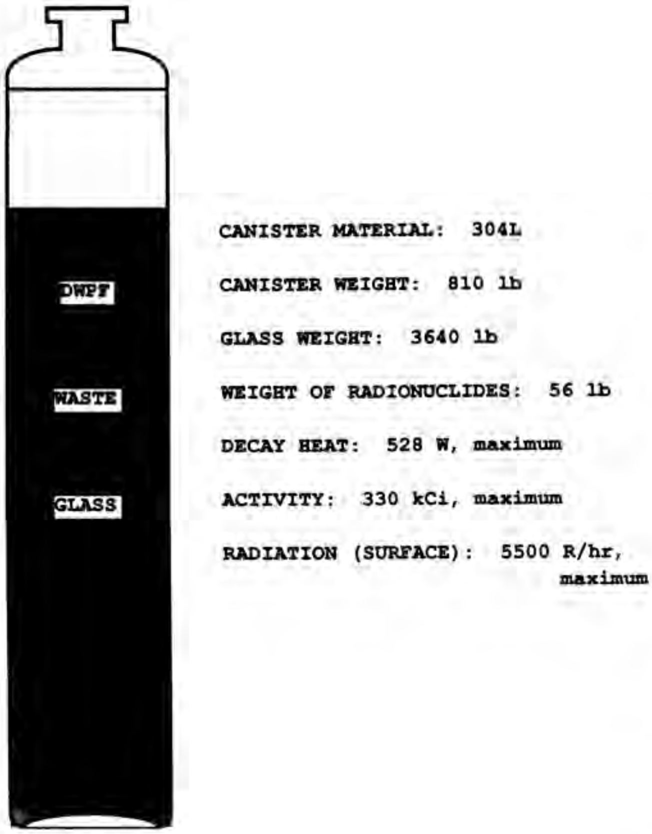

Fig. 2. Properties of DWPF glass and canister.

GLASS PERFORMANCE PROGRAMS

In accordance with the Nuclear Waste Policy Act of 1982, these canisters of waste glass will eventually go to a licensed federal repository for permanent disposal. The leading candidates for the first repository are tuff (Nevada Test Site - NTS), basalt (Hanford Reservation in Washington), and salt (Deaf Smith County in Texas). At the repository, the canister containing waste glass will be emplaced in the geology as part of a waste package. This package will contain the waste glass, the 304L stainless steel canister, a metallic overpack (to meet the containment requirement of 10 CFR 60), and possibly a packing material such as crushed rock or clay.

Reaction of waste glass with repository groundwater is the most likely mode of release of long-lived radioactive species to the environment. Thus, Savannah River Laboratory has focused on developing a quantitative understanding of this reaction over the range of conditions expected for groundwater/DWPF glass interactions in specific repository environments. The expected range of conditions for each of the candidate geologies is listed in Table I.

The SRL program, shown in Fig. 3, has two major components: modeling and verification. SRL's modeling efforts are directed toward development of a defensible model for long-term release from DWPF waste glass, while verification studies test the validity of the model and its predictions. Although these are separate functions, there is necessarily a large amount of interaction between the two components. For example, leaching models are used in the design of verification experiments to point out the appropriate parameters to measure. Conversely, verification tests can indicate phenomena not considered in the modeling program, and thus *are used to guide* modeling efforts.

TABLE I

Expected Repository Conditions For DWPF Glass

Parameter	Repository Conditions		
	Salt	Basalt	Tuff
Temperature, °C	34-90	57-150	30-95
Pressure, psi	2800	4700	Atmospheric
Groundwater	Brine	Silicate	Dilute Silicate
Eh	Neutral	Reducing	Oxidizing
pH	6	9.75	7.5
Flow	Static	Very Slow	Dripping
Amount of Water	Limited	Flooded	Limited

MODELING REACTIONS OF GROUNDWATER WITH WASTE GLASS

SRL's programs to model the reactions between waste glass and repository groundwater include:

- Fundamental studies to quantify the effects of parameters such as glass composition, groundwater composition (including Eh, pH, and dissolved gases), or radiation on glass durability.
- Laboratory tests to quantify glass performance under conditions simulating specific repository environments.

The first is exemplified by our development of the thermodynamic approach first suggested by Paul and Newton (2-4), which has enabled us to predict from their compositions the performance of a wide range of glasses and minerals on the standard MCC-1 static leach test. As Fig.4 shows, the durability of basalt (as measured by Si release to solution) is virtually identical to that of the DWPF product. Thus, the stability of this material, which has lead to its selection as a candidate for the first repository, is also indicative of the stability of DWPF waste glass in the same environment. These ideas are being expanded both by SRL (5-7) and by others (8), and will eventually become a powerful predictive tool.

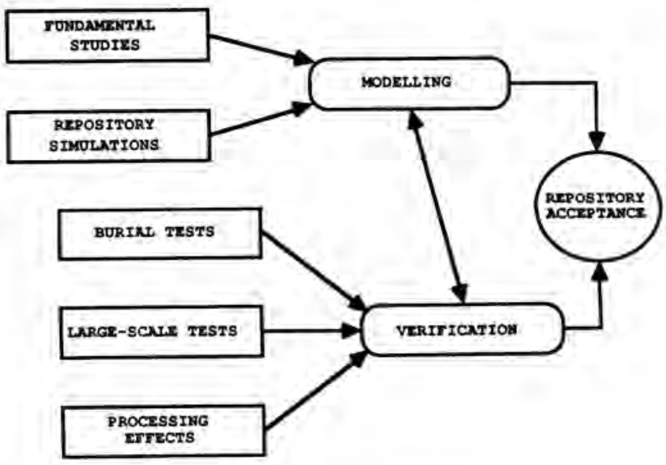

Fig. 3. Glass characterization programs at SRL.

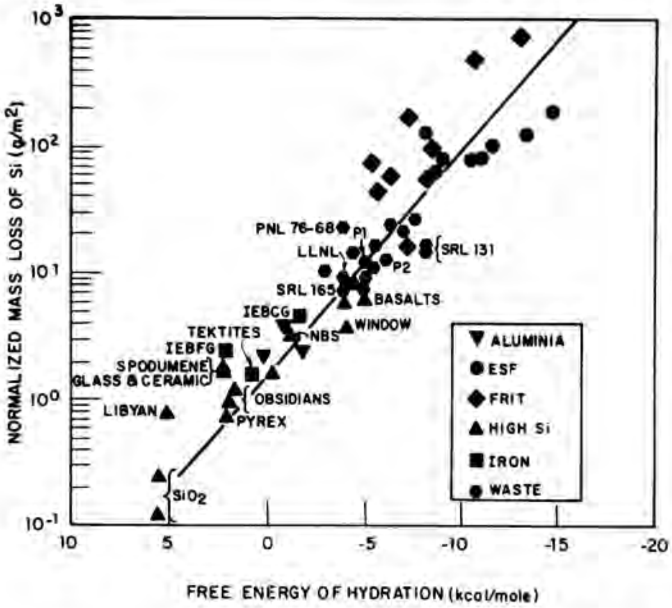

Fig. 4. Comparison of the durability of ancient glasses, natural analogues, and nuclear waste glasses.

SRL is also performing repository simulation tests in the laboratory, using both actual and simulated waste glasses. These tests are designed to provide data which will be used to determine the acceptability of DWPF glass in a specific repository environment. In these tests, samples of waste glass and stainless steel (simulating a breached canister) are placed in a reaction vessel made from rock cups, and the cups are closed. For the tests in tuff, actual groundwater from a well (J-13) at the Nevada Test Site is used. In the case of basalt, a synthetic groundwater (GR-4), prepared in an oxygen-free environment, is used (9). For the salt tests, both inclusion and intrusion brines are used.

Although these laboratory tests are not completed, they are indicating that the amount of radioactivity which will be free to travel with the groundwater will be a small fraction of the activity present in the waste glass (10,11). In Table II, the results for the radioactive tests in tuff cups are shown in terms of normalized mass losses.

TABLE II

Repository Simulation Results
For a Saturated Tuff Repository

Species	Normalized Release, g/m2	Fractional Release per year
Cs-137	0.022	5.8×10^{-8}
Sr-90	0.013	3.4×10^{-8}
Pu-238	0.0053	1.4×10^{-8}

Glass containing Tank 42 waste, exposed to J-13 water for 127 days, at 90°C.

In these tuff tests, solution concentrations of most elements were constant within experimental error after approximately 40 days, indicating that the rate of alteration of the glass had become very small. The final concentrations of species in solution were then used to provide estimates for the amount of material released by the waste glass. The concentrations were multiplied by an extremely conservative upper bound for the amount of groundwater which would be available for reaction (50 L), and then divided by the inventory of the individual species to give the fractional releases listed in Table II. The small fractions released are 500-1000 times less than the NRC requirement for the waste package as a whole. Thus, they are indicative of the very good performance to be expected of DWPF glass in this environment.

VERIFICATION TESTING

The results and conclusions from SRL's modeling efforts are being verified in several ways:

- Extensive testing of waste glass in burial experiments in underground laboratories, to relate performance in the laboratory to the actual repository.
- Large-scale leaching experiments using thick slices from full-scale canisters of simulated waste glass, to relate the performance of laboratory-sized samples to that of full-scale canisters of waste glass.
- Extensive testing of simulated and actual waste glasses prepared according to the DWPF process, to relate the performance of laboratory-prepared samples to that of glass made in the DWPF.

The most advanced of these verification programs is that in which samples of simulated waste glass have been buried in underground facilities. Extensive testing has been carried out in the Stripa mine in Sweden, where samples of several simulated waste glasses have been buried in granite for over a year. In this joint effort, scientists from SRL, KBS (the Swedish nuclear program), and the University of Florida have found only a slight interaction between glass and groundwater in the first month of testing, and virtually none thereafter (12). This agrees well with laboratory tests which also show that a steady-state is reached rather quickly (10).

A more extensive set of burial tests has just begun in the WIPP facility in New Mexico (13). In these tests, samples of simulated waste glasses from seven countries are being emplaced in salt approximately 2000 feet underground. These samples will be subjected to brine attack under both expected and unlikely conditions in a salt repository. In a later series of tests, full-scale canisters of radioactive glass from the DWPF will be placed in the WIPP salt, and their performance will be tested in a variety of ways. These tests are scheduled to begin in approximately 1990 and will demonstrate both glass durability and the retrievability of canisters from a salt repository.

Efforts have also recently begun to verify the relevance of the modeling results in another way. Full-scale canisters of nonradioactive simulated waste glass, filled according to the DWPF process in SRL's Engineering Test Facility, have been sliced into cylinders approximately 12 inches long. These large slices are being immersed in large leach vessels of deionized water, and will be leached under conditions approximating the standard MCC-1 test as closely as possible. The results will then be compared to a companion set of experiments being performed with laboratory-sized samples of the same glass to determine the relationship between laboratory and full-scale tests.

In later tests, similar comparative experiments will be performed for a brine/WIPP salt system, and for a basaltic groundwater/basalt system. These tests should finally demonstrate what effect, if any, cracking or stress (due to cooling) has on the performance of waste glass in repository environments. In particular, in the brine experiments, canister failure will be induced during the tests, to simulate the environment around the waste glass after canister failure has occurred.

SRL is also continuing to rigorously characterize and test glass samples made according to the DWPF process. The purpose of this effort is to establish that the results of tests of laboratory-prepared samples are relevant to the performance of DWPF glass. For example, samples of glass of the same composition were prepared in a 50 cc crucible, a 3 kg continuous electric melter, and in a 1500 kg capacity continuous melter. As shown in Fig. 5, the performance of the glass did not vary appreciably with the size of the melter. Thus, the performance of DWPF glass is likely to be insensitive to the size of the melter used to prepare it.

SUMMARY

Scientists at Savannah River Laboratory are characterizing the performance of DWPF glass under conditions expected in candidate repository environments. Preliminary indications from the many ongoing programs are that this glass will be an important barrier to the release of radionuclides to the environment, and that repositories containing the glass will meet emerging federal regulations.

ACKNOWLEDGEMENT

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Fig. 5. Effect of melter scale on leach rate.

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