Acc # 738280

DP-MS-75-48 (Rev 2)

PROCEDURE FOR DETERMINING LEACHABILITIES OF RADIOACTIVE WASTE FORMS

by

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Submitted to *Nuclear Technology* for publication

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration.

This document was prepared in conjunction with work accomplished under Contract No.
AT(07-2)-1 with the U.S. Department of Energy.

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ABSTRACT

A new and improved procedure was developed for determining leachabilities of proposed radioactive waste forms. Finely divided glass samples are leached in flowing deionized water; leached ions are continuously sorbed on ion exchange resins to control ionic quality. Sorbed ions are eluted from the resin columns for atomic absorption analyses. Leachabilities measured by this procedure are lower and more consistent than those made in stagnant water without continuous ionic control.

KEYWORDS: radioactive waste forms, leachability, leachant quality control, glass leaching in deionized water.

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* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration.

INTRODUCTION

Integrity and durability of solid radioactive wastes are related principally to rates at which waste constituents are leached into environmental water. While no laboratory procedure can be expected to duplicate all possible environmental conditions, a single test is desirable to compare the leaching properties of solid waste forms produced in different laboratories. Hespe[1] proposed such a test procedure, which comprises methods for specimen preparation, requirements for specimen and leachant container, and the leach procedure. Specimens are leached in stagnant demineralized water at 25°C, and the water is changed daily for the first week, once per week for the following eight weeks, and once per month during the next six months.

Hespe's procedure,[1] with minor variations, was used in a round-robin test sponsored by the Leach Rate Subcommittee of the Waste Solidification Development Working Group of the U. S. Energy Research and Development Administration. Participants were Pacific Northwest Laboratory (Battelle), Atlantic Richfield Hanford Company, Allied Chemical Company (Idaho), and Savannah River Laboratory (SRL). Each laboratory used samples of National Bureau of Standards (NBS) glass 710. Test results showed that leachabilities can vary by as much as a factor of 5 to 10, even in tests that are run exactly the same way. In some cases, the leachant pH increased to >9. Anomalous, sharp increases in leachability were also observed in some cases.

Because of the large variations in leachabilities and the instability of the leachant pH, an improved procedure for leaching radioactive waste forms was developed at SRL.

BASIS OF IMPROVED PROCEDURE

Diebold[2] showed that above pH 9, the silicate matrix in glass waste forms is attacked, and the leach rate increases sharply. Below pH 9, leachability in glass is mainly a diffusion process. Glass in the presence of H^+-form cation exchange resin is leached slower than in the absence of resin.[2] This difference was attributed to an exchange between matrix cations and resin H^+ ions; the leachant pH thereby remained reasonably constant. In addition, since the presence of leached ions in the leachant can affect subsequent leaching, continuous removal of leached ions by the cation exchange resin stabilized ionic quality of the leachant.

Since control of pH and ionic quality of leachant are therefore essential to performance of meaningful leach tests, we have controlled these parameters by leaching glass samples with flowing water that is continuously purified by both cation and anion exchange resin columns.

EXPERIMENTAL DETAILS

Description of Equipment

Two arrangements of equipment were used in these tests. In the first (Figure 1), the waste form is suspended in 50-100 ml of deionized water at ambient temperature. A basket, made of fine-mesh stainless steel screen or nylon mesh, can be used for crushed glass specimens. (Monolithic samples could be used with highly radioactive waste forms.) A plastic bottle holds the water, and the basket is suspended from the bottle lid. Alternatively, the glass could be placed on the bottom of the bottle without using a basket. One-eighth-inch-diameter polyethylene tubing is used for the circulation line. Polyethylene, *Teflon*,* or stainless steel *Swagelok*** fittings are used for connections. A filter is used between the leach bottle and pump to protect the pump from solids, such as glass fines, and to prevent solids from collecting on the ion exchange beds.

The ion exchange columns are 1/2-inch-diameter polyethylene tubing connected to 1/8-inch-diameter tubing. 2.5 ml of H^+-form, 50-100 mesh, *Dowex*† 50W-X8 resin is used in Bed C, and 2.5 ml of OH^--form, 50-100 mesh, *Dowex* 1-X4 resin is used in Bed A. The resin beds are supported with small polyurethane plugs.

Resin for the cation exchange column is prepared by washing H^+-form, 50-100 mesh, *Dowex* 50W-X8 resin with ~25 ml of 4M HCl to remove residual sodium. Resin is then washed with distilled water until the water leaving the column is near pH 7.

Resin for the anion exchange column is prepared by washing Cl^--form, 50-100 mesh, *Dowex* 1-X4 resin with ~60 ml of 2M LiOH.

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* Trademark of Du Pont.
** Trademark of Crawford Fitting Company.
† Trademark of Dow Chemical Company.

The resin is then washed with distilled water until the wash water is near pH 7. LiOH is used in preference to NaOH or KOH to eliminate Na^+ or K^+ contamination that would result from incomplete washing.

During leaching, Valves 1 and 2 (stainless steel construction) are open, and Valve 3 is closed. When the ion exchange beds are to be replaced, Valve 3 is opened, and Valves 1 and 2 are closed. It is not necessary to stop water circulation during this step. When new beds are in place, Valves 1 and 2 are opened, and Valve 3 is closed.

Operation of the second apparatus (Figure 2) is essentially the same as that of the first, except that a water reservoir is used, and the sample is contained in a Gelman filtration funnel. Water is passed upflow through the Gelman filter during leaching to remove air bubbles from crushed glass and to provide intimate contact between leachant and sample.

The Na^+, K^+, and Ca^{2+} ions that are sorbed on the 2.5-ml cation exchange columns can be eluted with 25 ml of 4M HNO_3. (4M HNO_3 is superior to 4M HCl for this elution.) In these elution tests, HNO_3 was pumped through the resin bed at 0.5 ml/min; higher elution rates have not been studied. The elements eluted were then analyzed by atomic absorption spectroscopy.

No attempts have been made to elute the anion resin since only silicon species will be sorbed from leach solutions of NBS glass 710.

pH measurements of leach water in this apparatus would probably be meaningless because of the very low ionic concentration. Measurements of pH with a glass electrode were not reproducible. A conductivity cell was therefore placed in the system to determine the purity of the water. The conductivity of leachant circulated through both columns and the sample was usually between 0.5 and 0.3 micromhos/cm, fairly close to the value for pure water of 0.04 micromhos/cm.

Leach Tests

Three samples of NBS glass 710 were leached at ambient temperature by this procedure. The glass was crushed and sieved, and the -40 +60 mesh fraction was retained. This fraction was washed with acetone to remove fines and dried prior to use in the leach tests. Two of the tests were run in the apparatus shown in Figure 1. The first sample was contained in a nylon bag suspended in the plastic leaching chamber; the second sample was simply placed on the bottom of the chamber. Leach water entered the top and exited the bottom at a turnover rate of ~20 minutes. A third sample was placed on the stainless steel support screen of a Gelman funnel, as shown in Figure 2, to allow upward leachant flow in intimate contact with the sample.

Leachabilities, L, were calculated from the formula

$$L = f \left(\frac{M}{A}\right) \frac{1}{t_n}$$

where f is the fraction of a particular ion leached during the leaching period t_n, and M/A is the ratio of mass to surface area of the sample. The ratio M/A was estimated to be 0.005 g/cm^2 by assuming all particles to be spheres with a diameter of 250 microns (the smallest particle that will not pass through a 60 mesh sieve), a density of 2.4 g/cm^3, and a roughness factor of 2.

DISCUSSION OF RESULTS

Leaching data are given for sodium, potassium, and calcium in Tables I through III and graphically for potassium in Figure 3. The general behavior of the initial part of the leaching curves was as expected; the leachabilities (in g/cm^2-day) were initially high and decreased with time. Results obtained with the two samples leached in the plastic chamber, Figure 1, agreed well; however, the leachabilities in the flow-through system (Gelman funnel, Figure 2) decreased much more rapidly with time than did the others and approached lower values. The lower leachability of glass in the flowthrough system is attributed to the removal of leached products from the glass surfaces by convection. These products can be removed in the other system only by diffusion from the bulk of crushed glass. Localized accumulation of leached products in the first apparatus could lead to conditions of locally high pH that would increase the leach rate.

In the samples leached in the first apparatus, the leachability increased sharply after 40 to 50 days. Leaching experiments were continued with these samples, and the results showed that the leachability remained high after additional leaching. Similar behavior was observed by others during the round-robin tests but was not observed in the present work with the flow-through system. The sharply increased leachability in later days probably resulted from sloughing of a protective silica coating that formed on the surface of the glass during early leaching of alkali and alkaline earth oxides. After prolonged leaching, this coating may become so thick and weak as to be unable to support itself or the glass within it and may slough off. Removal of this layer should manifest itself not only in an increased leachability but also in a change in the particle size distribution of the glass. A comparison of the particle size distribution of leached and unleached glass (Table IV) shows that the glass after leaching contains more fines than does the starting material.

ESCA analyses of the surfaces of leached glasses also indicate the formation of a silica layer. Most of the sodium and all of the potassium were leached from the glass surface. Other workers[3,4,5] have also found silica films on the surface of leached glasses. In one case,[5] the leached surface contained 93.5 mol % SiO_2.

CONCLUSIONS

This study demonstrated that large variations in leachabilities can be averted by using ion exchange resins to sorb leached ions from solution. However, in systems where localized stagnant films can form around glass particles, leachability is higher because of the localized high pH. This also is manifested in the decreased time required to form a thick silica film that eventually sloughs off. The flowthrough system prevents localized high pH around glass particles. This lowers leachability and delays formation of the film that falls off.

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LIST OF FIGURES

TABLE I

Leachability of Sodium from NBS Glass 710

Total Elapsed Time, days	*Leachability, g/(cm²-day)* *Glass in Nylon Bag*	*Glass on Bottom of Cell*	*Flowthrough System*
1	6.5×10^{-6}	4.7×10^{-6}	4.1×10^{-6}
2	2.1×10^{-6}	2.6×10^{-6}	5.5×10^{-7}
3	2.7×10^{-6}	1.8×10^{-6}	4.4×10^{-7}
4	1.6×10^{-6}	1.1×10^{-6}	4.2×10^{-7}
7	1.3×10^{-6}	2.0×10^{-6}	2.3×10^{-7}
14	5.5×10^{-7}	5.4×10^{-7}	1.8×10^{-7}
21	4.0×10^{-7}	2.8×10^{-7}	1.0×10^{-7}
28	2.8×10^{-7}	2.0×10^{-7}	7.8×10^{-8}
35	2.1×10^{-7}	1.8×10^{-7}	1.2×10^{-7}
42	1.7×10^{-7}	1.4×10^{-7}	1.2×10^{-7}
49	1.3×10^{-7}	2.4×10^{-7}	1.1×10^{-7}
56	6.3×10^{-7}	4.1×10^{-7}	9.4×10^{-8}
73	-	5.4×10^{-7}	-
86	7.3×10^{-7}	-	-

TABLE II

Leachability of Potassium from NBS Glass 710

Total Elapsed Time, days	*Leachability, g/(cm^2-day)*		
	Glass in Nylon Bag	*Glass on Bottom of Cell*	*Flowthrough System*
1	2.9×10^{-6}	2.5×10^{-6}	3.2×10^{-6}
2	1.4×10^{-6}	1.4×10^{-6}	3.4×10^{-7}
3	1.2×10^{-6}	1.0×10^{-6}	3.0×10^{-7}
4	8.9×10^{-7}	9.4×10^{-7}	2.5×10^{-7}
7	6.5×10^{-7}	6.4×10^{-7}	2.0×10^{-7}
14	3.9×10^{-7}	4.1×10^{-7}	1.2×10^{-7}
21	2.5×10^{-7}	2.3×10^{-7}	7.2×10^{-8}
28	1.5×10^{-7}	1.9×10^{-7}	6.6×10^{-8}
35	1.7×10^{-7}	1.3×10^{-7}	5.1×10^{-8}
42	1.1×10^{-7}	9.6×10^{-8}	4.9×10^{-8}
49	9.6×10^{-8}	2.1×10^{-7}	5.1×10^{-8}
56	6.8×10^{-7}	4.3×10^{-7}	4.8×10^{-8}
73	-	5.3×10^{-7}	-
86	7.3×10^{-7}	-	-

TABLE III

Leachability of Calcium from NBS Glass 710

Total Elapsed Time, days	*Leachability, g/(cm^2-day)*		
	Glass in Nylon Bag	*Glass on Bottom of Cell*	*Flowthrough System*
1	8.8×10^{-6}	7.0×10^{-6}	5.3×10^{-6}
2	9.8×10^{-6}	8.4×10^{-6}	1.2×10^{-6}
3	3.5×10^{-6}	4.5×10^{-6}	6.9×10^{-7}
4	2.4×10^{-6}	1.9×10^{-6}	4.0×10^{-7}
7	1.3×10^{-6}	1.0×10^{-6}	5.0×10^{-7}
14	7.3×10^{-7}	7.3×10^{-7}	5.4×10^{-7}
21	6.0×10^{-7}	3.3×10^{-7}	2.3×10^{-7}
28	5.1×10^{-7}	2.2×10^{-7}	1.6×10^{-7}
35	1.9×10^{-7}	2.3×10^{-7}	2.7×10^{-7}
42	1.8×10^{-7}	2.0×10^{-7}	2.3×10^{-7}
49	2.5×10^{-7}	3.7×10^{-7}	4.3×10^{-7}
56	8.4×10^{-7}	6.0×10^{-7}	4.0×10^{-7}
73	-	6.8×10^{-7}	-
86	9.3×10^{-7}		

TABLE IV

Effect of Leaching on Particle Size Distribution of NBS Glass 710

Particle Size, microns	*Particle Distribution*		
	Before Leaching, %	*After Leaching 86 Days in Nylon Bag, %*	*After Leaching 73 Days in Bottom of Cell, %*
350 - 250	93.8	85.1	85.4
250 - 125	5.3	13.4	13.5
<125	0.4	1.5	1.0

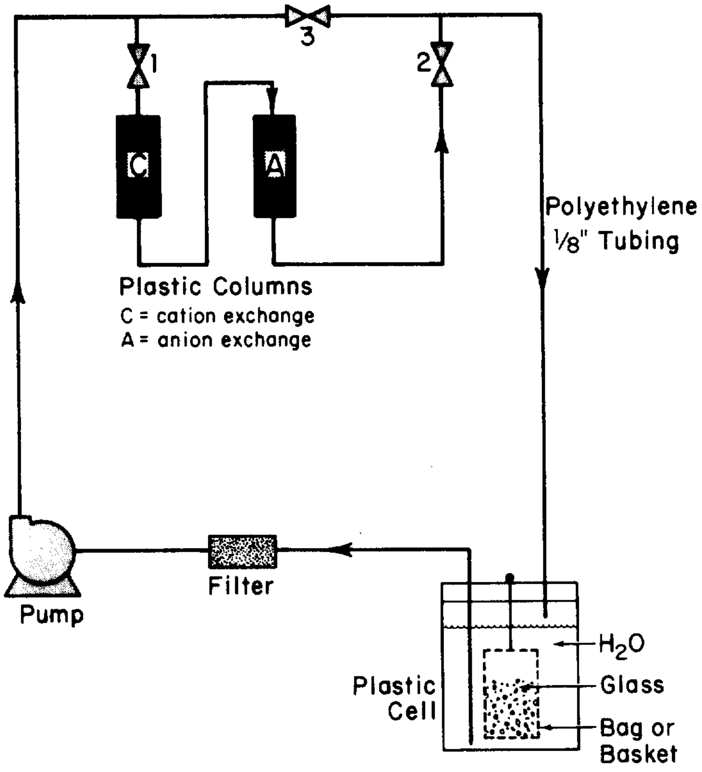

FIG. 1. First leach apparatus

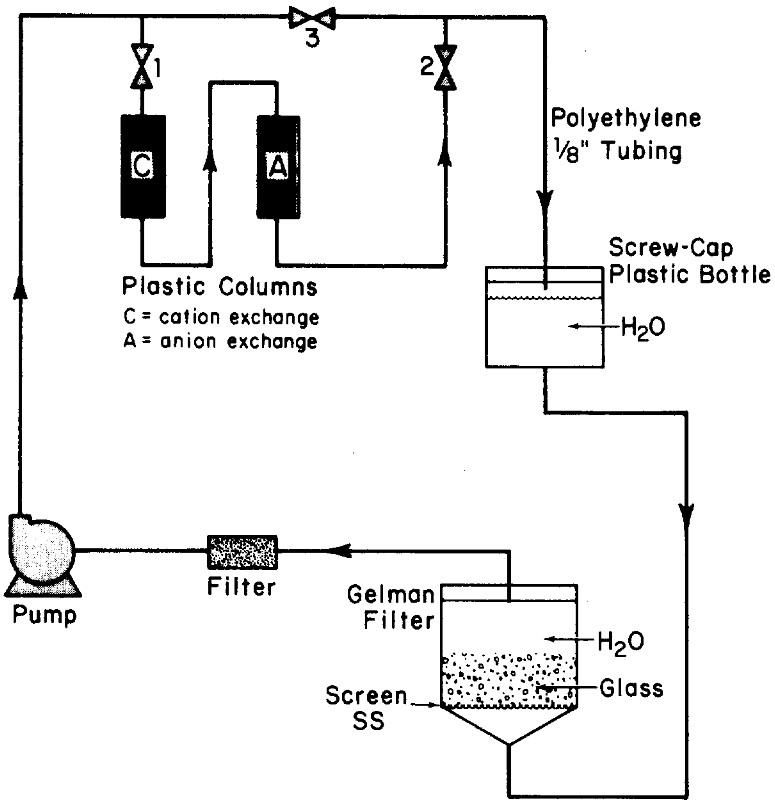

FIG. 2. Second leach apparatus

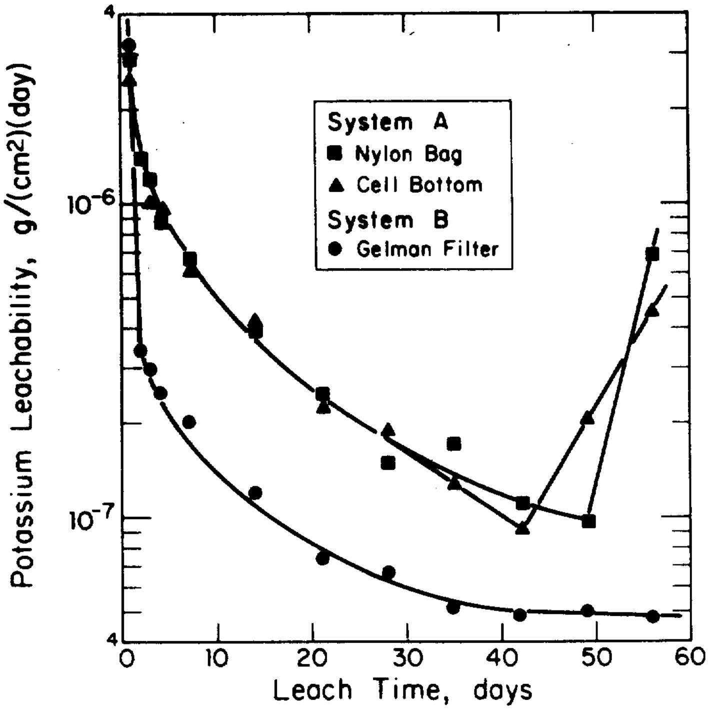

FIG. 3 LEACHING OF POTASSIUM FROM NBS GLASS 710 AT 25°C