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COMPARATIVE LEACH TESTING OF HIGH-LEVEL WASTE FORMS

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ABSTRACT

Four candidate waste forms (borosilicate glass, high-silica glass, tailored ceramic, and Synroc) for Savannah River Plant high-level nuclear waste were compared in MCC-1 standard static leach tests. Relative leaching behavior differed for each element, and none of the waste forms was clearly superior to the others.

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INTRODUCTION

More than 23 million gallons of defense high-level nuclear waste is stored at the Savannah River Plant (SRP), near Aiken, South Carolina. The U. S. Department of Energy (DOE) plans to build a Defense Waste Processing Facility (DWPF) at SRP to solidify this waste in a form suitable for permanent isolation in a mined geologic repository. Because the DWPF will be the first such facility in the United States, there has been considerable interest in the scientific and engineering community as to the type of waste form to be produced.

In 1977, the Department of Energy selected borosilicate glass as the reference waste form for design studies. Since then, alternative waste forms such as advanced ceramics, concretes, cermets, and composites also have been proposed. In the past two years, data on the waste forms have been gathered by waste-form developers that will allow DOE to decide on the form to be manufactured.

The principal requirements for a waste form are (1) that it be easy to make, and (2) that it have as low a leach rate as possible. These requirements are not always consistent with each other, and in fact are sometimes mutually exclusive. Thus, any comparison of leach rates must be tempered by the results of processability analyses. In this paper, I will present only the results of a Comparative Leach Test Program performed at the Savannah River Laboratory (SRL).

EXPERIMENTAL PROCEDURE

Four waste forms were selected for comparative leach testing (SLIDE 1). Each developer agreed to prepare waste form material from simulated Savannah River high-level waste sludges supplied by SRL. We gratefully acknowledge the cooperation of the following developers: SRL Chemical Technology Division for borosilicate glass; Catholic University of America for high-silica glass: Rockwell Energy Systems Group for tailored ceramic; Lawrence Livermore National Laboratory for Synroc.

The procedure for the Comparative Leach Test Program is given in SLIDE 2. Large batches of three different simulated sludges, designated Composite, High-Aluminum, and High-Iron, were prepared at SRL and distributed to the developers. The sludges were incorporated into state-of-the-art, laboratory-scale waste forms which were returned to SRL for evaluation. Samples were fabricated into leach specimens by core-drilling and sawing into thin discs. The discs were neutron activated and then leached by the MCC-1 static leach test procedure. The final step was radiometric analysis of the leachates for cesium, uranium, cerium, iron, zirconium, sodium, and aluminum.

The now-familiar MCC-1 Static Leach Test (SLIDE 3) required that Teflon® (trademark of Du Pont) leach vessels be maintained at constant temperature (40 and 90°C in the present tests) in an oven. Specimens were exposed to three aqueous leachants: deionized (DI) water, silicate water, or brine. Conditions were carefully specified in the standard test procedure.

RESULTS AND DISCUSSION

Results of the comparative leach tests are given in the next several slides. First, the observed effects of waste composition, leachant composition, and temperature will be discussed. Then, the four waste forms will be compared with respect to measured leach rates of cesium, uranium, sodium, and aluminum. Also, some strontium leaching data from other sources will be reviewed. Cesium, strontium, and uranium are important radwaste elements; sodium and aluminum are important inert matrix components.

Effects of Leaching Conditions

An example of the effect of sludge type is given in SLIDE 4, which is for 28-day leach rates of cesium from borosilicate glass in DI water at 90°C. This case is typical of most of the other conditions. Generally, the effect of sludge type was relatively small, with factors of only 3 to 5 difference in leach rates. The leach rates for different sludge types were usually in the following order, from best to worst:

High-Aluminum < Composite < High-Iron

The effect of leachant (SLIDE 5) also was relatively small, typically with factors of only 2 to 4 difference between leachants. The example is for 28-day leach rates of cesium from borosilicate glass with Composite sludge at 90°C. For most of the conditions, the leach rates with different leachants were in the following order, from best to worst:

Silicate Water, Brine < DI Water

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. Arrhenius plots (log L vs. 1/T) are shown in SLIDE 6 for some typical cases. The temperature dependence of 28-day leach rates of uranium and sodium from borosilicate glass with Composite sludge in DI water is shown. The points at 150°C are from the work of Wicks at SRL. Activation energies of 3 to 12 kcal/mole were found. 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.

Elemental Leach Rates

Cesium leach rates (SLIDE 7) of the waste forms span three orders of magnitude. Single tests were run for 3, 7, and 14 days; triplicate tests were run for 28 days. The data shown are for forms with Composite sludge in DI water at 90°C. In this case, a few of the single points appear to be outliers. There is a clear delineation between best and worst forms for cesium leaching.

Representative strontium leach rate data from individual waste-form developers are given in SLIDE 8. These are 28-day leach rates for forms with Composite sludge in silicate water at 90°C. There is a clear delineation between the very low strontium leach rates of borosilicate glass and tailored ceramic, and the much higher leach rates of high-silica glass and Synroc.

Uranium leach rates (SLIDE 9) of the waste forms span more than two orders of magnitude. The data shown are for forms with Composite sludge in DI water at 90°C. Synroc has exceptionally low uranium leach rates.

Sodium leach rates (SLIDE 10) also span nearly three orders of magnitude. The data shown are for forms with Composite sludge in DI water at 90°C. High-silica glass has exceptionally low sodium leach rates. The overall leaching behavior of sodium closely resembles that of cesium.

Aluminum leach rates (SLIDE 11) are shown for forms with Composite sludge in DI water at 90°C. For this case, the leach rates of the different waste forms fall into two groups separated by about one order of magnitude.

Leach rates also were measured for cerium, iron, and zirconium. Most of these data were less than detection limits, and thus few comparisons could be made. For cerium and iron, the leach rate of high-silica glass was significantly higher than the leach rate of the other three forms, which could not be distinguished from each other from the available data.

CONCLUSION

In conclusion, the relative order of leach rates of the four waste forms for each of the elements studied is summarized in SLIDE 12. A form ranked first has the lowest (best) leach rate, while one ranked fourth has the highest (worst) leach rate. In several cases, the complete ordering could not be determined from the data; these are considered ties, as shown. The important

point of this summary is that none of the forms is superior for all of the key elements. In particular, high-silica glass is best for cesium, borosilicate glass and tailored ceramic are best for strontium, and Synroc is best for uranium.

The implication of these results is that differences in ease of processing, rather than in leach rates, may very well be the deciding factor in selection of the DWPF waste form.

SLIDE 1

SRL COMPARATIVE LEACH TEST PROGRAM

WASTE FORMS

• BOROSILICATE GLASS	SRL
• HIGH-SILICA GLASS	CUA
• TAILORED CERAMIC	RES
• SYNROC	LLNL

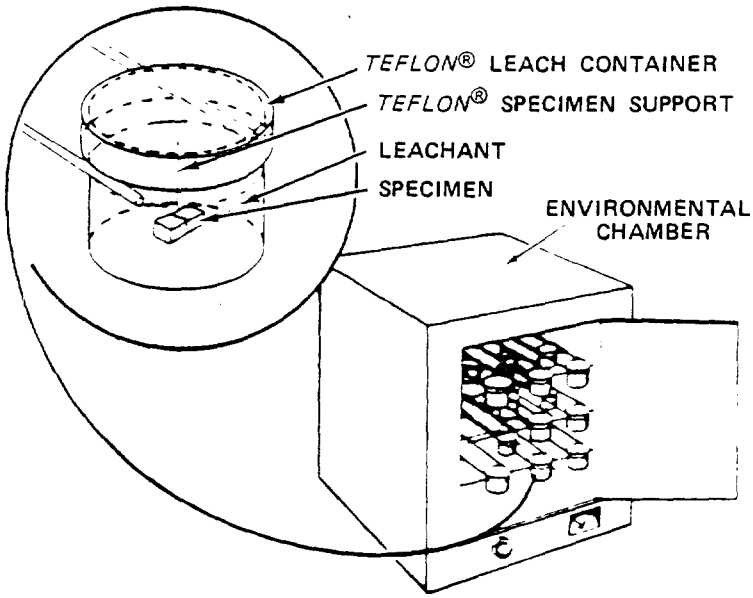
SLIDE 2

SRL COMPARATIVE LEACH TEST PROCEDURE

- PROVIDE DEVELOPERS WITH STANDARD SIMULATED SLUDGES
- OBTAIN STATE-OF-THE-ART WASTE FORMS FROM DEVELOPERS
- FABRICATE TEST SAMPLES
- NEUTRON-ACTIVATE SOLID SAMPLES (ANL PROCEDURE)
- LEACH ACTIVATED WASTE FORMS (MCC STATIC LEACH TEST)
- ANALYZE LEACHATES RADIOMETRICALLY

SLIDE 3

APPARATUS FOR MCC-1 STATIC LEACH TEST



SLIDE 4

EFFECT OF WASTE COMPOSITION

MCC-1 STATIC LEACH TEST, 28 DAYS, 90°C,
DI WATER, BOROSILICATE GLASS

	CESIUM LEACH RATE	
	$g/(m^2)(day)$	Relative
HIGH-IRON	3.24 ±0.25	2.1
COMPOSITE	1.54 ±0.03	1
HIGH-ALUMINUM	0.54 ±0.06	0.35

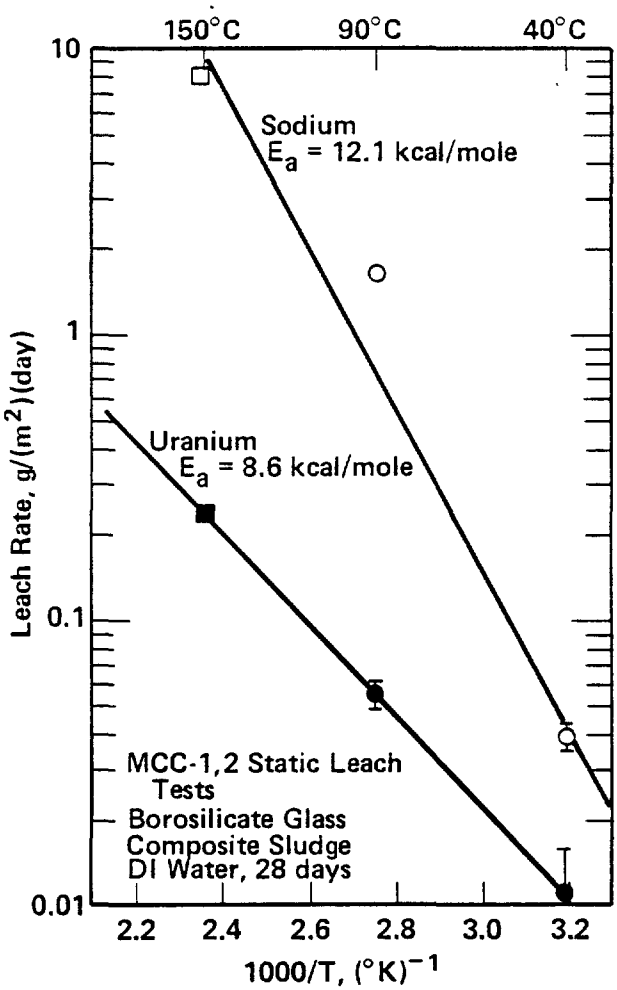
SLIDE 5

EFFECT OF LEACHANT COMPOSITION

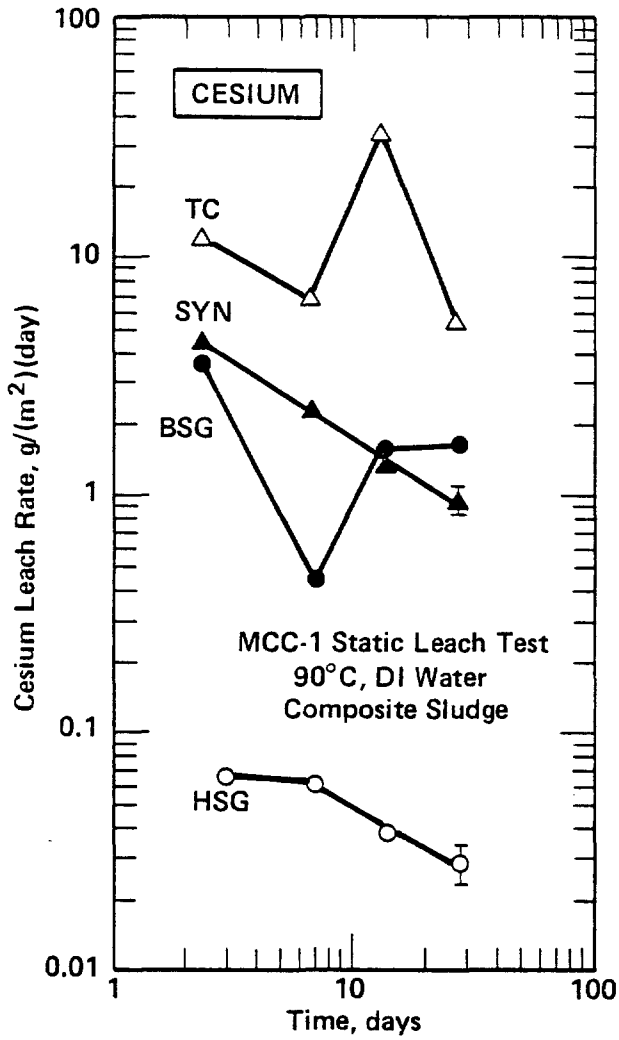
MCC-1 STATIC LEACH TEST, 28 DAYS, 90°C,
BOROSILICATE GLASS/COMPOSITE WASTE

	CESIUM LEACH RATE	
	$g/(m^2)(day)$	Relative
DI WATER	1.54 ±0.03	1
SILICATE WATER	0.76 ±0.04	0.5
BRINE	0.44 ±0.03	0.3

SLIDE 6


150°C
90°C
40°C
10
1
0.1
0.01
Leach Rate, g/(m²)(day)
Sodium
Ea = 12.1 kcal/mole
Uranium
Ea = 8.6 kcal/mole
MCC-1,2 Static Leach Tests
Borosilicate Glass
Composite Sludge
DI Water, 28 days
2.2
2.4
2.6
2.8
3.0
3.2
1000/T, (°K)⁻¹

SLIDE 7


CESIUM
TC
SYN
BSG
HSG
MCC-1 Static Leach Test
90°C, DI Water
Composite Sludge
Cesium Leach Rate, g/(m²)(day)
100
10
1
0.1
0.01
1
10
100
Time, days

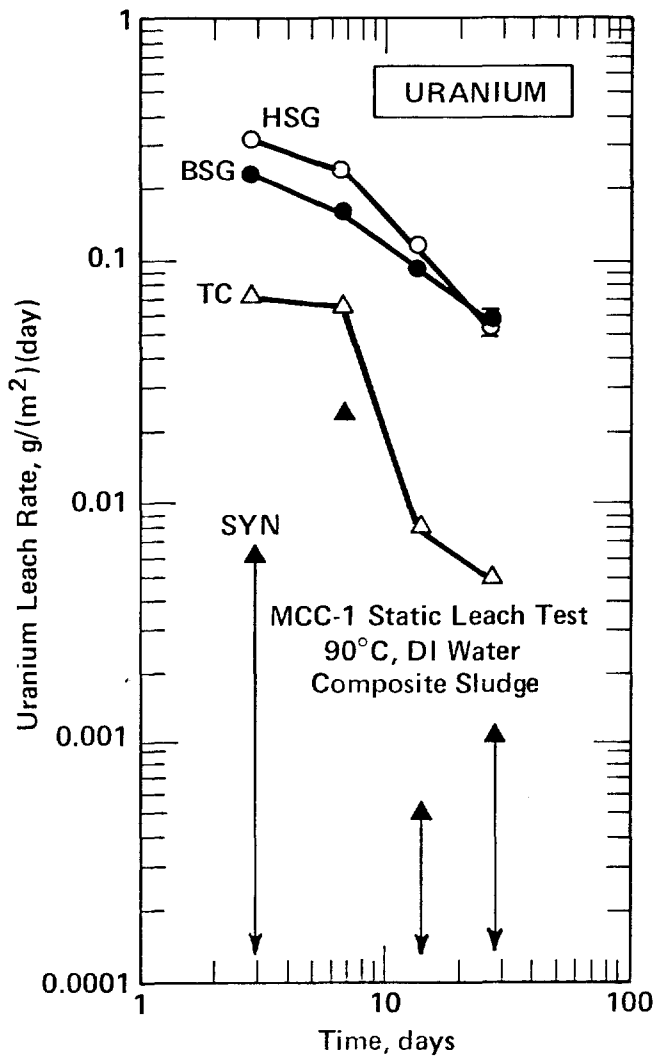
SLIDE 8

STRONTIUM LEACH RATES (LITERATURE DATA)

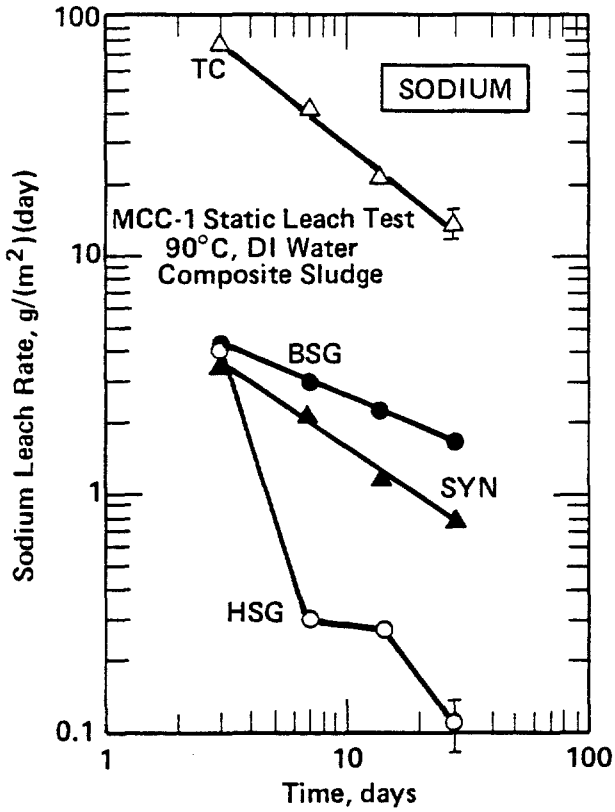
MCC-1 STATIC LEACH TEST, 28 DAYS, 90°C,
SILICATE WATER, COMPOSITE WASTE

	LEACH RATE, $g/(m^2)(day)$
SYNROC	0.099
HIGH-SILICA GLASS	0.043
BOROSILICATE GLASS	<0.001
TAILORED CERAMIC	<0.0004

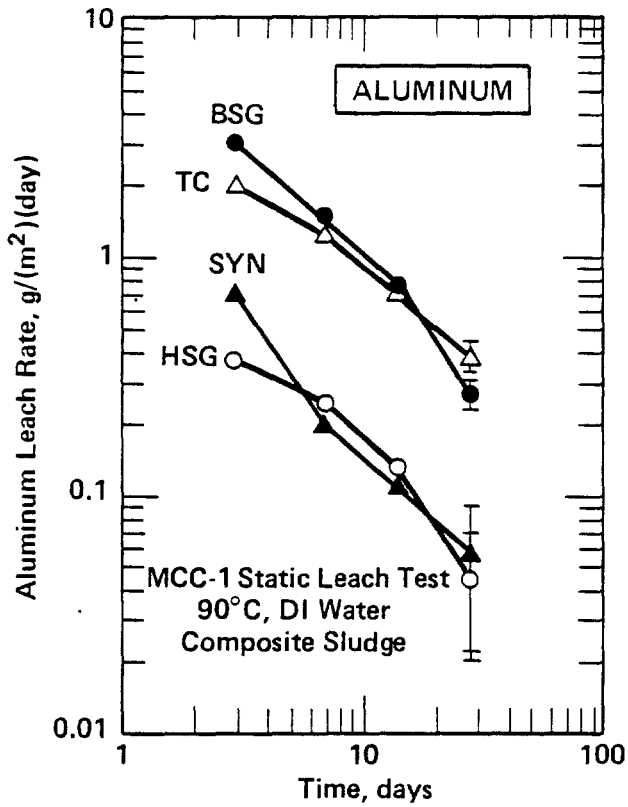
SLIDE 9


URANIUM
HSG
BSG
TC
SYN
MCC-1 Static Leach Test
90°C, DI Water
Composite Sludge
Uranium Leach Rate, g/(m²)(day)
1
0.1
0.01
0.001
0.0001
1
10
100
Time, days

SLIDE 10


SODIUM
TC
MCC-1 Static Leach Test
90°C, DI Water
Composite Sludge
BSG
SYN
HSG
Sodium Leach Rate, g/(m²)(day)
100
10
1
0.1
1
10
100
Time, days

SLIDE 11


ALUMINUM
BSG
TC
SYN
HSG
MCC-1 Static Leach Test
90°C, DI Water
Composite Sludge
Aluminum Leach Rate, g/(m²)(day)
10
1
0.1
0.01
1
10
100
Time, days

SLIDE 12

SUMMARY OF LEACHING BEHAVIOR

	1	2	3	4
CESIUM	HSG	BSG SYN		TC
STRONTIUM	BSG TC			SYN HSG
URANIUM	SYN	TC		BSG HSG
CERIUM	BSG TC SYN			HSG
SODIUM	HSG	SYN	BSG	TC
ALUMINUM	HSG SYN		TC	BSG
IRON	BSG TC SYN			HSG