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THE ENDOTHERMIC PROCESS--APPLICATION TO IMMOBILIZATION OF HANFORD IN-TANK SOLIDIFIED WASTE

Michael J. Kupfer
Wallace W. Schulz

Chemical Technology Laboratory
Research and Development
Chemical Processing Division

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ATLANTIC RICHFIELD HANFORD COMPANY
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ABSTRACT

Conversion of high-level solid radioactive waste to a nonleachable silicate glass is accomplished in the Endothermic process by simple melting of a mixture of the waste with crushed basalt. Dense (2.5 g cm^{-3}*) green-black glasses are obtained by melting mixtures containing 30 to 40 wt% Hanford In-Tank Solidified (ITS) waste, 50 to 70 wt% basalt, and 0 to 10 wt%* B_2O_3*. Addition of* B_2O_3 *to the process charge is desirable to lower its melting range from about 1100-1150 °C to 1000-1050 °C. Leach rates of these glasses (calculated from the sum of the concentrations of Fe, Na, Ca, Si, Mg, Al, Sr, and Cs in the leach liquor) in water at 25 °C range from* 10^{-7} *to* 10^{-5} *g/*cm^2 *day. The leach rate, based on* ^{137}Cs*, of a typical Endothermic process glass made from actual ITS waste, is* 3.0×10^{-8} *g/*cm^2 *day. This leach rate corresponds to removal of* 2.1×10^{-14} *g* ^{137}Cs *per day from a square centimeter of glass containing 57 μCi* ^{137}Cs *per gram. Judging from initial tests, the Endothermic process is a very promising scheme to increase immobilization of the ITS waste.*

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THE ENDOTHERMIC PROCESS--
APPLICATION TO IMMOBILIZATION OF HANFORD IN-TANK SOLIDIFIED WASTE

INTRODUCTION

Upon completion of the Hanford Waste Management Program[1] millions of gallons of salt cake generated by evaporation of aged, high-level, alkaline waste liquor will have accumulated in underground storage tanks. This In-Tank Solidifed (ITS) waste is essentially a mixture of $NaNO_3$, Na_2CO_3, $NaNO_2$, NaOH, and $NaAlO_2$; principal radioisotopes are strontium-90 and cesium-137. Ultimate disposition of this solid, high-level waste has not yet been determined; it may become necessary, however, in the future to convert the salt cake to a form more suitable for long-term storage.

High-temperature methods for conversion of ITS and other high-level wastes to immobile silicate and aluminosilicate forms suitable for long-term disposal and/or storage have been proposed recently.[2,3] Candidate feed materials, besides ITS waste, to these processes include calcined Purex process waste and the encapsulated $^{137}CsCl$ and $^{90}SrF_2$ which will be produced in the Hanford Waste Management Program. Proposed laboratory-scale studies to develop and demonstrate these immobilization processes have been outlined previously.[2]

This report is the second of a series intended to document progress of laboratory investigations of the various high-temperature processes. The first report[4] in this series concerned application of a thermite-type reaction (Exothermic process) to immobilization of ITS waste. Results of experiments to define suitable conditions for operation of a process to fix ITS wastes in molten basalt (Endothermic process) are summarized and discussed in this report. Incorporation of radioactive material into melted basalt was studied briefly earlier in Czechoslovakia by Saidl and Rálkovǎ.[5] Glasses obtained by these workers exhibited great stability to leaching by water.

SUMMARY AND CONCLUSIONS

In the Endothermic process a mixture of solid radioactive waste and crushed basalt is melted to produce a dense, nonleachable glass. Process tests with both simulated and actual ITS waste show that satisfactorily immobile glasses are obtained when the process charge contains 20 to 40 wt% waste. Leach rates in distilled water at 25 °C of typical glasses produced from such charges are in the range 10^{-8} to 10^{-5} g/cm^2 day.

Mixtures of basalt and ITS waste melt in the range 1100 to 1150 °C. However, mixtures heated to 1200 to 1300 °C are less viscous and, when cooled, yield a denser glass.

Addition of B_2O_3 to the basalt-ITS waste mixture is beneficial to reduce the maximum operating process temperature to 1200 °C or less. Endothermic process glasses made from charges containing 2 to 16 wt% B_2O_3 leach in water at rates comparable to those of ITS waste-basalt glasses containing no boron.

From 1 to 5% of the cesium in the synthetic ITS waste (containing 1.4 wt% cesium) volatilizes when charges containing 10 to 40 wt% waste are melted. The presence of 2 to 16 wt% B_2O_3 in such melts reduces cesium volatility to 1% or less. Only 0.27% of the ^{137}Cs volatilized during melting of a charge containg 70 wt% basalt-30 wt% actual ITS waste;

this ITS waste contained 0.00007 wt% ^{137}Cs.

Endothermic process glasses made from ITS waste stored at 350 to 550 °C for two weeks do not devitrify and do not exhibit increased leachability.

PROCESS DESCRIPTION AND FLOWSHEET

A conceptual flowsheet for application of the Endothermic process to immobilization of Hanford ITS waste is shown in Figure 1. Addition of small amounts of B_2O_3 to the mixture of basalt and ITS waste is beneficial, not only to lower the melting range from about 1100-1150 to 1000-1050 °C, but also to reduce volatilization of cesium. With charges containing 10 wt% B_2O_3, 1% or less of the cesium in the ITS waste volatilizes. In the absence of B_2O_3, from 1 to 5% of the cesium volatilizes during the melting step.

Typical glass products of the Endothermic process resemble obsidian (Figure 2). The volume of the glass obtained according to the flowsheet conditions of Figure 1 is equal to or only slightly less (10 to 15%) than the volume of the ITS waste in the original charge.

The gases evolved when the Endothermic process is operated with ITS waste contain, in addition to small amounts of ^{137}Cs, NO_x equivalent to the nitrate and nitrite content of the waste. Undetermined amounts of water are also volatilized. The off-gas may also contain CO_2 (from carbonate in the ITS waste) and ^{106}Ru; neither the presence nor the absence of these latter constituents have yet been established.

Thus far, the Endothermic process has been demonstrated only on a batch basis and then, with one exception,

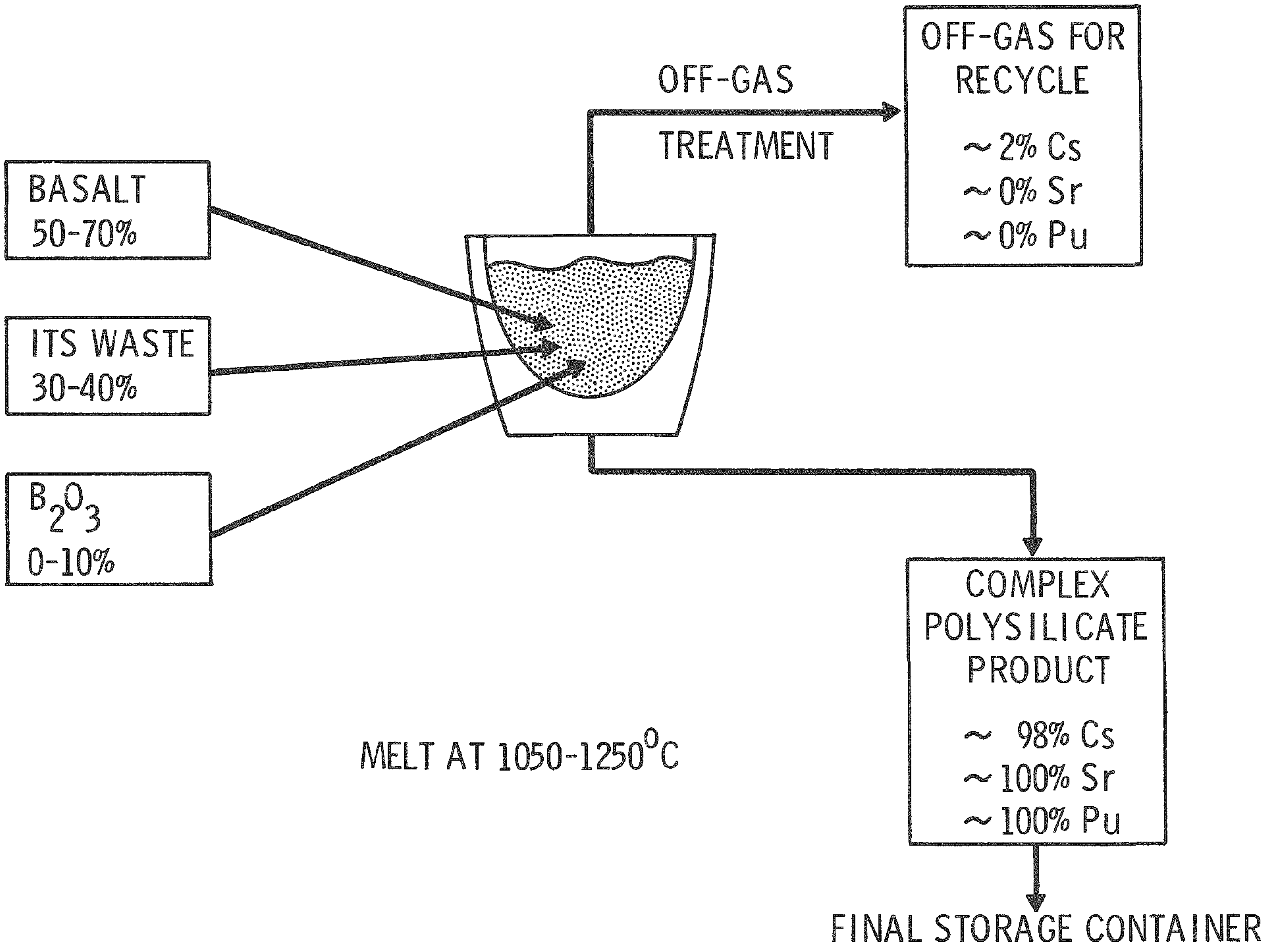

FIGURE 1

CONCEPTUAL FLOWSHEET FOR APPLICATION OF THE ENDOTHERMIC PROCESS TO ITS WASTE

FIGURE 2

TYPICAL ENDOTHERMIC PROCESS GLASSES MADE FROM SIMULATED ITS WASTE exclusively with simulated ITS wastes.* The process appears highly amenable to continuous operation, however, and tests to demonstrate such operation with both synthetic and actual ITS waste as well as with various other candidate feeds are planned.

EXPERIMENTAL

MATERIALS

In-Tank-Solidified (ITS) Waste

Table I lists the composition of the two simulated ITS wastes used in this work. The compositions of the simulated wastes were selected to take into account the variation in

TABLE I

ITS WASTE COMPOSITION

Simulated Wastes		
	Composition, wt%	
Component	ITS-1	ITS-2
$NaNO_3$	34.0	38.0
Na_2CO_3	22.0	13.8
$NaNO_2$	18.6	19.9
NaOH	12.4	1.8
$CsNO_3$	4.1	3.6
$NaAlO_2$	3.4	14.6
$Sr(NO_3)_2$	2.1	1.8
$SrCO_3$	2.1	1.8
NaH_2PO_4	0.7	1.3
Na_2SO_4	0.3	1.6
NaCl	0.3	0.9

Actual Waste[a]	
Component	Concentration
Na	32.8 wt%
NO_3	46.7 wt%
NO_2	1.3 wt%
CO_3	5.7 wt%
^{137}Cs	57. μCi/gram
$^{106}Ru-^{106}Rh$	0.51 μCi/gram
^{90}Sr	0.09 μCi/gram
Pu	10^{-5} mg/gram

[a] Sample from 116-TX Tank.

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* Two batch kilogram-scale tests of the Endothermic process with actual ITS waste have now been completed very successfully; properties of the resulting glasses were comparable with those described on p. 16 of this report.

NaOH and $NaAlO_2$ concentration of actual ITS material. The amounts of inert and radioactive cesium and strontium in actual ITS wastes are very low. Therefore, to facilitate determination of leach and volatility rates of products formed from the Endothermic process, additional strontium and cesium were added to the synthetic ITS waste.

Both the simulated ITS wastes were prepared by thorough mixing of finely ground dry ingredients. Actual ITS waste will contain varying amounts of water as associated mother liquor. One experiment was performed with ITS-2 waste to which sufficient water (≈ 0.2 ml g^{-1}) was added to make a paste; results with this "wet" waste are discussed on page 20.

One experiment was performed with a sample of actual ITS waste from the 116-TX Tank; radiochemical and chemical, insofar as the latter has been determined, compositions of this particular air-dried ITS waste sample are also listed in Table I. [The 116-TX Tank was one of the first tanks to be filled with ITS waste.] Compared with the synthetic wastes, the actual ITS waste contained considerably more nitrate, about as much sodium, slightly less carbonate, and considerably less nitrite. The sum of the nitrate and nitrite concentrations in the actual ITS was was about the same as in the synthetic waste, suggesting less radiolytic decomposition of nitrate to nitrite than expected.

Basalt

Basalt was available from a large stockpile used by local road maintenance crews and obtained originally by crushing surface outcroppings. The crushed basalt was screened and the portion finer than 30 mesh was used. Typical composition of Hanford basalt is shown in Table II; this material melts at approximately 1200 °C.

TABLE II

TYPICAL COMPOSITION OF HANFORD BASALT

Component	wt%
SiO_2	52.
FeO	14.
Al_2O_3	13.
CaO	8.
MgO	4.
Na_2O	3.
TiO_2	2.5
K_2O	1.5

Other Reagents

Boron trioxide (99.6% B_2O_3) powder was obtained from the Research Inorganic Company, Sun Valley, California. All other reagents were of reagent-grade quality.

PROCEDURES

Charge Preparation and Melting

Ordinarily, portions of ITS waste, crushed basalt, and, in some cases, B_2O_3 were thoroughly mixed in appropriately sized graphite-clay crucibles (Dixon Crucible Company). Charges weighing 50 to 75 grams were contained in No. 0000 crucibles while 500-gram charges were placed in No. 2 crucibles. In a few experiments 20-gram charges were contained in a 50-ml platinum crucible. In all cases the test charges contained from 20 to 50 wt% ITS waste.

In each experiment the crucible was placed in a crucible furnace (Lindberg Hevi-Duty Model 56953-S) and connected to the off-gas collection train. Approximately an hour was required to heat the charge to a temperature in the range 1050 to 1300 °C. Usually, when the desired temperature was attained, the furnace was shut off and the molten charge allowed to cool (*ca.* 4 hr) to room temperature without removing the crucible from the furnace. In a few tests the crucible was removed from the furnace as soon as the desired temperature was reached; in these cases the charge cooled to room temperature in about an hour.

The off-gas collection system shown in Figure 3 with the inverted quartz funnel simply suspended over the clay-graphite crucible was used in most tests. A few runs were made in a closed system with a platinum crucible completely contained in a quartz tube which was connected to the off-gas train. Runs with the closed system were made to insure that all volatilized cesium and strontium were collected and measured. Actually, however, as discussed later, cesium volatilization was about the same in both the closed and open systems.

Off-Gas Composition

Gas evolved from the molten charge was drawn, as indicated in Figure 3, through a water-cooled condenser, then through a trap containing either 1*M* NaOH or, occasionally, water, and finally through a glass wool filter. Sufficient vacuum was applied to the glass wool filter to insure that all the off-gas was collected. At the completion of each run, the various parts of the gas train including the glass wool filter were leached with 1*M* NaOH and water. Leachates as well as the liquid in the traps were analyzed for cesium and strontium.

Cesium was effectively removed from the off-gas in all cases. Most of the cesium deposited in the condenser; usually cesium was not found in the final glass wool filter. Much of the NO_x collected in the caustic traps, but some,

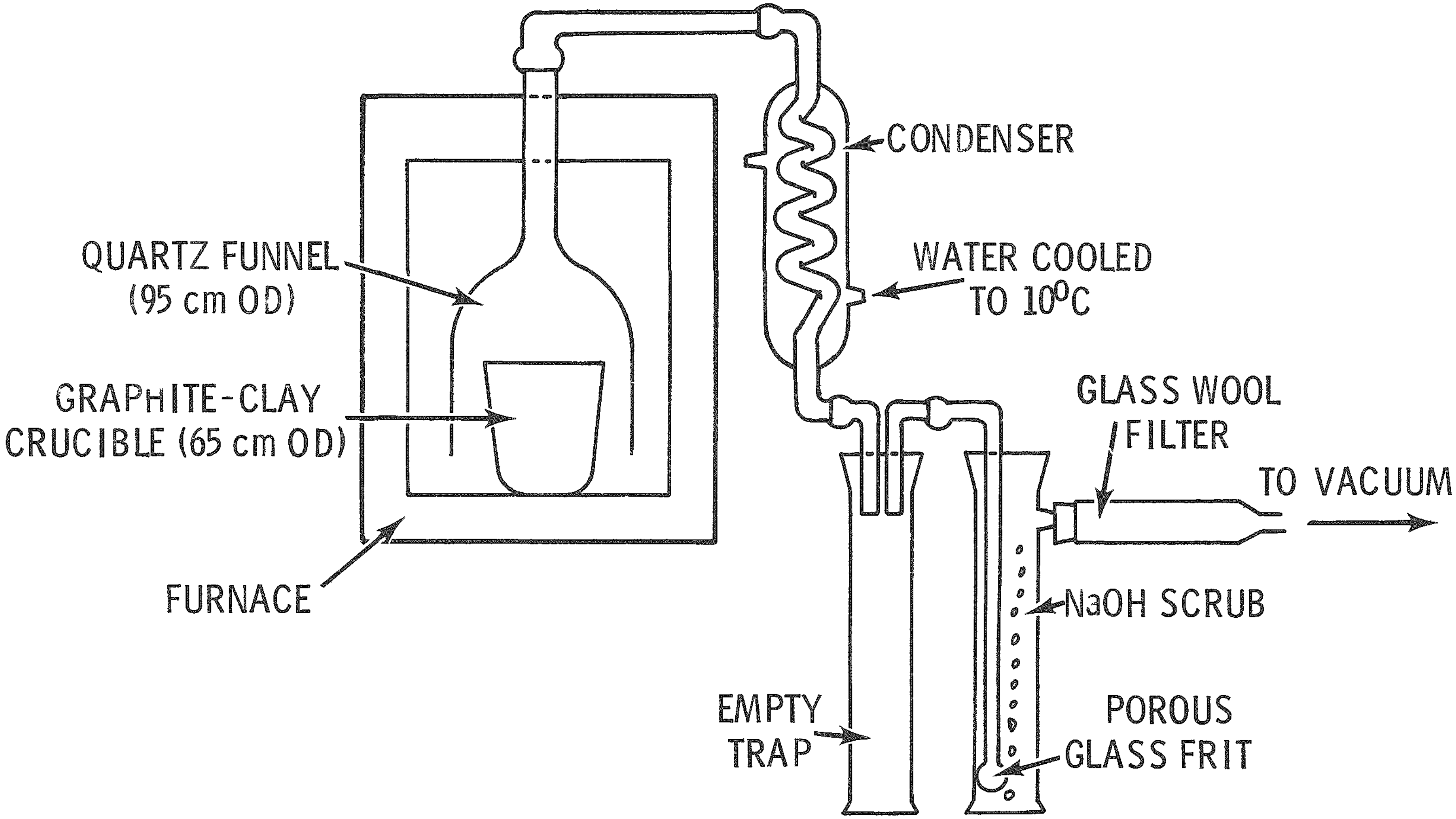

FIGURE 3

EXPERIMENTAL ARRANGEMENT FOR ENDOTHERMIC PROCESS TESTS because of inadequate residence time in the traps, passed completely through the gas train.

Product Quality Tests

Several properties of products from the Endothermic process were measured to evaluate effects of changes in reactant proportions, melting temperature, etc. These included:

1. Product Appearance

By inspection the silicate product was judged as either glassy or crystalline; X-ray diffraction techniques were used in some cases to confirm the presence or absence of crystalline materials. Qualitative estimates of product porosity were also made.

2. Product Density

Product density was calculated from the volume of water displaced by a weighed sample.

3. Leach Rates

A jaw-type rock crusher was used to break Endothermic process silicate products into small pieces. The crushed material was screened, and the 14 to 20 mesh (U.S. Standard Sieve series) fraction taken for leach tests. This fraction was rinsed with distilled water and then dried in air.

Leach tests were performed with 15 to 25 grams of the dried 14 to 20 mesh material which was assumed to consist of 0.11-cm diameter spheres. [The value of 0.11 cm is the average of the openings (0.14 and 0.084 cm, respectively) of 14 and 20 mesh screens.] Total surface area of the weighed leach samples was estimated from the weight and surface area of a counted number of the 0.11-cm diameter pieces.

Pyrex and quartz vessels described earlier[4] were used to perform leach tests. The test material was supported on a stainless steel screen, and airlift circulators were used to circulate 200 ml of distilled and deionized water over the sample pieces. Test samples were leach initially for 24 hours at 25 °C and then, after changing out the leach liquor, for 96 hours more at 25 °C. In all tests atomic absorption methods were used to analyze leach solution for iron, sodium, silicon, calcium, magnesium, aluminum, and strontium. Cesium in nonradioactive leach liquors was also determined by atomic absorption methods while ^{137}Cs in radioactive leach solutions was determined by gamma energy pulse height methods using a Ge(Li) detector.

From the concentration of iron, sodium, etc., in the leachate the sum of the FeO, Na_2O, SiO_2, CaO, MgO, Al_2O_3, Cs_2O, and SrO leached per day per square centimeter of glass was calculated. Values thus obtained are referred to as "bulk" leach rates (units of g cm^{-2} day^{-1}) in this report.

The formula

$$\text{Leach rate (g/cm}^2\text{ day) based on A} = \frac{\text{g of A leached}}{\text{[g of A/g of sample][sample area, cm}^2\text{][time, days]}} \qquad (1)$$

where "A" = Cs or Sr was also used to calculate leach rates of various glasses made from simulated ITS waste. The terms "based on cesium" or "based on strontium" are explicitly stated when referring to leach rates calculated by Equation 1. It is important to note that Equation 1 is equivalent to the expression "fraction A leached $(cm^2/g)^{-1}$ day^{-1}" recently recommended by Godbee[6] and Mendel.[7]

The procedure just described provided a rapid and convenient way of determining and comparing leach rates of the various Endothermic process products. However, leach rates determined by this procedure are uncertain to the extent of the errors involved in estimating the surface area of the test pieces. The assumption that the test pieces are spherical leads to calculation of minimum surface area; hence, leach rates quoted in this paper are believed maximum values.

In this latter connection, the surface area of three samples of crushed, screened (14 to 20 mesh) typical glasses were determined accurately by the Micromeritics Instrument Corporation of Norcross, Georgia, using their Model 2100 D Orr Surface Area-Pore Volume analyzer. In all cases (Table III) actual surface areas were from 3 to about 15 times larger than the estimated values.

TABLE III

LEACH TEST PARTICLES--
ACTUAL VERSUS ESTIMATED AREA

Sample No.	Surface Area, cm^2	
	Estimated	Actual
1	180	614
2	361	5940
3	519	7520

4. Devitrification Behavior

Propensity of the product of the Endothermic process to devitrify was studied with glasses obtained by melting (at 1200 °C) charges containing 20 to 40 wt% ITS-2 waste. The resulting melts were heated for two weeks at either 350 or 550 °C. After cooling to room temperature, the samples were examined (by visual inspection, and, in some cases, X-ray diffraction) for the presence of crystalline components and then leached in distilled and deionized water. Leach rates of the heated samples were compared with those for samples of the same glasses stored at room temperature.

RESULTS AND DISCUSSION

PROPERTIES OF ENDOTHERMIC PROCESS PRODUCTS

Table IV lists conditions and results of process tests with synthetic ITS wastes. Results of one test with actual ITS waste are summarized in Table V. Significant features of these data are discussed in the Sections immediately following.

Product Appearance

Glasses (Figure 2) are obtained with charges containing 20 to 30 wt% ITS waste irrespective of the rate at which the melt is cooled. Melts containing 40 wt% waste are glassy when cooled rapidly but are partly crystalline when cooled slowly. Melts containing 50 wt% waste are partly crystalline even when cooled rapidly. X-Ray diffraction patterns of the crystalline products could not be indexed to any specific mineral or compound.

Endothermic process products containing 20 to 40 wt% ITS waste are dense (≈ 2.5 g cm^{-3}) and nonporous; solidified melts containing 50 wt% waste exhibit some porosity. Melts heated to 1300 °C are definitely less viscous than those heated to 1200 °C and generally are denser.

When the initial charge contains about 40 wt% ITS the volume of the Endothermic process glass is about 15% less than the volume of the ITS waste. When the charge contains 30 wt% ITS waste, the volume of the glass product is about equal to the volume of the ITS waste.

Leach Behavior

For the Endothermic process conditions listed in Table IV bulk leach rates (96 hr) of immobilized ITS-1 and ITS-2

TABLE IV

ENDOTHERMIC PROCESS TESTS WITH SYNTHETIC ITS WASTES

Test Conditions			% Volatilized		Product	Wt% in Product[b]		Bulk Leach Rate g/cm² day		Leach Rate Based on Cs g/cm² day		Leach Rate Based on Sr g/cm² day	
Waste		Furnace											
Type	Wt%	Temp, °C[a]	Cs	Sr	Appearance	Cs	Sr	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
ITS-1	20	1200	2.5	[c]	Glassy[d]	0.6	0.7	2.1×10^{-6}	3.3×10^{-7}	4.3×10^{-6}	1.1×10^{-6}	3.9×10^{-6}	1.1×10^{-6}
	20	1300	2.7	[c]	Glassy[d]	0.6	0.7	9.5×10^{-7}	1.7×10^{-7}	$<4.2 \times 10^{-6}$	1.0×10^{-6}	3.0×10^{-6}	$<7.5 \times 10^{-7}$
ITS-1	30	1200	3.3	[c]	Glassy[d]	0.8	1.0	1.2×10^{-5}	1.1×10^{-6}	5.7×10^{-6}	7.1×10^{-7}	3.5×10^{-5}	6.3×10^{-7}
	30	1300	1.4	[c]	Glassy[d]	0.8	1.0	1.6×10^{-5}	2.9×10^{-7}	2.1×10^{-5}	1.3×10^{-6}	2.5×10^{-5}	5.5×10^{-7}
ITS-1	40	1200	5.0	[c]	Crystalline[d]	1.1	1.5	1.3×10^{-5}	6.3×10^{-6}	6.5×10^{-6}	1.6×10^{-6}	6.5×10^{-6}	3.2×10^{-6}
	40	1300	3.7	[c]	Crystalline[d]	1.1	1.5	3.9×10^{-5}	1.8×10^{-5}	1.5×10^{-5}	9.0×10^{-6}	6.4×10^{-5}	2.7×10^{-5}
ITS-1	50	1200	6.1	[c]	Crystalline[e]	1.4	1.8	4.2×10^{-4}	2.4×10^{-4}	8.0×10^{-3}	9.6×10^{-4}	5.1×10^{-4}	1.4×10^{-4}
	50	1300	6.3	[c]	Crystalline[d]	1.4	1.8	1.8×10^{-4}	8.3×10^{-5}	2.4×10^{-3}	4.8×10^{-5}	5.6×10^{-4}	2.6×10^{-4}
ITS-2	20	1200	1.3	0.003	Glassy[d]	0.6	0.7	2.8×10^{-6}	8.8×10^{-7}	5.4×10^{-6}	2.2×10^{-6}	8.4×10^{-6}	2.8×10^{-6}
	20	1200[f]	1.2[g]	[c]	Glassy[d]	0.6	0.7	4.6×10^{-6}	1.5×10^{-6}	9.6×10^{-6}	2.4×10^{-6}	1.6×10^{-5}	5.6×10^{-6}
	20	1300	2.0	0.003	Glassy[d]	0.6	0.7	5.0×10^{-6}	6.7×10^{-7}	$<4.0 \times 10^{-6}$	1.8×10^{-6}	5.3×10^{-6}	1.9×10^{-6}
ITS-2	30	1150	2.0	[c]	Glassy[h]	0.8	1.0	-	-	-	-	-	-
	30	1200	1.4[g]	[c]	Glassy[d]	0.8	1.0	-	-	-	-	-	-
	30	1200	3.2[g]	0.006	Glassy[d]	0.8	1.0	3.0×10^{-6}	1.1×10^{-6}	4.0×10^{-6}	1.1×10^{-6}	5.0×10^{-6}	5.2×10^{-7}
	30	1200[f]	[c]	[c]	Glassy[d]	0.8	1.0	3.0×10^{-6}	7.8×10^{-7}	4.4×10^{-6}	1.1×10^{-6}	$<3.3 \times 10^{-6}$	$<8.2 \times 10^{-7}$
	30	1300	1.6	[c]	Glassy[d]	0.6	1.0	-	-	-	-	-	-
	30	1300	4.9	0.003	Glassy[d]	0.8	1.0	1.4×10^{-6}	2.4×10^{-7}	$<3.3 \times 10^{-6}$	$<8.4 \times 10^{-7}$	$<2.5 \times 10^{-6}$	$<6.3 \times 10^{-7}$
ITS-2	40	1200	2.2[g]	[c]	Glassy[d]	1.1	1.5	-	-	-	-	-	-
	40	1200	3.7	0.006	Crystalline[d]	1.1	1.5	9.7×10^{-6}	3.2×10^{-6}	5.4×10^{-6}	$<1.1 \times 10^{-6}$	8.0×10^{-6}	1.6×10^{-6}
	40	1200[f]	[c]	[c]	Glassy[d]	1.1	1.5	9.2×10^{-6}	3.3×10^{-6}	1.2×10^{-5}	4.0×10^{-6}	6.3×10^{-6}	1.2×10^{-6}
	40	1300	3.0	0.007	Crystalline[d]	1.1	1.5	1.5×10^{-5}	1.9×10^{-6}	$<3.8 \times 10^{-6}$	$<9.5 \times 10^{-7}$	4.9×10^{-6}	1.3×10^{-6}
ITS-2	50	1150	7.8[g]	[c]	Crystalline[h]	1.4	1.8	-	-	-	-	-	-
	50	1200	[c]	[c]	Crystalline[e]	1.4	1.8	1.5×10^{-4}	7.5×10^{-5}	1.8×10^{-3}	4.7×10^{-4}	2.7×10^{-4}	2.9×10^{-4}
	50	1300	5.1	[c]	Crystalline[h]	1.4	1.8	8.7×10^{-5}	6.3×10^{-5}	2.6×10^{-4}	9.2×10^{-5}	2.7×10^{-4}	1.3×10^{-4}

[a] Melting range was 50° to 200° below furnace temperature.

[b] Determined by X-ray emission analysis of representative products.

[c] Not determined.

[d] Nonporous.

[e] Some pores present.

[f] Melt cooled to room temperature in *ca.* 1 hr; all other cooled to room temperature in *ca.* 4 hr.

[g] Volatility experiment performed in closed system; all others performed in open system (Figure 3).

[h] Quite porous.

TABLE V

APPLICATION OF ENDOTHERMIC PROCESS TO ACTUAL ITS WASTE

Conditions:

Charge composition - 30 wt% ITS waste[a] - 70 wt% basalt

Melt temperature - 1200 °C

Cooling rate - slow (4 hr to 25 °C)

Product Properties:

Appearance - dense, nonporous glass

^{137}Cs content - 57 μCi per gram

Leach Rates

	24 hr	96 hr
Bulk leach rate (g/cm^2 day)[b]	1.6×10^{-6}	2.3×10^{-6}
Leach rate based on ^{137}Cs (g/cm^2 day)[b]	8.8×10^{-8}	3.0×10^{-8}

[a] 15 g waste from Tank 116-TX dried 16 hr at 140 °C.
[b] Method for determining leach rates given on p. 12.

waste range from 1.7×10^{-7} to 2.4×10^{-4} and from 2.4×10^{-7} to 7.5×10^{-5} g/cm^2 day, respectively. The leach rates (96-hr) based on ^{137}Cs vary proportionately with bulk leach rates and for immobilized ITS-1 and ITS-2 waste range from 9.6×10^{-4} to 5.5×10^{-7} and from 4.7×10^{-4} to 5.2×10^{-7} g/cm^2 day, respectively.

Bulk leach rates of the one glass made from actual ITS waste (Table V) compare very favorably with those for glasses containing the same amount (30 wt%) of synthetic waste. However, for 96-hr leach periods the leach rate based on ^{137}Cs of the radioactive glass is about 20 to 40 times lower than that of glasses made from simulated waste--3.0×10^{-8} g/cm^2 day versus 1.3×10^{-6} to 7.1×10^{-7} g/cm^2 day. This difference in leach behavior is reasonable in view of the large difference in amount of cesium in the two glasses--0.8 wt% in glasses made from simulated waste and only 0.00007 wt% ^{137}Cs in glass made from actual ITS waste. The probability that all the cesium will be entrapped in an immobile silicate glass increases with decreasing amounts of cesium in the glass.

Because steady-state conditions may not have been reached after only 96-hr leaching, leach rates listed in Tables IV and V are likely somewhat higher than equilibrium values. Limited extended leach tests indicate that at least four weeks are required to reach steady-state leach rates, which may be an order of magnitude lower than those obtained after only 96 hr of leaching.

For the range of conditions listed in Table IV changes in the rate at which the melt was cooled did not affect leach rates of the resulting immobilized waste product. However, leach rates of glasses from melts heated to 1300 °C are slightly lower than those from melts heated to 1200 °C.

Leach rates of both immobilized ITS-1 and ITS-2 waste increase as the amount of waste in the melt increases. Leach rates of products containing 50 wt% waste are particularly high. Thus, to obtain satisfactorily immobile products, the Endothermic process charge should contain no more than 40 wt% ITS waste.

Just as observed in tests of the Exothermic process[4] (Hanford Thermite process), the increase in leach rates with increasing waste charge is more pronounced with ITS-1 waste than with ITS-2 waste. The ITS-1 waste contains about seven times as much NaOH and only about one-fourth as much $NaAlO_2$. This difference in composition is sufficient, apparently, to increase water solubility of immobilized ITS-1 waste.

Devitrification Behavior

Some of the glasses obtained by solidifying high-level Purex process wastes are known to crystallize (devitrify) when stored at high temperatures.[8,9] Devitrification is often accompanied by an increase in leach rate of one or more particular elements. Results in Table VI indicate silicate glasses made by the Endothermic process do not devitrify readily. Thus, none of the glasses treated for two weeks at either 350 or 550 °C contained detectable crystalline phases. Leach rates for the heated glasses were all equal to or slightly below those of the same glasses stored at room temperature.

It should be emphasized that because of their low radioisotopic content (*cf*. Table I) Endothermic process glasses made from ITS waste will never attain temperatures as high as 350 °C during storage. Chances of these glasses devitrifying thus become even more remote. The thermal conductivity of actual ITS waste at 25 to 30 °C is typically 0.7 to 0.8 watts/meter °C.[10] The thermal conductivity of Endothermic process products has not been measured yet but is thought to be in the same range.

EFFECTS OF ADDITION OF B_2O_3

Several processes for conversion of high-level Purex process wastes into immobile borosilicate glasses have been announced.[11-14] Incorporation of boron into silicate glasses is beneficial to reduce melting temperatures and, hence, to lower energy requirements for glass formation.

Addition of B_2O_3 to mixtures of ITS waste and basalt reduces their melting temperatures by 100 to 200 °C. Exact melting temperatures of ITS waste-basalt-B_2O_3 mixtures have not been measured. Qualitative measurements indicate,

TABLE VI

EFFECTS OF STORAGE TEMPERATURE ON PROPERTIES OF ENDOTHERMIC PROCESS GLASSES

Wt% ITS-2 Waste in Glass	Storage Temp, °C	Product Appearance		Bulk Leach Rate g/cm^2 day		Leach Rate Based on Cs g/cm^2 day		Leach Rate Based on Sr g/cm^2 day	
		Before Storage	After Storage	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
20	~25	Glassy	Glassy	2.8×10^{-6}	8.8×10^{-7}	4.5×10^{-6}	1.8×10^{-6}	9.0×10^{-6}	3.0×10^{-6}
20	350	Glassy	Glassy	1.7×10^{-6}	2.4×10^{-7}	3.5×10^{-6}	$<8.8 \times 10^{-7}$	$<5.3 \times 10^{-6}$	$<1.3 \times 10^{-6}$
20	550	Glassy	Glassy	1.9×10^{-6}	3.8×10^{-7}	$<3.0 \times 10^{-6}$	7.5×10^{-7}	$<4.6 \times 10^{-6}$	$<1.1 \times 10^{-6}$
30	≈25	Glassy	Glassy	3.0×10^{-6}	1.1×10^{-6}	4.0×10^{-6}	1.0×10^{-6}	5.0×10^{-6}	5.2×10^{-7}
30	350	Glassy	Glassy	2.3×10^{-6}	3.8×10^{-7}	$<3.0 \times 10^{-6}$	1.0×10^{-6}	$<4.0 \times 10^{-6}$	$<1.0 \times 10^{-6}$
30	550	Glassy	Glassy	5.5×10^{-6}	7.4×10^{-7}	$<3.0 \times 10^{-6}$	$<7.5 \times 10^{-7}$	$<4.0 \times 10^{-6}$	1.0×10^{-6}
40	≈25	Crystalline	Crystalline	9.7×10^{-6}	3.2×10^{-6}	4.9×10^{-6}	$<1.1 \times 10^{-6}$	8.0×10^{-6}	1.6×10^{-6}
40	350	Glassy	Glassy	9.2×10^{-6}	2.9×10^{-6}	2.5×10^{-6}	1.3×10^{-6}	7.3×10^{-6}	1.5×10^{-6}
40	550	Glassy	Glassy	6.1×10^{-6}	1.1×10^{-6}	2.0×10^{-6}	1.4×10^{-6}	5.2×10^{-6}	9.3×10^{-7}

however, that the melting range of such mixtures decreases from about 1150 °C to about 1000-1050 °C as the amount of B_2O_3 increases from 0 to 10 wt%.

Endothermic process glasses containing 2 to 16 wt% B_2O_3 leach in water at rates comparable to those of ITS waste-basalt glasses containing no boron (Table VII). [Except in the experiment with "wet" waste the waste:basalt ratio was held constant at 25:1 in these experiments.] At higher concentrations of B_2O_3, however, leach rates increase significantly. All of the melt composition listed in Table VII yielded dense, nonporous glasses.

In the test with "wet" waste about half of a mixture of 60 grams of basalt and 10 grams of B_2O_3 was placed in a graphite-clay crucible. The wet ITS waste (40 grams) was placed on top of the basalt-B_2O_3 mixture and then the remaining basalt-B_2O_3 charge was added. Melting of this charge at 1200 °C proceeded routinely with smooth evolution of water and NO_x vapors. The resulting glass appeared identical to glasses obtained with dry waste and exhibited very similar leaching behavior. Although not conclusive, these results suggest that extensive drying of the actual ITS waste may not be necessary to obtain satisfactory feed to the Endothermic process.

VOLATILIZATION OF CESIUM AND STRONTIUM

Only very small (≈0.01%) amounts of strontium volatilize when ITS waste is immobilized by the Endothermic process (Table IV). Considerably more cesium volatilizes, however, as is to be expected from the known volatility of cesium metal and oxide. [Even so, less than 5% of the cesium reported to the off-gas stream in any of the tests (Tables IV and VII) with 20 to 40 wt% simulated ITS waste.] For

TABLE VII

EFFECTS OF ADDITION OF B_2O_3 TO BASALT-ITS WASTE MELTS

Melt Composition, wt%			Furnace	Cs Volatilized	Bulk Leach Rate		Leach Rate Based on Cs		Leach Rate Based on Sr	
					g/cm^2 day		g/cm^2 day		g/cm^2 day	
Basalt	Waste[a]	B_2O_3	Temp[b], °C	%	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
70.	30.	0	1200	3.2	3.0×10^{-6}	1.1×10^{-6}	3.8×10^{-6}	1.0×10^{-6}	5.0×10^{-6}	5.1×10^{-7}
68.6	29.4	2	1200	2.5	3.3×10^{-6}	1.0×10^{-6}	3.0×10^{-6}	1.4×10^{-6}	$<2.4 \times 10^{-6}$	$<4.2 \times 10^{-7}$
63.7	27.2	9.1	1200	1.0	3.9×10^{-6}	6.0×10^{-7}	7.1×10^{-5}	2.9×10^{-6}	3.8×10^{-6}	6.7×10^{-7}
58.3	25.	16.7	1200	1.0	4.2×10^{-6}	1.1×10^{-6}	3.8×10^{-6}	2.1×10^{-6}	5.0×10^{-5}	3.2×10^{-6}
50.1	21.4	28.5	1200	0.2	4.3×10^{-5}	1.8×10^{-5}	7.6×10^{-5}	3.1×10^{-5}	1.2×10^{-4}	9.3×10^{-6}
63.7	27.2	9.1	1050	0.5	3.4×10^{-6}	7.7×10^{-7}	6.1×10^{-6}	1.5×10^{-6}	4.5×10^{-6}	1.4×10^{-6}
54.5	36.4[c]	9.1	1200	-	5.2×10^{-6}	1.5×10^{-6}	6.4×10^{-6}	2.6×10^{-6}	9.6×10^{-6}	1.4×10^{-6}

[a] ITS-2 waste; *cf*. Table I.
[b] Melting temperature was 50 to 150 °C below furnace temperature.
[c] "Wet" waste described on p. .

favored process flowsheet (Figure 1) conditions with actual ITS waste-basalt charges containing 10 to 15 wt% B_2O_3, only 0.5 to 1.0% of the cesium will volatilize.

Completely reliable and reproducible results for the amount of inert cesium volatilized in the various tests with simulated ITS waste were not obtained. Within the uncertainty of the data and for comparable experimental conditions, cesium volatilization determined with the "open" equipment arrangement (Figure 3) is the same as that measured in a "closed" system (p. 9). Cesium volatility appears to be insensitive either to differences in composition of the two synthetic wastes or to differences in the maximum furnace temperature. About the same amount of cesium volatilizes from charges containing from 20 to 40 wt% waste; cesium volatility increases markedly when the charge contains 50 wt% ITS waste. Finally, and most significantly, cesium volatility falls sharply when B_2O_3 is added to the waste-basalt charge (Table VII).

Only 0.25% of the ^{137}Cs in the 116-TX Tank waste volatilized when this waste was immobilized with basalt (Table V). This value is about 10 times less than observed (Table IV) for comparable melt conditions with ITS-2 waste. This difference in cesium volatility, just as for cesium leachability (p. 16) is likely related to the $\simeq 10^4$ lower cesium content of the radioactive ITS waste.

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REFERENCES

1. D. E. Larson, *Radioactive Waste Management Program*, ARH-2185, Atlantic Richfield Hanford Company, Richland, Washington, January 1971.
2. W. W. Schulz, M. J. Kupfer, and G. S. Barney, *Immobilization of High-Level Radioactive Wastes--Proposed Laboratory Studies*, ARH-2407, Atlantic Richfield Hanford Company, April 1972.
3. L. E. Brownell, R. E. Isaacson, M. J. Kupfer, and W. W. Schulz, *The Thermalt Process for Immobilization of Radioactive Wastes*, ARH-2059, Atlantic Richfield Hanford Company, April 1971.
4. M. J. Kupfer and W. W. Schulz, *Application of the Hanford Thermite Process to Increase Immobilization of In-Tank Solidified Waste*, ARH-2458, Atlantic Richfield Hanford Company, September 1972.
5. a. J. Saidl and J. Rálková, "Verfestigung Hochaktiver Abfälle. 2. Mitteilung: Basalt, Vorteilhaftes Inkorporierungs--und Fixerungsmediums," *Kernenergie 10*:129 (1967).
   b. *Ibid.* "3. Mitteilung: Diffusions--and Elutions--raten von in Basalten eingeschmolzenen Radionuckliden," *Kernenergie 10*:340 (1967).
   c. *Ibid.* "3. Mitteilung: Diffusions - and Elutions - raten von in Basalten eingeschmolzenen Radionukliden," *Kernenergie, 10*:340 (1967).

d. *Ibid.* "5. Mitteilung: Wärmeentwicklung und Temperaturverteilung in Basalt nach dem Verschmelzen mit hockaktiven Abfäll," *Kernernergie 10*:372 (1967).

6. H. W. Godbee, C. W. Clark, and C. L. Fitzgerald, "Physical Properties of Solids Incorporating Simulated Radioactive Wastes," *Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, February 14-18, Richland, Washington,* CONF-660208, November 1966.

7. *Quarterly Progress Report Research and Development Activities Waste Fixation Program December 1972 through March 1973*, A. M. Platt, compiler, BNWL-1741, Pacific Northwest Laboratories, Richland, Washington, April 1973.

8. R. G. Thompson, J. E. Mendel, and J. H. Kleinpeter, *Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste*, BNWL-1393, Pacific Northwest Laboratories, June 1970.

9. W. Heimerl, H. Heine, L. Kahl, H. W. Levi, W. Lutze, G. Malow, E. Schiewer, and P. Schubert, "Studies on the Behavior of Radioactive Waste Glasses," *Symposium on the Management of Radioactive Wastes from Fuel Reprocessing, Paris, France, 27 November-1 December 1972*, Hahn-Meitner Institute, Berlin, Germany, 1972.

10. D. G. Bouse, Unpublished Data, Atlantic Richfield Hanford Company, 1972.

11. J. R. Grover and B. E. Chidley, *Glasses Suitable for the Long-Term Storage of Fission Products*, AERE-R-3178, Atomic Energy Research Establishment, Harwell, England, July 1960.

12. N. N. Eillot and D. B. Auty, *The Durability of "FINGAL" Glass, Part I*, AERE-R-5151, Atomic Energy Research Establishment, Harwell, March 1967.

13. W. Heimeil *et al. Research on Glasses for Fission Product Fixation, Summary Report, January 1968-June 1971*, HMI-B109, Hahn-Meitner Institute, Berlin, September 1971.

14. J. E. Mendel and J. L. McElroy, *Waste Solidification Program, Volume 10, Evaluation of Solidified Waste Products*, BNWL-1666, Pacific Northwest Laboratories, July 1972.

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