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BNWL-200
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**FIXATION OF HIGH-LEVEL RADIOACTIVE WASTES
IN PHOSPHATE GLASS--
HOT CELL GLASS EXPERIMENT**

U. L. UPSON

JANUARY, 1966

DATE TO	DATE	EXAM	FORWARDED TO
<i>RJ Smith</i>	<i>30519</i>	<i>328</i>	<i>1230 1966</i>

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ERRATA

All activity data of Tables III and IV and Figures 24 and 25 are based on erroneously reported data. The corrected values are 1/10 the indicated values.

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FIXATION OF HIGH-LEVEL RADIOACTIVE WASTES
IN PHOSPHATE GLASS--
HOT CELL GLASS EXPERIMENT

By

U. L. Upson

Chemical Research Section
Chemistry Department

January, 1966

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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FIXATION OF HIGH-LEVEL RADIOACTIVE WASTES
IN PHOSPHATE GLASS - HOT CELL GLASS EXPERIMENT

SUMMARY

Phosphate glass has been produced from actual high-level fuel-reprocessing waste, demonstrating the technical feasibility of the Brookhaven continuous phosphate glass process. In this process, an aqueous waste is converted directly to a phosphate glass, with no intermediate drying or calcination step. The conversion to glass yields a waste product volume of about 5 gal per ton of uranium processed, a 15- to 20-fold reduction from that of currently stored liquid Purex wastes. In this demonstration, aged Purex 1WW waste, deficient in Ce^{144} and Zr-Nb^{95} , was converted to a glass with a density of 2.68 g/cm^3 , containing $\sim 400 \text{ Ci/liter}$ total gamma activity, and producing about 2 W/liter thermal power.

Demonstration of the Brookhaven process in the Hanford High-Level Radiochemical Facility was dictated by the need for a feasibility study prior to completion of the Waste Solidification Engineering Prototype facility at this site, as well as by the availability of suitable high-level liquid waste, and of existing hot-cell facilities and experienced personnel. A study of waste solidification by spray and pot calcination had just been completed, the calcination equipment was still in the cell, and much of the existing off-gas train was suitable for the glass process. To save time and expense, small-scale pilot-plant glassmaking equipment was installed in the limited remaining space, by remote handling, without decontaminating the cell or removing any of the calcination equipment. Four batches of glass were produced, but near the end of the last run, a melt pot failure destroyed the melter furnace and terminated the study. Difficulty was experienced in reconciling feed concentrator flow and adequate premelter concentration, and the actual waste was found to behave unlike the "simulated" wastes

of prior studies, possibly because of inadequate analytical data on the feed waste, and possibly because of radiolytic effects.

Leachability of the product glass was as good as that of similar "cold" glasses, and has remained substantially constant for glass stored in dry air. Storage in moist air yielded 5- to 10-fold increase in leachability in the same period. After 6 mo, microscopic exudations appeared on the surfaces of polished specimens of the glass. The cause could be either a radiolytic effect or excess phosphoric acid in the initial composition.

Contamination (especially by ruthenium) of the platinum melter lining was found to have penetrated throughout the metal, requiring dissolution and electrolytic separation for platinum recovery.

The inherent instability of the glassy state, especially at temperatures near the melting point, suggests that alternative polycrystalline forms also should be investigated.

INTRODUCTION

The advent of large-scale controlled nuclear fission has brought with it the problem of disposing of large quantities of highly radioactive wastes. In the processes for recovering uranium and plutonium from irradiated fuels, whether from weapons-production or power reactors, nearly all (> 99%) of the fission products are contained in the first stage chemical effluent wastes, typically about 1200 to 1600 gal of waste for each ton* of uranium processed.^(1b,1c) These wastes are stored either as highly concentrated acidic wastes (8-12 gal/ton U)^(1c) or as moderately concentrated alkaline wastes (60-500 gal/ton),^(1b) in stainless steel or

* The metric ton (1 tonne = 10^6 g = 1.1 U.S. short ton) will be used throughout this report.

or mild steel tanks, respectively. More than 75 million gallons of high-level wastes are now stored in underground tanks throughout the USAEC complex.^(1a,1b,2) These wastes will retain dangerous levels of radioactivity for hundreds of years, and will require cooling and controlled venting for much of this period.^(1b)

With the growth of the nuclear power industry, the activity levels and quantities of these wastes will increase markedly, greatly complicating an already burdensome problem. Moreover, while the earlier reactors were located distant from population centers, and were provided with adjacent fuel reprocessing and waste storage facilities, new power reactors are being built closer to the consumer markets, and probably will be dependent upon remote facilities for fuel reprocessing and refabrication.

The growing utilization of separated fission products for power generation in remote areas—or in space, for food sterilization, and for agricultural applications, as well as in medicine and research, inevitably will lead to the depletion of selected radioactive species in some future wastes and in some wastes now in storage. Nevertheless, the overall expectation is that increasing amounts of more highly radioactive wastes, originating in more widely scattered locations, will require some form of "ultimate" disposal. Although liquid storage in underground tanks has proven satisfactory during the last 20 yr, it does not constitute a desirable long-term solution.

The need for more economical and more permanent methods for the disposal of these wastes has led to extensive studies of various alternatives.⁽¹⁻³⁾ Conversion of the liquid waste to a stable, dense, solid medium is desirable for both storage and transportation.^(1d-f) Conversion to a glass offers the possible advantages of lower leachability, higher thermal conductivity and improved mechanical integrity; and considerable attention has been given to various methods for producing suitable glasses.^(1g-m) In all such

processes, the additives necessary for glass formation ordinarily do not adversely affect volume reduction, but may even enhance it, the added material usually resulting in increased density in the final product. Several of the processes under development throughout the world involve the formation of phosphate glasses,^(1a,g-j,m) and one of these^(1m) was the subject of this study.

In a process developed at Brookhaven National Laboratory (BNL), a phosphate glass is produced directly and continuously from an aqueous process waste, without a separate intermediate drying step.⁽⁴⁾ For a wide range of waste compositions, phosphoric acid is the only necessary additive, but metal ions can be added to improve the glass characteristics. Extensive testing by BNL's Nuclear Engineering Department showed this to be a feasible process,⁽⁵⁾ and the next logical step was to demonstrate the process with actual high-level wastes. Since BNL has no high-level engineering facilities and no easy access to high-level wastes, this demonstration, the Hot Cell Glass Experiment, was undertaken as a joint effort by BNL and Hanford Laboratories [now Pacific Northwest Laboratories (PNL)], and was carried out in one of the shielded cells (A-Cell) of the 325-A Building High-Level Radiochemistry Facility. The cell operations were conducted by Hanford personnel who had gained applicable experience in the immediately preceding work on waste calcination.^(1d, 6, 7)

The objectives of this experiment were:

1. to determine whether or not phosphate glasses could be formed by this process from highly radioactive wastes.
2. to evaluate the radiochemical problems associated with the process, and
3. to produce samples of phosphate glass, and to evaluate their mechanical and chemical stability and their resistance to leaching by water and other media.

Evaluation of the process with regard to engineering, equipment, and chemical behavior also was an objective of this study, but

primarily only insofar as the actual radioactive wastes differed from the simulated wastes, since these factors can be evaluated more easily in nonradioactive studies. Such "cold" studies have been extensive, both at PNL and at BNL, and are continuing at both sites.^(5,8) Semiplant studies of this process, among others, will be made with high-level wastes in the Waste Solidification Engineering Prototype to be installed in the Fuel Recycle Pilot Plant,* now under construction at Pacific Northwest Laboratories.

The Brookhaven Continuous Phosphate Glass Process

The Brookhaven continuous phosphate glass process consists simply of adding glass-forming chemicals (chiefly phosphoric acid) to the radioactive waste, evaporating the mixture to the maximum concentration consistent with reliable fluid flow, and continuously adding the concentrated mixture to a glass-forming crucible or "melter". The glass so formed can be retained for storage in an expendable melter, or can be dumped or poured batch-wise into separate molds or storage receivers, or continuously (or semicontinuously) delivered from the melter (e.g. by overflow) into receiving vessels—or a trough or "belt", for solidification, annealing, and cooling. The water and condensable volatile chemicals expelled from the evaporator and from the melter must be collected for recycle or storage, being too radioactive for casual disposal, and the off-gas must be decontaminated of airborne non-condensable or particulate radioactive material.

Two alternative flowsheets for the off-gas equipment employed in this study are shown in Figure 1. Both are modifications of the Brookhaven flowsheet, in which the concentrator and melter off-gas streams are completely separate and parallel.⁽⁴⁾ In our "basic" flowsheet, the only significant change is that of cascading the concentrator off-gas condensers (N-1 and N-2) behind the melter off-gas condensers (S-1 and S-2), yielding improved removal of fogs and entrained material from the melter off-gas. In the

* Later renamed Chemical and Materials Engineering Laboratory (CMEL).

FIGURE 1

Hot Cell Glass Experiment Flow Sheet

Neg. 0650957-1

second scheme, a fractionating absorption tower replaces the simple condensers in the melter off-gas line. The bottom section of the packed tower is saturated with refluxing sulfuric acid, greatly reducing sulfuric fog and entrainment in the melter off-gas. Introduction of the concentrator off-gas below the top of this column serves to remove from that stream any sulfuric acid evolving from the concentrator, and to combine it with that stripped from the melter off-gas and return it to the boiler of the fractionator. The boiler is provided with a trapped overflow tube, and the excess sulfuric acid constitutes a low-volume (<2 gal/ton), relatively non-corrosive "throwaway" stream which is 85-90% sulfuric acid and 2-10% phosphoric acid. In contrast, the "sulfuric" stream obtained by simple condensation contains in addition 5-10% of the water in the feed and a similar fraction of the nitric acid, and constitutes a fairly high-volume (4-12 gal/ton) and corrosive intermediate waste. (See also "The Sulfate Problem").

The "fractionator" flowsheet was employed for the first two runs to ensure favorable performance; but this arrangement does not yield samples for determination of the condensable constituents in the melter off-gas, since the volatile constituents are combined with the concentrator off-gas. The "basic" flowsheet was employed for the remaining runs in order to provide the requisite samples.

Feed Composition

An "ideal" feed composition would involve the best combination of low additive cost, a reasonably low glass-forming temperature, and low corrosivity (both feed and glass), as well as a product having low final volume (per unit processed fuel), high thermal conductivity and thermal stability (to minimize container size and cooling requirements), high mechanical integrity and strength, and low leachability. These characteristics will not all be optimal in any one feed composition, and in any given case the selected composition will depend on an evaluation of the relative importance of each characteristic. For this study, the feed composition was chosen to accommodate the available waste and yet yield a moderately dense, stable, and leach-resistant glass at a moderate temperature (1200 °C); and no attempt was made to optimize any characteristic. In view of the uncertainties in the composition of the "hot" feed and of the effects of radiolysis upon the reactions involved in the concentration and glass-formation steps, a "safe and simple" formulation was chosen for the initial studies. Plans to try other compositions were thwarted by equipment failure during the fifth run.

The Purex 1WW waste is considered characteristic of the general composition of anticipated power reactor feeds. A cask of this waste (~ 1000 MWd/ton, 56 gal/ton) was on hand in the 325-A Building, having been used in the preceding calcination studies, and this aged (~ 600 -day-old) Purex waste was used in this study.

Analyses of this waste are given in Table I, columns A and B. Also shown are the make-up compositions of simulated wastes used in the "cold" studies, and the anticipated compositions of wastes from processing high-burn-up power reactor fuels, normalized to the same fuel-equivalent concentration (parenthetical values).

TABLE I
PUREX HIGH-LEVEL WASTE COMPOSITIONS

Concentration, gal/ton uranium	Actual Purex HW Analyses				Simulated Purex Waste Make-Up			
	A	B	C		D	E	F	
	56	56	95	(56)*	-	-	100	(56)*
<u>Process Chemicals</u>								
Na	1.48M	1.5M	0.61	(1.03)M	1.5M	1.4M	0.35	(0.63)
Fe	0.41	0.37	0.29	(0.49)	0.30	0.37	0.080	(0.142)
Al	0.18	n.d. [†]	0.11	(0.19)	0.18	0.16	0.040	(0.071)
Cr	0.017	n.d.	n.d.		0.018	0.07	0.016	(0.029)
Ni	(0.008)**	n.d.	n.d.		0.008	0.035	0.008	(0.014)
H ⁺	2.9	3.2	2.4	(4.1)	~3.0	var.	Bal.	---
NO ₃	4.7	3.9	3.7	(6.3)	4.7	var.	4.64	(8.3)
SO ₄	0.47	n.d.	0.24	(0.41)	0.5	0.52	0.13	(0.21)
PO ₄	n.d.	n.d.			0	0	(0.005)	(0.009)
F	n.d.	n.d.	~0.002	(~0.003)	0	0		
SiO ₂	0.14	n.d.			0	0.016	(0.008)	(0.014)
<u>Fission Products</u>								
Zr					0.045	0.033	0.065	(0.116)
Ru					---	---	---	
Cs					0.027	0.015	0.035	(0.062)
Sr					0.012	0.0097	0.016	(0.029)
Ba					0.012	0.0072	0.020	(0.036)
Rb					---	0.0036 (K)	0.007	(0.013)
Re + Y					0.094 (Ce)	0.057 (Mx)	0.179	(0.212)
Mo					0.043	0.026	0.065	(0.115)
Total Fission Products			~0.02	(~0.03)	0.23	0.17 (var.)	(0.415)	(0.741)

* Normalized to 56 gal/ton for comparison

** Estimated

[†] Not determined

A Centrifuged waste used as feed for calcination and glass-making studies, analysis at age ~200 day (November, 1963) (Reference 6)

B Same waste at ~550 days (October, 1964) "Corroboration" analysis prior to glass runs.

C Earlier waste used in calcination studies, excessively diluted by jet steam (Reference 6).

D Cold simulated waste used in these studies, fission product levels equivalent to ~10,000 MWd/ton waste. Cerium "standin" for total rare earths and yttrium.

E Cold simulated waste used in G. B. Barton studies. Fission product ratios fixed but total fission product and HNO₃ necessary to dissolve variable (~10,000 MWd/ton shown here).

F Design base WSEP waste--20,000 MWd/ton, C. R. Cooley "Projected Waste Compositions for WSEP Studies," May 6, 1965.

The feed storage cask (Figure 2) was sparged with air through the dip leg for ~24 hr, and ~40 liters transferred to an intermediate, stirrer-equipped storage tank in one of the hot cells. Despite this precaution, the transferred feed is believed to have had disproportionately low solids content, since subsequent radio-analysis (~50 Ci/liter total) showed it to be lower than calculated

in Ce^{144} and in Zr-Nb^{95} , especially the latter. (It is believed that the precipitate had hardened on long standing, and that sparging merely tunneled a "well" through the caked precipitate.

For each "hot" run (except H-1), a 3-liter volume of feed waste was drawn from the in-cell storage tank, after agitation, and the phosphoric acid and ferric solutions (~ 1 liter total) added and mixed in a 4-liter Pyrex bottle, and allowed to stand overnight. Phosphoric acid* was added equivalent to the metal

FIGURE 2
Waste Storage Cask

* 820 ml of 85% H_3PO_4 per 3 liters of waste

cation analysis (including added iron) plus ~10% excess, to compensate for analytical error and P_2O_5 vapor loss from the melter (initial $M^+/P = 0.9$). This yields the metaphosphate compound, ($M^+/P = 1$) which forms the most stable glasses (See "The Cold Runs".⁽⁹⁾ To improve chemical durability (leach resistance), iron* was added to bring Fe^{+++} to 0.5M (Na/Fe = 3), for the "hot" feeds. (Other Na:Fe ratios, and other metal cation additions, were employed in some of the preliminary "cold" runs.) This feed has greater sodium content than believed typical of Purex wastes, and the resultant glass would be expected to have relatively high leachability at this iron content; but higher iron addition would have entailed higher glass-forming and melting temperatures, and for the initial runs formation of a true glass product was considered the most important objective.

In-Cell Operations

The prepared feed was transferred to the in-cell feed tank via the "load-in" line by applying vacuum to the feed tank. Solid material was kept in suspension by continuous circulation (at ~1 liter/min) through the splitter loop. The splitter could be controlled to divert from ~0.3 to ~10% of the recycle stream into the evaporator—i.e., from 3 to 100 ml/min. Normal flow to the evaporator was 8-12 ml/min, greater flow tending to yield a "wet" output (>20 gal/ton, bp <135 °C) which, in turn, lowered the melter temperature.

The concentrator effluent, a thick green "syrup" with "simulated" feeds, turned out with the actual waste to be a brown-gray mud with a watery liquid phase. The characteristic green color of the phosphoric complex was only faintly visible through the clear-glass periscope (undiscernible through the lead glass window). This failure to form the viscous green complex (which should have dissolved or "floated" the precipitate) is believed to have been due, at least in part, to radiolysis of the nitric acid. The situation was

* 240 g $Fe(NO_3)_3 \cdot 9H_2O$ per 3 liters of waste

alleviated, but not cured, by the addition of concentrated HNO_3 to increase the H^+ concentration in the feed by $\sim 1\text{M}$, to a nominal acidity of $\sim 4\text{M}$ (Runs H-4 and H-5). Plugging in the 1/4 in. OD concentrator-to-melter line was a severe problem in the first three runs, even though the line was heated. The problem may well be less troublesome with larger-scale equipment, but in any event appears to be much more severe with actual waste than with the not-too-well-simulated wastes used in the "cold" studies.

The melter operated with a bright cherry red ($\sim 1200^\circ\text{C}$) melt surface, with only a faint darkening at the drip point, when well-concentrated (15-20 gal/ton) feed was added at $\sim 3\text{ ml/min}$ or less—as observed during the cold runs. When surges or plug releases occurred in the concentrator, causing greater and/or wetter inputs to the melter, the melt surface tended to freeze over and "go black"; and in the case of substantial amounts of wet ($>25\text{ gal/ton}$) melter feed, heavy fogging occurred, exceeding the capacity of the fractionator. During normal operation, the fractionator functioned with no visible fog carry-through, in contrast to the simple condenser system, which always passed some visible fog.

A small flow of steam was injected following the last of the glass-process condensers (N-2), and condensed in the oversize Nionel condenser of the original calciner off-gas train, scavenging the residual radioactivity to a factor of $>10^8$ below the feed levels, except during upsets. A caustic scrubber, an electrostatic scrubber, and a silica gel bed were available between the final condenser and the final filters. These components were found to be unnecessary, but the silica gel bed was left in the line simply because it was more convenient to do so.

FIGURE 3
High-Level Radioactive Glass

TABLE II
GLASS LEACHABILITY - COMPARISONS

Glass	Storage Medium	Age, Days	Leaching Conditions			Leach Rate, (a) mg/dm ² day
			Medium	Temperature, °C	Period	
H-2	Air	20	H ₂ O	~25	24 hr	1.1
	Air	20	H ₂ O	~25	17 days	0.2
	Dry Air	37	H ₂ O	25	4 hr	1.1
	Saturated Air	37	H ₂ O	25	4 hr	2.1
	Water	37	H ₂ O	25	4 hr	1.1
Soda Lime ^(b)	Not Stated		H ₂ O	25	n.s.*	0.1
Borosilicate ^(c) (Pyrex 7740)	Not Stated		H ₂ O	25	6 hr	0.005
				100	6 hr	0.2
H-2 (Successive on same sample)	Air	62	2N NaOH	~25	10.5 hr	~2000
		63	H ₂ O	~25	10.5 hr	3.9
		64	2N HNO ₃	~25	4 hr	47
		65	H ₂ O	~25	4 hr	1.1
		66	2N NaOH	~25	4 hr	960
		67	H ₂ O	~25	4 hr	0.75
Borosilicate ^(d)	Not Stated		5% NaOH	40	n.s.	4
				65	n.s.	34
				100	n.s.	530
Borosilicate ^(b)	Not Stated		5% HCl	100	24 hr	0.5
Soda Lime ^(b)	Not Stated		5% NaOH	99	6 hr	320
			5% HCl	100	24 hr	5
			H ₂ O	25	n.s.	0.1

* n.s. = not stated

a Leach rate based on Cs¹³⁷ content of leach solution, for H-2 samples, and "as reported" for commercial glasses. (1 mdd = 1×10^{-5} g/cm² day)

b C. L. Mantell. "Engineering Materials Handbook," vol. 16, p. 27. McGraw-Hill, New York. 1958.

c Corning Glass Company (personal communication)

d H. H. Ohlig. "Corrosion Handbook," p. 355. John Wiley, New York. 1948.

In-Cell Equipment

The decision to install phosphate glass-making equipment in the calciner hot cell, without the expense and delay of removing the calcination equipment and decontaminating the cell, put rather severe restrictions on the size and arrangement of this equipment, and called for rather careful design. Except for the furnace, which could not be sufficiently reduced and which would have to be brought into the cell by an overhead crane—interrupting work in the other cells, all the equipment had to be designed so that it could be passed through an 8 x 8 in. transfer tunnel and remotely assembled inside the cell.

A small-scale apparatus for this purpose was fabricated at BNL, tested for 100 hr, and shipped to Hanford (Figure 4). This assembly was properly scaled (~0.5 liter/batch) and ingeniously devised, and served well to familiarize the writer with the process and its problems, but was considered too fragile for remote installation and operation.

During a series of "cold" runs in the BNL equipment, a number of modifications were made and tested, resulting in the flow-sheets of Figure 1. New components were designed, fabricated, and tested. Most of the new components were of stainless steel, and those in which glass or quartz were used (for corrosion resistance, process visibility, or ease of fabrication) were encased in protective sheathing. The final combination of components were assembled and tested, both for functional operation and for remote operability by manipulator, on a test stand which duplicated the calciner frame upon which the apparatus was to be mounted (Figure 5).

Equipment Assembly

The "cold" mock-up was disassembled and reassembled piecemeal in the hot cell. First to be installed was a crossbar which capped and clamped onto the two front jackleg housings of the

FIGURE 4
BNL Assembly

FIGURE 5
HCGE In-Cell Apparatus

Neg. 0642252-1

calciner.⁽⁶⁾ All other frame members were suspended from this crossbar and were steadied by clamping to a lower horizontal member of the calciner frame. Fortuitously, since the front of the calciner was the only available suitable space, mounting the equipment on the calciner made it possible to raise and lower the entire apparatus by means of the calciner jacks. This was a real advantage, both in assembly and in operation, since it gave a greater vertical range of manipulator access than otherwise available.

The feed tank assembly was mounted on a long, flat, U-shaped spine of 1/8 in. sheet, and was suspended from the left-hand clamping bolt of the crossbar. Next, the support rack was constructed in place by remote manipulation. This rack consisted of two 76-in. long 2 x 2 x 1/8 in. angles which were hung from stud bolts on the crossbar, and a "ladder" of eight 1/2-in. horizontal rods which fit into holes through the vertical angles. Each rod had preattached cross-rod connectors, with hex-head set screws in the open jaws. A vertical center rod with a preattached top connector was then installed to align and stiffen the cross-rods, and the furnace assembly, concentrator, and bottle holders (lower right) were then hung on the cross-rods. The fractionator and condenser assemblies were mounted on vertical rods which fit into prealigned fixed connectors on the cross-rods. The off-gas header was attached at the top of the frame, and connected by flexible tubing to the existing (calciner) off-gas train. The entire operation of conveying, assembling, and connecting the apparatus was completed without breakage or damage to any component, attesting to the high skill of the operators.

Equipment - Components

The feed tank assembly consisted of a 7-3/4 in. OD (11 liter) tank, a circulating pump, a magnetically operated stream splitter and associated valves and piping (Figure 6), and was installed as

FIGURE 6

Feed Tank and Melter Assemblies

Neg. 0641910-4

a prefabricated unit. All valves were placed and mounted so that the handles could fold into a 7-7/8 x 7-7/8 in. rectangle. Only the "Chem Add" funnel, the electrical outlet box (stud mounted through pear-shaped holes), the dip leg valve (front) and the tubing connections (to vacuum, load-in, air, water, and vent) required in-cell installation.

The "Chem Add" funnel permitted feed make-up in the feed tank, and was used during clean-up operations. It fed into a valved Y to permit either direct addition to the tank, or addition into the pump intake. Because of the high solids content in the feed, the tank was equipped with a spray head through which water additions were made (Figure 7). The nozzle was made from a short piece of 1/2 in. rod drilled to 3/16 in. ID which was inserted through a bulkhead fitting in the center of the tank top. Various angled milled slots provided fan-shaped curtains of water which effectively washed the tank walls. A float valve indicated the liquid level, and was provided with a top fitting to permit flushing the sight glass. The pump (an inexpensive unit with a polyethylene body) was accessible for replacement by raising the calciner to its highest position.

The stainless steel stream splitter (Figure 8) was provided with a lamp and a methacrylate window. A magnetic stainless pad was welded to the diverting tube, and was actuated by a coil (from a solenoid valve) mounted on a soft-iron-wire-filled tube stub, and energized by a 15-sec cycle "percentage" timer. An unbalanced Y in the splitter input yielded ~900 ml/mm by-pass and ~100 ml/mm flow to the diverter, providing adequate total flow for stirring and low enough splitter flow for a usable "on" time. To provide more nearly continuous flow to the concentrator, 3/32 in. bore tubing was used for the output from the "hopper", and this was coiled around a thermocouple well inside the concentration off-gas stack (1/2 in. tubing) to preheat the feed (to reduce the load on

FIGURE 7
Feed Tank Washdown Nozzle

FIGURE 8
Stream Splitter

the concentrator) and to reflux to the concentrator most of the sulfuric acid in the concentrator off-gas (Figure 9).

The concentrator consisted of a cylindrical pot with a conical bottom sloping downward from the center (Figure 1). Heat was applied to the bottom in two zones by a round (pancake) and a ring heater, and temperature was sensed and controlled by well thermocouples near the inlet (center) and outlet (wall) and by a thermocouple bonded to the pot wall near the outlet. Three C-shaped baffles served to direct the flow in a series of semi-circular paths from the center section to the outlet, to prevent mixing of the fresh and concentrated feeds* (Figure 10).

An experimental concentrator used in the cold runs consisted of a long tube (1/2 in. OD x 0.065 wall x ~16 ft long) coiled around and bonded to a 4-in. diam brass core (Figure 11). The core was heated by a ring of twelve 90 W rod heaters, controlled by a thermost switch in the center, and the upper half of the core was hollowed out with a tapered wall to give a temperature gradient (from ~105 to ~135 °C) down the top half of the coil. The feed ran down the coil in gutter flow, and the off-gas flowed upward counter-current to the liquid, giving excellent concentration and denitration with negligible sulfate vaporization or entrainment in the off-gas. On one occasion, however, a change in feed composition (the inclusion of lithium) resulted in excessive precipitate formation at the controlled temperature (which had not been readjusted for this feed), and the tube became so thoroughly plugged that cleaning by remote manipulation would have been extremely difficult. Because of this, since so little was known of

* This appears necessary in that there seems to be a minimum required "residence time" for the formation of a good glass-forming complex. Mixed solutions of the same averaged concentration and residence time do not behave in the same manner.

FIGURE 9
Preheat-Reflux
Unit

FIGURE 10
Baffled Concentrator

FIGURE 11
Inclined Tube
Concentrator

Neg. 0652195-2

how the actual waste would behave on concentration, this concentrator was not installed in the hot cell, but was replaced by the above less efficient unit which could be dismantled for cleaning.*

The line from the concentrator to the melter was provided with a glass section to permit visual observation of the flow— via the magnifying periscope (Figure 12). This section was connected to the stainless steel lines by spherical joints, and was formed in a trap which could be filled or drained by rotating in the joints. This trap served to prevent pressure transients from producing off-gas cross flow from the melter to the concentrator off-gas line.

* Actually, although quite seriously plugged on several occasions, the pot evaporator was cleaned up in each instance without removing the baffled cover plate.

FIGURE 12

Concentrator Assembly

Neg. 0642277-3

Plugging in this transfer line—or at the concentrator outlet, was by far the greatest operating difficulty. In this small-scale equipment, heated lines are necessary to prevent "freezing" of the concentrated feed, and even with the more tractable simulated feed occasional plugging occurred. A Variac-controlled heat lamp on an adjustable arm was found more convenient and effective than heating tapes, and permitted heating the glass section without impairing visibility. This worked well during the cold runs, but the altered nature of the actual waste, especially without added acid, made operation very difficult in the hot-cell runs. Quite likely, improved design or at least larger lines would have improved this situation; and, although their experience has been with simulated feeds only, BNL personnel anticipate no difficulty here in pilot plant or production scaled equipment.

The feed entered the melter through a water-cooled nozzle to prevent its being prematurely dried or calcined by radiant heat from the bottom of the melter and from the melt. The cooling jacket contained a small amount (~50 ml) of water which boiled furiously in the nozzle jacket, but which was retained and returned by a condenser coil in the jacket vent tube* (Figures 12 and 13). The cooled melter head refluxed condensible off-gas from the melter, keeping the head clean of scale and splatter. The melter head was equipped with a 1 in. quartz window through which (by means of periscope and mirror) the "color" of the surface melt could be observed.

Figure 13
Melter Head

Neg. 0652195-3

* This Hanford-originated technique has replaced the earlier method of pumping phosphoric acid coolant through the nozzle jacket and through a heat exchanger.

The melter pot consisted of a 90-mil thick Inconel 702 pot with a thin (7 to 15-mil thick) platinum liner. Although overflow-tube pots had been used in the "cold" studies, and were on hand for continuous operation, simple, untubulated pots were used for all the completed "hot" runs (Figure 14). The pots were ~3 in. diam x 10 in. high, with a flanged lip to which the head was clamped, pinching the platinum flange between the head and pot flanges. It was found necessary to groove the pot flange to accept a platinum wire (14 gage) O-ring, to prevent in-leakage between the pot and liner; and a small pinhole leak was put in the top of each liner, just below the flange, to prevent collapse of the liner under high temperature in a reduced pressure system. Such collapse occurred during a cold test of the equipment. As a further precaution, a water manometer and bubble manostat were installed in the off-gas header to limit the system "vacuum" to 3-4 in. of water. No liner collapses occurred during in-cell operation. Lining failures did occur, however, through pinhole leaks in the welds, both during the "cold" tests and during the final "hot" run, terminating the experiment (See "Pot Failures and Platinum Contamination").

The furnace element was a Kanthal type REH 10-30 (about 4 in. diam x 7-7/8 in. high, about 2 kW at 35 V) enclosed in a 9 x 9 x 12 in. high sheet metal (stainless steel) box in which it was supported on firebricks and insulated with Tipersul* and Fiberfrax**. Enclosed in the firebrick floor was a platinum-wound "freeze valve" heater, to surround the drain tube of the "continuous" melter liner. Below the furnace, and suspended therefrom, was a clamshell annealing furnace which clamped around a quartz tube collection and annealing compartment

* Fibrous potassium titanate (registered tradename of the E. I. du Pont de Nemours and Company).

** Ceramic fibers (registered tradename of the Carborundum Company).

(a) Continuous-Flow and Liner

(b) Batch Pot and Liner

FIGURE 14
Melter Pots and Liners

(Figures 7 and 15). The collection pot (a stainless steel beaker—see Figure 5) was raised into the annealing zone by a screw elevator in the pneumatically-operated platform which sealed the chamber during glass collection, and which lowered the pot for glass removal and pot replacement. (This feature was never used in the "hot" runs, owing to destructive equipment failure during the batch runs.)

FIGURE 15

Annealer

Neg. 0642277-4

The melter off-gas was conducted by two quartz ball-joint adapters* to a point near the bottom of the packed (1/2 in. berl

* To prevent fracture of socket sections, especially when the ball section is the hotter component (or for Pyrex balls in quartz sockets) the rim of the ball should be ground off to reduce the contact arc to ~150 degrees.

saddles) section of the 51 mm OD Vycor fractionator (Figure 16). The bottom 6 in. of the fractionator served as a wall-heated boiler, filled to overflow with concentrated sulfuric acid. Vapor from the boiler passed axially up the fractionator for 6 in. through an inverted funnel section which supported the packing, refluxing downward in the annular space up which the off-gas flowed. Sulfuric acid overflow (due to off-gas stripping) was through an axial tube with a pigtail trap at the top and a drip tip inside a larger ball-joint section at the bottom.

FIGURE 16
Melter
Off-Gas Connections

Samples of the hot concentrated acid overflow were obtained by tilting an offset adapter (by means of a jack under the "sulfuric tank") to provide a temporary cooling reservoir (Figure 17).

FIGURE 17

Annealer, "Sulfuric" Tank, and Sampler

The overhead from the fractionator, essentially the concentrator off-gas, was refluxed at $\sim 105^{\circ}\text{C}$ by a cold finger condenser at the top of the column, and then passed through two (entrance and exit) water-cooled condensers to yield the "nitric" condensate. (Cooling water flowed through all these condensers in series, counter-current to process flow.) The residual off-gas (mostly leakage air) was drawn into the manifold and to the large Nionel scavenging condenser in the calciner off-gas train (See Figure 1).

The sulfuric acid boiler section of the fractionator was heated by a cylindrical furnace element (Hevi-duty 82SP, 580 W), and the column temperature gradient was obtained by means of four heater tapes separately controlled by well thermocouples in the column. All heaters were wrapped in Fiberfrax blanket and protected by an aluminum outer shell.

"Nitric" samples were obtained by means of a hold-up sampler inserted on the entrance port of the "nitric tank" and a collection pocket (with stopcock drain) was added to the long glass off-gas tube from the concentrator to the fractionator (or S-1), to yield separate condensate samples at this point. (These samplers are not shown in Figure 5).

Off-gas samples were collected on Millipore filters in the same samplers used in the calcination study.⁽⁶⁾ An additional "roving" ball connector on a flexible tube was used to sample the melter off-gas line at the "sulfuric" tank vent-return socket.

The "Cold" Runs

A number of runs and tests were made with simulated or experimental feeds with various components and flow sheets, not only for familiarization with the process prior to "going hot", but also to evaluate component designs and to determine the permissible limits and effects of variations in feed composition and operating conditions.

For example, it was found that for the selected pot size and furnace element, melter temperature could not exceed $\sim 1250^{\circ}\text{C}$ at any appreciable input rate, even with well concentrated feed. By increasing the size and power of the concentrator by a factor greater than two (above that of the original glass equipment), simulated feeds could be concentrated ~ 3 -fold at up to ~ 20 ml/min input, and that at 10-12 ml/min input and concentration to equilibrium at 150°C the output was sufficiently dry that, with the furnace at 1300°C , the melter could maintain a high enough temperature ($\sim 1200^{\circ}\text{C}$) at the top of a 5-in.-deep melt to form a good glass.

On this basis a nominal hot-cell rate of 0.5 liters/hr and a nominal melt depth of 3-5 in. were selected.

For a nominal melter temperature of 1200 °C, some limits on feed composition were imposed. It had been shown that insufficient residence time in the melter resulted in a poor, quite soluble glass—milky green rather than black for the same feed. Also, while many compositions and residence times gave a good appearing glass on air quenching, many of these devitrified on being annealed or slowly cooled, and hence would be unsuitable for furnace-cooled batches or for a self-heating waste. Resistance to devitrification is maximum in glasses of the metaphosphate composition, that is, those of the cation equivalence-to-phosphate ratio $M^+/P = \sim 1$.⁽⁹⁾ Except in experiments substantiating this characteristic, all the "cold" run feeds were of metaphosphate-ratio composition, and the "hot" feeds also were adjusted to yield a nominal metaphosphate glass. Addition of calcium or aluminum to the simulated Purex 1WW waste both resulted in higher melting and more durable glasses. On "soaking" at 1200 °C the high calcium glass, on cooling, formed a hard, shiny microcrystalline "rock". The aluminum glass ($Na/Al \approx 2$) not only taxed the temperature capacity of the furnace, but formed a melt of very high surface tension, the molten drops from the melter dancing and rolling like water on waxed paper, rather than forming a stalagmite as was usual. High addition of iron ($Na/Fe = 1$) did not excessively increase the glass-forming or melting temperatures, and usually improved resistance to leaching.* Probably a much higher level of iron than $Na/Fe = 3$ could have been tolerated in the "hot" glass with

* Occasional anomalous leachability results indicate that glass thermal history, as well as composition, is a major factor in this regard.

good effect. However, in view of the uncertainty as to the true composition of the waste, this more cautious iron content was chosen. Most of the "shakedown" tests of equipment, as well as the "hot" runs, were made with the "safe" 0.5M iron level. This glass, from simulated feed, slowly formed, reliably remained in the glassy state on slow cooling, and on being annealed for up to 6 hr at 600 °C. On being left at 800 °C overnight, however, even this glass devitrified on cooling. For reasons unknown, the "hot" glass of the same nominal composition was found to devitrify quite easily.

During the "cold" runs a test was made of one of the Inconel 702 pots with a 7-mil platinum liner which had been supplied by BNL as a simple pot, but which had been locally modified to incorporate a drain tube for a freeze valve and an overflow tube for continuous melting. No X-ray or dye tests were made of these welds, which must have contained a pinhole or hairline crack. On heating to 1200 °C, this opened enough to let a little phosphate glass come in contact with the Inconel, and thus initiate an intense reaction (Figure 18). It is believed that chromium reduces the phosphate glass (P_2O_5 + metal oxides) to elemental phosphorous, which attacks the platinum and initiates a thermite-like reaction with the nickel, yielding a relatively low-melting "alloy" (~45% Pt + nickel phosphide). Large and small globules of this composition were found in the glass dumped from the furnace. The tubulated liners for hot-cell use were fabricated of 15-mil platinum by an experienced vendor and were tested before acceptance.

The "Hot" Runs

Only five runs were undertaken before a similar catastrophic pot failure destroyed the furnace and thus terminated the study. All of these were "batch" runs in which the melter served as the final container, and only one of these was successful in producing a stable glass.

(a) Cold Run Pot

(b) Detail

FIGURE 18

"Cold" Pot Failure

Run H-1 (9/21/64)

The alternative flow sheet (Figure 1), employing a sulfuric acid fractionating tower, was selected for the initial runs, since this scheme was expected to yield a lesser hazard of exhaust air contamination by fog transport. The first run was started up on simulated feed (1.4 liters) to "prove" the in-cell installation, and was switched to actual 1WW (3.0 liters) for the remainder of the run—the product thus being two-thirds full level. The run was plagued by equipment difficulties: manipulator failures (four), a power outage, a plugged air jet, inadequate feed-rate control, and a fused controller contact. The latter trouble caused a temperature excursion in the concentrator from the set point (150 °C) to well over 200 °C, resulting in a caked concentrator and a plugged line. This was corrected by the use of wire probes and by the addition of nearly 500 ml excess phosphoric acid to the concentration. The melter operated at ~1250 °C, and yielded about 0.5 liter of solid product; but this was not a good glass, since it devitrified on slow cooling (Figure 19).

The volume reduction obtained was only ~9 relative to the raw waste, or ~11 relative to the waste plus additives, whereas those factors should have been 9.5 to 10 and ~13, respectively, for a good glass from this feed composition.* Failure to produce a good high-density glass probably was due to the excess phosphoric acid added to the concentrator to dissolve the plugs ($M/P = \sim 0.67$), so that even batchwise formation at 1250 °C was insufficient to expel the excess P_2O_5 and the associated traces of water. No leaching tests were performed in this material.

* A piece of this glass was later remelted and allowed to cool in air, and formed an excellent glass.

FIGURE 19

High-Level Glass
(Run H-1)

Run H-2 (9/30/64)

In this run only the actual waste was used, 3.0 liters of Purex 1WW plus the standard additives, and no additional phosphoric acid was added during the run. Equipment difficulties had been corrected and, except for one "upset" (See "Off-Gas Decontamination"), the run went smoothly, being completed in 9 hr (from start of feed-to-concentrator to furnace shut-down), as compared to 24 hr for run H-1. Average feed rate, excluding the one interruption, was 500 ml/hr —the nominal design rate.

The smaller batch size permitted premixing the feed and additives in a 4-liter bottle, and reduced heat loss to the cooled feed nozzle by reducing the final melt level. Heating was continued at full power for 30 min after cessation of feed to the melter, to insure adequate residence time at full temperature for all the feed; and the cooling coil was removed from the nozzle cooler, and the jacket allowed to boil dry and heat up, to reduce end losses from the melter.

The product appeared to be an excellent glass (Figure 20). It was extremely hard, and on being sectioned (by a diamond saw) overheated and fell apart with typical conchoidal fractures. Small coupons were carefully sawn from this specimen for subsequent leachability tests, and two faces, axial and transverse, were mounted and polished for "metallurgical" examination.

Run H-3 (10/23/64)

For the remaining runs, the system was converted to "basic scheme" operation (Figure 1), which permits better determination of fission product behavior. Run H-3 was intended to duplicate the successful preceding run (H-2), except for this equipment change, but one operational change also was made. In the "cold" runs, it had been found that, with care, the concentrator could be operated with minimum hold-up (and hence with minimum delay between start of feed to the concentrator and overflow to the melter) if initially operated with

FIGURE 20
High-Level Glass
(Run H-2)

Neg. C-5937, C-5892

the lower drain valve open. This procedure was tried on this "hot" run, but in this case not only was the feed insufficiently concentrated, but also it proved to be heavily loaded with a precipitate which repeatedly plugged the concentrator outlet and/or the melter feed line. Changing back to overflow operation did not alter the two-phase nature of the feed, and after ~24 hr of unsuccessful effort to establish operation, the run was abandoned. The voluminous precipitate in the concentrator effluent was shown by gamma analysis to be high in Zr-Nb⁹⁵, suggesting insufficient acidity in the feed. This was unexpected, since the raw feed analyzed 2.9M H⁺ before addition of the phosphoric acid, and since much lower acidity had been found adequate in the "cold" runs.

Run H-4 (11/12/64)

After thorough clean-up of the concentrator and feed lines—but with a small "heel" of the H-3 product in the bottom of the melt pot—a second attempt was made to duplicate the H-2 run in the "basic scheme" equipment. In view of the previous difficulty, two precautionary steps were taken: 1. nitric acid (400 ml; 16N) was added to the feed to bring the total acid to ~5M H⁺, and 2) startup concentrator temperature was reduced to 115 °C, to avoid precipitate formation. No plugging was experienced throughout the entire run. The concentrator temperature gradually was raised to 145 °C, but the feed was exhausted just as the concentrator effluent approached adequate concentration. The feed to the melter was excessively "wet" during the entire run, and the run was characterized by excessive fog in the melter off-gas, which frequently was visible passing through the "sulfuric" condensers and into the "nitric" system. Thus, the "sulfuric" stream was abnormally high in both volume (40% of feed) and nitric acid (4M). Although the furnace and melter thermocouples indicated normal temperatures (above 1200 °C), apparently not all the melt was thoroughly dehydrated, desulfated, and converted to glass. On cooling, the melt devitrified to a glassy matrix containing needle-like crystals, which shattered on sectioning (Figure 21). On remelting and cooling a sample of this glass devitrification did not recur.

FIGURE 21
High-Level Glass
(Run H-4)

Neg. C-9462 , C-7017

Run H-5 (12/16/65)

In view of the apparent efficacy of added nitric acid, this procedure was repeated for the fifth run, but only in the amount (200 mil) to bring the total acidity to $\sim 4M H^+$. Startup of the feed to the melter was by normal concentrator overflow at $\sim 150^\circ C$. Although there was occasional slight plugging (which possibly might have been prevented by higher acidity), the run went exceptionally well until the feed was about 90% depleted. At that time, foaming in the concentrator caused a small amount of the concentrated feed to be carried over into the "nitric" stream.

The feed was turned off while the concentrator off-gas line was rinsed, to minimize carry over into the "nitric" stream. On resuming feed flow (perhaps slightly prior thereto) the current to the melter furnace became erratic, and within a few minutes dropped to zero, and the run had to be discontinued. The power failure was first thought to have been due to corrosion or burn-out at the cable connection to the furnace, so on the following morning the melter pot was removed from the furnace preparatory to dismantling the furnace for repair. The bottoms of the Inconel 702 melt pot and of the platinum liner had been completely destroyed (Figure 22), and the molten glass had dissolved away the lower Kanthal furnace windings, and had dripped into the annealing section (Figure 23).^{*} No product glass was recovered from this run, but off-gas data had been collected, so in view of the delays and difficulties inherent in remotely replacing the furnace element, and the urgent need for the cell facility for another project, the Hot Cell Glass Experiment program was terminated at this point.

* The photographs of Figures 22 and 23 were taken by means of a through-the-wall periscope and a manipulator-held mirror.

FIGURE 22

Failed Pot (Terminating "Hot" Runs)

FIGURE 23

H-5 Glass Leakage from Furnace After Pot Failure

Neg. 0643561-2, 0643561-5

POT FAILURES AND PLATINUM CONTAMINATION

The occurrence of two pot failures (Figures 18 and 22. See also page 34), apparently by the same mechanism, clearly demonstrates the inadvisability of using a base-metal pot with a thin platinum lining. Experience with a thicker (90 mil) platinum pot, supported only by a refractory ceramic plate, disclosed no sign of failure in over a dozen prolonged "cold" runs. Thus, despite the higher initial cost of an all-platinum (or platinum alloy) pot, its greater reliability—and the extreme nature of bimetallic failure—make it appear to be the only acceptable choice.

A section of the H-5 pot was subjected to successive rinse and dissolution steps to determine the nature and distribution of the fission product contamination (Tables III and IV). The effects of the rinses, and the profile of permeation into the 11 mil thick platinum are shown in Figures 24 and 25.

The profile and the data of Table IV show that although most of the contamination is on or near the surface of the platinum, there is sufficient permeation to render a platinum melter incapable of being decontaminated to the extent necessary for refabrication or repair. Moreover, although the persistent surface contamination is mostly cerium and cesium (Table III), ruthenium has penetrated more deeply into the metal, and is the most abundant contaminant in the center section, as was anticipated. Thus, salvage of the platinum of a defective melter may be expected to require electrochemical separation and purification. This consideration might well be a determining factor in the choice of a process for waste solidification.

TABLE III

PLATINUM FISSION-PRODUCT SURFACE CONTAMINATION

Effect of successive 10 min, 100 ml 1M HCl washes
at 25 °C. No significant weight losses.
Area = ~17 cm² (both sides).

Rinse No.	Activity Removed, mCi			
	Ce	Ru	Cs	Zr-Nb
1	4500	200	2000	81
2	2700	54	900	42
3	1400	40	580	24
4	900	24	350	15
5	720	18.5	270	12
6	630	18	210	9.0
7	550	21	230	9.5
8	300	5.8	85	3.6
9	290	5.4	77	3.2
10	270	4.3	63	2.8
11	320	5.0	63	2.8
12	360	5.4	63	2.8

TABLE IV

PLATINUM FISSION-PRODUCT PERMEATION

Effect of successive dissolutions in aqua regia

Dissolution, No.	Weight Loss, g	Depth, (a) mils	Activity in Platinum, mCi			
			Ce	Ru	Cs	Zr-Nb
1	0.005	0.01	36,000	207,000	8,000	--
2	0.005	0.01	7,100	48,000	1,600	--
3	0.005	0.01	4,100	29,000	1,100	--
4	0.284	0.31	38	260	8.6	--
5	0.234	0.26	87	1.6	16.5	0.73
6	4.499	4.90	4.1	37	1.0	--

- (a) Depth of platinum dissolution, each side, assuming symmetrical etching. Activity/gram is calculated on basis of both sides of platinum sheet, although probably nearly all on inside surface.

FIGURE 24
Effect of HCl Rinses

FIGURE 25
Fission Product Permeation of Platinum

The "Sulfate" Problem

High-level wastes derived from processes employing sulfamic acid contain substantial amounts of sulfate on concentration. In the calcination of such wastes, most of the sulfate remains in the calciner, and indeed contributes to its meltability,⁽⁶⁾ but some is lost to the off-gas condensates, rendering them more corrosive. In the production of a phosphate glass from such wastes, nearly all the sulfate is expelled from the melt. Thus, the melter off-gas condensate, also containing the residual nitric acid and water from the melter feed, can be quite corrosive. Also, if not recombined with the high-volume concentrator condensate, it constitutes a separate medium-activity stream requiring storage and/or treatment (See also page 6).

The acid-tower fractionator employed in the alternative flowsheet (Figure 1) was designed to minimize this problem by separating the sulfuric acid, plus a small amount of phosphoric, as a concentrated, small-volume stream. The off-gas from the melter may contain the various oxides of phosphorus, sulfur, and nitrogen, and their hydrates. Under equilibrium conditions, in the cold runs, the phosphorus and sulfur oxides and equivalent water are absorbed by refluxing H_2SO_4 (from a boiler at the base of the column) producing a constant-boiling heavy-acid overflow stream; and low-sulfate nitric acid and steam pass out the top of the column. Sulfate separation can exceed 50:1. In the "hot" runs, however, as in some "cold" runs, occasional flow surges of wet feed to the melter would momentarily upset the fractionation, sweeping H_2SO_4 vapor into the "nitric" stream, depleting the "inventory" of H_2SO_4 in lower column section, and substantially reducing the overall effectiveness of this mode of operation. In fact, for the two "hot" runs made with the fractionator, the total sulfate in the "nitric" streams (composite) appeared not to be significantly less than obtained without the fractionator. These runs, however, were too few and too variable to yield reliable

evaluation. On the other hand, the volumes and acid concentration of the "sulfuric" streams were demonstrably different (Table V).

TABLE V
COMPOSITIONS OF "SULFURIC" CONDENSATE STREAMS

<u>"Flowsheet"</u>	<u>Volume % of Feed</u>	<u>$\underline{M} \text{ NO}_3^-$</u>	<u>$\underline{M} \text{ SO}_4^{=}$</u>	<u>$\underline{M} \text{ PO}_4^{\equiv}$</u>
With Fractionator (H-2)	5*	<0.01	16*	n.d.**
Without Fractionator (H-5)	23	2.4	4.2	0.26

* Diluted below constant-boiling H_2SO_4 concentration by "wet" surges which caused momentary dilute overflow.

** n.d. = not determined

Thus it appears that the practicality of adding fractionating equipment depends upon reasonable control of the melter feed rate, and adequate fractionator capacity (neither of which obtained here), as well as the relative costs of alternative means of sulfate disposal.

Fission Product Release

Fission product release from the glassy melts was less abundant than from the previously studied calcines,⁽⁶⁾ which was somewhat surprising in view of the higher melt temperatures involved. In the only full-level fractionator run (H-2), the total release was only about 0.5% of the total feed activity, and less than 1% of the ruthenium was released, in contrast to about 20% Ru release on calcination. The distribution of the fission products in the various H-2 condensates is shown in Table VI.

TABLE VI
RUN H-2 (FRACTIONATOR) DISTRIBUTION OF FISSION PRODUCTS

	Percent of Feed ^(a)			
	Ce	Ru	Cs	Zr-Nb
Nitric Composite	0.03	0.13	<0.001	0.02
Sulfuric Composite	--	0.4	--	--
Fractionator Packing ^(b)	--	0.02	--	--
Steam Scavenge Condensate	<u>0.3</u>	<u>0.2</u>	<u>--</u>	<u>0.08</u>
Total Fission Products in Condensates	0.33	0.75	<0.01	0.10
Concentrator Off-Gas ^(c)	0.03	0.07	--	0.02
Melter Off-Gas ^(d)	0.3	0.68	<0.01	0.08

(a) Values are in percent of each radioisotope. Weighted "Total Fission Products Released" is 0.37%.

(b) NaOCl rinse of fractionator packing

(c) Average of grab-sample values

(d) Total fission products minus concentrator off-gas.

In the better of the two "basic" runs (H-5), the fission product release appears to have been much greater than in the H-2 run, total release being about 10% of the ruthenium, and ~4% of the total fission product content of the feed. The distribution data on this run are given in Table VII.

TABLE VII
RUN H-4(BASIC) DISTRIBUTION OF FISSION PRODUCTS

	Percent of Feed ^(a)			
	Ce	Ru	Cs	Zr-Nb
Nitric Composite	0.006	4.0	0.003	0.064
Sulfuric Composite	0.8	3.0	1.0	2.1
Steam Scavenge Condensate ^(b)	<u>0.8</u>	<u>3.0</u>	<u>1.0</u>	<u>2.1</u>
Total Fission Products in Condensates	1.6	10.0	2.0	4.3
Concentrator Off-Gas ^(c)	0.09	1.0	0.06	0.3
Melter Off-Gas ^(d)	~1.5	~9	~2	~4

(a) Values are in percent of each radioisotope. Weighted "Total Fission Products Released" is 4.2%.

(b) "Steam scavenge" values believed to be erroneously high, affecting subsequent data (see text).

(c) Average of grab-sample values

(d) Total Fission Products minus concentrator off-gas.

While it appears that fission product release was much higher during the H-5 run than during H-2, the operation of the two runs, except for the equipment changes, was quite similar. The preceding "wet" run (H-4), however, was characterized by excessive fogging in the melter off-gas, with consequent high entrainment and transport through the condensers. The condensates of that run, however, were generally slightly lower in fission product content (except for 5.6% of the ruthenium in the "sulfuric") than those indicated for Run H-5. Thus it appears likely that hold-up on internal surfaces depleted the H-4 condensates, and subsequently enriched the H-5 condensates—especially in the relatively large-scale steam scavenge condenser and associated piping. On the other hand, a similar adsorption effect may also have contributed to the much lower values obtained earlier (Table VI). Surely, at least, the problem is no greater than indicated by the Table VII data.

Off-Gas Decontamination

Although off-gas contamination frequently passed the small glass condensers of the "nitric" and "sulfuric" systems, as shown in Tables VI and VII, it was effectively trapped in the steam scavenge condensate (5 to 10 ml/min) of the large Nionel condenser. The decontamination factor ($DF = \frac{\text{concentration in feed}}{\text{equiv. conc. in off-gas}}$) through the final condenser usually being about 10^8 . The final filters between the condensers and the exhaust jet normally reduced contamination by another order (i.e., to 10^9 or greater) before discharge to cell air.

On one occasion during Run H-2, on the release of plugging in the melter feed line, an excessive quantity of concentrated feed was suddenly dumped into the glowing melt pot. The melter off-gas became voluminous, heavily fogged, and colored by nitrogen oxides, and both fog and nitrogen oxides appeared at the top of the "fractionator". The ruthenium DF dropped to 3×10^5 , and had not

fully recovered 2 hr later. Moreover, although the ruthenium did not immediately pass the final filters, it did appear in the postfilter off-gas at the later time. Also, some cesium appeared in the off-gas, although previously it had not been present in detectable quantities. This upset yielded the lowest momentary DF of any run. The data are shown in Table VIII.

TABLE VIII
RUN H-2 OFF-GAS DATA - FILTER SAMPLES

	Decontamination Factors			
	Ce ^(a)	Ru	Ce	Zr-Nb
At 3 hr ("normal")				
Before Final Filters	2×10^8	5×10^9	*	5×10^9
After Final Filters	2×10^8	*	*	*
At 5 hr ("upset") ^(b)				
Before Final Filters	2×10^7	3×10^5	*	2×10^7
After Final Filters	8×10^7	*	1×10^9	*
At 7 hr ("recovery")				
Before Final Filters	7×10^6	6×10^7	1×10^8	1×10^8
After Final Filters	6×10^7	4×10^8	3×10^9	*

* Indicates apparent DF of 10^{10} or greater, beyond reliability of counting data.

(a) Cerium levels high and unreliable, owing to high cerium contamination in cell (from previous experiment).

(b) Plugged feed line to melter caused buildup in concentrator and subsequent high flow melter, resulting in high fogging and overloading of fractionator.

Although the "worst" run (H-4) had consistently high fog and carry-over, none of the filter samples showed ruthenium or total DF's through the condensers below 10^7 , and the decontamination data were remarkably consistent (Table IX).

TABLE IX
RUN H-4 OFF-GAS DATA—FILTER SAMPLES

		<u>Decontamination Factors</u>	
		<u>Ru</u>	<u>Total Fission Products (a)</u>
(F-1)	Melter Off-Gas*	640	980
(F-2)	Sulfuric Condenser, Top*	$\sim 10^6$	2×10^7
(F-3)	Nitric Condenser, Top*	$\sim 10^8$	$\sim 10^8$
(F-5)	Before Final Filter		
	Minimum	4×10^8	5×10^8
	Maximum	8×10^8	1.1×10^9
(F-6)	After Final Filter		
	Minimum (b)	1.6×10^7	3.7×10^7
	Maximum	1.2×10^8	1.4×10^8

* Single value

(a) Excepting cerium, results for which were erratic, owing to high-level contamination in cell from other (unrelated) work.

(b) First sample after start up. High count may have resulted from between-run alterations or sampler contamination. Consistently higher filter counts from this sampler (F-6) than from F-5 indicate sampler contamination.

Glass Leachability

As previously indicated, a series of leaching tests have been carried out on coupons of the H-2 glass. These coupons have surfaces produced by a 100-grit diamond saw. Only the gross dimensional areas (e.g., 10 cm^2 for a $22 \times 13 \times 6.1 \text{ mm}$ coupon) are used for the calculated leachabilities—since this type of area is the kind calculable for a cast block, etc. The intrinsic leachabilities probably are less than half those given here.

Three pairs of samples have been tested repeatedly to determine the effects of aging and radiation damage, and those of mode of storage. One pair is stored in desiccated air, one under water, and the third pair is stored in saturated air.

The latter condition probably most closely simulates underground storage, and this mode is the most damaging. The same effect is also true for ordinary window glass—or for any alkali-containing glass. On any such surface, there will be some exposed alkali oxide molecules and these will absorb moisture from the air to form the hydroxide in contact with the glass surface, with subsequent etching. This action does not occur in dry air, nor under water, since in the latter case the alkaline hydroxide is immediately diluted and transported from the surface.

The leach tests were performed as timed "soaks" (usually 4 hr) at 25 °C, in either double-distilled or well water. Coupons were rinsed and dried before each leach, to avoid counting interim damage, and were weighted to verify identity and check against possible mechanical damage and surface area change. Each leach solution was acidified (to prevent precipitation) and diluted to volume (100 ml) and aliquots taken for gamma analysis. For water leaches, there was no evident selectivity in leaching, and leach rates obtained for the different isotopes were in reasonable agreement with their average. However, since the Cs^{137} data seemed most consistent, all final leach rates have been determined on that basis.

Well water was obtained from a well near the Hanford burial grounds, to compare its leach effect with that of distilled water. This water (kept in polyethylene bottles) has a pH of 7.88, and contains about 50 ppm Na^+ , ~140 ppm HCO_3^- , and lesser amounts of other ions, to a total hardness (as CaCO_3) of ~125 ppm. Leachability in this water is about twice that in distilled water. The data on these tests are shown in Table X and in Figure 26. The figure quite graphically shows that although there has been little aging or radiation effect on the glasses stored either in dry air or in water, the glasses stored in moist air are deteriorating

TABLE X

LEACHABILITY OF H-2 GLASS (AT 25 °C)

Age, Days	Storage Medium	Leach Medium	Leach Period	Leach Rates		
				mdd ^(a)	μ/yr	Ci/ft ² yr ^(b)
20	Room Air	Distilled Water	24 hr	1.1	15	1.4
20	Room Air	Distilled Water	17 days	0.2	3	0.25
37	Dry Air	Distilled Water	4 hr	1.1	14	1.3
37	Saturated Air	Distilled Water		2.1	28	2.6
37	Water	Distilled Water		1.1	14	1.3
140	Dry Air	DDW ^(c)	4 hr	0.7	9	0.9
140	Saturated Air	DDW		4.8	65	6
140	Water	DDW		1.4	20	1.8
140	Dry Air	Well ^(d)	4 hr	0.8	11	1.0
140	Saturated Air	Well		9.0	120	11
140	Water	Well		3.3	44	4.1
390	Dry Air	DDW	4 hr	2.3	31	2.9
390	Saturated Air	DDW		6.7	91	8.5
390	Water	DDW		1.0	14	1.3
390	Dry Air	Well	4 hr	2.8	38	3.6
390	Saturated Air	Well		14.4	196	18
390	Water	Well		2.0	27	2.5

(a) $1 \times 10^{-5} \text{ g/cm}^2 \text{ day} = 1 \text{ mg/dm}^2 \text{ day (mdd)}$

(b) Activity release rate for 1 KCi/liter glass

(c) Double-distilled water

(d) Well water, 7.8pH (see text)

FIGURE 26

Effects of Age-Radiation and Mode of Storage
on Glass Leachability

quite rapidly. Apparently this degradation is due predominantly to storage mode, rather than radiation damage, since the other samples are showing only slight increases in leachability, which may be partly due to repeated testing.

Even at the initial leach rate of 1-2 mmd, and even for this relatively low-level (~ 400 Ci/liter) glass (compared to those from anticipated power fuel wastes), the leached activity in contact with the exposed glass (at 1 gal/yr ft²) would exceed the MPC in Sr⁹⁰ by a factor $>10^9$, and a dilution flow >2000 gpm would be required for each square foot of exposed glass to yield an acceptable effluent stream. Quite obviously even the most leach-resistant solidified waste will still require containment, even at today's level; and future wastes are expected to be of much higher activity. For example, for 10,000 MWD/ton exposure at 12 MW/ton, the following thermal powers have been calculated:⁽¹⁰⁾

TABLE XI
ISOTOPIC SELF-HEAT IN WASTES

<u>Age Since Discharge</u>	<u>Beta Curies</u>		<u>Beta + Gamma Power</u>	
	<u>Ci/Ton Uranium</u>	<u>Ci/Liter Glass</u>	<u>W_t/Ton Uranium</u>	<u>W_t/Liter Glass</u>
200 days	1.1×10^6	5.5×10^4	4600	230
1 yr	6.5×10^5	3.2×10^4	2800	140
2 yr	3.2×10^5	1.6×10^4	1300	65
5 yr	1.2×10^5	0.6×10^4	473	24

Leachability of the glass samples to other than water also was investigated. An early investigation at rather high acid and alkaline concentrations is reported in Table II, and compared with ordinary glasses. A further study involving the phosphate system was made at age 267 days, on the same samples used for the earlier acid-base study. In this case, there appears to be some selective leaching, since the isotopic ratios in the leach solutions vary

from the original feed, and from each other. Therefore, the results (Table XII) are expressed in terms of the isotopic activities in the leach solutions. Nominal leach rates, based on cesium activity, are included for comparison to the preceding data. The leach rate appears to be sensitive to pH in either direction from 7, rather than just to the presence of sodium ions.

TABLE XII
H-2 GLASS LEACHABILITY IN PHOSPHATE SOLUTIONS

Glass Age ~240 Days

(Each test for 4.0 hr at 25 °C in 100 ml; water rinse between tests)

Leach Medium	pH	Apparent Glass Dissolution, g/cm ²				Leach Rate,* mdd
		Ce	Ru	Cs	Zr-Nb	
0.001M H ₃ PO ₄	3.05	4.0 x 10 ⁻⁴	6.0 x 10 ⁻⁵	1.3 x 10 ⁻⁵	2.1 x 10 ⁻⁵	7.6
0.001M NaH ₂ PO ₄	5.0	8.2 x 10 ⁻⁶	2.8 x 10 ⁻⁶	5.4 x 10 ⁻⁷	4.9 x 10 ⁻⁷	0.32
0.001M Na ₂ HPO ₄	8.1	6.1 x 10 ⁻⁵	3.0 x 10 ⁻⁶	9.0 x 10 ⁻⁷	2.4 x 10 ⁻⁶	0.54
0.001M Na ₃ PO ₄ **	--	---	---	---	---	--
0.003M NaOH	10.5	2.55 x 10 ⁻⁴	4.1 x 10 ⁻⁵	3.9 x 10 ⁻⁵	2.1 x 10 ⁻⁵	23

* Leach rate based on Cs¹³⁷ (1 mdd = 1 x 10⁻⁵ g/cm² day)

** Tests in 0.001M Na₃PO₄ were omitted inadvertently, and might be expected to indicate intermediate leachability (i.e., ~10 mdd).

Glass Stability

In addition to the leaching coupons, metallographic specimens were cut from the H-2 product—one longitudinally, along the axis, and one transversely, parallel to and about 1/4 in. above the bottom. On initial metallographic examination of the polished surfaces, no structure of any kind was visible; and none was visible on reexamination at age 140 days. On repolishing and examining at age ~7 mo however, small exudations appeared on the surface. Since these were somewhat more abundant on the upper portion of the longitudinal surface than on the transverse surface,

it seems likely that these exudations are due to excess incompletely bound P_2O_5 , or possibly even traces of partially hydrated phosphoric acid. On the other hand, they may result from radiation-induced changes in the glass, possibly cross-linking which reduces the number of available sites. At age 1 yr, the specimens were repolished and reexamined. Although the exudations still are formed, they appear less numerous than previously. Metallographic photomicrographs of the specimen surfaces are shown in Figures 27 and 28. It can be seen that the discontinuities do not yet constitute significant flaws in the glassy structure, being observable only at high magnification, and that their appearance was not accompanied by any significant breakdown in leachability.

It may be significant that similar-appearing discontinuities were observed in the specimens of waste glass produced by Zimakov et al, as reported at the Vienna Symposium in October, 1962.⁽¹¹⁾

Materials of Construction

The problem of equipment corrosion, while not insuperable, must remain a significant factor in evaluating waste fixation in phosphate glass, especially when formed directly from an aqueous solution. The hot concentrated phosphoric feed is corrosive to both AISI 304 and 316 SS, but it can be handled in Carpenter 20. The fractionating absorption tower used in some of these runs was fabricated of quartz and packed with ceramic saddles, and showed no significant damage following the "cold" runs; but a suitable large-scale unit may be difficult to construct, and may make this feature impractical for a production unit.

Perhaps the most demanding materials problem is that of the melt pot, for which only platinum metals appear to be satisfactory. Ceramic crucibles have insufficient thermal conductivity to permit desirable feed rates, and have marginal thermal shock resistance for use with aqueous feeds. The use of thin platinum liners in

(3X)

(75X)

(250X)

FIGURE 27
H-2 Glass at Age 7 Months
Neg. C-9052,9041,9043,9042.

(75X)

(250X)

(250X)

FIGURE 27

H-2 Glass at Age 7 Months

Neg. C-9052,9041,9043,9042.

Neg. 2660, 2661

FIGURE 28
H-2 Glass at Age 1 Year
(250X)

metal pots is not recommended, since these have failed in both "cold" and "hot" runs. Solid platinum melters, supported on ceramic plates, have been quite satisfactory, but involve considerable capital investment coupled with substantial recovery costs. Moreover, although recovery of such highly contaminated platinum surely is possible, the procedures for doing so have not yet been demonstrated.

CONCLUSIONS

The Hot Cell Glass Experiment demonstrated the technical feasibility of producing a phosphate glass directly from a high-level aqueous waste. The off-gas decontamination problem was found to be minimal, and under controlled operation substantially all the fission products are retained in the glassy product. With correct additive proportions, a stable homogeneous nondevitrifying, high-density product of low leachability can be produced.

The equipment and operating problems, however, are formidable. Corrosion will be difficult and/or expensive to combat in both the concentrator and melter off-gas equipment, as well as in the high-temperature melter assembly. The combination of aqueous feed and high melt temperature may impose an unnecessary burden, and glass formation from dried or calcined waste, and dry additives, may prove to be a less difficult route.

The successful operation of a feed concentrator with "simulated" waste is now routine, but this operation is yet to be demonstrated consistently with an actual waste—the behavior of which is largely unpredictable from "simulated" experience. Fortunately, the Waste Solidification Engineering Prototype facility of the Fuels Recycle Pilot Plant* will soon be in a position to attain the requisite experience, and to resolve many of these problems.

One question yet to be resolved is whether a glass is indeed the optimal form for waste solidification. The formation of a nondevitrifying glass requires much closer control of the product composition

* Later renamed Chemical and Materials Engineering Laboratory.

than do sinters or porcelains and other ceramics. This, in turn, demands accurate knowledge of the waste composition—beyond that easily obtained. Moreover, it probably is impossible to produce a truly nondevitrifying glass in terms of reasonable waste storage conditions. Economical storage of any solidified waste will require that it be "packaged" in reasonably large units. To be competitive with other forms, glass packages will probably need to be large enough that the center-line temperatures are at or above the glass liquidus temperature, from fission product decay heat. In such cases, it appears inevitable that eventually nearly all of the glass will devitrify. While it may be possible to select compositions in which devitrification involves negligible mechanical damage, the glassy state is inherently unstable, as evidenced by its rarity in nature. A more stable waste storage form might be that of a polycrystalline ceramic or porcelain, in which crystallization takes place without undercooling, and with negligible volume change; and a nucleated microcrystalline material (similar to Corning's Pycoceram) might prove a superior form for long storage, now that the theory and techniques of nucleated crystallization are becoming sufficiently known for practical application.^(11,12)

Whatever solid form eventually emerges as most nearly optimum, surely accurate control of its composition will be necessary; and to this end accurate knowledge of waste compositions and characteristics will be required. Precise and extensive characterization of wastes, in turn, might be justifiable only for fairly large, well-mixed composites, sufficiently aged and blended to retain their determined characteristics for an extended period; and this, in turn, indicated prior cooling and storage for at least 4 or 5 years.

ACKNOWLEDGMENTS

The author is indebted to numerous individuals for their contributions to this study, including people in the Analytical Laboratories, Technical Shops, and Radiometallurgical Operation of Hanford Laboratories.

Special thanks are due to J. C. Gibson and his technicians, G. B. Becker, R. C. Britton, G. N. Buck, C. A. Fulcher, J. L. Green, G. O. Hammer and T. R. Myers for their skillful installation, assembly and operation of the in-cell equipment; to G. B. Barton for technical advice; to W. A. Emel and Barbara Van der Cook for special analytical effort; and to W. J. Gruber and R. Teats and their crews for excellent metallurgical assistance. The advice and criticism of R. L. Moore, under whose direction this work was carried out, also is appreciated; and particular recognition is due to G. C. Weth and E. J. Tuthill, Brookhaven National Laboratory, who cooperated fully in support of this project.

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