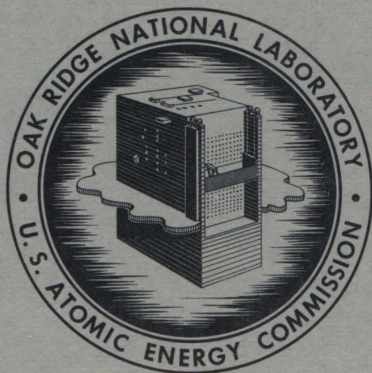ORNL-3640
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LABORATORY DEVELOPMENT OF PROCESSES FOR

FIXATION OF HIGH-LEVEL RADIOACTIVE WASTE

IN GLASSY SOLIDS. 3. WASTES FROM THE

PUREX SOLVENT EXTRACTION PROCESS

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operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

Glassy solids suitable for the long-term storage ("ultimate disposal") of radioactive wastes were prepared from solutions simulating those obtained or expected from the processing of nuclear fuel by the Purex solvent extraction process. The studies were applicable to both rising level (RL-Potglass) and continuous glass (Con-Potglass) processes.

The simulated waste solutions studied varied from those in which sodium sulfate was the principal constituent to those which contained no sulfate. Simulated fission products varied from zero to amounts expected from a burn-up of 35,000 Mwd/metric ton. Actual radioactivity was limited to tracer amounts used in determining leaching rates and volatilities. Minimum volumes of "glass" obtained (at 0.2% simulated fission products) corresponded to about 2.7 gallons of solid per ton of uranium processed. This solid contained 46% (by weight) waste oxides (process oxides plus simulated fission products), 31.5% P_2O_5, 11.8% Al_2O_3, 7.4% Li_2O, and 4.9% CaO. Melts incorporating higher concentrations of fission products required higher percentages of fluxing agents to keep melting temperatures and viscosities low enough for practical operation in stainless steel equipment. Maximum temperatures allowable are about 1050° and 900°C for the rising level (RL-Potglass) and the continuous melting glass (Con-Potglass) processes, respectively; lower operating temperatures are desirable in both cases.

Phosphate, aluminum, sodium, lithium, and calcium were the principal fluxing agents used for sulfate-containing wastes. The most glassy non-sulfate melts were obtained with phosphate and lead as fluxes. Increasing the content of aluminum or of fission products generally increased softening and melting temperatures but resulted in a more uniform product. Addition of lithium to give a final ratio, $Na/Li \cong 1$ usually resulted in less soluble, more homogeneous, and lower melting solids than when only sodium was present. Volatility of sulfate was minimized by keeping the ratio

$$\frac{\text{chemical equivalents (alkali + alkaline earths)}}{\text{chemical equivalents } (PO_3^{3-} + SO_4^{2-} + \text{other nonvolatile anions})} \gtrsim 1.1$$

to form a "neutral" glass. Leaching rates of ^{137}Cs from two sulfate-containing ceramics corresponded to penetration rates

of about 10^{-4} g cm^{-2} day^{-1}. The thermal conductivity of a true "glass" product was 1.3 to 1.7 Btu hr^{-1} ft^{-1} °F^{-1} vs 0.2 to 0.7 Btu hr^{-1} ft^{-1} °F^{-1}, for a calcined product.

Vapor-liquid equilibria and densities were measured for sulfate-containing waste solutions.

Titanium was the most resistant material tested for use in the evaporator, condenser, and off-gas lines. The maximum rate observed was 3.3 mils/month; expected rates are $\ll 1$ mil/ month. Stainless steel and nickel alloys suffered severe intergranular attack under the most aggressive conditions. Wastes of low acidity (i.e. "acid killed") wastes were relatively noncorrosive ($\lesssim 0.3$ mil/month) toward stainless steel and nickel alloys and even less corrosive toward titanium. Stainless steel is sufficiently resistant to serve as the fixation-storage vessel for the RL-Potglass process in spite of relatively high corrosion rates. Stainless steel is also suitable to contain waste for final storage in salt.

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1. INTRODUCTION

The accumulation of large volumes of highly radioactive waste material poses a problem in an expanding nuclear power industry. Occasional leakage may occur in spite of elaborate safety precautions. It is therefore desirable that at least those wastes with high levels of radioactivity be immobilized for ultimate disposal or storage to minimize contamination of the biosphere in the event of accidental release.

The greatest volumes of radioactive wastes currently in existence in the U.S. are derived from the Purex solvent extraction process. There is a very wide range of solution compositions in this waste class, ranging from those which contain large amounts of iron and sulfate to those that consist almost entirely of sodium nitrate plus fission product nitrates.

For maximum safety, the volumes of the wastes should be reduced as much as possible, converted to an insoluble form, and stored in an impervious container in a remote and dry environment. Many different

workers have approached the problem from various angles. Some of this work has been referred to in a previous report[1] on fixation of other types of wastes, and the references given there will not be repeated here.

The purpose of this report is to point out the criteria for acceptable products, discuss briefly the problems that arise from the volatile substances in the original wastes, summarize the developmental work, and summarize the corrosion studies.

2. FIXATION CRITERIA AND WASTE TYPES STUDIED

The criteria for fixation established in the chemical development work are as follows:

1. Retain in the solid, when possible, all materials stable at the temperatures and in the radiation fields expected, thus eliminating or minimizing side streams in the process.

2. Produce an insoluble solid which has long-term chemical and mechanical stability and high thermal conductivity.

3. Achieve a high volume reduction.

4. Develop a fixation process that will be economical and consistent with the above three criteria.

The steps in the rising liquid-level process emphasized here include:

1. evaporating the waste solution with or without additives, with recycle of the off-gas to an evaporator to reduce the amount of volatile radioactive isotopes in the off-gas (Fig. 1);

2. calcining and melting the solids produced;

3. "soaking" at the maximum temperature expected during storage to remove traces of unstable components such as nitrate and water;

4. sealing the container; and

5. transporting the glassy waste to the final storage site.

Simulated waste compositions studied (Table 1) varied in composition from those in which sodium and iron sulfates were the principal constituents to those containing predominantly sodium nitrate. Wastes that contain

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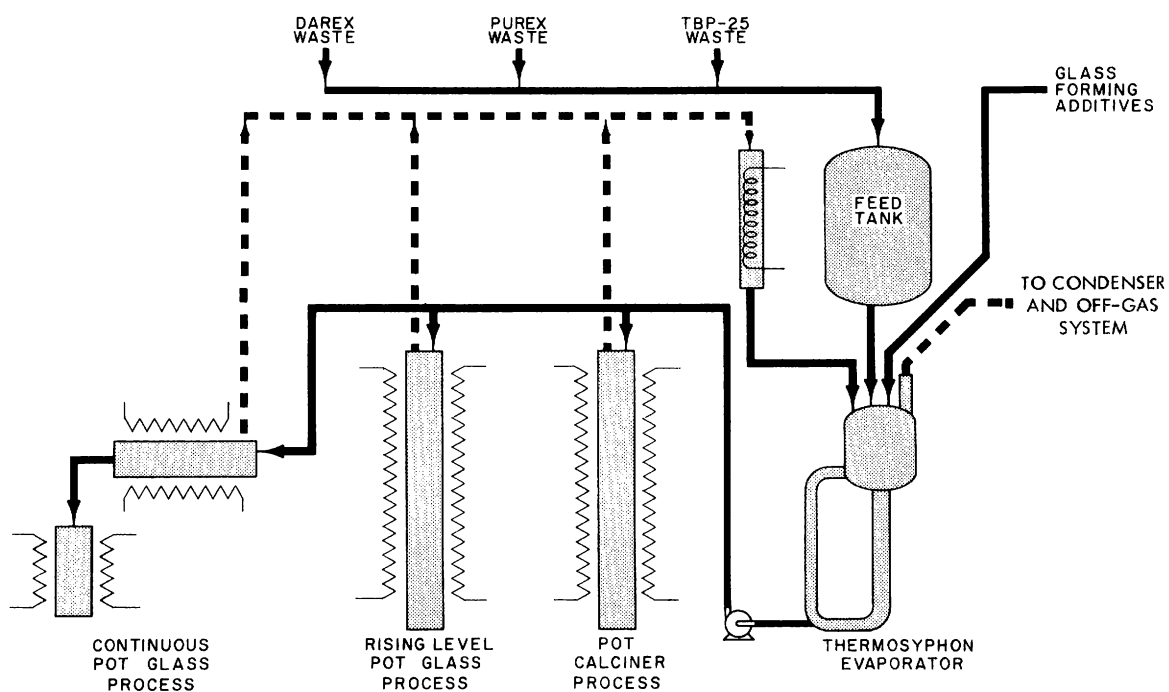
Fig. 1. Pot Processes for Solidification of High Level Wastes. All three fixation processes developed at ORNL use the same evaporator, condenser, and off-gas equipment.

Table 1. Compositions of High-Radioactive-Level Purex Waste

Constituent (g-moles per liter waste)	Purex FTW-65 Single Conc'n, 82 gal per ton U	X3[a]	High Sulfate Purex, 1WW, 40 gal per ton U	FT-1WW[e] Purex, 20 gal per ton U	Reacidified Purex	Non-Sulfate Purex[b]
H^+	0.5	1.5	5.6	0.3	0.5	3.0
Na^+	0.30	0.9	0.6	1.2	1.2	0.6
Al^{3+}	0.05	0.15	0.1	0.2	c	0.2
Fe^{3+}	0.10	0.30	0.5	1.0	0.1	0.05
Cr^{3+}	0.02	0.06	0.01	0.02	.01	0.006
Ni^{2+}	0.01	0.03	0.01	0.02	.02	0.006
Hg^{2+}	0.0035[d]	0.0105[d]	c	c	0.005	c
Ru	0.002	0.006	0.002	0.004	c	c
SO_4^{2-}	0.15	0.45	1.0	2.0	0.2(6)	c
PO_4^{3-}	0.005	0.015	c	c	c	0.02
SiO_3^{2-}	0.01	0.03	c	c	c	c
F^-	0.0005	0.0015	0.0005	c	0.0005	c
NO_3^- [f]	~1.0	~3.1	~6.1	1.2	~1.6	~4.3

[a]The FTW X3 represents the highest concentration of this waste type that can be conveniently simulated by direct makeup from laboratory reagents without heating the solution.

[b]Estimated from consideration of various Savannah River Plant flowsheet wastes.

[c]Content not specified.

[d]Maximum.

[e]The solution resulting from formaldehyde treatment of 1WW waste accompanied by a volume reduction of 2.

[f]Enough NO_3^- to balance in each waste.

sulfate are a particular problem because of the volatility and corrosivity of the sulfate at the high temperatures required for fixation. One approach has been to convert all sulfate to Na_2SO_4, which is nonvolatile as such. In addition, Na_2SO_4 serves as a fluxing agent, producing a non-

porous but rather soluble solid product.[2] In this case, primary dependence for containment must be placed upon the container material itself. A second approach is to drive off nearly all the sulfate by heating with an excess of some less volatile fluxing agent, such as phosphoric acid.[3] The sulfuric acid would then form a low- or intermediate-level waste stream that would require further processing before disposal. Preparation of a glass from the material remaining after removal of the sulfate is considerably simplified because of such removal.

None of the waste compositions listed in Table 1 can be melted to form satisfactory solid products without some additive. Even the simple calcination of "non-sulfate" or sulfate-deficient Purex wastes to form porous solids requires the addition of some other material or materials to prevent loss of sulfate and of cesium, as well as to prevent gross displacement of solids from a pot calciner.[4] However, all these types can be melted to produce satisfactory solid products by addition of the proper additives, as described hereafter.

Most of the tests described here were performed in the absence of simulated fission products. For some elements (cesium, ruthenium), tracer levels of fission products were employed. Simulated fission product compositions employed are listed in Table 2. Much current waste-disposal effort in the U.S. and abroad is now devoted to the development of waste fixation in glass. Glassy solids can be formed from many simulated waste types, particularly in small batches that can be quenched. Although it appears likely that glassy solids incorporating large amounts of radio-activity will devitrify with time because of the internal heat generated by the fission product decay, this is not necessarily undesirable. Glasses do indeed have smaller surface areas than their microcrystalline counter-parts and consequently show smaller fission product losses, particularly at the beginning of a leaching process. Yet, if the basic material is fundamentally insoluble, a small difference in leaching rates should not be sufficient to rule out the use of microcrystalline materials as disposal media. Furthermore, the thermal conductivity and the mechanical strength of crystalline materials are generally higher than those of glasses. Thus, there is no reason to believe that an insoluble crystalline

Table 2. Concentrations of Simulated Fission Product

| | g-moles/liter waste for 333 liters waste/tonne U (80 gals/ton U) | | |
| | 10,000 Mwd per metric ton | | 35,000 Mwd per metric ton |
Element	Hanford-BNL[a]	ORNL[b]	ORNL[c]
Zr	0.021	0.045	0.1675
Mo + Te	0.025[d]	0.044[d]	0.1643[d]
(Mo)		(0.035)	(0.1321)
(Te)		(0.009)	(0.0322)
Y + Lanthanides	0.045	0.081[e]	0.2966[e]
(Ce)		(0.022)	(0.0741)
(others)		(0.059)	(0.2225)
Rb + Cs	0.014	0.025	0.0982
(Rb)	(0.007)	(0.006)	(0.0209)
(Cs)	(0.007)	(0.019)	(0.0773)
Sr + Ba	0.011	0.022	0.0832
(Sr)	(0.0055)	(0.014)	(0.0503)
(Ba)	(0.0055)	(0.008)	(0.0329)
Ru, Rh, Pd	0.028[f]	0.016[f]	0.0841[f]
IO_3^-	--	0.0017	0.0068
Total g-moles	0.144	0.2347	0.8871

[a]Personal communication from G. Rey, HAPO, to BNL Waste Disposal Group, March 10, 1964.

[b]Calculated from J. O. Blomeke's and M. F. Todd's Uranium-235 Fission Production as a Function of Thermal Neutron Flux, Irradiation Time and Decay Time, ORNL-2127, II Vols., 1 and 3, "Summations of Individual Chains, Elements, and the Rare Gas and Rare-Earth Groups, Assuming 3×10^{13} nvt (thermal), Decay Time of 10^7 secs, Irradiation Time of 3×10^7 secs, $N_{25}^O = 5.1 \times 10^{25}$ (2% ^{235}U)."

[c]Calculated from ORNL-2127, II, Vols., 1 and 3 (see b above), Assuming 10^{13} nvt (thermal), Decay Time of 10^7, Irradiation Time of 10^8 secs, $N_{25}^O = 1.72 \times 10^{26}$ (6% ^{235}U).

[d]All added as MoO_3.

[e]Added as "Didymium Nitrate" plus cerous nitrate.

[f]All added as $RuCl_3$.

material will not be satisfactory for disposal, particularly if the container remains intact or that the storage environment is dry.

At ORNL, studies on the fixation of highly radioactive waste has resulted in the development of three processes (Fig. 1) as follows:

1. Pot-calcination process (Potcal). The final evaporation of the waste and its conversion to a porous mixture of oxides and salts is carried out in the final storage container ("pot").[5]

2. Rising-level Pot-glass process (RL-Potglass), the process emphasized in this report. Final evaporation, calcination, and melting to form a glass or ceramic product is carried out semicontinuously in the storage pot. The pot is identical with that used in the Potcal process.[6]

3. Continuous pot-glass process (Con-Potglass). Final evaporation and melting is done in a continuous melter, which discharges to the storage pot.[7]

All three processes have been successfully demonstrated on an engineering scale with simulated Purex waste and other waste types.[7,8,9]

3. EXPERIMENTAL RESULTS

3.1 Physical Characteristics of the Wastes

Vapor-liquid equilibria and solution densities were determined for both 1WW and FTW-65 types of Purex wastes without simulated fission products over the probable range of salt and acid concentrations (Appendix). Simple boildown experiments indicated that the 1WW type can be concentrated by a factor of at least 2 and that the FTW-65 type can be concentrated by a factor of 4 before the solution becomes noticeably unstable upon cooling.[*] Vapor-liquid equilibria and solution density data are presented in the Appendix.

Similar characterization tests were not made on the other types of solutions listed in Table 1.

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[*]The presence of fission products will produce appreciable quantities of solid material in all actual waste solutions.

3.2 Volatility Problems

Whether the aim is to produce a crystalline solid, as in the pot-calcination process, or whether the aim is to produce a glassy solid, the waste must be evaporated to dryness. Some of the volatile products, discussed below, require special attention to ensure a useful process.

Ruthenium Volatility

A cursory review of the literature reveals that reducing agents are effective in reducing the volatility of ruthenium during volume reduction of acid nitrate solutions. There is little or no volatilization of ruthenium from boildown and calcination of neutralized wastes. However, it is undesirable to store large volumes of radioactive wastes in an alkaline form if these are to be later removed from the storage tank and converted to solids. Addition of reducing agents, on the other hand, appears to be a practical means of reducing ruthenium volatility. The use of formaldehyde and/or sugar to reduce the amount of free acid in nitrate wastes results in the volatilization of less ruthenium from these solutions. Among inorganic reducing agents that can possibly be used for ruthenium control, phosphite and hypophosphite appear unique since they are not volatilized on oxidation and are oxidized to phosphate, which is a glass former.

Phosphite (Fig. 2) and hypophosphite were quite effective in reducing the volatility of ruthenium during fixation of Purex wastes in small-scale experiments. This was true in both calcination and meltdown experiments. Phosphite was also effective in reducing ruthenium volatility in semiengineering-scale experiments in which a fixed liquid level was used for calcination (Potcal process).[10] It was not effective in lowering it when the rising liquid level method of operation was used in connection with glass production in the fixation pot (RL-Potglass process).[6] The reason for this lack of control by phosphite is not thoroughly understood, but appears to be caused by the fact that when the rising-liquid-level method is used, much of the feed spatters on exposed hot walls, where the nitrates decompose in the absence of phosphite. Under these
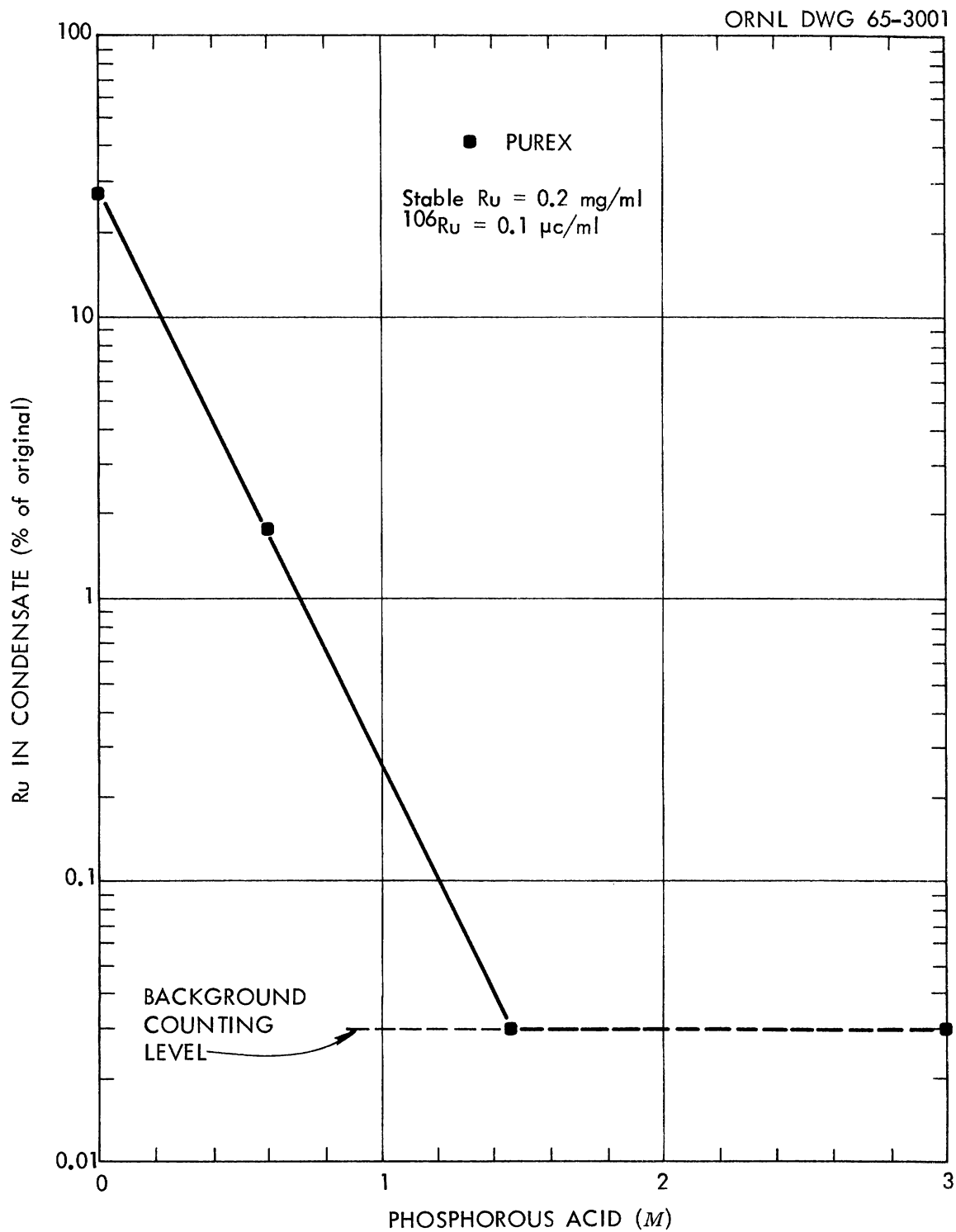
Fig. 2. Effect of Phosphorus Acid on Ruthenium Volatility from Purex
1WW Waste Solution During Batch Calcination to 500°C.

circumstances ruthenium probably first volatilizes and then forms an aerosol that is entrained by the off-gas.

Investigation of ruthenium volatility from nitric acid solutions with and without aluminum present showed that its volatility is a direct function of nitric acid volatilized at least when the ruthenium is added to the solution in the form of chloride.[1,10] Allowing the solutions to age reduces the volatility somewhat. These results are in general agreement with those of other investigators who used actual radioactive waste solutions.[11,12,13]

Phosphorus acid added to 1WW Purex waste solution in the extent of 0.1 $\underline{M}$ reduced the ruthenium volatility during distillation by a factor of 48.8 from that observed in the absence of phosphite. The current ORNL plans for processing waste (Fig. 1) entail the recycle of off-gases from the fixation vessel to a close-coupled evaporator. Nitric acid in the evaporator overhead is kept at an average concentration of about 1 $\underline{M}$ by adding excess water to the evaporator.* Ruthenium in the off-gas from the evaporator was thus kept between 0.1 and 1.0% of the total present (i.e., DF = 10^2 to 10^3) in engineering-scale calcination tests.[5] If it is desirable or necessary to limit ruthenium carryover to the amount physically entrained, it should be possible to do so by adding 0.1 $\underline{M}$ phosphite to the evaporator.[10]

Mercury Volatility

The presence of mercury in waste solutions is likely to create a problem in the high-temperature fixation of any waste, regardless of the method used for fixation, because mercury forms no compounds that are stable at high temperatures.

Thermogravimetric analysis in air of mercury and mercury compounds collected in the off-gas line during the calcination process indicated that mercury could probably be retained in an off-gas trap operated at

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*The operation of this "evaporator" might more accurately be described as steam-stripping of nitric acid rather than as evaporation. Depending upon the composition of the waste solution used for feed, some volume reduction is usually achieved in spite of the addition of water to the evaporator.

about 150°C. Attempts to do this on laboratory, semiengineering, and engineering scales were all unsuccessful. At most, 50% of the solids were trapped, and usually the amount was considerably less. The rest of the mercury was distributed between the fixation pot, the off-gas lines, the condensate, and the off-gas scrubber solution.

There was considerable variation in the appearance and the composition of the mercury compounds deposited. The composition is obviously a function of acid, oxidant, water, etc., in the off-gas, and probably of the flowrate in the off-gas line.

Subsequent work indicated that it may be advantageous to remove mercury from the waste solution before the fixation step. In laboratory-scale tests, as much as 99.9% of the mercury was removed by passing simulated waste solution through beds packed with copper.[14] This process works well in simulated wastes in which the concentration of free acid is no more than about 0.5 $\underline{M}$. Substitution of aluminum for the copper in the bed was feasible for FTW-65 waste that had acid concentrations no more than about 1.5 $\underline{M}$.

Iron Volatility

There was some indication that large amounts of iron were volatilized during semiengineering-scale fixation of FTW waste solutions (Table 3). This conclusion is based on a comparison of the percentages of iron and of phosphate volatilized during fixation of simulated FTW waste solution. Phosphate volatility varied only between 0.18 and 0.4% of the total present, while the iron volatility amounted to between 3 and 15% of the total present (Table 3). This gross difference between iron and phosphate is difficult to explain by the simple entrainment or by corrosion in the off-gas system. The phenomenon needs further investigation.

Sulfate and Cesium Volatility

Volatilization of sulfate is one of the principal problems associated with fixation of sulfate-containing wastes. Though it is chemically feasible to remove all sulfate by adding an excess of a non-

Table 3. Summary of Semiengineering-Scale, RL-Potglass Fixation Experiments with Purex Waste

Experiment No.	1	2	3	4	5	6	7	8	9
Waste Type	1WW		FTW-65 X3						
Additives (g-moles/liter waste)									
H_3PO_3	--	0.4	1.02	1.02	1.18	1.0	--	1.0	--
H_3PO_4	--	1.12	--	--	--	--	1.0	--	1.0
H_3PO_2	0.38	--	--	--	--	--	--	--	--
$NaH_2PO_2 \cdot H_2O$	0.5	--	--	--	--	--	--	--	--
NaH_2PO_4	0.76	--	--	--	--	--	--	--	--
$Al(NO_3)_3 \cdot 9H_2O$	--	--	0.24	0.24	0.153	0.5	0.5	0.5	0.5
$Na_2B_4O_7 \cdot 10H_2O$	0.13	0.13	--	--	--	--	--	--	--
NaOH	0.038	1.58	1.14	1.14	--	--	--	--	--
$LiOH \cdot H_2O$	--	--	--	--	1.25	1.14	1.14	1.14	1.14
$Ca(OH)_2$	--	--	0.21	0.21	--	--	--	--	--
$Ca(NO_3)_2 \cdot 4H_2O$	0.5	--	--	--	0.25	0.2	0.2	0.2	0.2
MgO	--	0.81	--	--	--	--	--	--	--
Ratio[a]	0.86	0.86	1.24	1.24	0.92	1.2	1.2	1.2	1.2
Wt % waste oxides, theoretical	35.7	40.3	45.0	45.0	42.4	44.5	44.5	44.5	44.5
Volatility and Entrainment (% of total present)									
SO_4^{2-}	29.8	31.3	1.8	1.4	40.3	6.1	1.1	0.5	22.5
Ru	23.6	21.9	24.2	2.6	26.6	20.7	37.1	29.7	22.3
Fe^{3+}	--	--	--	4.9	5.8	6.4	14.9	6.8	3.1
PO_4^{3-}	0.7	0.07	--	0.54	0.23	0.4	0.4	0.4	0.18
Average feed rate (ml/min)	35.5	68.8	--	--	35.5	36.9	41.8	38.0	38.4
Apparent volume reduction	--	--	--	--	--	36	36	36	36
Corrosion	Medium	--	Medium	Medium	Excessive	Negligible	Negligible	Negligible	Excessive
Remarks	Relatively good product; excessive sulfate loss	Short run; off-gas line plugged; unsatisfactory product	Fairly satisfactory melt; viscosity too high at 900°C for best operation		Satisfactory product but too corrosive; excessive sulfate loss	Very satisfactory in all respects			Melt sparged with N_2; pot corroded through

a $\dfrac{\text{Chem. equivalents } (Na^+ + Li^+ + Ca^{2+} + Mg^{2+})}{\text{Chem. equivalents } (SO_4^{2-} + PO_3^- + BO_2^- + SiO_3^{2-} + F^-)}$.

volatile acid (e.g., phosphoric acid), the result is an extra sidestream
that requires further decontamination, volume reduction, and storage.
Also, the volatilized sulfuric acid increases the corrosion of the fixa-
tion container. Consequently, retention of sulfate and simultaneous
production of desirable solid products continue to be major objectives
of the ORNL developmental program on waste disposal.

It is necessary that some nonvolatile anion be present in the waste
to prevent volatilization of cesium and sodium. The latter are vola-
tilized in gross amounts and caused plugging of the off-gas system during
calcination to 900°C. Excess of an anion less volatile than sulfate re-
sults in volatility of sulfate if the latter is present and if the only
other anion is nitrate. For calcining wastes containing only the anions
nitrate and sulfate, Godbee and Roberts[15] found that alkali metals were
not volatilized if the ratio

$$\frac{\text{chem. equivalents sulfate}}{\text{chem. equivalents alkali metals}} \geqq 1 \, ,$$

and that no sulfate was volatilized if the ratio

$$\frac{\text{chem. equivalents (alkalis + alkaline earths)}}{\text{chem. equivalents sulfate}} \geqq 1 \, .$$

A value of about 1.1 was found to be practical for this latter ratio when
either calcium or magnesium was the additive by which the cation ratio
was increased. Subsequent work[8] indicated that calcium is preferable to
magnesium as an additive because of the nature of the solids obtained.
Aluminum slows down the rate of sulfate loss and is very effective in
suppressing alkali volatility.[16]

The added criterion of meltdown to form an insoluble ceramic vastly
complicates the fixation problem, since gross amounts of fluxing agents
(e.g., phosphate, borate, silicate) must be added, and since one cannot
assume the existence of stoichiometric chemical compounds in the molten
state. Nevertheless, postcalcination weight losses of solids resulting
from evaporation and calcination to 650°C of waste plus additives indicated
that the above relationship between chemical equivalents of cations and

sulfate is generally valid when the added anions were included in the ratio as metaphosphate, metasilicate, or metaborate in the anion total. At temperatures greatly above the softening point,[*] sulfate tends to become increasingly volatile from all melts studied. Consequently, the values for sulfate volatilization reported in the tables (see below) were determined at the lowest temperature at which the mixes were considered to be sufficiently fluid for use in a fixation process. This was usually about 100°C above the temperature listed as the "melting temperature." The sulfate loss reported was determined thermogravimetrically. Analysis of the condensate and off-gas scrubbers always gave lower values for volatility than those determined thermogravimetrically. Quantitative measurements of melt viscosity are being determined and will be reported later.

Sulfate can also be lost by volatilization resulting from hydrolysis of residual water retained in the melt. X-ray patterns of solids resulting from certain melts have revealed the presence of hydrates[17] (Table 4). Similar hydrolysis can be expected with fluoride. In both cases, hydrolysis to form the acid at elevated temperatures will result in a very corrosive condition as well as in volatilization of the anion. Fortunately, the fluoride content of most Purex wastes is quite low (Table 1).

It is generally accepted that a solution consisting mostly of sodium nitrate cannot be calcined without additives because of the volatilization of the alkali oxides and/or salts. Attempted calcination of a waste consisting primarily of sodium nitrate with a relatively smaller amount of sodium sulfate ("Reacidified Purex," Table 1) resulted in displacement of gross amounts of the solids from the waste fixation container at temperatures far below those normally necessary for calcination. Both sodium and sulfate were detected in some quantity in the condensate (Fig. 3). Rather than add extra sulfate to this waste, it appears more logical to add either phosphate, which is a glass former, or aluminum, which is amphoteric and compatible with either calcination or fixation in glass.

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[*] "Softening" and "melting" temperatures as used herein are arbitrarily defined respectively as the temperatures at which melting was first detected and at which the melt flowed readily. Such measurements are highly dependent upon the judgment of the observer. The values listed may be considered as usually accurate to ±50°C, with occasional deviation of ±100°C.

Table 4. Nominal Compositions and Results of X-Ray Investigations of Solids Prepared from Simulated High-Sulfate Purex Waste[a]

	Melt Number						
	1	2	3	4	5	6	7
Waste Oxides (W.O.) (wt %)							
Fe_2O_3	11.4	10.7	10.7	11.9	10.4	11.8	11.7
NiO	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Cr_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al_2O_3	1.5	1.4	1.4	1.5	1.3	1.5	1.5
Na_2O	5.3	5.0	5.0	5.5	4.8	5.5	5.4
SO_3	22.9	21.5	21.6	23.9	20.9	23.7	23.5
RuO_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
% W.O.	41.6	39.1	39.2	43.3	37.9	43.0	42.6
Theoretical Additive Oxides (wt %)							
Na_2O	14.8	16.8	10.3	19.6	29.6	15.6	19.3
CaO	--	--	16.6	--	--	--	6.6
MgO	9.2	8.7	--	4.8	4.2	9.5	--
P_2O_5	30.9	29.0	28.9	32.2	28.2	31.9	31.6
B_2O_3	3.4	6.4	5.2	--	--	--	--
Total	99.9	100.0	100.2	99.9	99.9	100.0	100.1
Species Indicated by X-Ray							
Na_2SO_4	minor	minor (>No.1)	--	sig.	sig. (=No.4)	minor	trace?
Fe_2O_3	sig.	major	--	trace	trace (<No.4)	sig. (=No.1)	minor
Acid sodium orthophosphate	--	--	--	--	major	trace?	sig.
α-calcium orthophosphate	--	--	sig.	--	--	--	trace
β-calcium orthophosphate	--	--	minor	--	--	--	--
Unknown "d"[b]							
3.44	sig.	sig.	--	--	--	minor	--
5.37	sig.	sig.	--	trace	--	sig.	--
6.18	major	major	--	minor	trace	major	--
Approx. softening temp. (°C)	850	840	900	830	875	850	900
Melting temp. (°C)	900	900	950	900	900	1000	1000
% SO_3 lost at 950°C (100 min)	63.0	51.2	42.1	53.2	9.54	45.4	44.8

[a]Specimens prepared at ORNL. X-ray studies by R. W. Pelz of the Ferro Corporation.

[b]Pattern was similar to $Mg_3(PO_4)_2 \cdot 3H_2O$ but was shifted enough to cause suspicion of a solid solution with Fe_2O_3 or some other iron compound.
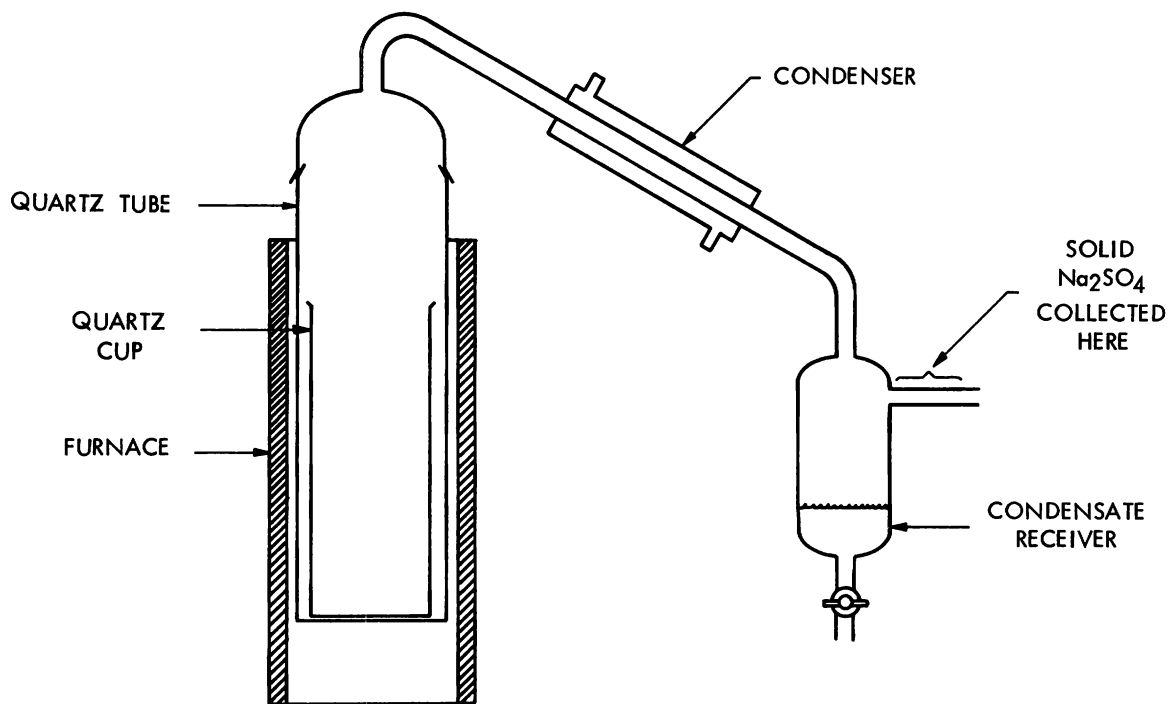
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Fig. 3. Apparatus for Studying Volatility from Sulfate-Deficient Purex Waste During Fixation.

Experiments in which aluminum was added in amounts equivalent to or greater than the equivalent amount of sodium (i.e., to form the hypothetical Na_3AlO_3) indicated that volatility of both sodium and sulfate can be reduced to levels considerably less than 0.1% of the total present. The limiting factor is that of physical entrainment. Tracer experiments with ^{137}Cs confirm results obtained when sodium was the only alkali metal present (Table 5). The calcination step in these experiments was accompanied by considerable foaming.

3.3 Semiengineering-Scale Experiments

Nine semiengineering-scale experiments were run using a semicontinuous method of operation (Figs. 4, 5, and 6, Table 3). The first two were attempted by using a fixed-level method of operation similar to that employed in the pot-calcination work. These two (experiments 1 and 2, Table 3) were run using 1WW Purex waste (Table 1), with an insufficient amount of active cations added to prevent sulfate volatility. The results of these two were therefore rather unsatisfactory from a practical standpoint and led to the development of the rising-level type of operation.[6] Seven experiments were then run utilizing FTW-65 waste with three different additive combinations. The results of these indicated that: (1) the rising-level method (RL-Potglass) is practical; (2) sulfate-retention and low corrosion can be achieved by the use of proper additives; and (3) products obtained by adding lithium to the waste solution (e.g. to give a Na/Li ratio $\cong$ 1) are generally fluid at lower temperatures than those which contain only sodium (see Sec 3.4).

Average feed rates to the 4-in.-diam fixation pot (Figs. 5 and 6*) varied between about 30 and 42 ml/min. Corrosion rates for the "best" composition (experiments 6 to 10) were almost negligible except when the melt was sparged (experiment 9) or when the experiment was stopped, allowed to cool, and operation restarted. These experiments served as a basis for full-scale engineering tests of the RL-Potglass process.[9] The results of subsequent semiengineering-scale continuous-fixation (Con-Potglass) experiments will be reported separately.

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*Minor experimental details such as the positioning of thermocouples, the use of pots with flanged vs welded bottom closure, etc., were changed from experiment to experiment. Figures 5 and 6 illustrate two different variations employed.

Table 5. Suppression of the Volatility of Sodium, Cesium, and Sulfate During Calcination of Sulfate-Deficient Purex Waste[a] in the Presence of Aluminum

Experiment No.	1	2	2a	3	3a	4	4a
$Al(NO_3)_3$ added, g-moles/liter waste	0	0.27	0.27	0.54	0.54	0.80	0.80
Mole ratios: $Al/NaNO_3$[b]	0	0.34	0.34	0.675	0.675	1.0	1.0
Al/total Na + ^{137}Cs	0	0.225	0.225	0.45	0.45	0.566	0.566

Volatility and Entrainment (% of total)

$^{137}Cs^+$

Total in off-gas line, condenser and condensate receiver	--		0.010		0.012		0.006

Na^+

In off-gas line and condenser	0.25	0.13	Not	0.005	Not	negligible	Not
In condensate receiver	0.15	0.12	analyzed	0.004	analyzed	0.018	analyzed
Total	0.45	0.25	for	0.009	for	0.018	for

SO_4^{2-}

In off-gas line and condenser	0.29	0.12	Not	<0.003	Not	negligible	Not
In condensate receiver	0.17	0.10	analyzed	0.004	analyzed	0.014	analyzed
Total	0.46	0.22	for	<0.007	for	0.014	for

| Observations | c | No gross displacement of solids; some white solids in off-gas system | | No gross displacement of solids; solids slightly visible in the off-gas system | | No solids visible in off-gas system | |

[a]Future acid Purex waste. Composition (g-moles/liter): H^+, 0.5; Na^+, 1.2; Fe^{3+}, 0.1; SO_4^{2-}, 0.2; NO_3^-, ~1.6 (to balance).

[b]More precisely, moles $Al/[$moles Na - (2 x moles $SO_4^{2-})]$.

[c]Gross displacement of solids took place from inner cup to cooler parts of ignition tube; some white solid in exit tube from condensate receiver.

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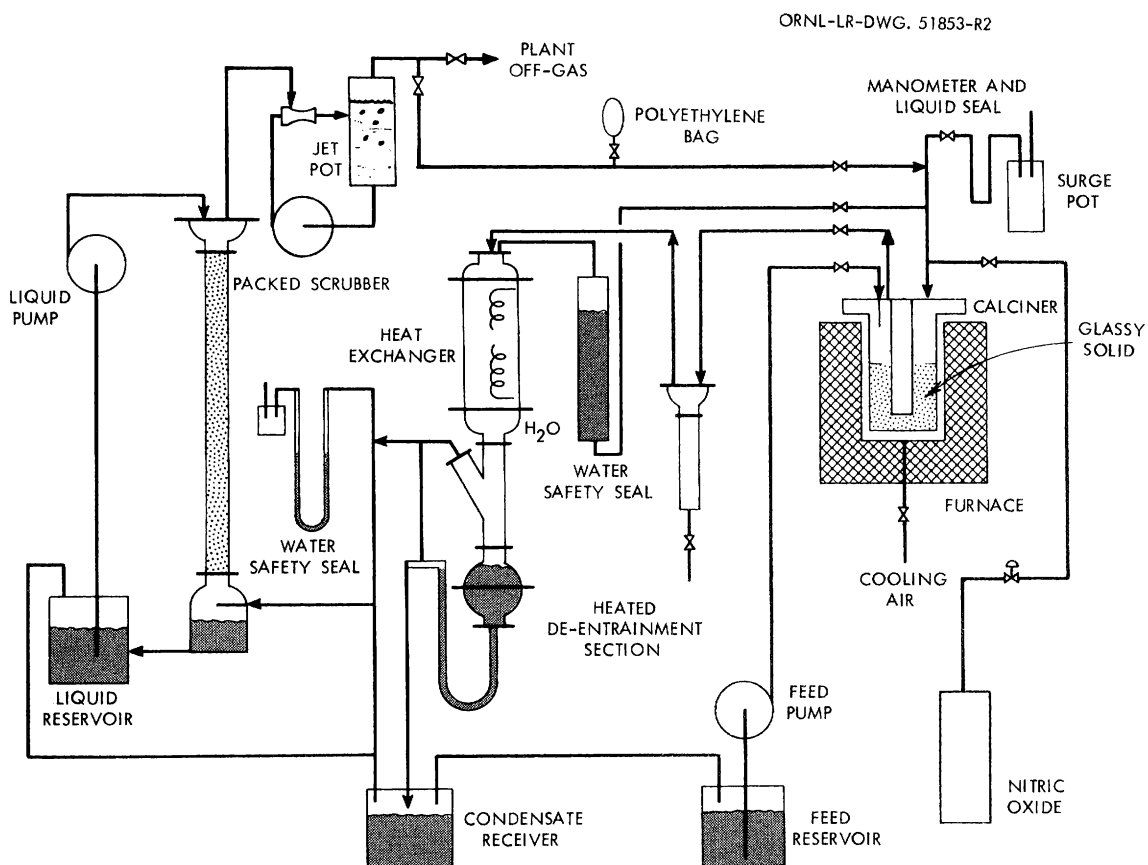Fig. 4. Experimental Equipment for Conversion of High-Level Radio-active Waste Solutions to Glassy Solids.
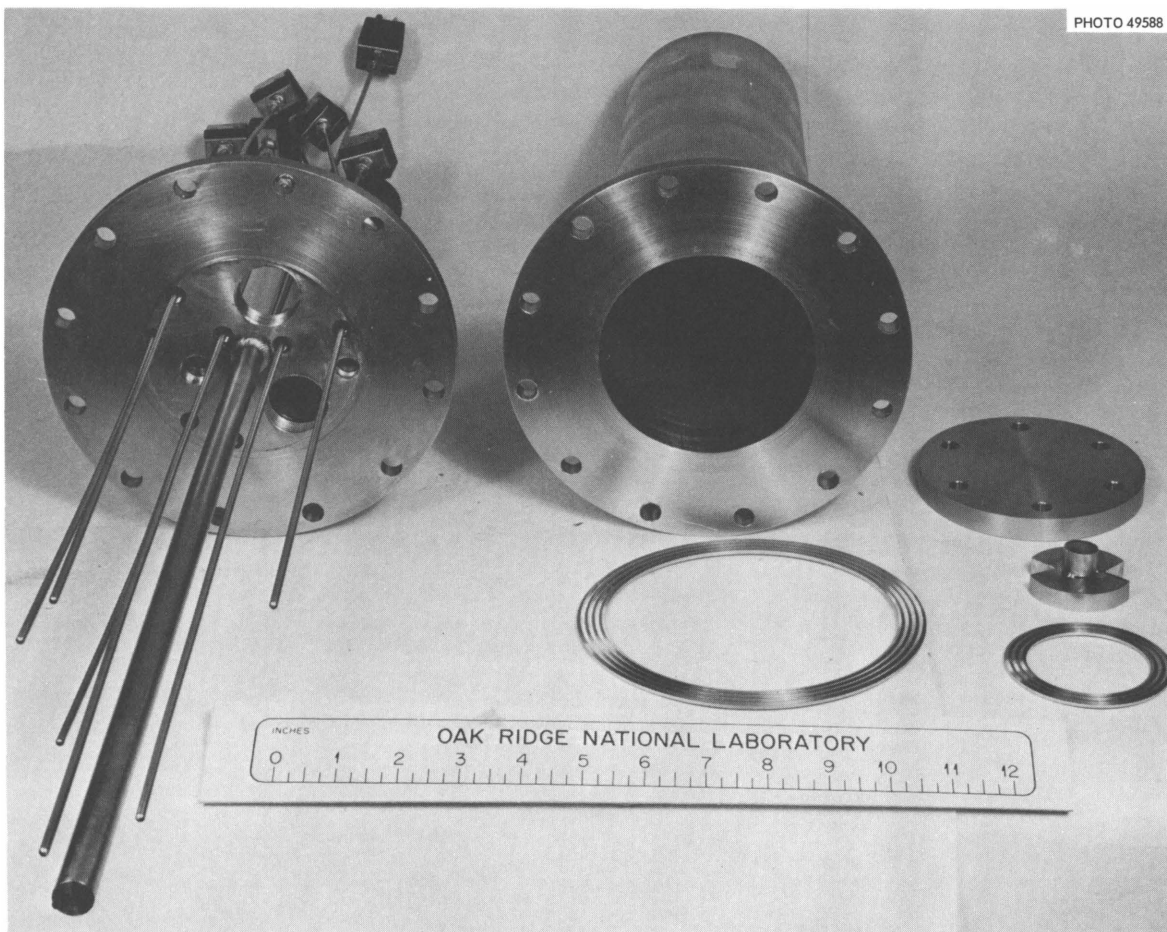
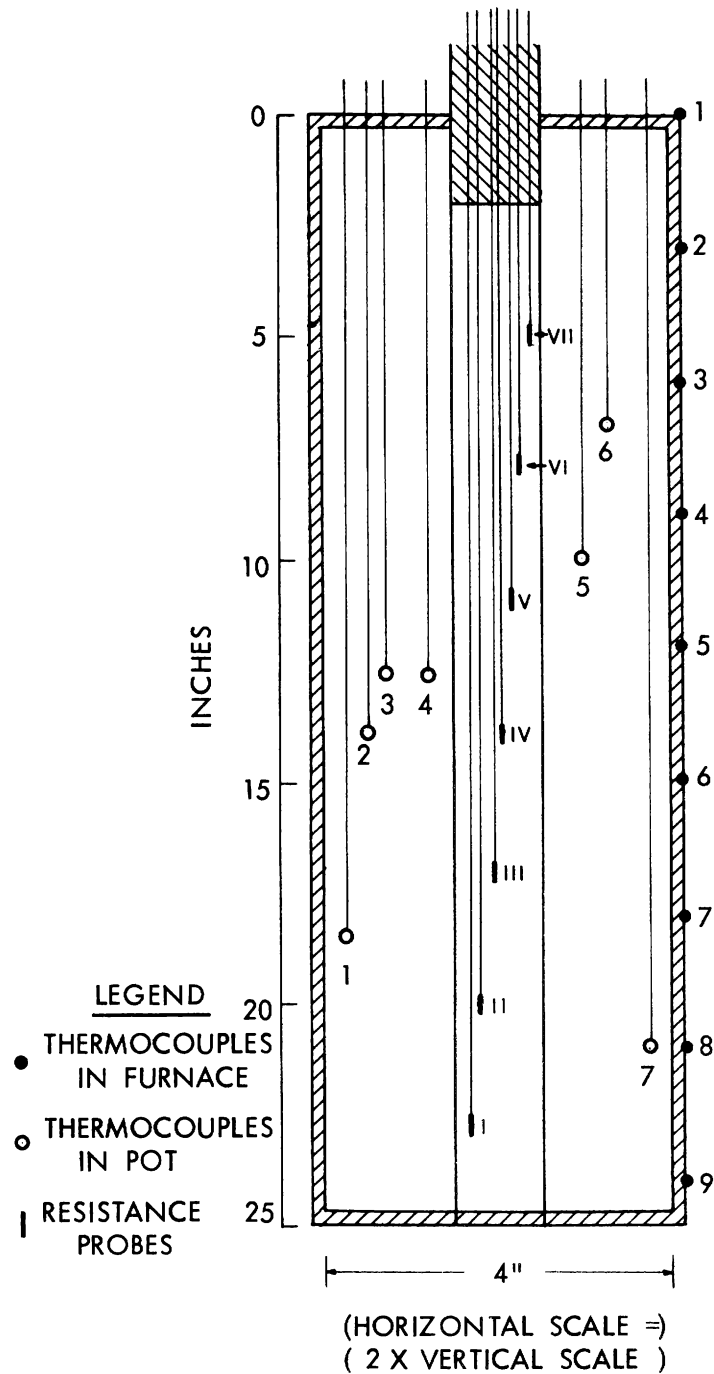Fig. 5. Stainless-Steel Calciner-Melter Pot, Disassembled.

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Fig. 6. Locations of Thermocouples and Electrical Conductivity Probes in Fixation Pot. The usefulness of conductivity probes was demonstrated in three of the nine semiengineering-scale, rising-level fixation experiments.

As indicated above, volatility of ruthenium was excessively high in all rising-liquid-level tests, and the volatility of iron was occasionally much higher than expected (Table 3). Sulfate volatility was variable, depending upon the melt composition and the method of operation. Excessive sulfate volatility was usually accompanied by excessive corrosion (Table 3).

3.4 Laboratory Development of Solid Products ("Glasses")

Briefly, the fluxing agents (H_3PO_4, LiOH, $Al(NO_3)_3$, etc.) were added to simulated waste solutions, which were then evaporated to dryness on a sand bath. The residues were calcined and melted in a muffle furnace, then were either allowed to cool slowly (anneal) or were quenched.

The wide variation in Purex waste compositions makes it impractical to reach a simple solution to the glass-mix formulation problem without compromising some of the other criteria adopted for the ORNL developmental program. The greater part of the work done was applied to sulfate-containing wastes since volumes of these wastes are greater and their incorporation in insoluble solids is more difficult than that for other Purex waste types. The development of phosphate glassy ceramics has been emphasized since initial experiments indicated these to have lower softening temperatures and to be more compatible with sulfate waste than either borates or silicates.

Very satisfactory products have been prepared for the fixation of the specific waste compositions, designated as FTW-65 and 1WW (Table 1). Leachability of solids containing large percentages of sulfate was high ($\sim 10^{-4}$ g cm^{-2} day^{-1})[*] in the two cases tested, compared with the rate for true glasses (10^{-6} to 10^{-7} g cm^{-2} day^{-1}) but was not appreciably different for two specimens one of which retained >95% sulfate while the other retained only about 80% (Fig. 7). Because of the immense number of possible

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[*] $\dfrac{\text{activity leached/cm}^2 \cdot \text{day}}{\text{activity/g of product}} = \text{g cm}^{-2}\ \text{day}^{-1}$.
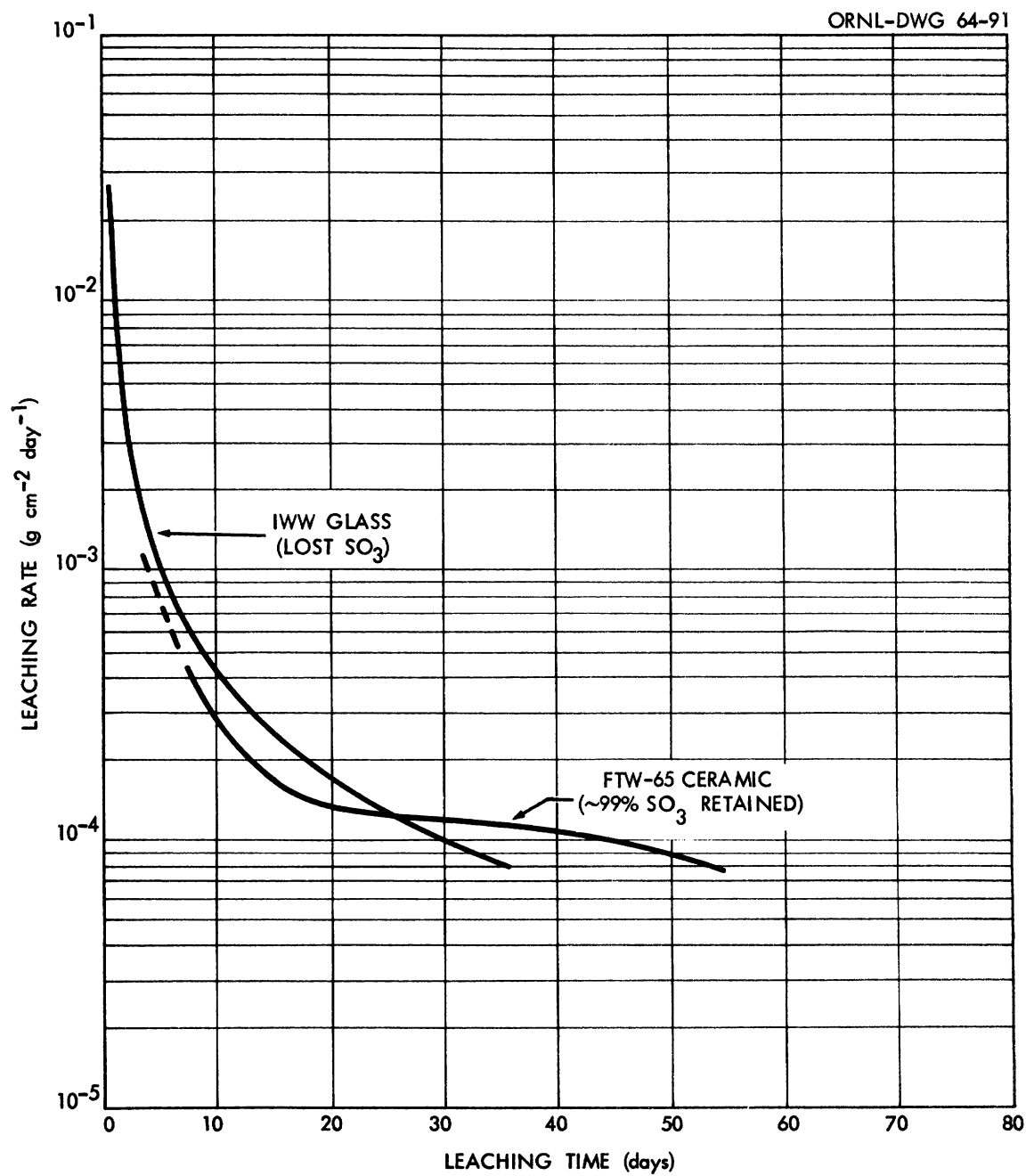
Fig. 7. Leaching Rates of 1WW and FTW-65 Purex Solid Fixation Products.

compositional variables, the optimization of the melts and the resulting solids produced is a particularly complicated problem. A computer code is being developed for correlating the data from this study.

Substituting lithium for sodium as an additive for fixing waste that contains sodium sulfate so as to give an Na/Li ratio $\cong$ 1 usually resulted in lowering the softening and melting temperatures of the solid products without increasing sulfate volatility or product solubility (Figs. 8 and 9). In fact, the lithium-sodium ceramics were usually more insoluble and were more often homogeneous in appearance than their sodium counterparts. Since the Purex waste always contains sodium, the properties of the pure lithium melts are of academic interest only. Adding potassium to the sulfate waste usually resulted in more soluble materials than were obtained by adding either sodium or lithium. Increasing the aluminum content usually raised the softening and melting temperatures, increased the viscosity of the resulting melt, and decreased the solubility of the solid product.

The usefulness of phase diagrams in these studies is very limited because the large number of components makes exact phase studies impossible. However, the use of pseudo phase diagrams proved to be of some value in correlating an otherwise unmanageable mass of data. Of a number of such diagrams tried, probably the most useful was a triangular plot on which the three apices represented the alkali oxide content (Na_2O, Li_2O, K_2O, etc.), the R_2O_3 oxides (primarily Al_2O_3, Fe_2O_3), and the nonmetal oxides or anions (primarily P_2O_5, SO_3, and B_2O_3). On such a diagram, the most satisfactory products obtained for sulfate wastes fell in a very roughly triangular area between the lines representing 35-75 mole % alkali oxide, 0-40% R_2O_3, and 25-65% nonmetallic oxides (Fig. 10). All the solids within this area are not satisfactory; even when simulated fission products are absent, allowance must be made for variations in the Na_2O/Li_2O ratio, the Al_2O_3/Fe_2O_3 ratio, and the SO_3/P_2O_5 ratio. Also there is no way to indicate the variable amounts of divalent metal oxides such as CaO. Nevertheless, the diagram has proved to be helpful as a condensed though empirical method of correlating data.
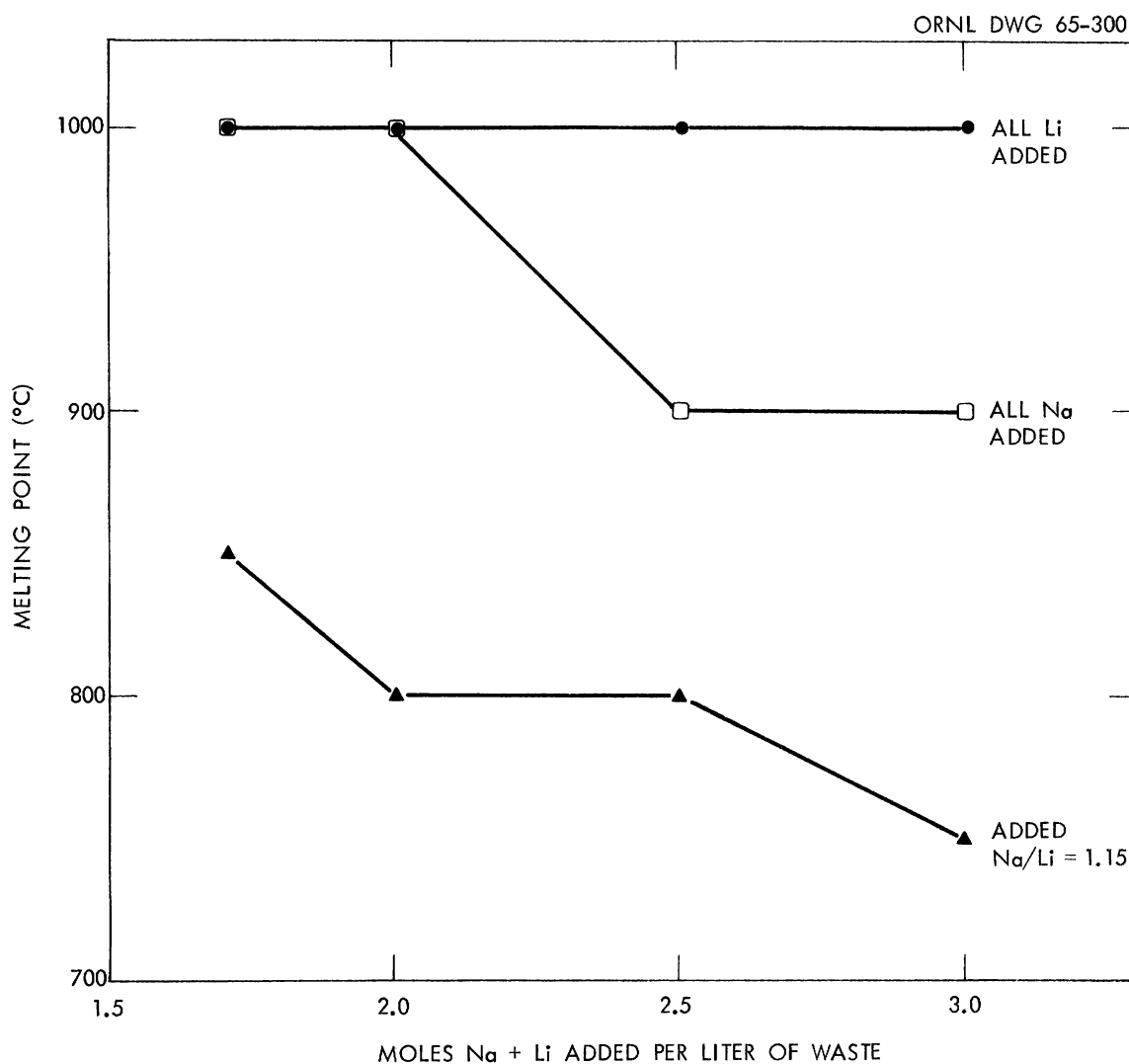
Fig. 8. The Effect of Lithium on the Melting Temperature of Solids Prepared by Fixation of Purex FTW-65 Waste. Sodium ion in waste (not included in abcissa) = 0.45 g-mole/liter. Phosphate added in 1:1 atomic ratio to added (Na + Li). Aluminum added = 0.5 to 0.6 g-mole/liter of waste.

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MOLE FRACTION OF Li_2O IN M_2O CONTENT OF MELT
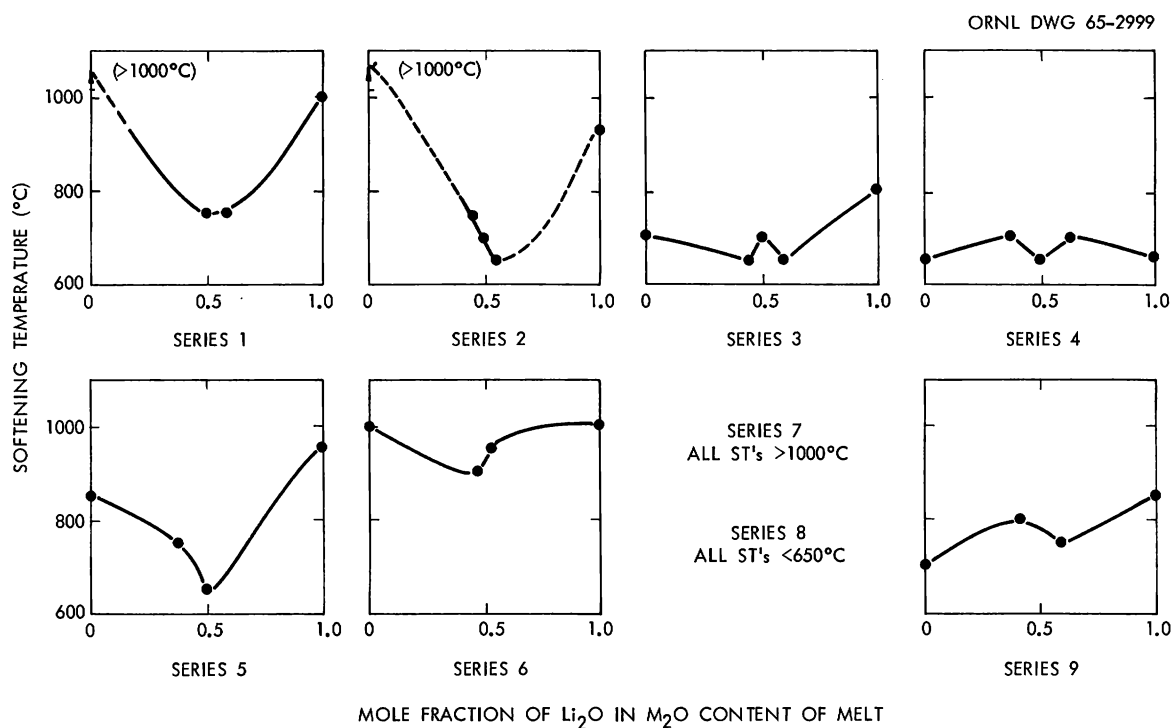
Fig. 9. The Effect of the Na_2O/Li_2O Ratio on the Softening Temperatures (ST's) of Seven Series of Melts. Composition (mole fraction) and mole ratios:

Series No.	M_2O	M_2O_3	Fe_2O_3/Al_2O_3	Anions	SO_3/P_2O_5
1	0.6	0.05	(1.0)	0.35	(0.75)
2	0.55	0.1	(0.33)	0.35	(0.33)
3[a]	0.5	0.1	(0.33)	0.4	(0.33)
4	0.4	0.1	(0.33)	0.5	(0.25)
5	0.4	0.2	(0.33)	0.4	(0.33)
6	0.45	0.25	(0.33)	0.3	(0.26)
7	0.55	0.2	(0.33 to 0.50)	0.25	(0.20 to 1.0)(All ST's >1000°)
8	0.35	0.05	(0.20 to 1.0)	0.6	(0.085 to 0.33)(All ST's <650°)
9	0.35	0.2	(0.33)	0.45	(0.29)

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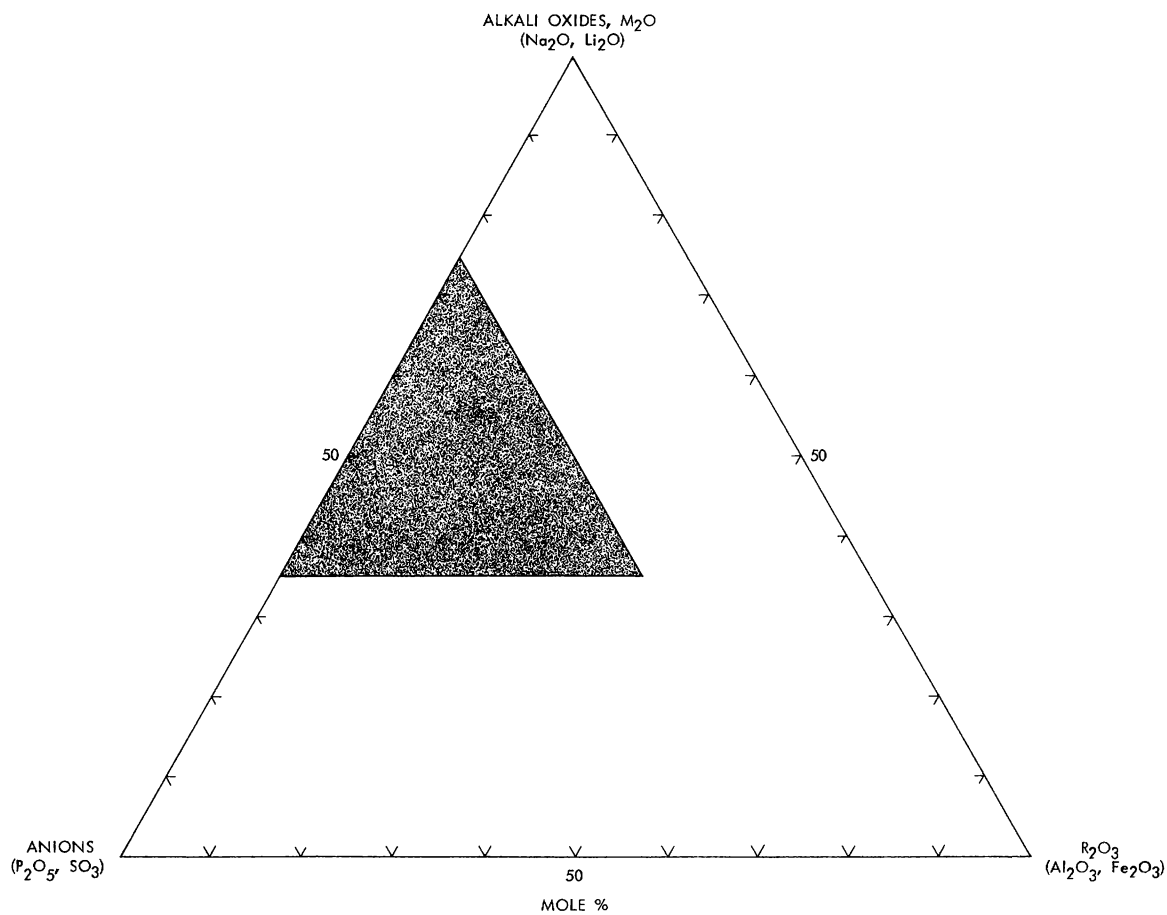
Fig. 10. Pseudo Phase Diagram Used in the Correlation of Melt Compositions and Properties. Shaded area includes the compositions of the best melts developed.

Within the indicated optimum composition range, the Na_2O/Li_2O ratio appears to be optimum at about 1 (Figs. 8 and 9), and the SO_3/P_2O_5 ratio at ≤ 1. The nature of the solid product is less sensitive to the Fe_2O_3/Al_2O_3 ratio than to the other two within the ranges studied. This ratio has not yet been investigated over as wide a range as the other two.

Increase in the total M_2O content beyond the indicated range usually resulted in either a higher melting mix or a heterogeneous solid or both. Increase in total R_2O_3 content tended toward raising the softening and melting temperatures. Excessive amounts of anions increased the loss of sulfate and/or increased the leachability of the material. As a rule, the addition of alkaline-earth oxides (e.g., CaO, BaO) decreased the solubility of the resulting solid and increased the melting temperature. Adding simulated fission products corresponding to burnups of 10,000 to 35,000 Mwd/metric ton increased the melting temperature but improved the physical properties of the product (Fig. 11).

Much less effort has been expended on the development of solids for fixation of non-sulfate Purex waste, and no semiengineering scale experiments have thus far been made on this waste type.

Fairly typical examples of the solid products obtained are described in Table 6 for high-sulfate (FTW-65 and 1WW) and in Table 7 for non-sulfate waste types. Examples have been selected to show unsatisfactory as well as satisfactory types of products. It is rather interesting to note that the majority of the more satisfactory melts developed for the non-sulfate waste fall into the same compositional triangle as that for the sulfate-containing waste (Fig. 10). It may be significant that this "best" region is almost entirely included with the area on the triangular plot, Na_2O-Al_2O-P_2O_5, designated as "glass" by Takahashi[18], though in our studies most of the non-sulfate melts were excessively soluble in water, too viscous for practical operation below 900°C, or devitrified rapidly unless substantial amounts of lead oxide were added.

The more satisfactory solids from fixation of the two waste types generally fell within the following mole-percent ranges:
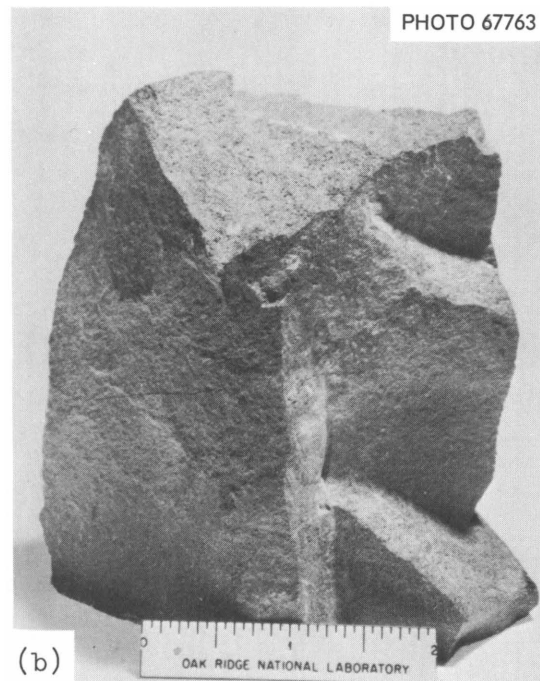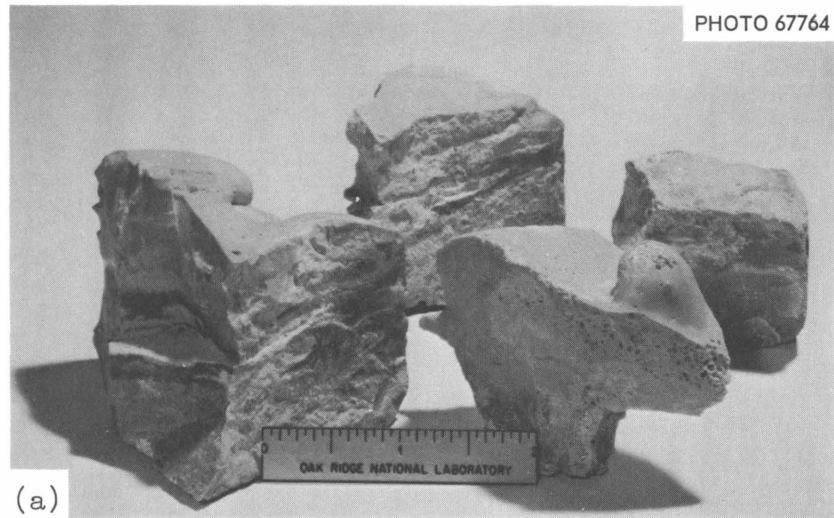
Fig. 11. Solids Obtained by Fixing Simulated Purex FTW-65 Waste.
(a) With no simulated fission products; (b) with simulated fission
products expected from fuel burnup of 10,000 Mwd/metric ton.

Table 6. Examples of Solid Products from Fixation of Simulated Sulfate-Containing Purex Waste Solutions
(No simulated fission products except Ru)

Waste Type	FTW X3	FTW X3	FTW X3[b]	FTW X3	FTW X3	FTW X3	1WW	1WW	1WW[b]	1WW	1WW
Additives (g-moles/liter waste)	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11
H_3PO_4, H_3PO_3, or H_3PO_2[a]	1.02	1.50	2.0	0.66	1.02	4.5	2.27	1.02	2.0	1.7	3.0
$Na_2B_4O_7 \cdot 10H_2O$	--	--	--	--	--	0.4	--	--	0.1	--	0.2
$Al(NO_3)_3 \cdot 9H_2O$	0.5	0.5	--	0.24	--	--	1.0	0.5	--	--	2.4
$LiOH \cdot H_2O$	1.14	1.50	--	0.68	--	--	2.53	1.14	--	--	--
$NaOH$[a]	--	--	--	--	1.14	1.8	1.4	--	2.0	1.3	2.6
$Ca(NO_3)_2 \cdot 4H_2O$ or $Ca(OH)_2$	0.2	0.2	--	--	0.2	1.2	--	0.2	--	1.1	0.8
$Pb(NO_3)_2$	--	--	0.5	--	--	--	--	--	1.0	--	--
$Fe(NO_3)_2 \cdot 9H_2O$	--	--	--	--	--	--	0.16	--	--	--	--
Wt % waste oxides, theoretical	44.5	39.6	29.5	60.6	47.1	16.8	32.2	53.5	24.5	39.8	22.5
Composition, mole %, theoretical											
Al_2O_3	11.8	10.2	2.7	9.6	3.0	1.1	10.4	9.6	1.0	1.2	17.8
CaO	7.2	6.2	--	--	8.3	17.7	--	6.4	--	26.3	11.4
Na_2O	16.3	14.1	16.4	22.1	40.3	25.6	18.9	9.6	28.5	22.2	25.7
Li_2O	20.6	23.5	--	16.7	--	--	23.9	18.1	--	--	--
Fe_2O_3	5.4	4.7	5.5	7.4	5.9	2.2	6.2	8.0	5.1	6.0	3.6
Cr_2O_3	1.1	0.9	1.1	1.5	1.2	0.4	0.1	0.2	0.1	0.1	<0.1
NiO	1.1	0.9	1.1	1.5	1.2	0.4	0.1	0.2	0.2	0.2	0.1
RuO_2	0.2	0.2	0.2	0.2	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PbO	--	--	18.2	--	--	--	--	--	--	--	--
SO_3	16.3	14.1	16.4	22.1	17.8	6.6	18.9	31.8	20.3	23.9	14.3
P_2O_5	18.4	27.3	36.7	16.6	20.1	33.7	21.5	16.2	20.3	20.1	--
B_2O_3	--	--	--	--	--	11.5	--	--	4.1	--	5.7
SiO_2	1.1	0.9	1.1	1.5	1.2	0.4	--	--	--	--	--
F^-	0.5	0.5	0.6	0.7	0.6	0.2	--	--	--	--	--
Approx. softening temp., °C	750	700	800	800	900	800	750	800	850	1000	950
Ratio[c]	1.22	1.17	--	--	--	--	1.06	0.71	--	--	--
Percent SO_3 lost (100 min at temperature)	5.3(900°)	19.6(900°)	--	--	--	--	6.2(900°)	33.5(950°)	--	--	--
Description	Brown rock; insoluble	Brown rock; insoluble	Crystalline; homogeneous	Glassy; segregated	Crystalline; segregated	Homogeneous glassy	Hard, brown rock; insoluble	Hard, black rock; voids	Crystalline; homogeneous	Never completely melted	Glassy; segregated

[a] Na, P, and B may be added as sodium phosphates and borates or as the respective acids and NaOH.

[b] Large amounts of lead and phosphite or hypophosphite should not be mixed because of the possibility of an explosive reaction on heating.

Table 7. Examples of Solid Products from the Fixation of Simulated Non-Sulfate Purex Waste
(No simulated fission products)

Additives (g-moles/liter waste)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
H_3PO_4	0.75	1.0	1.25	1.5	1.0	1.5	1.5	1.5	1.5	1.5	1.0	1.25	1.5	1.5
$Pb(NO_3)_2$	0.2	0.2	0.3	0.3	--	--	0.2	0.3	0.3	--	--	--	0.4	0.5
$Al(NO_3)_3 \cdot 9H_2O$	--	--	--	--	--	--	--	0.1	0.2	0.3	0.3	0.2	--	--
Wt % waste oxides, theo.	26.5	23.4	18.5	16.9	33.3	24.9	19	16.5	16.2	22.5	29.1	26.3	15.3	14
Mole % theoretical oxides														
Al_2O_3	9.8	8.7	7.3	6.7	10.6	8.4	7.2	12.5	17.7	26.8	32.2	23.6	6.3	5.9
Cr_2O_3	0.3	0.3	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Fe_2O_3	2.5	2.2	1.8	1.7	2.6	2.1	1.8	1.6	1.5	1.7	2.0	2.1	1.6	1.5
Na_2O	29.4	26.2	21.9	20.1	31.8	25.1	21.5	18.8	17.7	20.1	24.1	23.6	18.8	17.7
NiO	0.6	0.5	0.4	0.4	0.6	0.5	0.4	0.4	0.4	0.4	0.5	0.5	0.4	0.4
P_2O_5	37.8	44.6	46.4	50.9	54.0	63.7	54.5	47.7	44.9	50.9	41.0	50.0	47.7	44.9
PbO	19.6	17.5	21.9	20.1	--	--	14.3	18.8	17.7	--	--	--	25.1	29.5
Approx. softening temp.,°C	700	750	700	<650	800	<500	500	750	800	900	775	900	600	600
Approx. melting temp.,°C	800	850	750 (viscous)	<650	850 (viscous)	500	600	850 (viscous)	900 (viscous)	950 (viscous)	875 (viscous)	--	700 (viscous)	700 (viscous)
Description	Dark green, very hard; near glass; insoluble	Pale-green rock; crumbly; soluble	Pale-green rock; soluble	Clear-green glass; insoluble	Two phase; some green glass, some rock; insoluble	Two phase; green glass and rock; insoluble	Green glass; insoluble	Green rock	Green rock; voids	Very hard, dense; some segregation	Coarse, green rock; voids	Coarse, green rock; voids	Fine-grained green rock	Fine-grained green rock

	Sulfate	Non-Sulfate
P_2O_5	18-28	50-55
SO_3	<17	---
Na_2O	6-24	20-25
Li_2O	21-32	---
PbO	---	14-21
Al_2O_3-Fe_2O_3	8-20	8-12

By analogy with previous work on fixation of high-aluminum waste[1] the range of composition for the nonsulfate type waste should prove to be much wider than is indicated here.

It will be noted that the experiments listed in Tables 6 and 7 included only ruthenium to simulate the fission product material. These obviously represent greater volume reductions than those obtainable in fixation of actual waste. The minimum volume of solid product obtained in these experiments (Melt No. 1, Table 6) was equivalent to 2.7 gal of solid per ton of uranium processed. This particular product contained 44.5% waste oxides and 11.8% Al_2O_3, 31.5% P_2O_5, 7.4% Li_2O, and 4.9% CaO as fluxing agents. Results of scoping experiments in which simulated fission products were included are listed in Table 8. More complete results will be presented in a separate report after the data have been subjected to analysis by the computer program.

No quantitative measurements of mechanical strength were made on the solid products. In general, strength will vary considerably for different samples of the same composition depending largely upon cooling time (e.g., quenched or annealed). As a rule, crystalline materials do not shatter as readily as glasses but may fracture along cleavage planes. In any case, mechanical strength for almost any massive solid produced by melting will be more than sufficient to withstand any shocks or strains (including those resulting from dropping) as long as the container remains essentially intact.

The thermal conductivity of a satisfactory lithium-aluminum-phosphate ceramic (No. 1, Table 5) varied between about 1.3 and 1.7 Btu hr^{-1} ft^{-1} $°F^{-1}$

Table 8. Purex "Glasses" with Fission Products (FP's)

Additives (g-moles/liter)	FTW-65 (x3)		Non-Sulfate	
	1	2	1	2
H_3PO_4	1.5	3.6	2.0	2.0
$LiOH \cdot H_2O$	1.5	2.4	--	--
NaOH	--	2.7	--	--
$Ca(NO_3)_2 \cdot 4H_2O$	0.2	--	--	--
$Al(NO_3)_3 \cdot 9H_2O$	0.5	0.75	--	--
$Pb(NO_3)_2$	--	--	0.2	0.3
wt % waste oxides (including FP's)				
No FP's	40	20	--	--
FP's	52	30	24	22
Approx. mp (°C)				
No FP's	800	700	--	--
FP's	1000	800	800	800
Sulfate loss (%)				
No FP's	19.6	10.2	--	--
FP's	--	10.6	--	--

over the temperature range from 300 to 1600°F. This is higher than that for a calcined Purex product by a factor which decreases from about 8 at 300°F to about 2 at 1600°F (Fig. 12). The rather complex nature of the thermal conductivity curve for the Purex ceramic indicates probable transition from a crystalline to an amorphous state at about 570°F, followed by gradual softening of the latter beginning between 1000 and 1100°F. Between 300 and about 600°C, the thermal conductivity is still slightly greater than that of the aluminum (TBP-25) glass previously reported.[1]

It appears that the majority of glasses and ceramics can be expected to have thermal conductivities between about 1 and 2 Btu hr^{-1} ft^{-1} $°F^{-1}$ between 600°F (316°C) and the softening temperature. The calcined products, on the other hand, can apparently be expected to have thermal conductivities
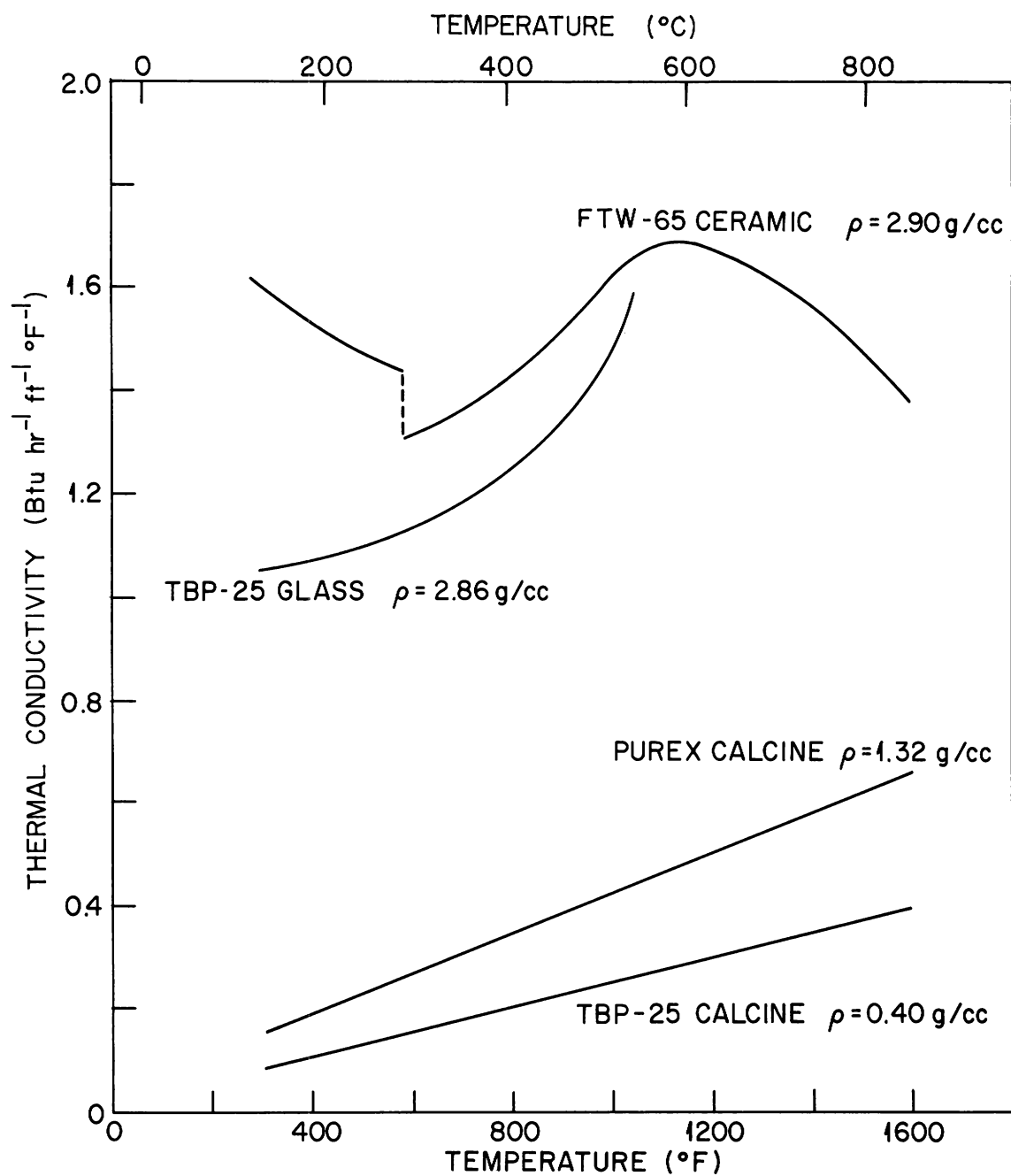
ORNL-DWG 63-4346R2

Fig. 12. Thermal Conductivity of a Lithium Aluminum Phosphate Ceramic Solid Incorporating 44.5 Weight % Solids from Simulated FTW-65 Waste. Thermal conductivities of TBP-25 glass and calcine and of Purex 1WW calcine are included for comparison.

which increase from about 0.1 Btu hr^{-1} ft^{-1} $°F^{-1}$ at 200°F to 0.3-0.8
Btu $hr^{\pm1}$ ft^{-1} $°F^{-1}$ at 1600°F. [1,19]

3.5 Materials of Construction[*]

The final fixation container (pot), whether used as the evaporation-
calcination vessel (Potcal Process), the evaporation-meltdown vessel (RL-
Potglass Process) or simply as the final melt receiver and storage vessel
(Con-Potglass Process, Fig. 1) can be designed with sufficient wall
thickness to withstand severe corrosion for the relatively short periods
that it will be held at high temperature. The continuous evaporator (plus
the condenser and off-gas system) common to all three processes, and the
continuous melter for the Con-Potglass Process, must, on the other hand,
be made of material that has a relatively long service life since replace-
ment of these items in a highly radioactive environment will be difficult
and expensive. All such permanent equipment must be resistant over a
fairly wide range of environments to allow for probable variations in the
composition of the waste solutions to be processed. A general summary
of the corrosion data is given here. Detailed data will be presented in
a separate report.

Titanium was found to be a very satisfactory material of construction
for the continuous evaporator, the condenser, and the off-gas system. Cor-
rosion rates varied from negligible during evaporation of FTW-65 waste,
both with and without glass-making additives, to a maximum of 2 to 3
mils/month in refluxing 15 $\underline{M}$ HNO_3--1.0 $\underline{M}$ H_2SO_4 (Table 9). The latter
solution is not expected to result from any of the three ORNL processes,
but might result from calcination of a Purex waste in which the sulfate
is not balanced by cations.

Stainless steel is sufficiently resistant for use in an evaporator
for the FTW-65 waste. The maximum corrosion rate was about 0.3 mil/month.
It corroded about 10 times faster and developed intergranular attack in

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[*]Corrosion tests were run by L. Rice, P. D. Neumann, and J. L. English of
the ORNL Reactor Chemistry Division.

Table 9. Summary of Corrosion Tests in Sulfate-Containing Purex Waste Evaporator Environments
(All specimens were welded)

| Test Conditions | Exposure Time (hr) | Maximum Corrosion Rate, mils/month, in Vapor (V), Interface (I), or Solution (S) for Alloys Listed | | | | | | | |
| | | 347 | 304L | Coupled | | Ti-45A | Hastelloy F | LCNA[f] | LCNA[f] 0.2% Pd |
				304L	Ti-45A				
FTW-65 waste environments (all reflux)									
"Initial" solution (FTW-65)	1300-1600	--	a	0.3 (V)	a	a	a	--	--
"Final" solution[b]	1008	--	$\leq$0.1 (all)	$\leq$0.1 (all)	$\leq$0.1 (all)	$\leq$0.1 (all)	$\leq$0.1 (all)	--	--
"Initial" solution plus "glass" additives[c]	1008	--	0.2 (S)	0.2 (S)	<0.01	<0.01	0.1 (S)	--	--
"Final" solution plus "glass" additives[d]	1008	--	0.3 (V)	0.2 (V)	a	a	0.2 (V)	--	--
1WW waste environments									
(all reflux except superheat experiment)									
"Initial" solution (1WW waste)	300-500	4.2 (V)[e]	2.8 (V)[e]	--	--	0.04 (V,I)	2.0 (S)	0.67 (S)	--
	840-1000	3.3 (V)[e]	2.8 (V)[e]	--	--	0.04 (S)	3.3 (S)[e]	0.82 (S)[e]	
"Final" solution[g]	72	--	--	--	--	--	0.2 (S)	0.1 (S)	--
Super-heated (150-305°C) vapor above boiling, 1WW waste solution	1008	<0.1	<0.1	--	--	--	--	--	--
Simulated waste condensate									
"Average" (6 $\underline{M}$ HNO$_3$--0.05 $\underline{M}$ H$_2$SO$_4$)	144	--	--	--	--	2.1 (S)	0.58 (S)	0.16 (S)	7.2 (S)[e]
	520	--	--	--	--	--	2.9 (V)	2.7 (V)	--
	1000	--	--	--	--	1.5 (S)	--	--	--
"Final" (15 $\underline{M}$ HNO$_3$--1.0 $\underline{M}$ H$_2$SO$_4$)	144	--	--	--	--	--	9.8 (V)[e]	1.0 (S)	--
	360-520	--	--	--	--	3.3 (S)[h]	11.2 (V)[e]	9.9 (V)[e]	--
	1145	--	--	--	--	2.0 (S)	--	--	--

[a]Indicates slight weight gain.

[b]Solution composition ($\underline{M}$): H$^+$, 1.5; Na$^+$, 1.2; Al^{3+}, 0.2; Fe^{3+}, 0.4; Cr^{3+}, 0.08; Ni^{2+}, 0.04; Hg^{2+}, 0.014; UO$_2^{2+}$, 0.013; Ru^{3+}, 0.008; SO$_4^{2-}$, 0.6; PO$_4^{3-}$, 0.2; SiO$_3^{2-}$, 0.04; F$^-$, 0.08; Cl$^-$, ~0.024; NO$_3^-$, to balance.

[c]Additives (g-moles/liter waste): H$_3$PO$_4$, 1.0; LiOH·H$_2$O, 1.4; Al(NO$_3$)$_3$·9H$_2$O, 0.5.

[d]Additivies (g-moles/liter concentrated waste): H$_3$PO$_4$, 4.0; LiOH·H$_2$O, 5.6; Al(NO$_3$)$_3$·9H$_2$O, 2.0.

[e]Intergranular attack observed.

[f]A special low-carbon alloy (0.005% C) with the nominal composition of Ni-o-nel.

[g]Solution composition ($\underline{M}$): H$^+$, 0.3; Na$^+$, 1.3 to 1.8; Al^{3+}, 0.2 to 0.3; Fe^{3+}, 1.0 to 1.5; Cr^{3+}, 0.02 to 0.03; Ni^{2+}, 0.02 to 0.03; Ru, 0.004 to 0.006; SO$_4^{2-}$, 2.0 to 3.0; Cl$^-$, ~0.12 to 0.02; NO$_3^-$, to balance (~1.2 to 1.8).

[h]Slight localized attack in the heat-affected zone near weldments.

the highly acid vapor phase and condensate from 1WW waste. Type 304L stainless steel is slightly but consistently superior to type 347 for service in all Purex waste environments investigated.[1,20] The high-nickel alloys, Hastelloy F and LCNA*, were more resistant to the acid sulfate-nitrate solutions than was stainless steel, but developed inter-granular attack on long exposure in the more aggressive environments. Tests not listed on Table 9 confirmed previous observations that ruthenium accelerates the attack on stainless steels and nickel alloys. Constant addition of small amounts of H_2O_2 to simulate radiolysis of water had no noticeable effect on the corrosion rate.

Stainless steel has been used for construction of the "pot-head" for connecting the pot to the condenser and off-gas system in engineering-scale experiments here.[21] Titanium is undesirable because of its tendency to gall. Stainless-steel pot heads used for several hundred hours showed no appreciable attack. This lack of attack in the superheated vapor (150 to 305°C) was confirmed by laboratory experiment; rates for both 304L and 347 stainless steel were less than 0.1 mil/month (Table 9). Coupling the stainless steel to titanium (e.g., the pot head to the off-gas line) resulted in no marked acceleration of corrosion.

Corrosion of the fixation pot is dependent upon both the fixation temperature and the composition of the waste plus additives. Since the cost of the pot is a major item in the overall cost of waste disposal in the Potcal and RL-Potglass processes, it is imperative that the material of construction be no more expensive or difficult to fabricate than stain-less steel. The use of stainless steel imposes a maximum temperature limit of about 1050°C on the process.** This maximum must be lowered for longer-term operation or for use with corrosive melts. RL-Potglass experiments employing stainless steel pots, 88 in. long and 8 in. in diameter (i.e., practical engineering scale) have been run at temperatures as high as 950°C, with occasional temperature excursions to 1050°C. Maximum penetration

*A special low-carbon nickel alloy (0.005% C) with the same nominal composition as Ni-o-nel.
**RL-Potglass fixation of aluminum type (TBP-25) waste have been success-fully carried out on a semiengineering scale at operating temperatures of 1000°C with occasional excursions to about 1050°C. A lower tempera-ture is advisable, particularly with sulfate-containing wastes since a small mistake in fluxing additives may considerably increase the vapor pressure of SO_3 above the melt.

observed was about 120 mils vs an arbitrary corrosion allowance of 150 mils out of a total wall thickness of 320 mils.[9]

A number of pot-corrosion tests were run by evaporating waste solutions plus additives to dryness and then heating to operational temperatures for periods of several days. The results (Table 10) indicate (1) that corrosion is less in the calcination (Potcal) process than when a melt is produced, (2) that the worst corrosion in the glass-making (RL-Potglass) process normally occurs during the period when the last of the volatile material (water, SO_3, etc.) is driven off,[*] and (3) that corrosion varies markedly with different compositions of melt plus additives. Depending upon melt composition and operating temperature, corrosion rates varied from almost negligible to catastrophic.

Corrosion tests and operating experience alike showed that the worst corrosion was associated with loss of sulfate (or of fluoride when present) from the melt. Even in melts which contain excess alkali and alkaline earth metals, such loss can occur through hydrolysis of sulfates with steam. This was apparently the mechanism of the rapid failure of the pot in the "sparged-glass" experiment (Table 3, No. 9). Likewise, the occasional local attack observed in Potcal experiments was usually associated with adherence of wet calcine to the pot wall at the point of attack. The presence of the magnetic oxide of iron, Fe_3O_4, at the point of attack is circumstantial evidence that the steam-iron reaction is involved in the corrosion process. Very rarely another type of attack was observed with the sulfate-containing waste. In this latter case no Fe_3O_4 was detectable, but SO_2, SO_3, and/or H_2S were detectable by odor. This type of attack was observed when the sulfate melts were held at temperatures well above their melting points for substantial periods of time after the initial meltdown. This type of attack is obviously caused by oxidation of the stainless steel container by the sulfate. Temperature cycling of the container (i.e., allowing the melt to solidify and then remelting) seems to invite this type of attack.

"Neutral" glasses which contain enough alkalis plus alkaline earths to neutralize the nonvolatile acid anions and which are "buffered" with

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[*]For example, 304 stainless steel in FT-1WW waste + additives at 900°C corroded at 133 mils/mo for a 24 hr exposure but at only 80 mils/mo for a 78 hr exposure. At 950° rates were 1330 mils/mo for a 2 hr exposure vs 19 mils/mo for a 75 hr exposure.

Table 10. Summary of Corrosion Tests During Calcination and Fixation of Simulated Sulfate-Containing
Purex Waste
(All specimens welded)

Environment[a]	Material	Maximum Temp. °C	Expo-sure Time (hr)	Overall Corrosion Rate, mils/mo	Remarks
Air (no waste)	304L	900	24	1.4	
FT-1WW[b] calcined solids after calcination to 1000°C	304L	900	123	3.6[c]	
FT-1WW	304L	900	24	7.3[c]	
FT-1WW plus "glass" making additives[d]					
Expt. No. 1	304L	900	24	133	Intergranular attack
Expt. No. 2	304L	900	78	80	Intergranular attack
Expt. No. 3					
- Part A	304L	850	1	~0	
- Part B	304L	950	2	1330	Very aggressive inter-granular attack
- Part C	304L	950	75	19	
FTW-65 plus 0.0135 $\underline{M}$ $Ca(NO_3)_2 \cdot 4H_2O$	304L	1050	168	2.5	10 mils total penetration
	Ti-45A	1050	168	Failed	Specimen completely dis-integrated
	Ti-0.2% Pd	1050	168	Failed	Specimen completely dis-integrated
FTW-65 plus "glass" making additives[f]					
Expt. No. 1 - Sodium flux[g]		1050	29	283	15.4 mils total penetra-tion
Expt. No. 2 - Lithium flux		1050	24	--	<31 mils total. Heavy exfoliation
Expt. No. 3 - Lithium "reducing" flux		1050	24	Failed	>31 mils total penetra-tion

[a]Except as otherwise indicated, the waste with or without additive was evaporated, brought to the temperature indicated, and held there for the time indicated.

[b]Formaldehyde-treated 1WW. Solution composition ($\underline{M}$): H^+, 0.3; SO_4^{2-}, 2.0; NO_3^-, 1.2; Na^+, 1.2; Al^{3+}, 0.2; Fe^{3+}, 1.0; Cr^{3+}, 0.02; Ni^{2+}, 0.02; Ru, 0.004.

[c]Average of two experiments.

[d]Additives (g-moles/liter waste): $Na_2B_4O_7 \cdot 10H_2O$, 0.13; $NaH_2PO_4 \cdot H_2O$, 0.76; H_3PO_2, 0.76; $Ca(OH)_2$, 1.1; NaOH, 0.22. Subsequent work showed that this melt loses gross amounts of sulfate at the test temperature.

[e]Parts A, B, and C of this experiment were done in sequence, i.e., the solution was evaporated and calcined to 850°, the corrosion measured, specimen replaced, heated to 950°, etc.

[f]Additives (g-moles/liter waste): H_3PO_4 (H_3PO_3 for reducing flux), 1.33; $LiOH \cdot H_2O$, 1.52; $Ca(OH)_2$, 0.27; $Al(NO_3)_3 \cdot 9H_2O$, 0.67.

[g]This melt was developed before the lower-melting lithium counterparts. Additives (g-moles/liter waste): H_3PO_4, 1.33; NaOH, 1.52; $Ca(OH)_2$, 0.27; $Al(NO_3)_3 \cdot 9H_2O$. Concentration of Al.

an amphoteric element such as aluminum were found to be generally less corrosive than glasses containing an excess of either sulfate or phosphate.

The elongation of a stainless steel pot loaded with glass is almost negligible below 1050°C. Small pots placed under a tension of 315 lb/in.^{2} * were subjected to a Purex evaporation-melting cycle and then held at 1050°C for 96 hr. The maximum elongation observed was 1.5×10^{-3} in./in., which is equivalent to less than 150 mils for a pot 8 ft long.

Storage of the loaded pot in a salt mine does not present a significant corrosion problem. Stainless steel specimens exposed at 300°C for six months in salt (NaCl) containing up to 2% water, 5% $CaSO_4$, and 0.25% $MgCl_2$ corroded at maximum overall rates of about 0.03 mil/month and showed maximum total local attack amounting to 6-10 mils. In any event, the integrity of the pot is not significant once the pot is placed in the salt environment.

It is almost certain that the relatively low-melting (e.g., 700 to 800°C) ORNL Purex glasses developed for the continuous glass (Con-Glass) process can be contained in platinum for an indefinitely long period. Hatch[22] reports negligible attack on a platinum continuous melter for melts containing 50 to 65% P_2O_5 at temperatures between 1000°C and 1200°C for 1400 hours. Short-term exposures of platinum to sulfate-containing Purex melts in a laboratory-scale continuous melter tend to confirm this conclusion. However, the possibility remains that the Con-Potglass process may be contained in cheaper and more conventional materials of construction. Finding such a material is one objective of the continuing ORNL development program. A 304L stainless steel continuous melter of practical size (40 in. long and 12 in. in diameter) was operated for about 250 hr at temperature without failure.[21] Although stainless steel is not sufficiently resistant to make its use attractive in an operating plant, certain of the nickel-chromium alloys (e.g., Inconel, Corronel 230, and 50% Cr-50% Ni) have performed much better than stainless steel in short-term tests. These tests are still in the early stages and will be continued.

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*This is the calculated maximum stress to which any part of a pot 8 ft long and 24 in. in diameter would be subjected if filled with melt.

Use of protective coatings (e.g., flame-sprayed Al_2O_3 or ZrO_2) may
be worthwhile even though the coating is not self-healing. A lithium-
aluminum phosphate Purex "glass" (No. 1, Table 6) was melted in two 304
stainless steel beakers coated with Al_2O_3 and ZrO_2, respectively, held
at 900°C for 16 hr and then sectioned. The bond between the metal and
the protecting oxide appeared to be essentially intact in both cases.
Exposure of flame-coated specimens in a continuous melter indicated that
the coatings were porous at sharp edges and possibly at other locations
as well.

4. SUMMARY AND CONCLUSIONS

1. Sulfate-containing Purex wastes can be fixed in insoluble solids
(i.e., ones that leach at a rate corresponding to a penetration of $\sim 10^{-4}$ g
cm^{-2} day^{-1}). Ninety-five percent (95%) or more of the sulfate can be
retained in the glassy product. Phosphate, aluminum, sodium, lithium,
and calcium were the fluxes used with the greatest success. The minimum
volume of satisfactory solid product formed was 2.7 gallons per ton of
uranium processed. Further work is needed to establish optimum composi-
tional limits and operational conditions. Fixation is technically feasi-
ble by either the rising-level technique (RL-Potglass Process) or by a
continuous melting technique.

2. Non-sulfate Purex wastes can be fixed in insoluble glass by
fluxing with phosphate and lead. Much less work has been done with this
waste type than with the sulfate-containing waste.

3. Elements simulating fission products resulting from fuel burnups
of 10,000 and 35,000 megawatt days per metric ton were successfully in-
corporated into the glassy solids produced from sulfate and non-sulfate
Purex waste types, respectively. The presence of these elements usually
increases both the melting temperatures and the viscosities of the resul-
tant melts and therefore requires the addition of extra fluxing additives
in order to maintain low melting temperatures and fluidities.

4. Stainless steel is a satisfactory material of construction for
the fixation pot-storage container in the RL-Potglass process. The

extreme maximum temperature for the use of stainless steel is about 1050°C; operation at 800° to 900°C allows a margin of safety. The composition of the melt can be very critical from a corrosion standpoint. Those compositions which tend to hold water at high temperatures and those which contain an excess (in chemical equivalents) of nonvolatile anions over the alkali and alkaline earth metals (i.e., "acid" glasses) are more corrosive than those which lose water before or upon melting or the "neutral" glasses which contain a slight excess of strong cations plus a "buffer" such as aluminum.

5. The long-term containment of the continuous melting (Con-Potglass) process in materials other than platinum has not been demonstrated but remains a principal objective of this program. Titanium is by far the most resistant material of construction tested for the waste evaporator. In strongly acid sulfate-containing wastes the long-term maximum rate was 3.3 mils per month but in low acid wastes the corrosion was negligible. Both stainless steel and the common nickel alloys suffer aggressive intergranular attack in high acid waste solutions and condensates but in low-acid wastes rates were less than 1 mil per month.

6. Methods are available for lowering the volatility of ruthenium and cesium to approximately entrainment quantities.

7. Mercury can be removed from the waste by displacement with copper or aluminum.

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APPENDIX
Vapor-Liquid Equilibrium Data for Simulated Purex 1WW and FTW-65
Waste Solutions

Knowledge of the compositions and densities of expected condensate and thick liquor streams is a prerequisite to intelligent design of a continuous evaporator. High-level waste disposal plants built for operation within the near future must be prepared to handle a range of waste compositions within one general "type" of waste (e.g., "Purex," "TBP-25," etc.). The data presented here are for a range of concentrations of two different subtypes of sulfate-containing Purex waste solutions designated as "1WW" and "FTW-65," respectively (Table A-1). The solutions studied contained no simulated fission products.

The vapor-liquid equilibrium studies were made in Gillespie stills. Distillations were carried out for ten times the length of time required for a single filling of the condensate receiver. It has been shown that no further change in the composition of the condensate takes place after this point; in fact it appears that this is very conservative and that equilibrium is probably reached after as few as 3 or 4 condensate volumes have been distilled in the cases studied. Temperatures were measured in the stillpot and in the vapor-liquid disengagement chamber. Studies were carried out on both types of solutions at ambient pressures (745 to 750 mm Hg). The 1WW solution was also investigated at ~564 mm. Samples of feed, thick liquor, and distillate were analyzed for the principal constituents (Tables A-2 and A3).

Equilibrium data for 1WW waste are plotted as functions of acid concentration (Fig. A-1) and of Fe(III) concentration (Fig. A-2) since the compositional variations of this waste subtype included both acid and metal ion concentrations. Data for nitric acid alone (i.e., molarity of Fe(III) = 0) is included in these plots.[*] Equilibrium data for FTW-65 are plotted as a function of acid concentrations only (Fig. A-4).

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[*]These data were obtained from the <u>International Critical Tables</u>, vol. III, p 305, McGraw-Hill, New York, 1928 .

The densities recorded and plotted for the 1WW waste (Table A-2 and Fig. A-3) were determined for the thick liquor from the Gillespie-still studies using picnometers. The densities recorded and plotted for the FTW-65 waste (Table A-3, Fig. A-5), on the other hand, are for the original solutions used for still feed. These densities were determined by means of a Westphal balance. The difference in shape between the curves for the more concentrated FTW-65 solutions compared with that for the other density-concentration curves probably indicates that there was some evaporation of water from the solutions during the Westphal-balance determinations.

Table A-1. Nominal Compositions of Simulated Waste Solutions

Solution No.	Solution Composition (M)								
	H^+	Al^{3+}	Fe^{3+}	Na^+	Hg^{2+}	NO_3^{-*}	Cr^{3+}	Ni^{2+}	SO_4^{2-}
I. Purex 1WW									
1WW - 1	5.6	0.1	0.5	0.6	--	6.05	0.01	0.01	1.0
- 1a	7.0	0.1	0.5	0.6	--	7.45	0.01	0.01	1.0
- 1b	4.0	0.1	0.5	0.6	--	4.45	0.01	0.01	1.0
- 1c	2.0	0.1	0.5	0.6	--	2.45	0.01	0.01	1.0
1WW - 2	5.6	0.05	0.25	0.3	--	5.825	0.005	0.005	0.5
- 2a	7.0	0.05	0.25	0.3	--	7.225	0.005	0.005	0.5
- 2b	4.0	0.05	0.25	0.3	--	4.225	0.005	0.005	0.5
- 2c	2.0	0.05	0.25	0.3	--	2.225	0.005	0.005	0.5
1WW - 3	5.6	0.2	1.0	1.2	--	6.50	0.02	0.02	2.0
- 3a	7.0	0.2	1.0	1.2	--	7.90	0.02	0.02	2.0
- 3b	4.0	0.2	1.0	1.2	--	4.90	0.02	0.02	2.0
- 3c	2.0	0.2	1.0	1.2	--	2.90	0.02	0.02	2.0
II. Purex FTW-65									
FTW x 1	0.55	0.05	0.10	0.2	0.0035	0.997	0.02	0.01	0.15
x 2	1.10	0.10	0.20	0.4	0.0070	1.994	0.04	0.02	0.30
x 3	1.65	0.15	0.30	0.6	0.0105	2.991	0.06	0.03	0.45
x 4	2.2	0.20	0.40	0.8	0.014	3.988	0.08	0.04	0.60
x 5	2.7	0.25	0.50	1.0	0.0175	4.935	0.10	0.05	0.75
x 7	3.5	0.35	0.70	1.4	0.0245	6.629	0.14	0.07	1.05
x 9	4.5	0.45	0.90	1.8	0.0315	8.523	0.18	0.09	1.35

*Calculated by difference.

Table A-2. Vapor-Liquid Equilibrium and Density Data for Simulated
1WW Purex Waste

Solution	H+ Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) of Thick Liquor			
				25°C	50°C	75°C	100°C
			Pressure 744-751 mm Hg				
PS-1	5.35	110.5	---				
pot	5.52			1.3175	1.2994	1.2773	1.2505
distillate	1.43						
PS-1a	6.75	113	747.7	1.3548[b]	1.3347	1.3096	1.2824
pot	6.88						
distillate	2.81						
PS-1b	3.70	107.5	747.7				
pot	3.92			1.2736	1.2565	1.2377	1.2106
distillate	0.58						
PS-1c	1.88	104	750.5				
pot	1.91			1.2115	1.1974	1.1804	1.1536
distillate	0.091						
PS-2	5.50	109	747.7				
pot	5.57			1.2653	1.2470	1.2246	1.1947
distillate	1.10						
PS-2a	6.78	111	747.7				
pot	6.89			1.2944	1.2738	1.2376	1.2217
distillate	2.12						
PS-2b	3.80	106	750.5				
pot	4.08			1.2133	1.1973	1.1776	1.1487
distillate	0.44						
PS-2c	1.82	103	750.5				
pot	1.95			1.1423	1.1297	1.1129	1.0800
distillate	0.058						
PS-3[a]	5.25	113	750.4				
pot	5.36			1.4470	1.4272	1.4032	1.3770
distillate	2.67						
PS-3a[c]	6.67	116	750.4				
pot	6.81						
distillate	4.88						
PS-3b	3.67	110	744.4				
pot	3.77			1.3991	1.3810	1.3603	1.3334
distillate	1.05						
PS-3c	2.22	106.5	747.5				
pot	2.38			1.3778	1.3612	1.3426	1.3144
distillate	0.25						

Table A-2. (Cont'd.)

Solution	H$^+$ Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) of Thick Liquor			
				25°C	50°C	75°C	100°C
Pressure 564-568 mm Hg							
PS-1s	5.35	101	563.6				
pot	5.53			1.3319	1.3103	1.2845	1.2508
distillate	0.95						
PS-1as	6.75	105	567.1				
pot	6.73			1.3543	1.3324	1.3076	1.2777
distillate	2.42						
PS-1bs	3.70	99.5	567.1				
pot	3.83			1.2747	1.2575	1.2376	1.2114
distillate	0.44						
PS-1cs	1.88	96	566.6				
pot	1.85			1.2104	1.1963	1.1791	1.1480
distillate	0.056						
PS-2s	5.50	103.5	563.6				
pot	5.38			1.2663	1.2474	1.2252	1.1950
distillate	1.49						
PS-2as	6.78	103	567.1				
pot	6.66			1.2953	1.2725	1.2469	1.2167
distillate	1.94						
PS-2bs	3.80	98.5	567.1				
pot	3.92			1.2131	1.1959	1.1773	1.1451
distillate	0.37						
PS-2cs	1.82	95	566.6				
pot	1.87			1.1457	1.1331	1.1150	1.0884
distillate	0.048						
PS-3s	5.25	106	566.6				
pot	5.63			1.4552	1.4331	1.4112	1.3833
distillate	2.64						
PS-3bs	3.67	103	566.6				
pot	4.17			1.4037	1.3844	1.3639	1.3395
distillate	0.99						
PS-3cs	2.22	99	566.6				
pot	2.16			1.3777	1.3602	1.3416	1.3155
distillate	0.19						

[a]Solution precipitated on standing.

[b]Measurements made on duplicate samples.

[c]Densities of solution not determined because of solution instability.

Table A-3. Vapor-Liquid Equilibrium and Density Data for Simulated FTW-65 Waste Solutions

Solution	H^+ Analyzed (M)	Fe Analyzed (mg/ml)	Equilibrium Boiling Point (°C)	Density (g/ml) of Still Feed			
				23.5°C	50.0°C	75.0°C	100.0°C
FTW-Conc. x 1*	0.55	5.40	101	1.064	1.056	1.043	1.018
pot	0.56						
distillate	<0.02						
FTW-Conc. x 2	1.07		102				
pot	1.08						
distillate	<0.02						
FTW-Conc. x 3	1.65	16.40		1.194	1.181	1.165	1.135
pot							
distillate							
FTW-Conc. x 4	1.87		105				
pot	2.09						
distillate	0.17						
FTW-Conc. x 5	2.68	23.6	108	1.317	1.301	1.273	1.265
pot	2.91	29.0					
distillate	0.55	<0.005					
FTW-Conc. x 7	3.44	36.0	114	1.413	1.395	1.373	1.354
pot	3.76	42.0					
distillate	1.40	<0.005					
FTW-Conc. x 9	3.70	47.3	115	1.441	1.423	1.397	1.386
pot	3.85	54.5					
distillate	2.53	<0.005					

*Composition, g-moles/liter: H^+, 0.5; Na^+, 0.3; Al^{3+}, 0.05; Fe^{3+}, 0.1; Cr^{3+}, 0.02; Ni^{2+}, 0.01; Hg^{2+}, 0.0035; SO_4^{2-}, 0.15; PO_4^{3-}, 0.005, SiO_3^{2-}, 0.01; F^-, 0.002, NO_3^- to balance.
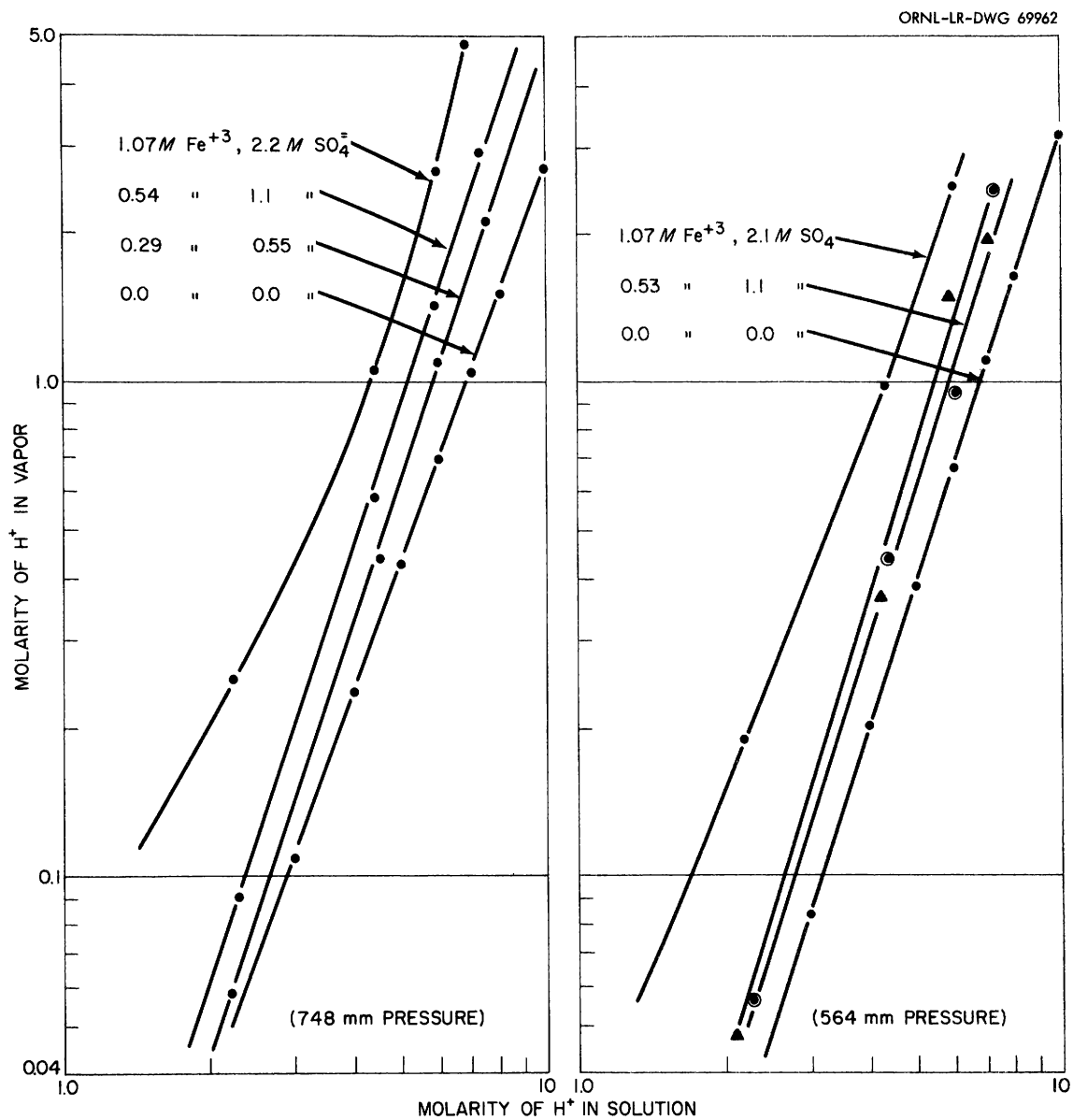
Fig. A-1. Vapor-Liquid Equilibrium of Simulated Purex 1WW Waste.
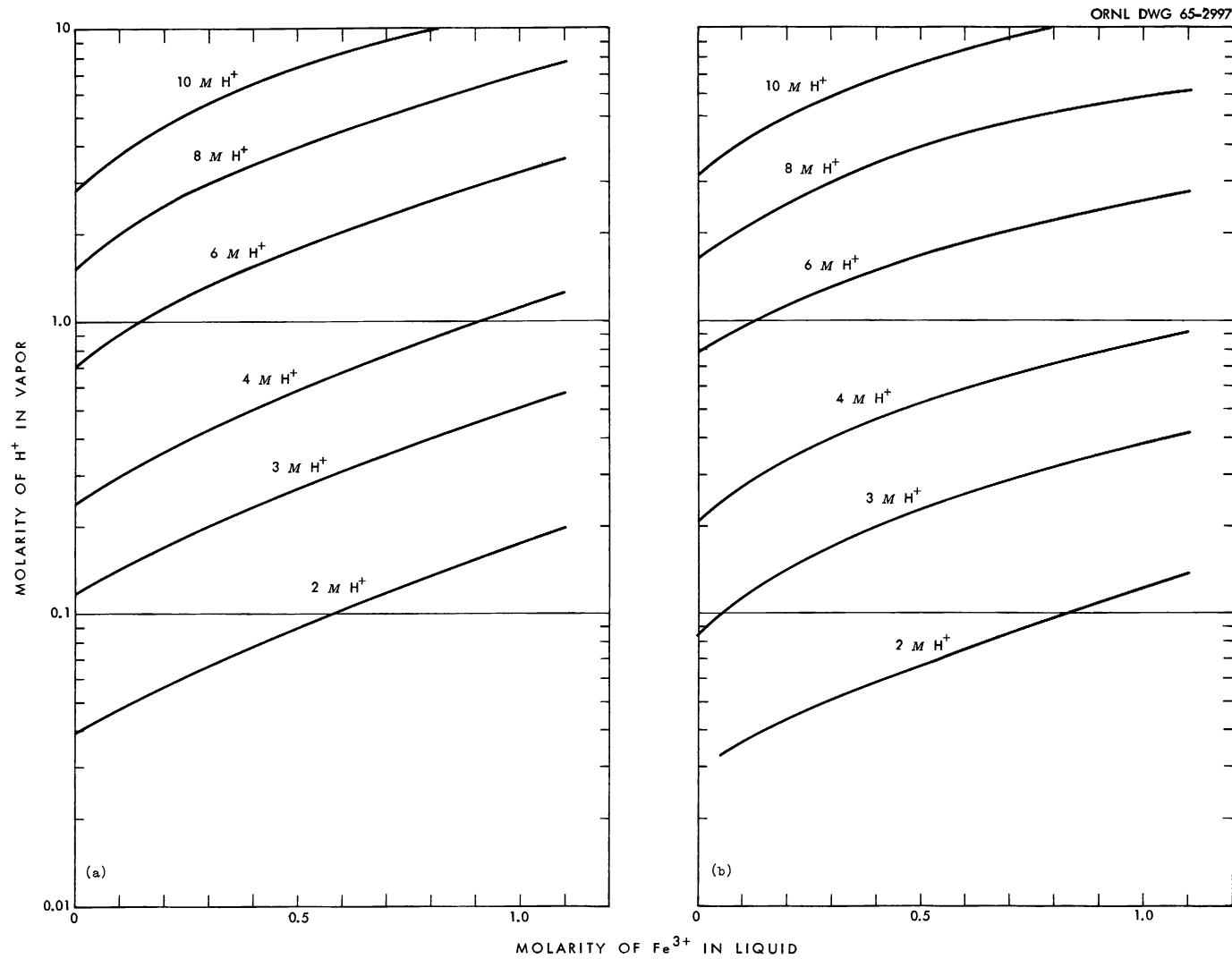
Fig. A-2. Vapor-Liquid Equilibrium in Simulated 1WW Purex Waste.
(a) 744-751 mm Hg; (b) 564-568 mm Hg.

Fig. A-3. Density of Simulated Sulfate-Containing Purex Waste Solutions.
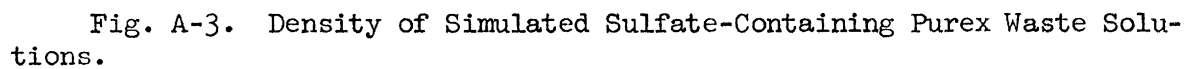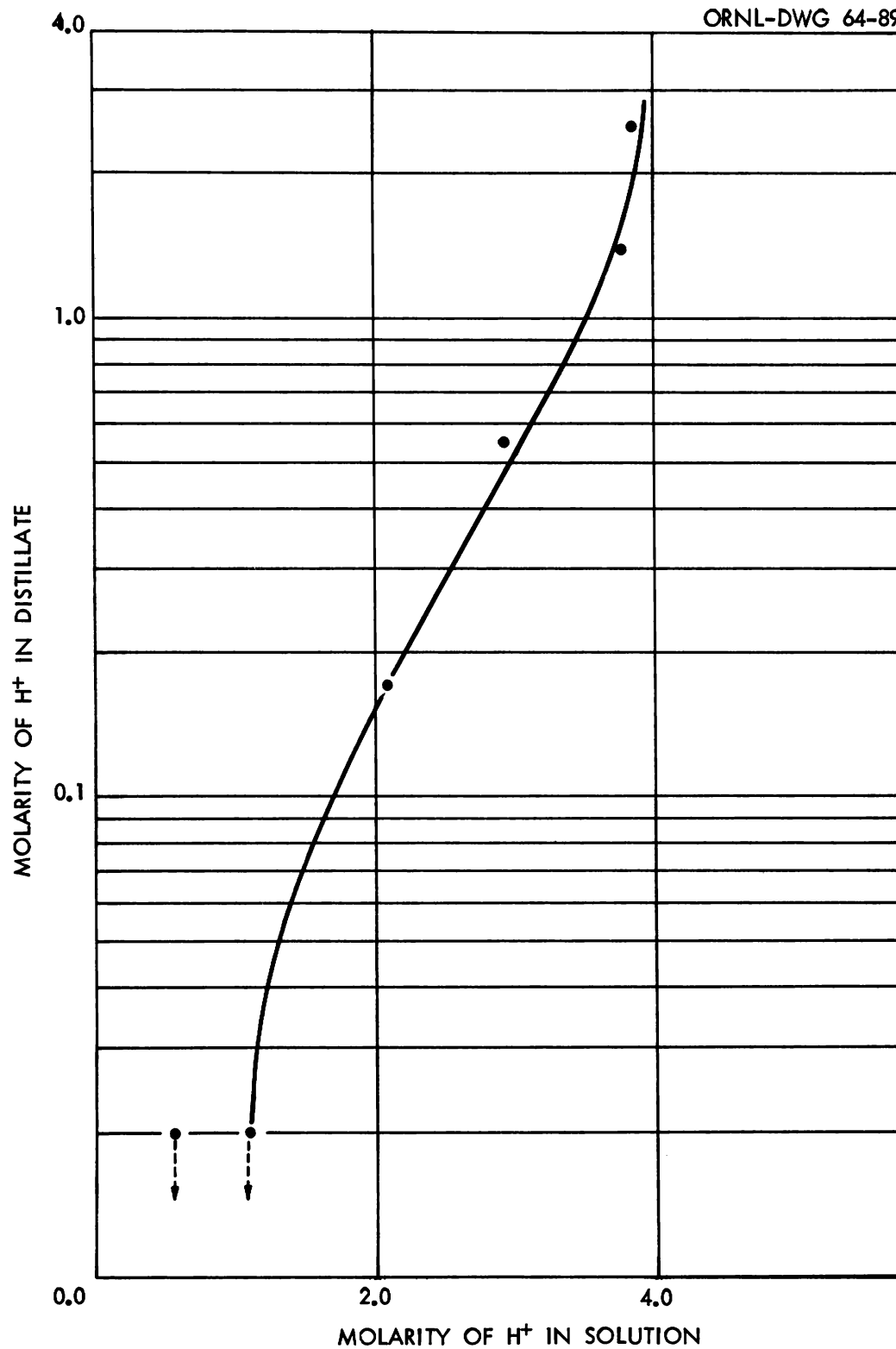
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Fig. A-4. Vapor-Liquid Equilibrium in FTW-65 Waste Solutions.

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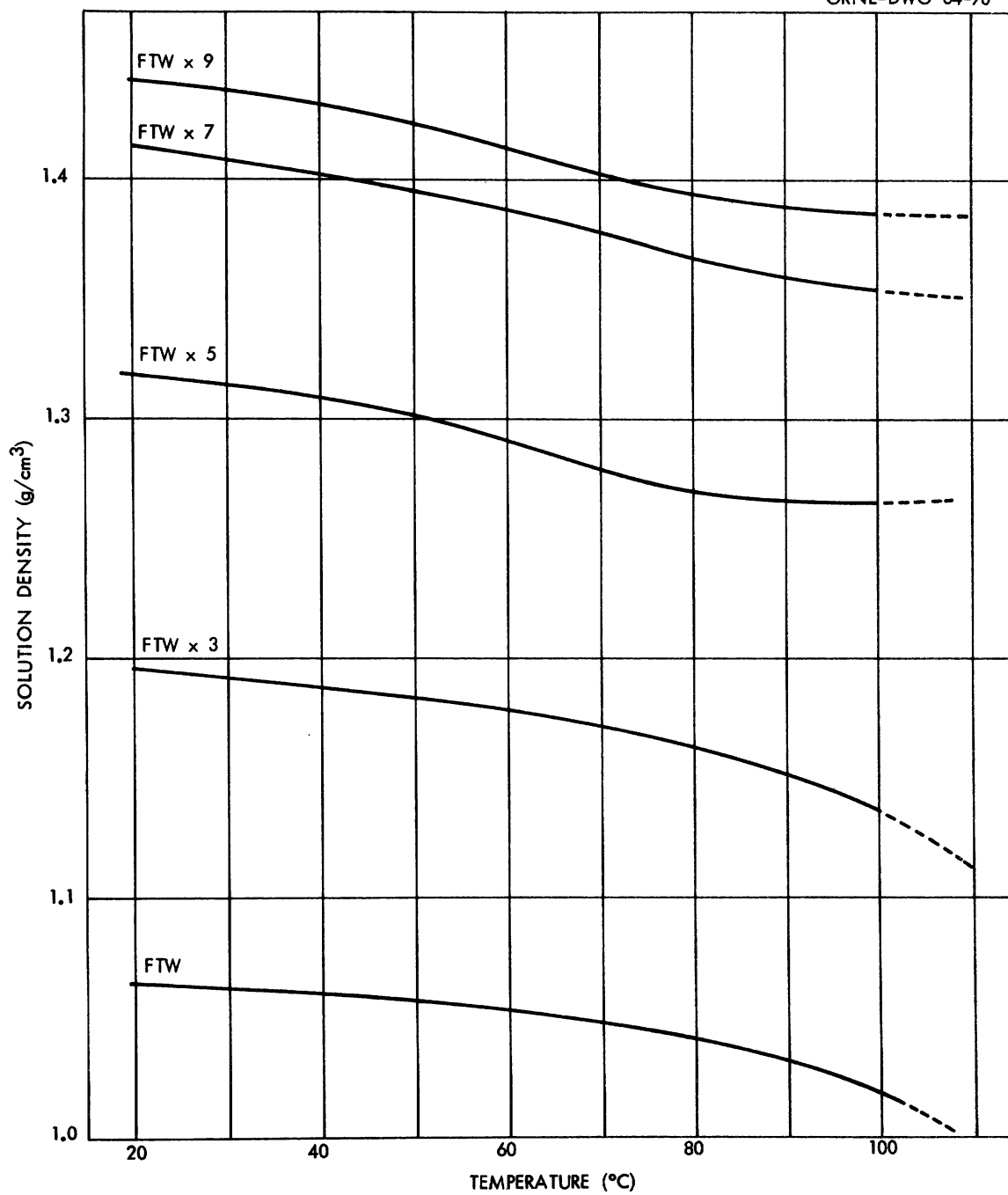
Fig. A-5. Densities of FTW-65 Waste Solution at Various Concentrations.

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