

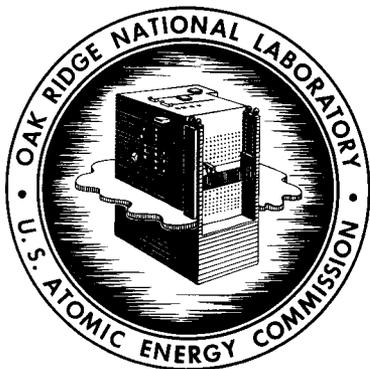


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LABORATORY DEVELOPMENT OF PROCESSES FOR
FIXATION OF HIGH-LEVEL RADIOACTIVE WASTES
IN GLASSY SOLIDS: WASTES CONTAINING
(1) ALUMINUM NITRATE AND (2) THE NITRATES
OF THE CONSTITUENTS OF STAINLESS STEEL

W. E. Clark
H. W. Godbee



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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JULY 1964

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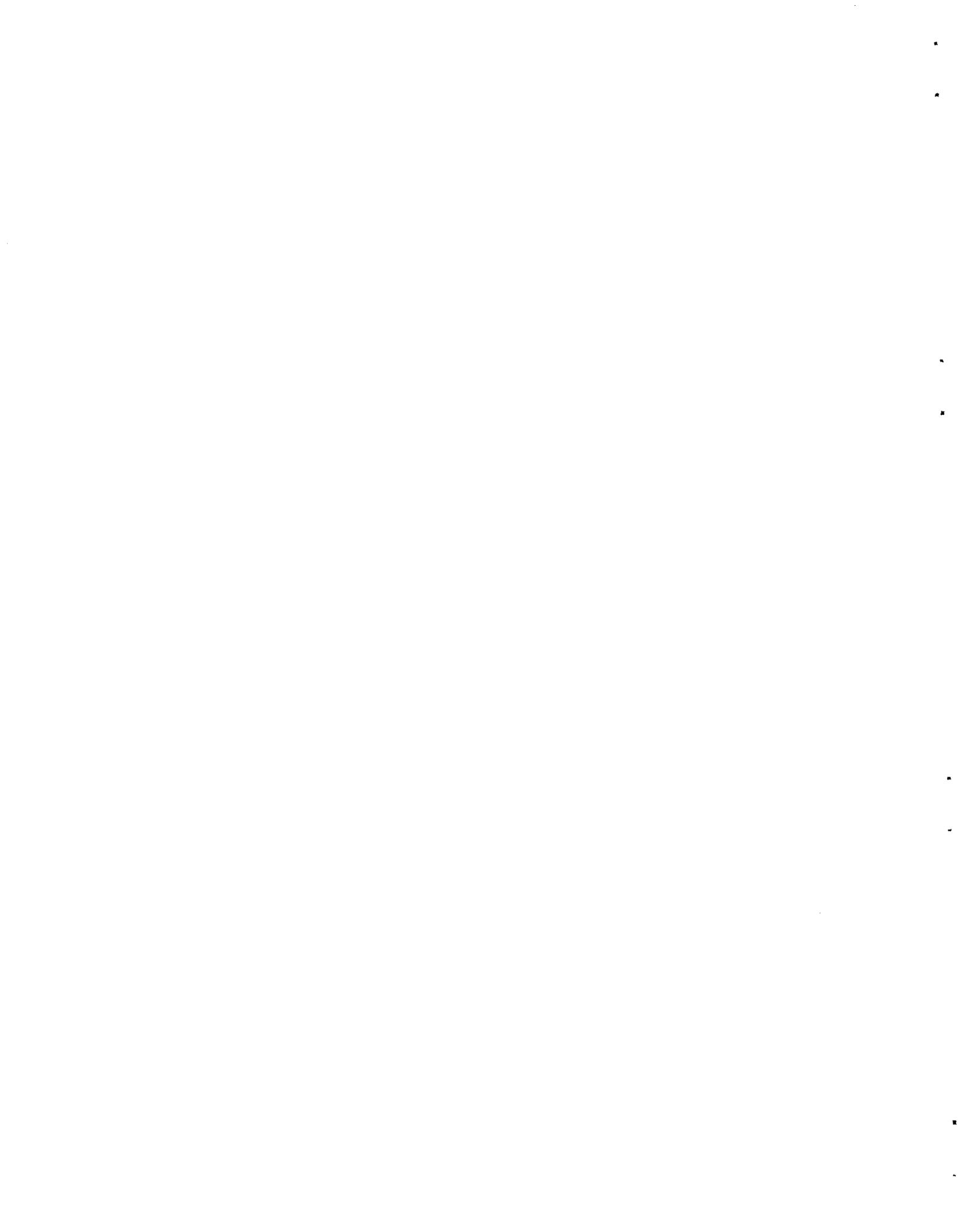


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ABSTRACT

Glassy solids satisfactory for the long-term storage ("ultimate disposal") of radioactive wastes were prepared from solutions simulating those obtained or expected from aqueous reprocessing of aluminum- and stainless steel-bearing fuel elements. Only tracer levels of radioactivity were tested. Vapor-liquid equilibria and solution densities were determined for both waste types over wide ranges of composition.

Phosphate was the principal fluxing agent in all products reported. Borate and sodium were employed as other additives with both waste types. Aluminum generally improved the glassiness of the products obtained with stainless steel waste, while lead was helpful in lowering the softening temperature of the melts obtained with the aluminum waste.

Volume reductions (volume of waste solution/volume of glass) varied from 7.2 to 9.3 for the aluminum waste and from 2.5 to 6.6 for the stainless steel waste.

Leaching tests on small specimens of the more satisfactory solids prepared from both waste types gave dissolution rates of about 10^{-6} g/cm².day based on the fraction of Cs¹³⁷ spike leached from the product.

Semicontinuous fixations of both waste types were run on a semi-engineering scale. These were highly successful for the aluminum waste. The melt used for fixation of the stainless steel waste was excessively corrosive and produced a solid containing excessive voids.

Use of stainless steel fixation pots appears feasible with both waste types, but titanium is preferred for the construction of an evaporator for concentration of the waste solution.

Thermal conductivity of one aluminum-type glass varied from 1.05 Btu hr⁻¹ ft⁻¹ °F⁻¹ at 300°F to 1.60 Btu hr⁻¹ ft⁻¹ °F⁻¹ at 1050°F.

Fixation of both waste types in phosphate "glasses" is feasible on the basis of current technology. Further work needs to be done to define the compositions of products having optimum properties.

1. INTRODUCTION

The advent of large-scale nuclear power necessitates the development of radioactive waste disposal of such a nature as to ensure that there is no appreciable escape of the waste to the biosphere for indefinitely long storage periods (e.g., more than 300 yr). The most certain method appears to be fixation in an insoluble solid form contained in a corrosion-resisting material which, in turn, is stored in a dry medium in an area of geologic tranquillity. How much of this ideal procedure is adopted will depend upon economic pressures for inexpensive waste disposal and upon social pressures for completely safe waste disposal.

In many respects glass is the ideal solid for the incorporation of waste, provided that it retains its glassy nature. All other conditions being equal, a glass should have less exposed surface than a crystalline material of the same volume and geometric configuration, and thus should dissolve more slowly. Retention of the glassy structure is unlikely for long storage times. Fixation in intrinsically insoluble solid materials is, therefore, desirable.

The process criteria currently guiding the chemical development of waste disposal at the Oak Ridge National Laboratory (ORNL) are these: (1) All radioactive and other constituents possible are to be retained in the solid product to eliminate intermediate and low radioactive level side streams. (2) Volume reductions of waste to solid product are to be large. (3) The solid form is to be insoluble, heat conductive, stable for long-term storage, homogeneous, and mechanically strong. (4) The waste disposal process is to operate as economically as possible.

Numerous agencies both in the United States and abroad are working on this fixation problem. In Canada the approach has been to incorporate the waste in a glass formed by the addition of nepheline syenite which, when combined with the waste,

results in a glass of low leachability.¹ In the United Kingdom the principal approach has been to fix the waste in borosilicate glasses,² though other types of glass have been considered. In France, several different approaches are being tried,³ including a rotary calciner coupled to a continuous fusion furnace. ORNL^{4,5} is considering the pot calcination process in which the waste is disposed of in its original container either as calcine (without melting) or as a glass. Hanford Atomic Products Operation (HAPO) is developing spray calcination,⁶ possibly followed by melting in the disposal container ("pot"). Idaho Chemical Processing Plant (ICPP) is investigating fluidized-bed calcination.⁷ The Brookhaven National Laboratory (BNL) is developing a process in which the waste is continuously converted to a phosphate glass in an all-liquid system.⁸ A rotary calciner has also been studied at BNL.⁹ In addition to these methods, numerous other approaches have been tried, such as incorporation in molten sulfur,¹⁰ and in ceramic sponges,¹¹ fixation by adsorption or ion exchange on minerals,^{12,13} and coprecipitation.¹⁴

As currently envisioned, the ORNL Pot Fixation process for high level waste would involve the following steps: (1) interim storage of acid solutions in tanks; (2) concentration by evaporation with recycle of all vaporized activity; (3) final evaporation and calcination or melting in the waste storage pot itself; (4) heating the product to a high temperature in order to remove the last traces of water and nitrate; (5) sealing the container; and (6) transportation of the container to the final storage site which, according to present plans, would be either a dry salt mine or a specially prepared concrete vault. Economic estimates have been made for waste management involving several variations of this general scheme.¹⁵

The waste types that have been investigated at ORNL include: (1) aluminum nitrate wastes from the reprocessing of aluminum-type nuclear fuels (TBP-25 process), (2) wastes resulting from the reprocessing of stainless steel fuel elements by either the Darex process or the electrolytic process (hereafter abbreviated as Darex waste) and (3) wastes resulting from the Purex solvent extraction process. Satisfactory processes have been developed at ORNL for all three types of wastes, though more work needs to be done on each in order to optimize the conditions and the products formed.

Since it is more convenient to handle solutions than solids or slurries, phosphate, rather than silicate, was chosen as the major fluxing additive. In addition, scouting experiments at ORNL,¹⁶ as well as work elsewhere, indicated generally lower melting temperatures for phosphate glasses than for their silicate counterparts. The possibility of using phosphite for ruthenium control was an added incentive for development of phosphate glasses.

The purpose of this report is to summarize the work done on aluminum and stainless steel waste types. Work on the Purex types of wastes will be the subject of a future report.

2. EXPERIMENTAL METHODS ADAPTED TO THE TWO KINDS OF WASTES

Evaporation characteristics of the waste types considered (Table 1) were studied in a small-scale pot and condenser system equipped with an off-gas train. Equilibrium evaporation studies were made in Gillespie stills. Most of the solution densities were determined by pycnometric techniques at four different temperatures. Densities of low-acid (0.5 to 1.0 \underline{M} H^+) solutions of stainless steel were determined with a Westphal balance.

Small specimens of solid products were obtained by evaporation of the solution on a sand bath followed by calcination and possibly melting in a muffle furnace. The proposed use of stainless steel for the fixation pot limited the maximum practical operating temperature to about 1050°C. Promising products obtained in this way were then produced in small-scale semicontinuous equipment (Fig. 1) equipped with a condenser and off-gas train.

The next step in fixation was carried out in a stainless steel cylinder (pot) 4 in. in inside diameter x 24 in. long (Fig. 2). Feed was pumped continuously to the pot at a rate which allowed the formation of a melt covered by a relatively thin layer of calcine which was in turn covered by a thin layer of aqueous solution. This method of operation, designated as "The Rising Liquid Level Method," is similar to the method developed in the United Kingdom² and is described in detail elsewhere.¹⁷

Table 1. Compositions of Simulated High-Activity Wastes

Component	Aluminum (TBP-25) Waste (106 gal/kg U-235 Processed)	Stainless Steel (Darex) Waste (24 gal/kg U-235 Processed)
Al ³⁺	1.72 <u>M</u>	---
Fe ³⁺	0.16 mg/ml	1.25 <u>M</u>
Cr ³⁺	---	0.38 <u>M</u>
Ni ²⁺	---	0.18 <u>M</u>
Mn ²⁺	---	0.04 <u>M</u>
H ⁺	1.26 <u>M</u>	0.75 <u>M</u>
Hg ²⁺	4.02 mg/ml	---
NH ₄ ⁺	0.05 <u>M</u>	---
Na ⁺	2.4 mg/ml	---
NO ₃ ⁻	6.6 <u>M</u>	6.0 <u>M</u>
SO ₄ ²⁻	---	---
Cl ^{-a}	160 ppm	260 ppm
Ru	0.2 mg/ml	0.2 mg/ml
Density, g/ml	1.32	1.33

^aExcept for Darex waste, which normally contains about 100 ppm Cl⁻, all Cl⁻ present was added with Ru as RuCl₃.

Operation was continued until the pot was about one-half to two-thirds full of melt. The pot was not filled any closer to capacity since the upper section of the pot served for the de-entrainment of vapors and also since the rate of melt formation decreased as the pot became more nearly full. (The fraction of the pot volume that must be left unfilled should decrease with increasing length of the pot. The figures listed here are not, therefore, applicable to larger-scale fixation processes.) Thermal conductivity of this large-scale product was determined in situ by a steady-state method employing

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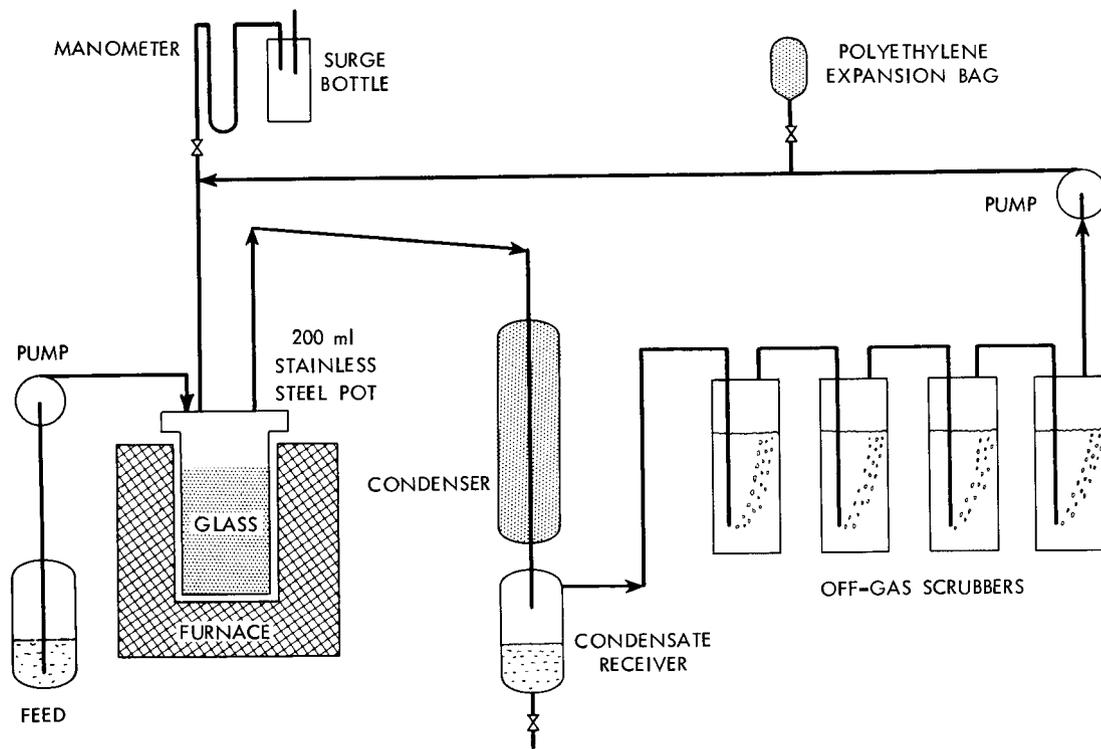


Fig. 1. Schematic Diagram of Small-Scale Equipment for Semicontinuous Production of Glass.

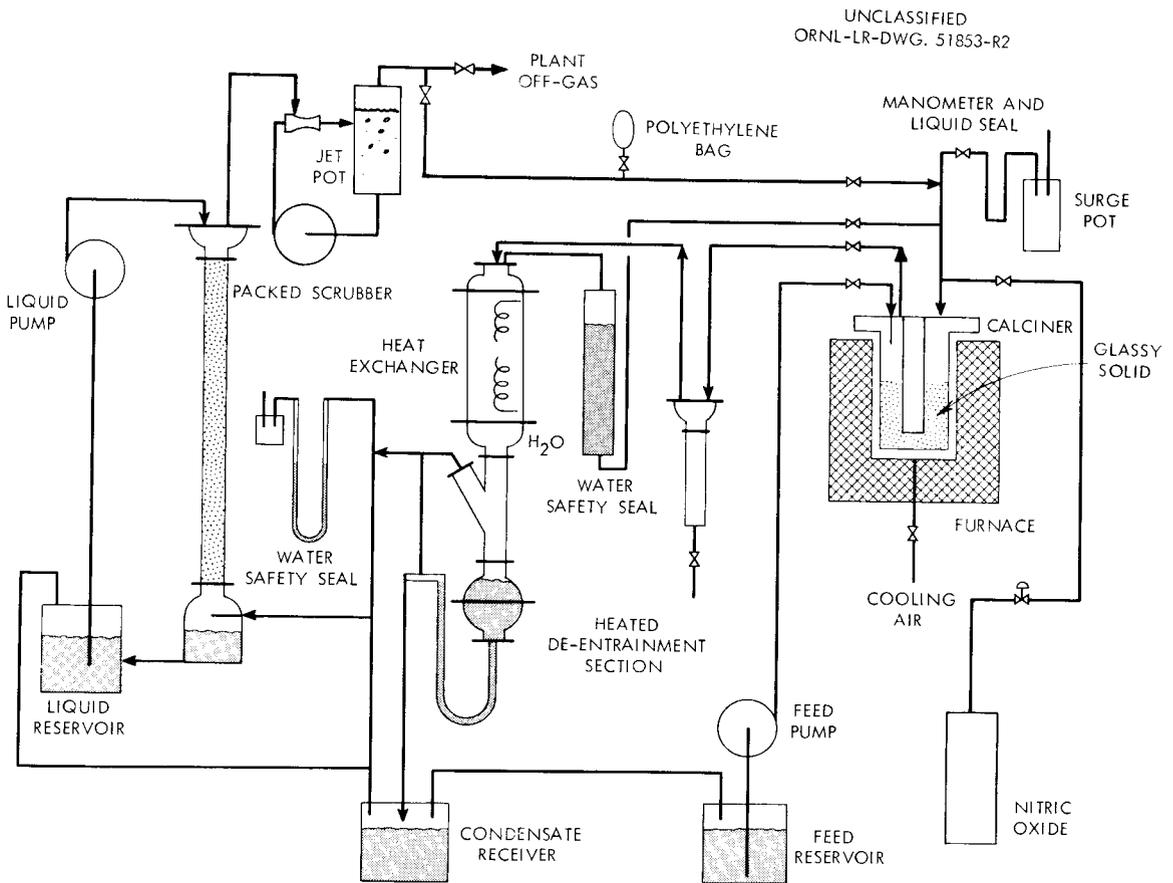


Fig. 2. Equipment for Semicontinuous Fixation of Simulated Waste Solutions in Solids.

radial heat flow outward through a hollow cylinder (the sample). Thermal stability of this product was studied by heating the material to the desired temperature in a system closed except for an off-gas train (Fig. 3).

Leaching tests to determine the probable solubility of fission products incorporated in the solid were carried out on small specimens (buttons) spiked with Cs^{137} and produced in a platinum crucible which was later peeled from the button, allowing a fairly accurate estimate of apparent area to be made. These buttons were then exposed in polyethylene equipment through which distilled water was circulated (Fig. 4). The water was changed and the dissolved activity was measured at intervals of about one week.

Ruthenium volatility during evaporation, calcination, and melt down was investigated by using Ru^{106} tracer and also by neutron activation of stable ruthenium in the condensate. In two instances, volatile activity due to the ruthenium was distinguished from entrainment by the addition of Pm^{147} tracer to the simulated waste solution. These two activities could be easily distinguished from each other since Pm^{147} is a pure beta emitter.

3. WASTES CONSISTING PRINCIPALLY OF ALUMINUM NITRATE

Evaporation characteristics and densities of simulated waste for four different acid concentrations and three concentrations of salt up to the limit of solubility were investigated (Table 2). Densities were measured at four different temperatures, and evaporation characteristics were measured at two different pressures for most of the solutions studied (Tables 2, 3, and 4; Figs. 5 and 6). Densities of the most concentrated solutions could not be determined because precipitation occurred at room temperature.

Aluminum wastes were readily incorporated in phosphate and borophosphate glasses to the extent of 26 to 35 wt % waste oxides, giving products with volume reductions varying from 7.2 to 9.3 (Table 5). Both types of melt gave very glassy materials (Figs. 7 and 8). Generally, borate and borophosphate glasses were more

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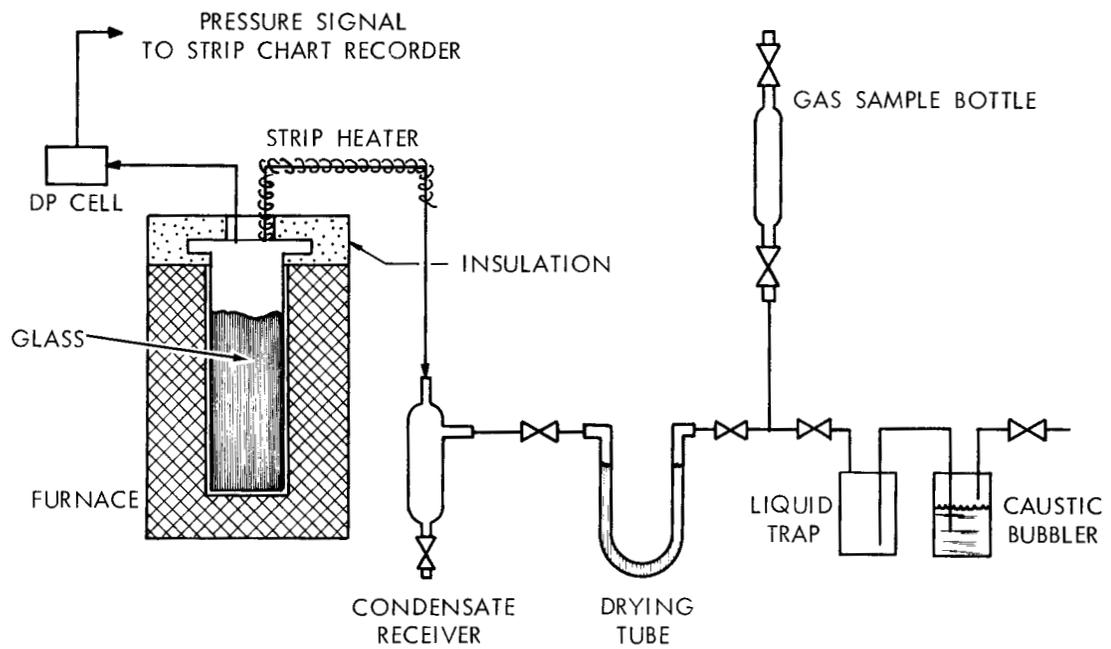


Fig. 3. Schematic Diagram of Apparatus to Measure Pressure in Sealed Waste-Fixation Pot During Prolonged Heating.

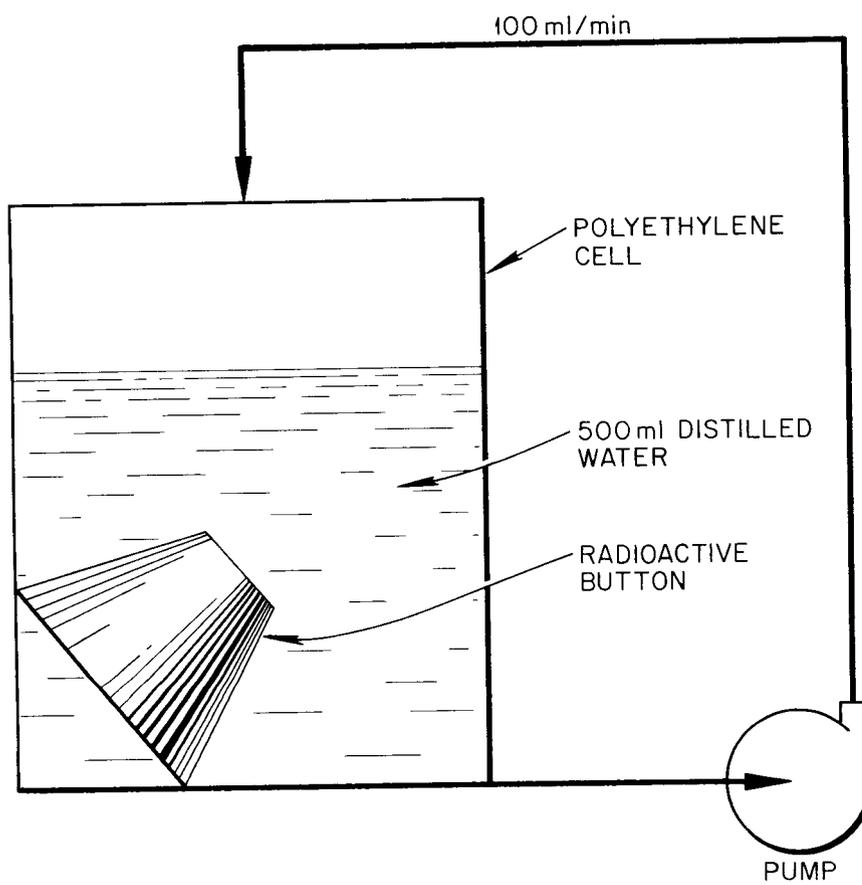
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Fig. 4. Diagram of Apparatus for Leaching of Radioactive Samples.

Table 2. Compositions of Simulated Waste Solutions

Solution Designation	Solution Composition (M)									
	H ⁺	Al ³⁺	Fe ³⁺	Na ⁺	Hg ²⁺	NO ₃ ⁻	Cr ³⁺	Ni ²⁺	Mn ²⁺	Cl ⁻
A. Aluminum (TBP-25) Waste										
T-1	1.26	1.72	0.003	0.01	0.02	6.48				
T-1a	0.5	1.72	0.003	0.01	0.02	5.72				
T-1b	3.0	1.72	0.003	0.01	0.02	8.22				
T-1c	5.0	1.72	0.003	0.01	0.02	10.22				
T-1d	1.26	1.72	0.003	0.1	0.02	6.57				
T-2	1.26	0.86	0.0015	0.005	0.01	3.87				
T-2a	0.5	0.86	0.0015	0.005	0.01	3.11				
T-2b	3.0	0.86	0.0015	0.005	0.01	5.61				
T-2c	5.0	0.86	0.0015	0.005	0.01	7.61				
T-3**	1.26	2.6	0.0045	0.015	0.03	9.15				
T-3a*	0.5	2.6	0.0045	0.015	0.03	8.39				
T-3b*	3.0	2.6	0.0045	0.015	0.03	10.89				
T-3c*	5.0	2.6	0.0045	0.015	0.03	12.89				
B. Stainless Steel (Darex) Waste										
D-1	0.50		1.21			5.69	0.38	0.17	0.04	0.001
D-1a	1.00		1.21			6.19	0.38	0.17	0.04	0.001
D-1b	2.001		1.21			7.19	0.38	0.17	0.04	0.001
D-1c	3.002		1.21			8.19	0.38	0.17	0.04	0.001
D-1d	5.003		1.21			10.19	0.38	0.17	0.04	0.001
D-1e	7.004		1.21			12.19	0.38	0.17	0.04	0.001
D-2	0.50		0.6			3.08	0.19	0.085	0.02	0.0005
D-2a	1.00		0.6			3.58	0.19	0.085	0.02	0.0005
D-2b	2.001		0.6			4.58	0.19	0.085	0.02	0.0005
D-2c	3.002		0.6			5.58	0.19	0.085	0.02	0.0005
D-2d	5.003		0.6			7.58	0.19	0.085	0.02	0.0005
D-2e	7.004		0.6			9.58	0.19	0.085	0.02	0.0005
D-3	0.5		1.82			8.30	0.57	0.255	0.06	0.0015
D-3a	1.00		1.82			8.80	0.57	0.255	0.06	0.0015
D-3b	2.001		1.82			9.80	0.57	0.255	0.06	0.0015
D-3c	3.002		1.82			10.80	0.57	0.255	0.06	0.0015
D-3d	5.003		1.82			12.80	0.57	0.255	0.06	0.0015
D-3e*	7.004		1.82			14.80	0.57	0.255	0.06	0.0015

* These solutions could not be made up due to solubility limitations.

** This solution was not stable at room temperature.

Table 3. Vapor-Liquid Equilibrium and Density Data for Simulated Aluminum Waste

Local atmospheric pressure, 744 to 749 mm Hg

Solution	H ⁺ , Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml)			
				25°C	50°C	75°C	100°C
Pressure 744-749 mm Hg							
T-1	1.26	109.5	748.3				
pot	1.28			1.3238	1.3072	1.2818	1.2688
distillate	0.52						
T-1d	1.32	109.5	741.1				
pot	1.35			1.3194	1.3049	1.2885	1.2672
distillate	0.52						
T-1a	0.50	107.5	748.3				
pot	0.58			1.2963	1.2819	1.2580	1.2443
distillate	0.15						
T-1b	2.91	113.5	748.5				
pot	2.96			1.3725	1.3512	1.3317	1.3124
distillate	2.10						
T-1c	4.85**	117	746.3				
pot	4.86			1.4249	1.4034	1.3811	1.3574
distillate	5.45						
T-2	1.26	104	746.3				
pot	1.34			1.1922	1.1803	1.1593	1.1341
distillate	0.13						
T-2a	0.50	102.5	746.4				
pot	0.54			1.1669	1.1531	1.1361	1.1087
distillate	0.04						
T-2b	2.97	107.5	746.6				
pot	3.17			1.2478	1.2319	1.2131	1.1833
distillate	0.60						
T-2c	4.96	111.5	745.7				
pot	5.10			1.3039	1.2811	1.2609	1.2385
distillate	2.01						
T-3		117	746.6				
pot	1.26						
distillate	1.92						
T-3-1*		119	745.7				
pot	2.22						
distillate	4.11						
T-3-2*		120.5	745.7				
pot	3.03						
distillate	6.24						
T-3-3*		121.5	744.8				
pot	3.70						
distillate	8.24						
T-3-4*		122	744.8				
pot	4.22						
distillate	9.84						
T-3-5*		122.5	744.8				
pot	4.64						
distillate	11.00						

*T-3 was not stable at room temperature. In order to obtain equilibrium data on this and the following solutions, concentrated acid was added to the pot after each distillation. Pot compositions for T-3-1 through T-3-5 are, therefore, calculated values.

Table 4. Vapor-Liquid Equilibrium and Density Data for Simulated Aluminum Waste
Reduced pressure, 563 to 568 mm Hg

Solution	H ⁺ , Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml)			
				25°C	50°C	75°C	100°C
Pressure 563-568 mm Hg							
T-1s	1.26	101.5	567.5				
pot	1.32			1.3242	1.3099	1.2938	1.2710
distillate	0.51						
T-1ds	1.32	102	563.9				
pot	1.41			1.3279	1.3141	1.2963	1.2731
distillate	0.58						
T-1as	0.50	100	566.7				
pot	0.56			1.2961	1.2837	1.2632	1.2443
distillate	0.17						
T-1bs	2.91	105	566.7				
pot	3.02			1.3699	1.3522	1.3339	1.3102
distillate	2.03						
T-1cs**	4.85	110	---				
pot	5.12			1.4286	1.4069	1.3842	1.3589
distillate	5.95						
T-2s	1.26	96	567.5				
pot	1.41			1.1914	1.1786	1.1581	1.1320
distillate	0.58						
T-2as	0.50	94	566.7				
pot	1.34			1.1647	1.1532	1.1344	1.1087
distillate	0.092						
T-2bs	2.97	99	566.7				
pot	3.21			1.2444	1.2295	1.2110	1.1800
distillate	0.51						
T-2cs	4.96	104	---				
pot	5.25			1.3041	1.2818	1.2603	1.2356
distillate	1.88						
T-3s*		109	566.4				
pot	1.26						
distillate	1.86						
T-3-1s		111.5	566.4				
pot	2.22						
distillate	3.83						
T-3-2s		113	563.9				
pot	3.03						
distillate	5.89						
T-3-3s		113.5	563.9				
pot	3.70						
distillate	7.81						

* T-3 was not stable at room temperature. In order to obtain equilibrium data on this and the following solutions, concentrated acid was added to the pot after each distillation. Pot compositions for T-3-1s through T-3-3s are, therefore, calculated values.

** Apparent analytical error probably due to solution instability at room temperature.

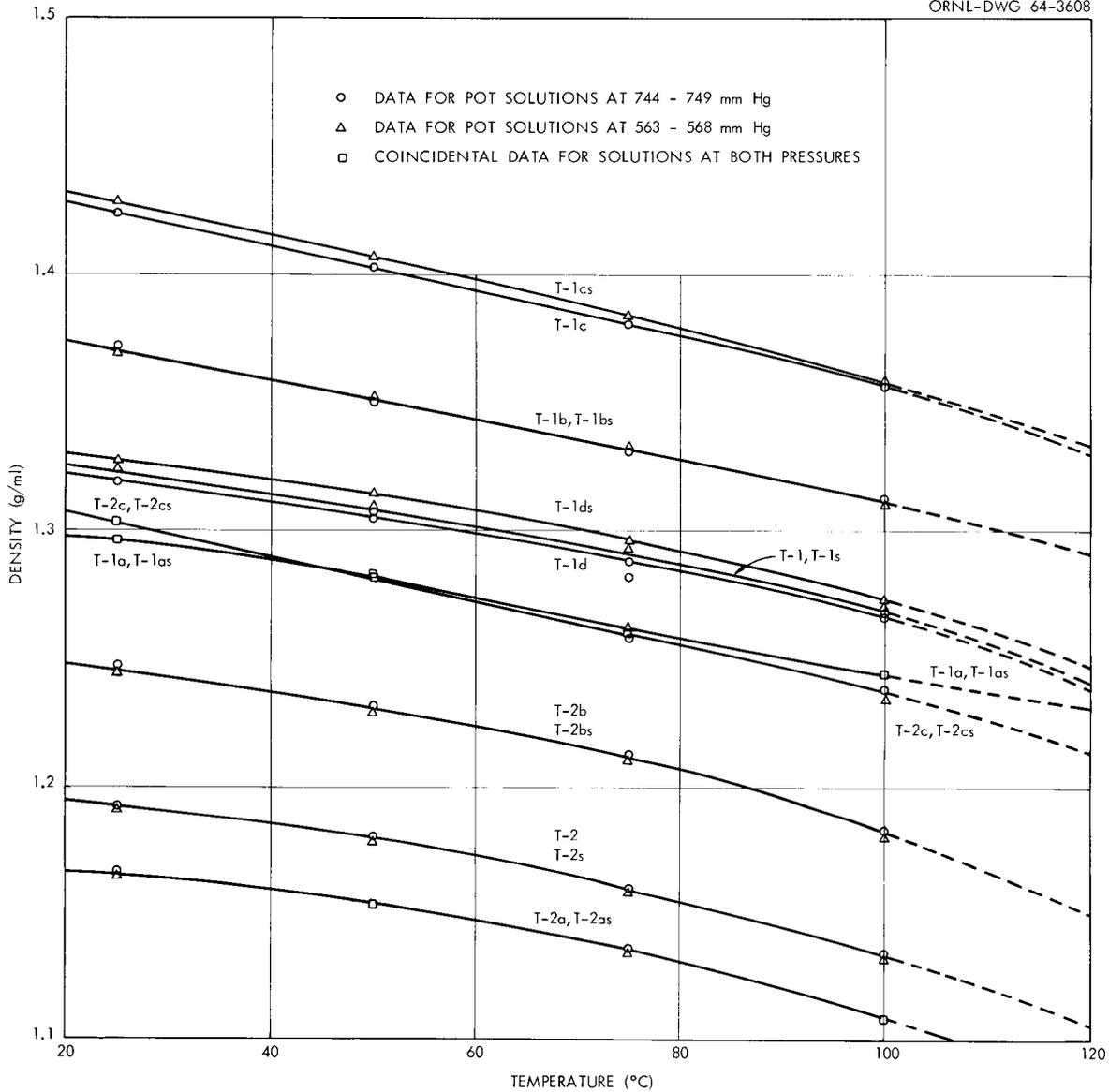
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Fig. 5. Density of Thick Liquor from Evaporation of Simulated Aluminum (TBP-25) Waste Solutions. Data are listed in Tables 3 and 4.

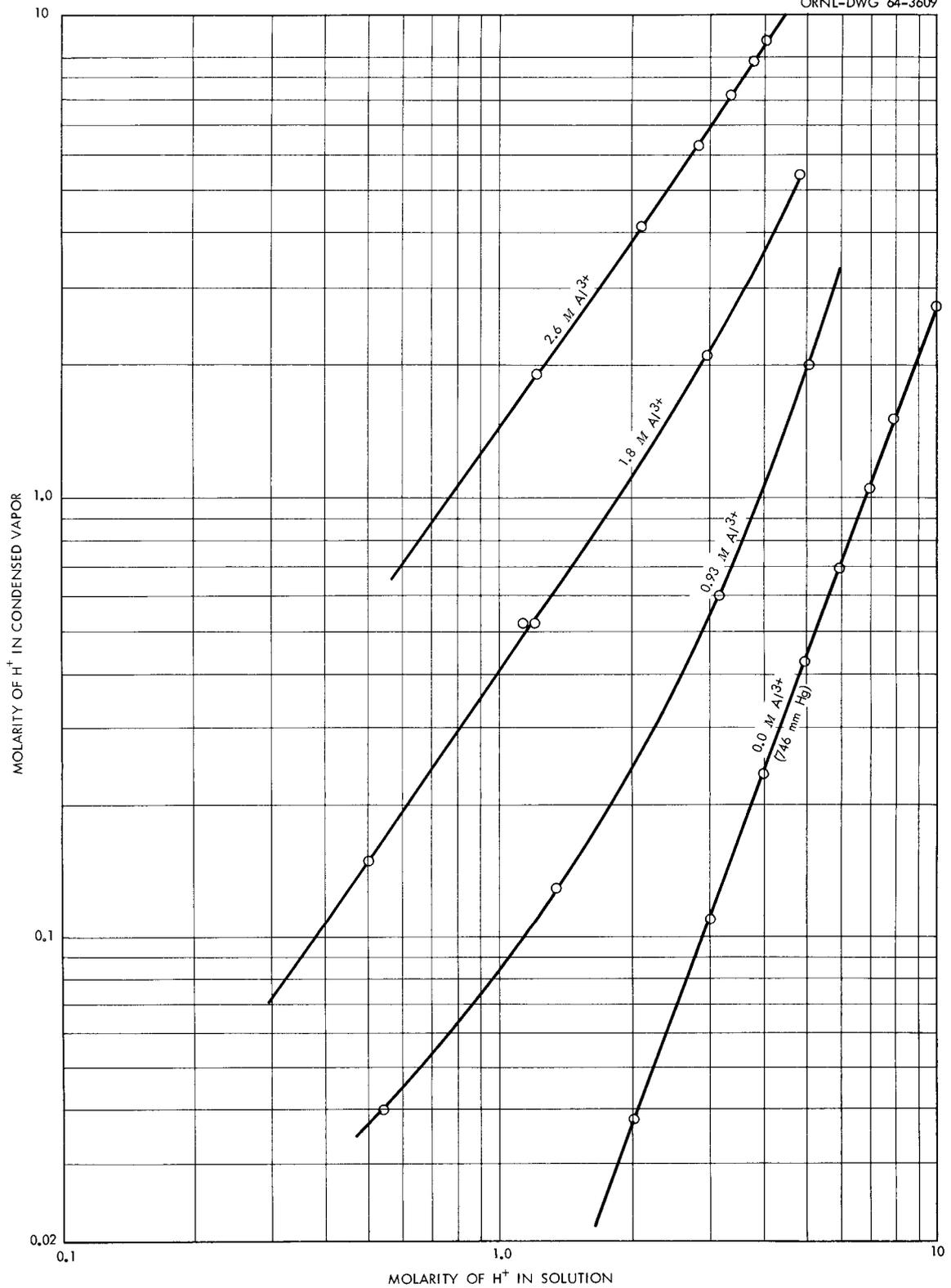


Fig. 6a. Vapor-Liquid Equilibrium of Simulated Aluminum (TBP-25) Waste at 744-749 mm Hg Pressure.

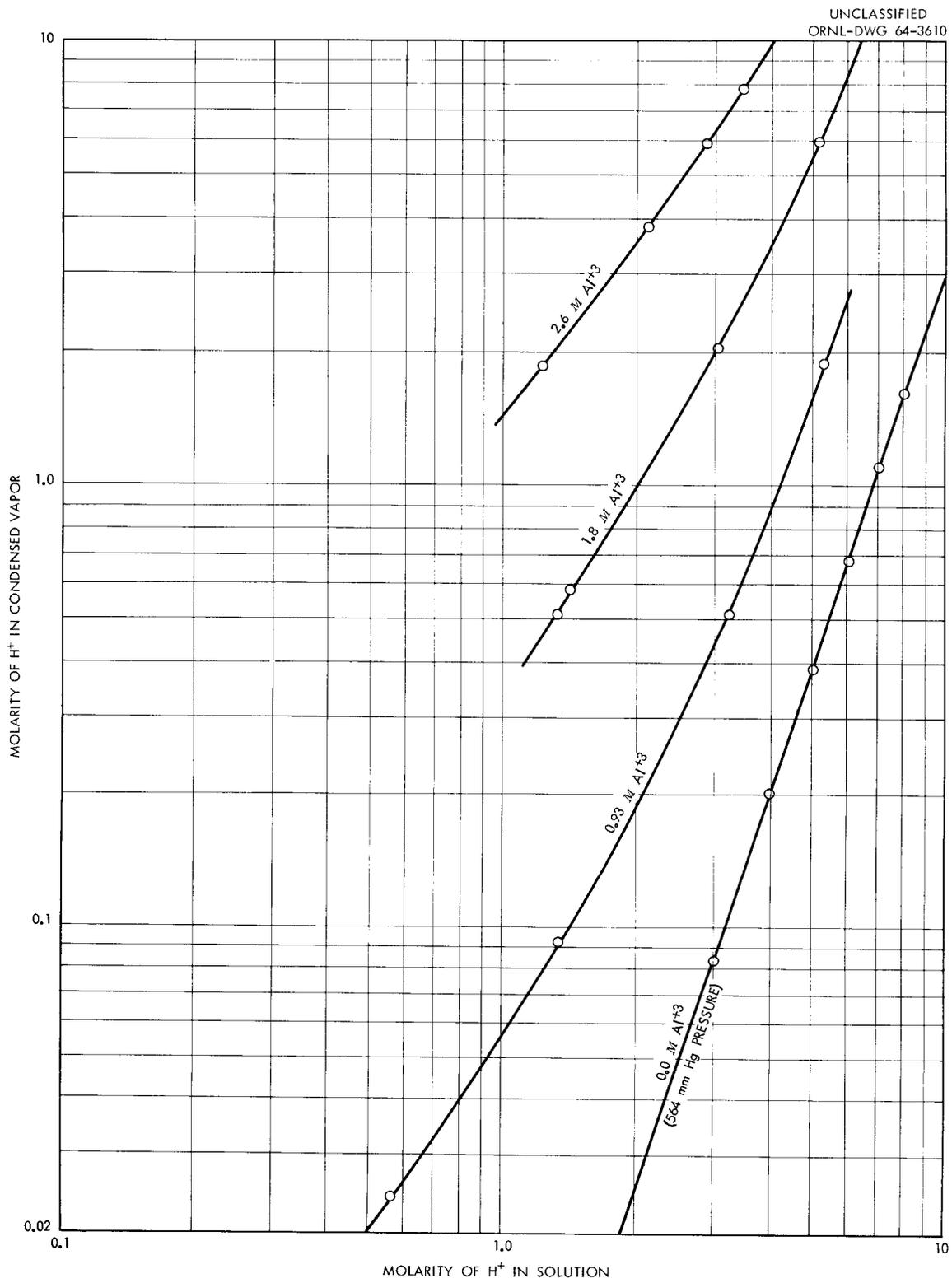


Fig. 6b. Vapor-Liquid Equilibrium of Simulated Aluminum (TBP-25) Waste at 563-568 mm Hg Pressure.

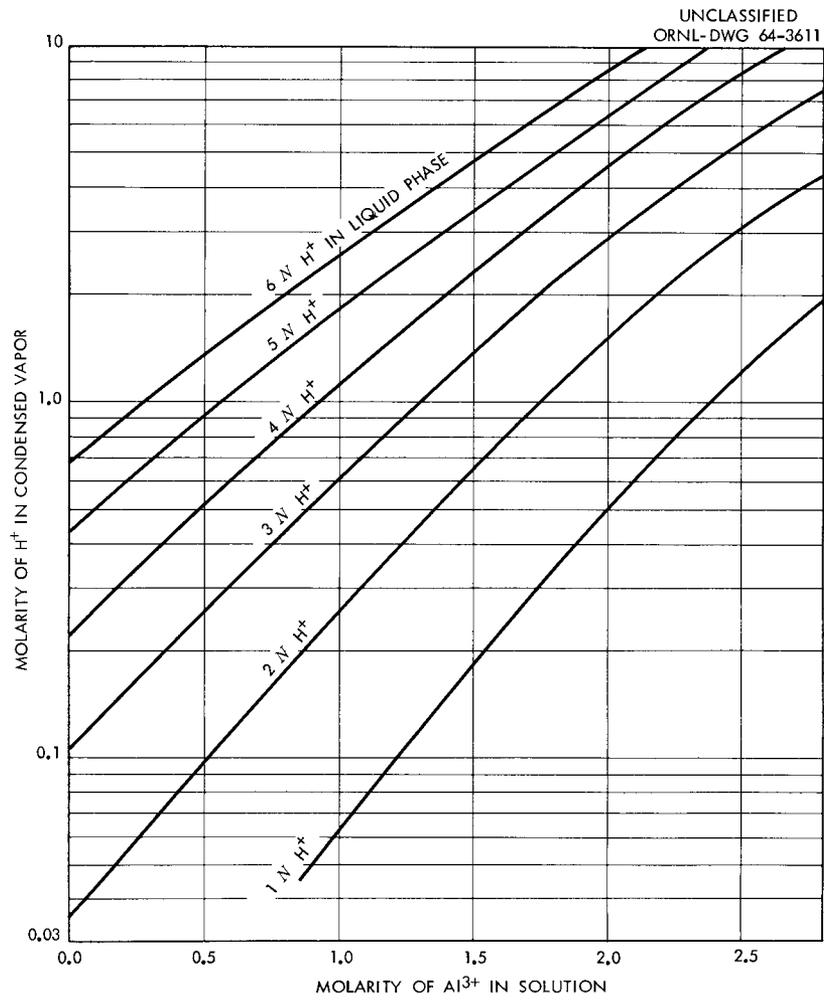


Fig. 6c. Vapor-Liquid Equilibrium in Simulated Aluminum (TBP-25) Waste at 744-760 mm Hg Pressure.

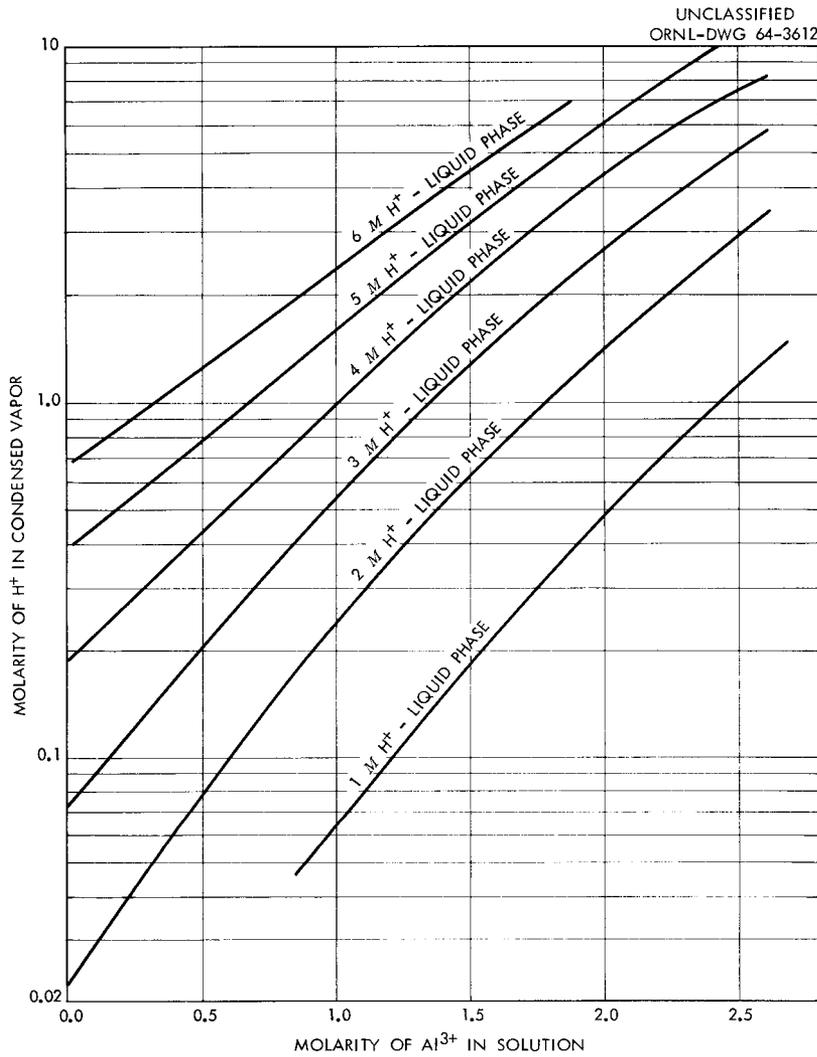


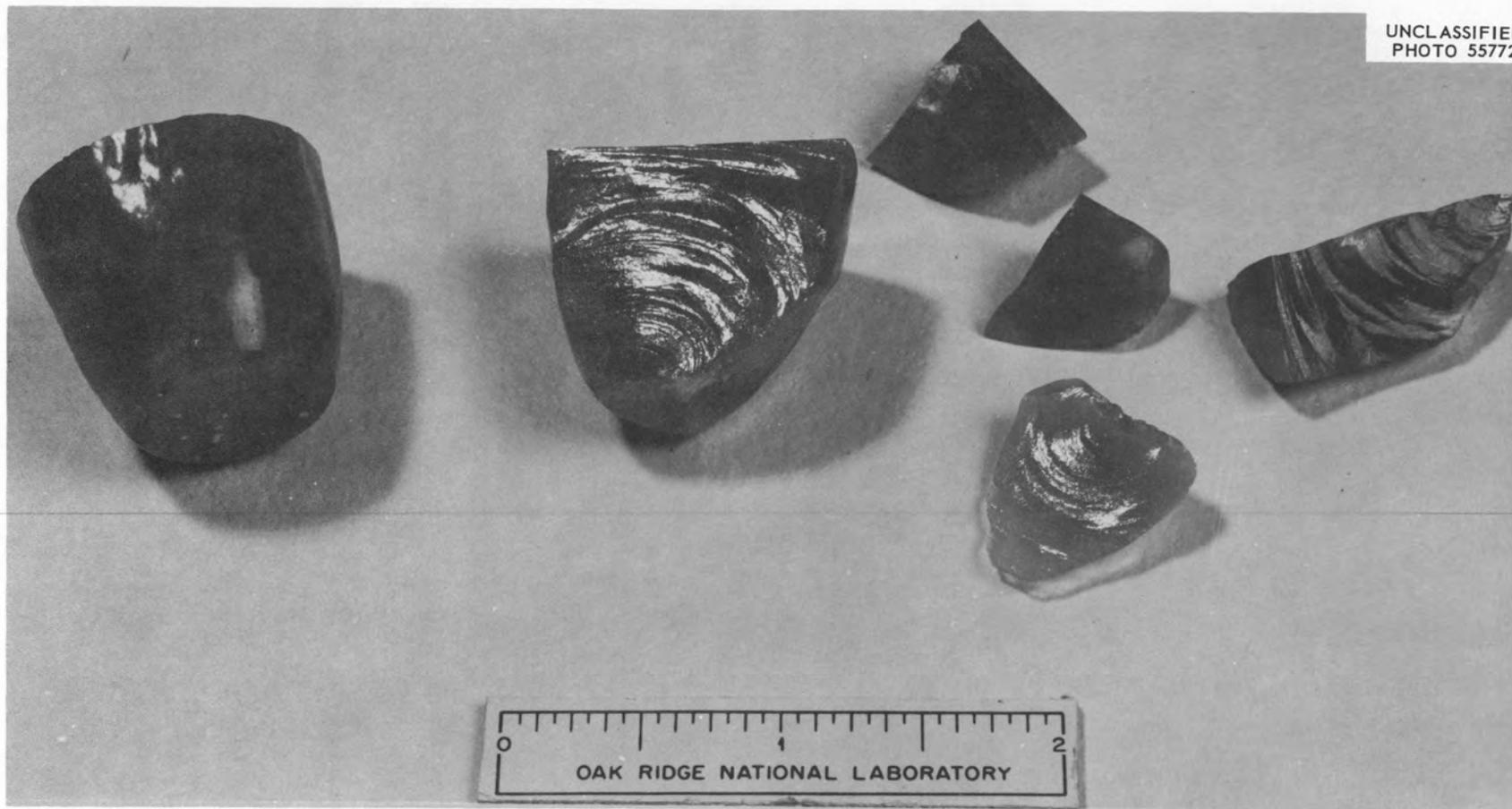
Fig. 6d. Vapor-Liquid Equilibrium in Simulated Aluminum (TBP-25) Waste at 563-600 mm Hg Pressure.

Table 5. Phosphate and Borophosphate Glasses Incorporating Aluminum Type (TBP-25) Waste Oxides.
Preparation of Phosphate Glasses from This Waste Type is Relatively Simple.

TBP-25 Waste (M): 6.60 NO₃⁻, 1.72 Al³⁺, 1.26 H⁺, 0.10 Na⁺, 0.05 NH₄⁺, 0.003 Fe³⁺, 0.002 Hg²⁺, 0.002 Ru
with 160 ppm Cl⁻

Melt	1	2	3	4	5	6	7	8	9	10	11	12
Additives, moles/liter												
NaH ₂ PO ₄ ·H ₂ O	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.52	1.52	1.52	2.00	2.00
Na ₂ B ₄ O ₇ ·10H ₂ O	0.065	0.065	--	0.032	--	--	--	0.13	--	0.26	--	0.13
NaOH	0.060	--	1.20	0.025	--	--	--	0.16	--	0.42	--	0.16
MgO	--	0.30	--	--	--	--	--	--	--	--	--	--
SiO ₂	--	--	0.52	0.26	--	--	--	--	--	--	--	--
PbO	--	--	--	--	0.125	0.188	0.250	--	--	--	--	--
NaH ₂ PO ₄ ·H ₂ O	--	--	--	--	--	--	--	--	0.13	--	--	--
Composition of melt wt % of oxides												
Al ₂ O ₃	28.4	28.4	26.7	27.6	27.1	26.0	25.0	31.6	33.8	28.2	29.7	26.9
Na ₂ O	22.7	22.4	20.4	21.4	20.2	19.4	18.6	22.9	21.0	25.5	22.1	24.0
P ₂ O ₅	45.9	46.0	43.3	44.6	43.9	42.1	40.5	38.9	45.1	34.6	48.1	43.5
B ₂ O ₃	2.9	2.9	--	1.4	--	--	--	6.5	--	11.6	--	5.6
SiO ₂	--	--	9.5	4.9	--	--	--	--	--	--	--	--
PbO	--	--	--	--	8.6	12.4	15.9	--	--	--	--	--
MgO	--	0.2	--	--	--	--	--	--	--	--	--	--
Fe ₂ O ₃	0.07	0.07	0.07	0.07	0.07	0.07	0.06	0.08	0.09	0.07	0.08	0.07
RuO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Approximate softening temperature, °C												
	875	900	1000	950	975	925	900	850	950	950	950	850
Bulk density, g/cc												
	2.36	2.45	2.36	2.38	2.71	2.75	2.84	2.47	2.42	2.41	2.44	2.47
Waste oxides in glass, wt %												
	29.5	29.5	27.8	28.7	28.2	27.1	26.0	32.9	35.2	29.3	30.9	28.0
Volume reduction, vol TBP-25/ vol glass												
	7.6	7.9	7.2	7.5	8.4	8.2	8.1	8.9	9.3	7.7	8.3	7.6
Appearance												
	Pale yellow, clear glass	Pale greenish-white glass	Grayish-green glass	Grayish-green glass	Green glass, mottled with white	Green glass	Greenish white glass	Light-green glass	Greenish white glass	Light-green glass	Green glass mottled with white	Light-yellow glass

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Fig. 7. Phosphate-Lead Glass Incorporating 26 wt % Aluminum Type (TBP-25) Waste Oxides. Volume reduction, 8.1; density, 2.8 g/cc, softening point, 900°C (No. 7, Table 5).

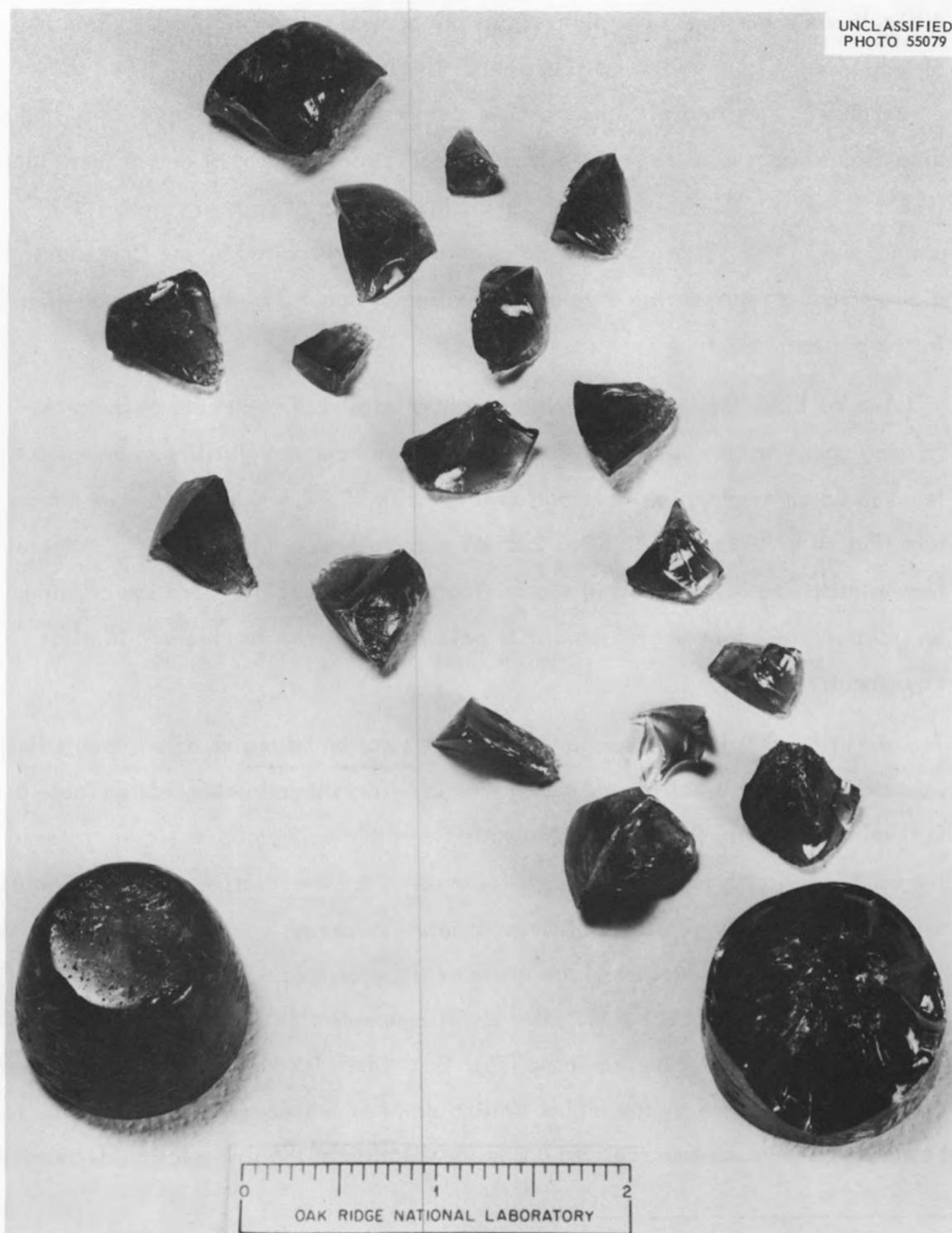


Fig. 8. Phosphate-Borate Glass Incorporating Aluminum-Type (TBP-25) Waste Oxides. Additives (moles/liter waste): 1.52 $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 0.13 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.16 NaOH (Table 5, No. 8).

difficult to de-gas than were plain phosphate or lead phosphate glasses. The addition of lead usually lowered the melting point. The lead was partially reduced to metal, presumably by reaction with the stainless steel container, but this apparently had no deleterious effect upon the nature of the glass. Leaching tests of one of these glasses (Table 5, No. 7) indicated a long-term dissolution rate of approximately 1×10^{-7} g cm⁻² day⁻¹ (Fig. 9) or about twice as great as that reported by the Canadians¹ for a glass product representing a volume reduction of about 3 vs a volume reduction of 8 in the present case.*

Use of 1.52 M phosphite or hypophosphite instead of phosphate as the glass-forming agent in the waste solution lowered the ruthenium volatility to background level in batch evaporation-calcination tests when 500°C was the maximum temperature (Fig. 10). In tests to 1000°C, 2.25 M phosphite was necessary to hold the ruthenium volatility to 0.1% or less of the original present (Fig. 11). Sorption of ruthenium on stainless steel lowered the volatility below that which was observed in glass equipment.

Addition of 0.1 M phosphite to the waste solution before equilibrium distillation lowered ruthenium volatility by a factor of 227 from the untreated waste (Table 6). Ruthenium volatility from an aluminum nitrate-nitric acid solution closely resembling the aluminum waste was lowered by a factor of 208. The relative volatilization of ruthenium and nitric acid from nitric acid solutions during equilibrium distillation was found to be a linear function of the nitric acid concentration in the distillate until the latter was as high as about 4 M. Above this concentration of nitric acid the relative volatility of the ruthenium increased (Fig. 12). There is some indication that this increased rate is caused by the higher boiling point of the more concentrated solution. Lowering the atmospheric pressure during distillation of the salt solution decreased the

* Actual storage volume of Canadian waste was about twice as large as that of the original solution (i.e., a volume increase of 2) because of the size of the crucible used. A corresponding figure for the ORNL process is not yet available but should correspond to a volume reduction somewhere between 4 and 8.

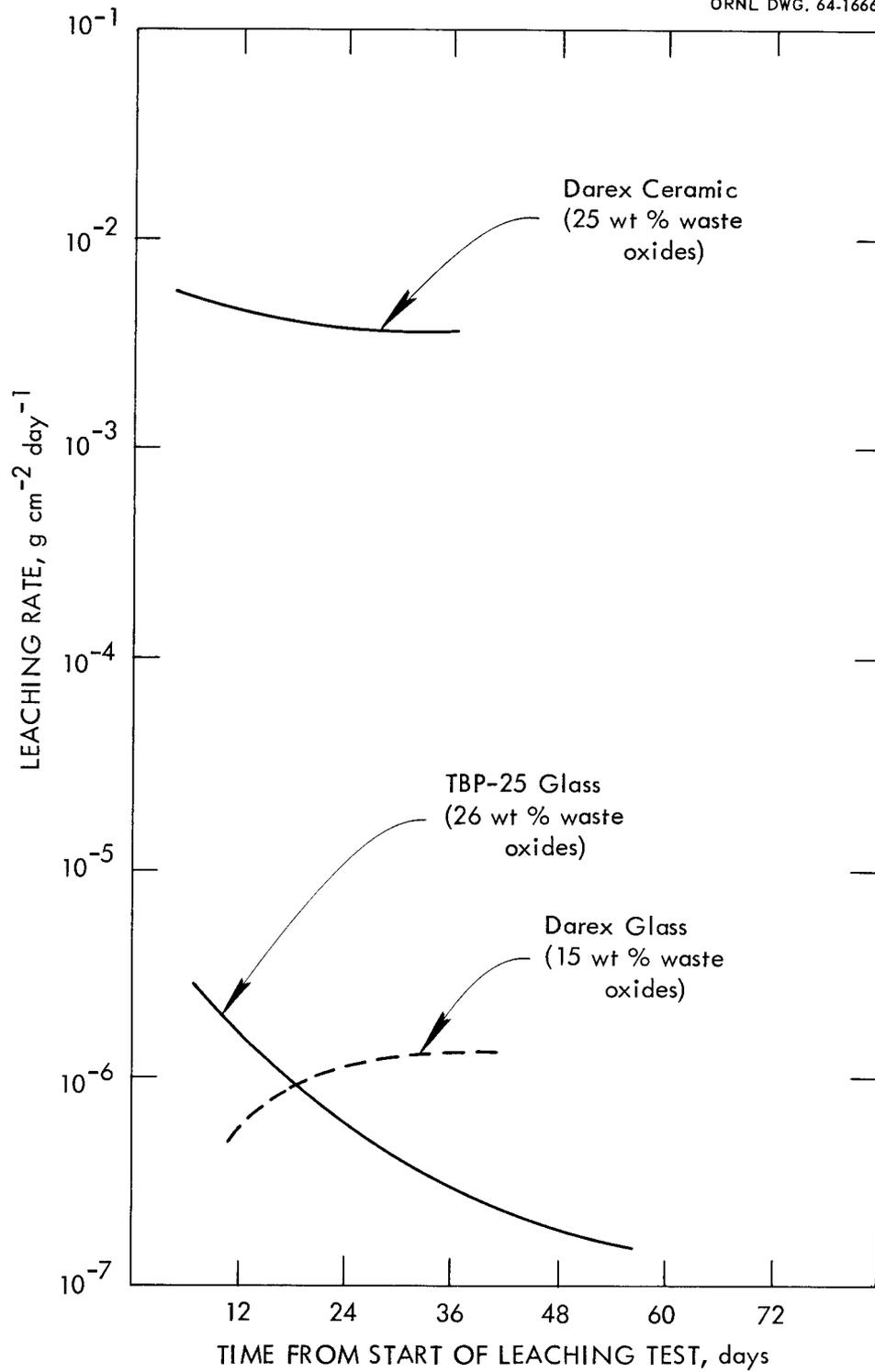


Fig. 9. Leach Rate of Glasses Made from Aluminum Type (TBP-25), and Stainless Steel Type (Darex) Waste Solutions. Rates are Much Lower for Glasses Than for Crystalline Ceramics.

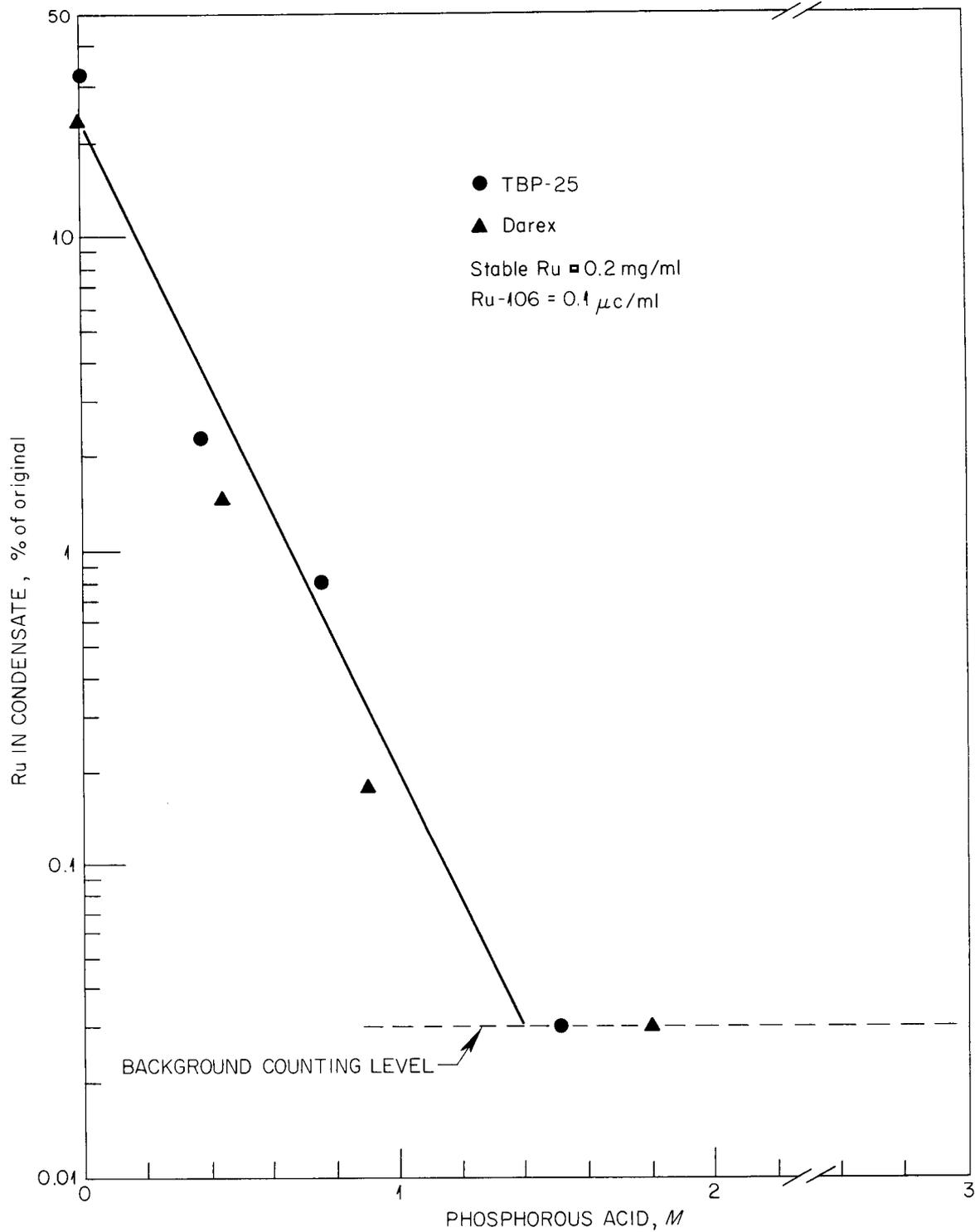


Fig. 10. Effect of Phosphorous Acid on Ruthenium Volatility from Stainless Steel (Darex) and Aluminum-Type (TBP-25) Waste Solutions on Batch Calcination to 500°C. Use of Phosphite Greatly Improves Retention of Ruthenium in the Solid.

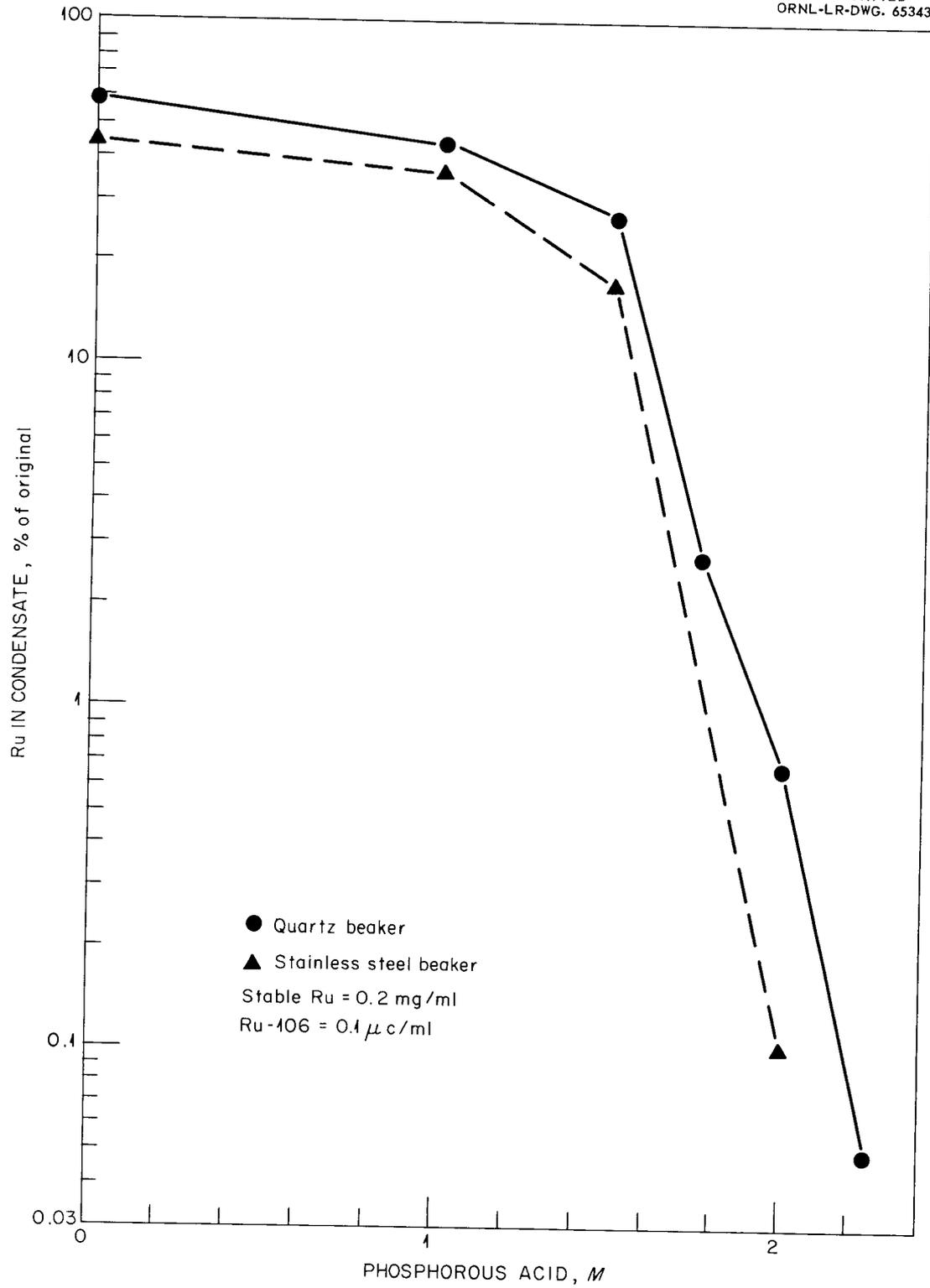


Fig. 11. Effect of Phosphorous Acid on Ruthenium Volatility from Aluminum-Type (TBP-25) Waste on Batch Calcination to 1000°C.

Table 6. Effect of 0.1 M H₃PO₃ on Volatilization of Ruthenium During Distillation of Nitrate Solutions. Even Small Additions of Phosphite Greatly Increase the Separation Factor for Nitric Acid From Ruthenium.

Ru added as RuCl₃, 0.002 M, except as indicated; all solutions contained about 1 μc Ru¹⁰⁶Cl₃.

Solution	Reduction Factors		Increase in Separation Factor for HNO ₃ from Ru, $\left(\frac{\text{HNO}_{3v}/\text{HNO}_{3l}}{\text{Ru}_v/\text{Ru}_l}\right)$ with H ₃ PO ₃ ÷ $\left(\frac{\text{HNO}_{3v}/\text{HNO}_{3l}}{\text{Ru}_v/\text{Ru}_l}\right)$ no H ₃ PO ₃
	Distillation Factor		
	$\frac{\text{Ru}_v, \text{ no H}_3\text{PO}_3}{\text{Ru}_l, \text{ with H}_3\text{PO}_3}$	$\frac{(\text{Ru}_v/\text{Ru}_l), \text{ no H}_3\text{PO}_3}{(\text{Ru}_v/\text{Ru}_l), \text{ with H}_3\text{PO}_3}$	
12 M HNO ₃ ^a	420	447	395
6 M HNO ₃ ^b	2593	2920	2866
1.7 M Al(NO ₃) ₃ ^a + 2 M HNO ₃	208	204	186
Aluminum type (TBP-25) waste ^c	227	225	356
Purex waste ^d	48.8	50.4	53.0
Stainless steel type (Darex) waste ^c	38.4	38.8	38.4

^aData from ORNL-TM-133, Table 2.2.

^bRuthenium added as the nitrosohydroxide.

^cSee Table 1 for solution compositions.

^dSolution composition (M): Al³⁺, 0.1; Fe³⁺, 0.5; Cr³⁺, 0.01; Ni²⁺, 0.01; H⁺, 5.6; Na⁺, 0.6; SO₄²⁻, 1.0; Ru, 0.002; NO₃⁻, 8.05.

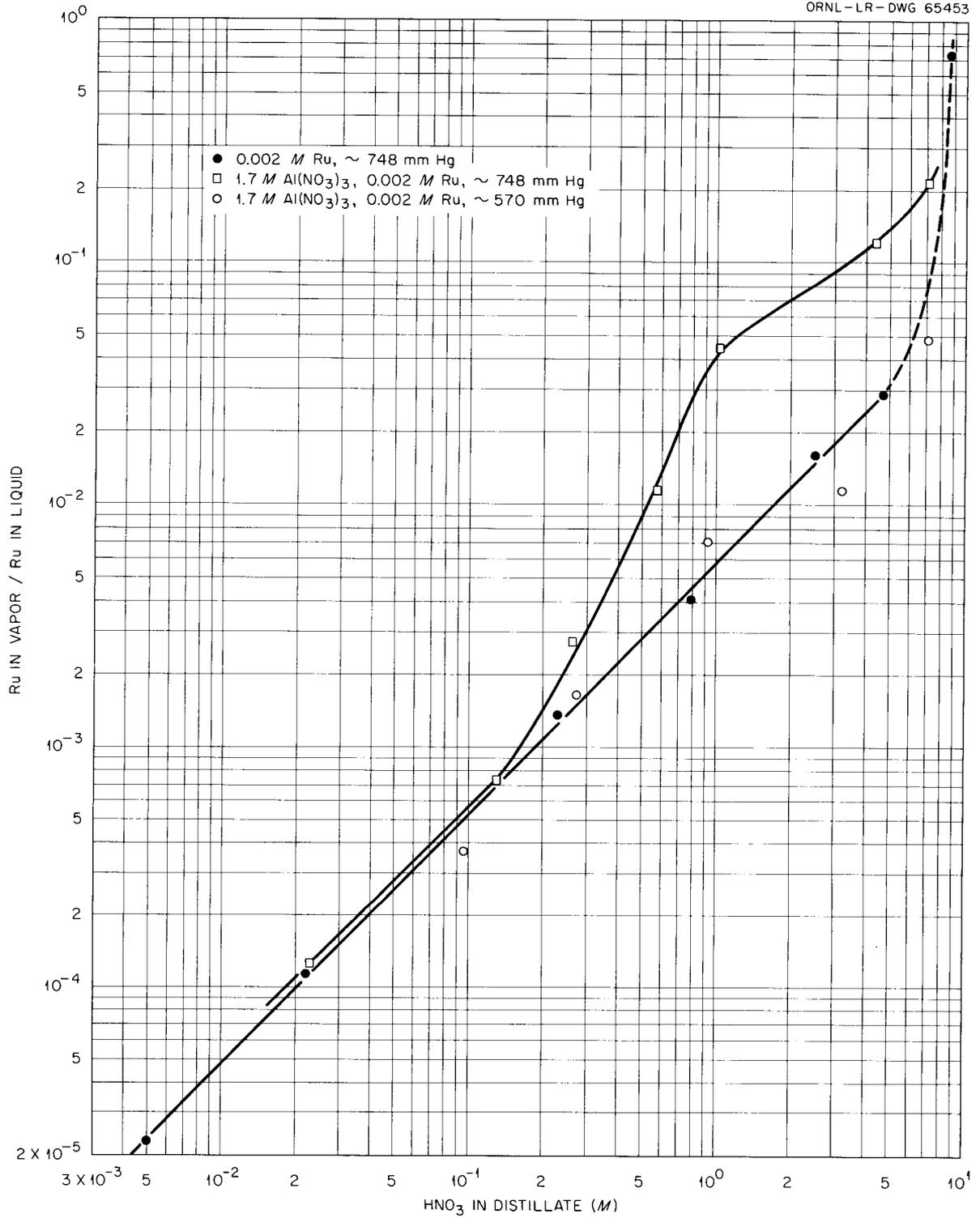


Fig. 12. Volatilization of Ruthenium from Acid Nitrate Solutions as a Function of Nitric Acid Volatility.

relative volatility of ruthenium, but this was not true for the solution of nitric acid alone. The separation factor for distillation of nitric acid from ruthenium increased sharply as free nitric acid in the feed was decreased below 2 \underline{M} , but the factor was about 60 at 570 mm of mercury vs about 10 at 748 mm of mercury (Fig. 13).

Six semicontinuous, semiengineering-scale experiments were made in the 4-in.-diam by 24-in.-long pot using essentially the same glass composition as that tested in the leach test (Table 7). The product formed was quite similar to that formed in small-scale experiments. Increasing the phosphite addition by 12.5%, that is, from 2 to 2.25 \underline{M} , or the substitution of phosphate for phosphite had a negligible effect on ruthenium volatility. This is believed to be caused by oxidation of the ruthenium on the hot, dry walls of the pot. Prior experiments that had shown a marked reduction in ruthenium volatility were carried out at a fixed liquid level, whereas, with glass it was necessary to operate with a slowly rising liquid level in order to minimize pressure variations in the pot. This resulted in spattering of the melt on the wall and the decomposition of solid nitrate in the absence of contact with phosphite. The variation in ruthenium volatility observed under supposedly identical operating conditions (from 12.5 to 21.0%; Table 7) is difficult to explain. There is a possibility that there was some buildup of ruthenium in the stainless steel piping and that the buildup tended to cause the apparent volatility to be higher for the later experiments. These lines were, however, flushed out thoroughly between experiments by distilling nitric acid through the system.

Entrainment observed was rather consistently about 0.1%, as indicated by the amounts of Pm^{147} tracer and phosphorous in the condenser system. Analysis for iron gave results indicating entrainment in the range of 1 to 3%. This higher value may have been caused at least partially by corrosion of the stainless steel off-gas line by the distilled acid. Subsequent results with a sulfate-containing nitrate waste^{18a} and somewhat different additives indicate that some volatile compound of iron may be formed during the fixation process and then decomposed in the vapor phase. This point needs further investigation.

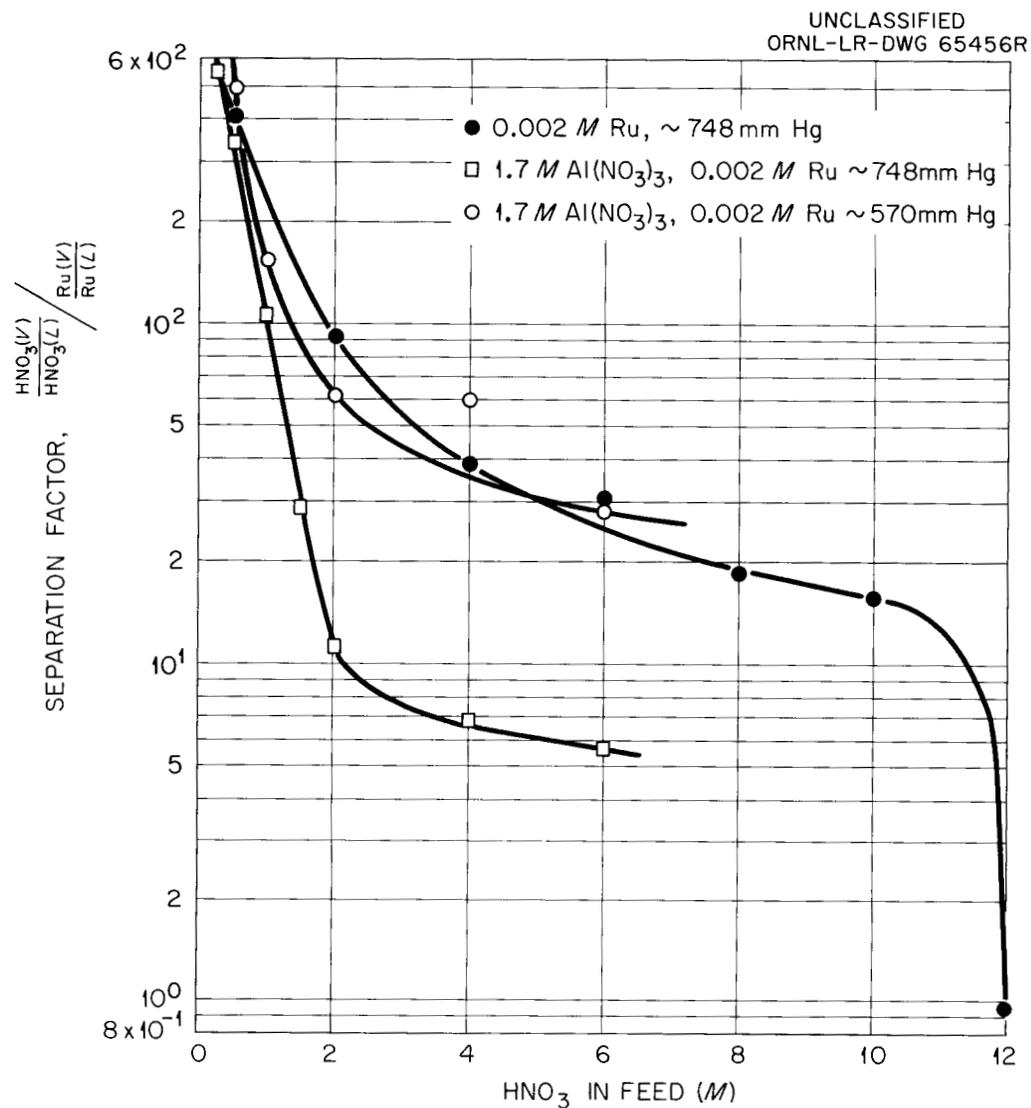


Fig. 13. Ratio Between Nitric Acid and Ruthenium Distillation Factor as a Function of Nitric Acid Concentration in Feed.

Table 7. Summary of Semiengineering-Scale Semicontinuous Fixations of Simulated Aluminum (TBP-25) Waste^a

Additives (g-moles per liter waste sol'n)		Constituents in Condensate (% of Total Present)					Average Feed Rate (ml/min)
		Ru	Hg	Pm ¹⁴⁷	Fe	P	
NaH ₂ PO ₂	2.0	27.5	90.6	---	2.6	0.085	45
PbO	0.25						
NaH ₂ PO ₂	2.0						
PbO	0.25	18.4	---	---	---	0.122	32
NaH ₂ PO ₂ ^b	2.0						
PbO	0.25						
Ru ¹⁰⁶	(0.1 μc/ml)	12.5	54.1	0.019	---	---	36
Pm ¹⁴⁷	(2 μc/ml)						
NaH ₂ PO ₂ ^b	2.25						
PbO	0.25	16.5	---	< 0.11	2.4	---	40
Ru ¹⁰⁶	(0.2 μc/ml)						
Pm ¹⁴⁷	(2 μc/ml)						
Na ₂ HPO ₄ ^b	0.5	22.6	76.7	---	1.4	---	44
NaH ₂ PO ₄	0.84						
H ₃ PO ₄	1.17						
PbO	0.25						
NaH ₂ PO ₂ ^b	2.0						
PbO	0.25	21.0	---	---	---	---	33
Ru ¹⁰⁶	(0.2 μc/ml)						

^aVolume reductions from waste solution to glass were about 8 in every case; density of glass was about 2.9 g/cm³.

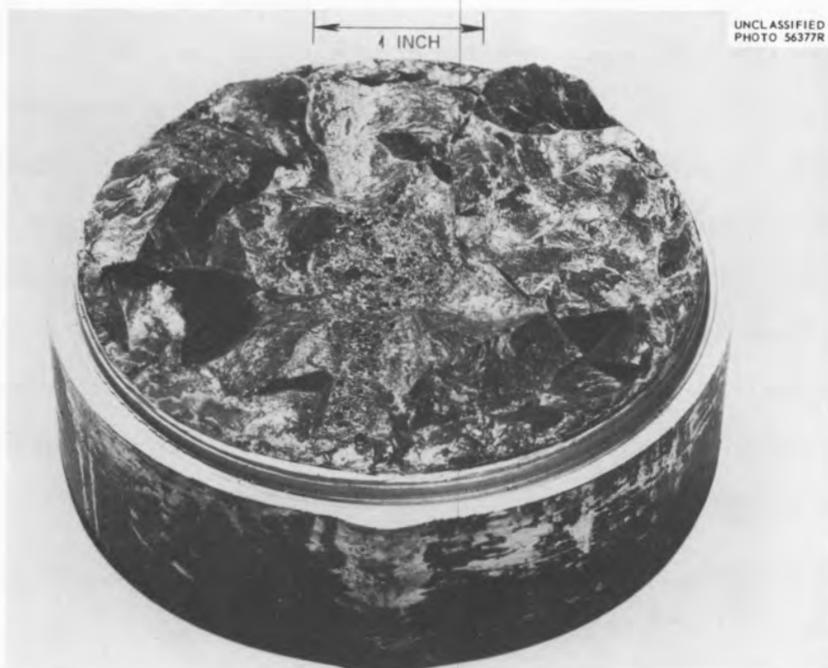
^bEquipment was flushed with NO before starting feed.

Heating the glass produced in one of these tests to 900°C for 24 days in a closed container resulted in lowering the internal pressure by about 30 in. of water. No appreciable corrosion was observed on the stainless steel container at the end of the test. The glass had turned slightly brown, and lead had accumulated at the bottom of the container, but otherwise the appearance of the material was very nearly the same as before (Fig. 14). This particular glass has also been prepared successfully on an engineering scale in an 8-in.-diam by 8-ft-long pot.^{18b} About 6 ft of the pot was filled with glass, leaving about 2 ft of void space at the top. The solid formed in this larger-scale demonstration was as glassy in appearance as that prepared in the 4-inch-diameter pot but gave an x-ray pattern for aluminum phosphate.

The measured thermal conductivity values for this lead phosphate glass varied from about $1.05 \text{ Btu hr}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$ at 300°F to about 1.60 at 1050°F (Fig. 15). The glass had a positive temperature coefficient of thermal conductivity, which is characteristic of amorphous solids. For purposes of comparison the conductivities of three common glasses from reference 19 are plotted in Fig. 15. The measured conductivity values are larger by factors of more than 10 than the $0.1 \text{ Btu hr}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$ that has been calculated as probably high enough for the storage of calcined wastes.²⁰

The presence of mercury in the waste solution (Table 1) represents a source of potential operational difficulty since all mercury compounds are unstable at the temperatures required for either calcination or glass making. Mercury and mercury compounds, varying greatly in appearance and composition, collected in the off-gas system during calcination and fixation. Thermogravimetric study of these solids indicated ranges of rapid weight loss between 100° and 400°C and above 500°C. Small specimens heated in open containers volatilized completely and rapidly at 600°C.

Attempts to collect the mercury in a trap located in the off-gas line were unsuccessful. Neither laboratory nor semiengineering-scale attempts ever collected more than 50% of the total mercury, and the amount collected was usually less than this. The remainder was scattered throughout the system from the fixation pot through the entire off-gas system to the liquid condensate.



(a)



(b)

Fig. 14. Sectioned Stainless Steel Fixation Pot Containing Aluminum Type (TBP-25) Waste in Lead Phosphate Glass: (a) As Prepared; (b) After One Month at 900°C. Prolonged Heating Produced no Deleterious Effects Upon Either the Glass or the Container.

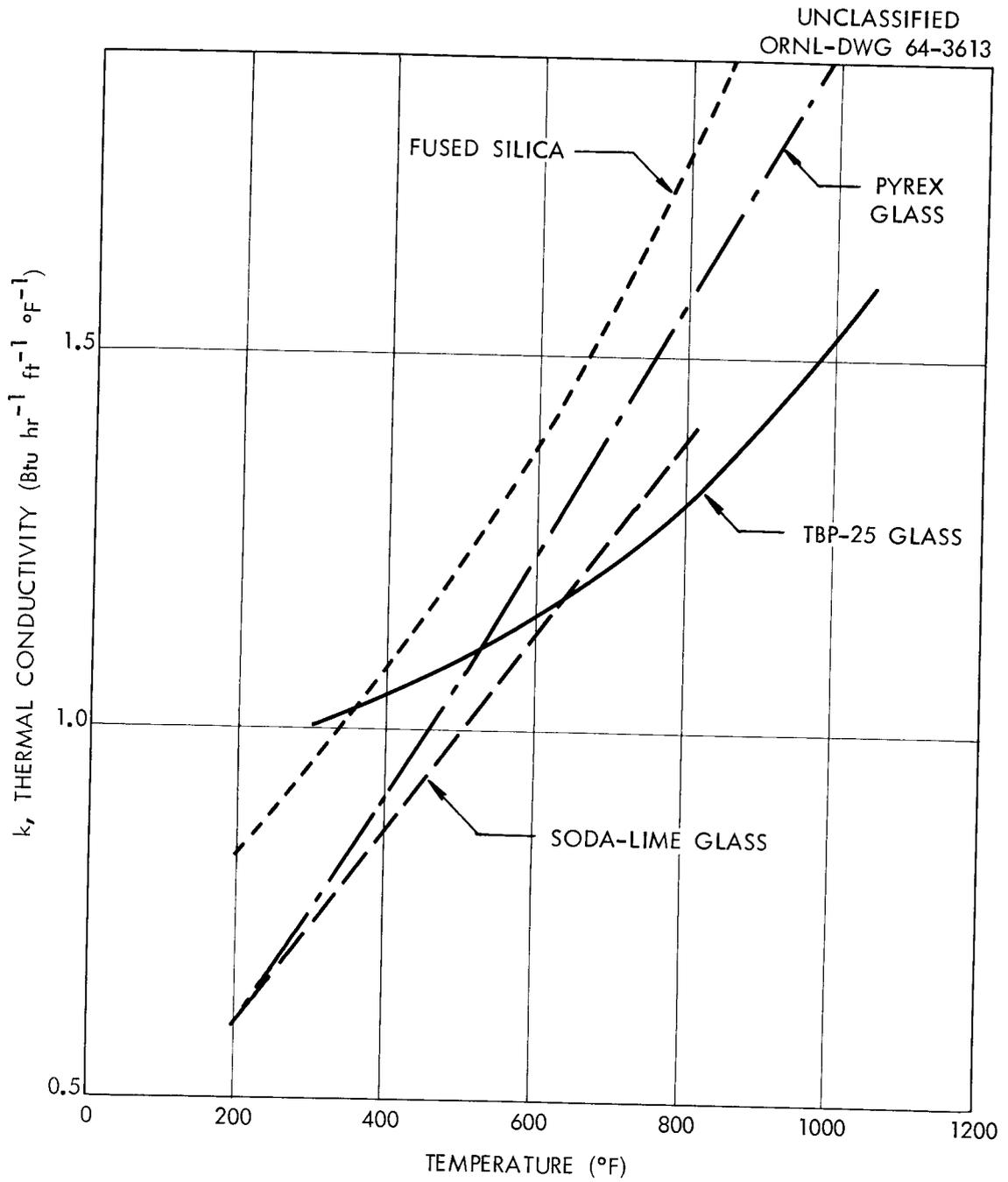


Fig. 15. Thermal Conductivity of Several Glasses.

Consequently, the removal of mercury prior to waste calcination or fixation is proposed as a general solution for the mercury problem for all waste solidification methods. A simple method for removal of more than 99% of the mercury directly from the waste solution was demonstrated on a laboratory scale.²¹ The waste solution containing no more than 1.5 M free acid was passed upflow through a column packed with shot or turnings of copper or aluminum. In principle any metal more active than mercury would serve provided it is not attacked rapidly enough to produce gas evolution and does not form insoluble compounds which prevent further attack or which plug the column.

Corrosion tests in simulated waste solutions of high aluminum concentration without fluxing additives showed overall rates of 5.1 and 10.5 mils/month for welded types 304L and 347 stainless steels, respectively, in 24 hr, and 1.59 and 1.95 mils/month in 68 hr. These results indicate that aggressive corrosion ceases after volatilization of the free acid and water. This was also found to be true for the waste to which glass-making ingredients had been added;* in two tests of 19 and 345 hr, overall corrosion rates were calculated to be 42.2 and 5.4 mils/month, respectively. No serious localized attack was apparent. In semiengineering-scale tests, attack on the center tube was greater than on the wall of the pot. Such attack as did occur resulted in the formation of magnetite from the stainless steel. Figure 16 illustrates this type of attack. The specimen shown was the type 347 stainless steel spider used to position the center tube in the fixation pot. This would seem to indicate that the attack was due primarily to water vapor trapped in the melt at high temperatures. In areas where little or no corrosion took place, the phosphate glass bonded tightly to the stainless steel, making separation of the specimen from the glass extremely difficult.

The most extreme conditions to which the fixation pot is to be exposed are represented by a temperature of 1050°C in a pot full of high-density glass. Under these conditions the entire weight of the pot plus the glass will be carried by the outside wall of the pot near the top, since the pot is suspended from the top flange. Accordingly, tests were carried out in which a small 304L stainless steel pot was filled with

* Additives (g-moles per liter of waste solution) were $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 2.0 M; and PbO , 0.25 M.

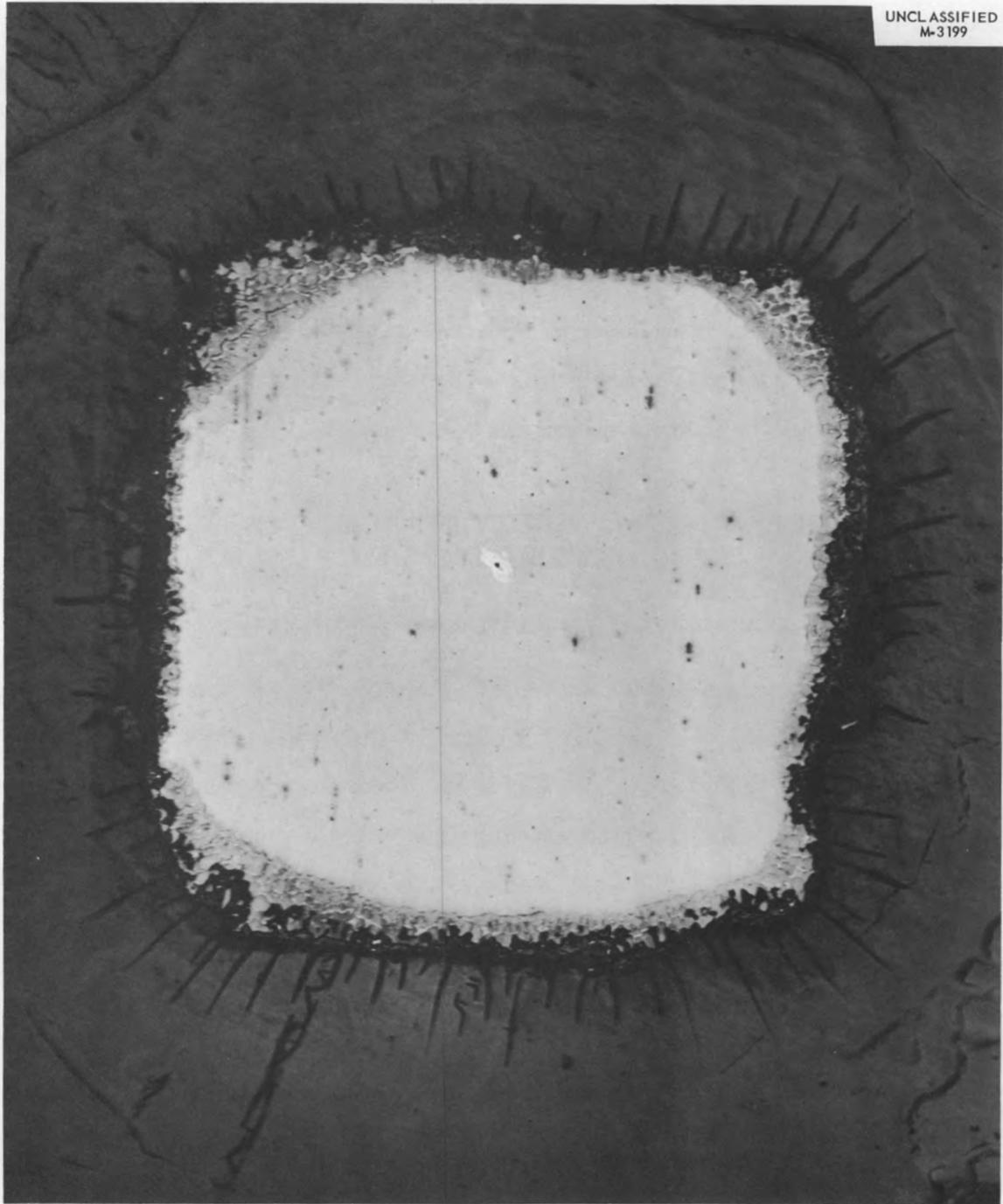
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Fig. 16. Corrosion of Type 347 Stainless Steel "Spider" in Pot During Formation of Glass from Aluminum Nitrate Waste. Corrosion was Worse on Unheated Interior Surfaces Than on the Interior Pot Walls. 20X. Reduced 16%.

simulated high-sulfate Purex waste plus fluxing additives. (Purex waste was used because it is more corrosive than the other two types.) The pot was then subjected to a tensile stress of 315 psi and simultaneously to an evaporation-calcination cycle. After 96 hr at 1050°C one side of the pot showed an elongation of 1.49×10^{-3} in./in., while the other side showed no measurable change. This indicates that the maximum elongation in an 8-ft-long pot over a normal evaporation-calcination cycle (cycle time is estimated to be 80 hr) should be about 0.15 in.

In all tests thus far in which types 304L and 347 stainless steels have been compared, 304L was equal to or superior to 347. It is probable that either of these two types of steel could be used for the pot.

4. WASTES CONSISTING PRINCIPALLY OF NITRATES OF THE CONSTITUENTS OF STAINLESS STEEL

(From Darex or Electrolytic Fuel Dissolution Processes)

Simulated Darex waste solutions were characterized as to vapor-liquid equilibria and solution densities. The compositions of the solution varied from 0.5 to 7 M in free acid and from 0.06 to 1.82 M in iron (Table 2). These iron concentrations correspond to 1/2 to 1-1/2 times the expected concentration of the waste as listed in Table 1. It was impracticable to make and study a solution corresponding to twice this concentration of iron. Vapor-liquid equilibrium data and densities are presented in Tables 8 and 9 and are plotted in Figs. 17, 18, and 19.

Stainless steel wastes are not as amenable to fixation in good glass as are aluminum wastes, but a series of apparently satisfactory products was obtained by the addition of borate and aluminum as well as phosphate (or phosphite). These were glasses only if they contained less than about 20 wt % waste oxides. Above this amount a number of apparently satisfactory solids were not glassy unless quenched (Tables 10 and 11). Volume reductions obtained varied from 2.5 to 6.6 from the unconcentrated waste. Softening temperatures varied from 800 to 1100°C.

Table 8. Vapor-Liquid Equilibrium and Solution Density Data for Simulated Stainless Steel (Darex) Waste at Atmospheric Pressure (746 to 749 mm Hg)

Solution	H ⁺ , Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml)			
				25°C	50°C	75°C	100°C
D-1*	0.79	107	747.0	1.344	1.323	1.304	1.294 (95°)
pot	0.86						
distillate	0.29						
D-1a*	1.26	108.5	747.0	1.352	1.328	1.308	1.296 (95°)
pot	1.35						
distillate	0.46						
D-1b	1.83	110	746.7				
pot	1.97			1.3844	1.3665	1.3470	1.3203
distillate	0.94						
D-1c	2.75	112.5	747.1				
pot	2.99			1.4129	1.3941	1.3727	1.3469
distillate	1.86						
D-1d	4.41**	116	750.4				
pot	4.92			1.4595	1.4370	1.4126	1.3829
distillate	4.46						
D-1e	6.70	119	750.4				
pot	6.80			1.5080	1.4813	1.4485	1.4175
distillate	8.51						
D-2*	0.63	102.0	747.0	1.178	1.158	1.143	1.098 (95°)
pot	0.72						
distillate	0.025						
D-2a*	1.04	103.0	747.0	1.194	1.176	1.158	1.149 (95°)
pot	1.18						
distillate	0.073						
D-2b	1.88	105.5	747.1				
pot	2.06			1.2380	1.2200	1.2011	1.1732
distillate	0.26						
D-2c	2.80	107.5	750.4				
pot	3.11			1.2731	1.2555	1.2374	1.2149
distillate	0.59						
D-2d	4.77	111	750.4				
pot	5.16			1.3289	1.3077	1.2746	1.2602
distillate	1.81						
D-2e	6.39	114.5	749.3				
pot	7.05			1.3765	1.3513	1.3237	1.2947****
distillate	4.02			1.3764	1.3514	1.3260	1.2965
D-3*	0.98	104.5	748.5	1.473	1.448	1.432	1.415 (95°)
pot	1.24						
distillate	1.04						
D-3a*	1.31	105.0	748.5	1.481	1.455	1.436	1.417 (95°)
pot	1.14						
distillate	1.70						
D-3b***		117	749.3				
pot	1.98			1.5363	1.5167	1.4869	1.4650
distillate	3.19						
D-3c***		118.5	750.1				
pot	2.75			1.5563	1.5356	1.5100	1.4814
distillate	4.74						
D-3d***		121	750.1				
pot	4.58			1.5841	1.5598	1.5319	1.4992
distillate	8.57						

* Westphal balance data on feed solutions.

** Apparent analytical error.

*** Not stable at room temperature.

**** Duplicate determinations.

Table 9. Vapor-Liquid Equilibrium and Solution Density for Simulated Stainless Steel (Darex) Waste at Subatmospheric Pressure (559 to 569 mm Hg)

Solution*	H ⁺ , Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml)			
				25°C	50°C	75°C	100°C
D-1bs pot distillate	1.83 1.97 0.80	103	566.0	1.3874	1.3701	1.3455	1.3265
D-1cs pot distillate	2.75 2.90 1.66	105	566.0	1.4168	1.3993	1.3763	1.3506
D-1ds pot distillate	4.41 4.86 4.12	108.5	562.4	1.4628	1.4396	1.4040	1.3847
D-1cs pot distillate	6.70** 6.87 8.10	111.5	559.8	1.5101	1.4831	1.4537	1.4216
D-2bs pot distillate	1.88 2.00 0.20	97.5	566.0	1.2300	1.2151	1.1908	1.1707
D-2cs pot distillate	2.80 3.09 0.53	99.5	566.0	1.2709	1.2539	1.2354	1.2063
D-2ds pot distillate	4.77 5.18 1.67	103	562.4	1.3257	1.3066	1.2838	1.2573
D-2es pot distillate	6.39 7.07 3.79	106.5	559.8	1.3768	1.3529	1.3269	1.2961
D-3bs*** pot distillate	1.94 2.91	109.5	568.1	1.5320	1.5117	1.4873	1.4587
D-3cs pot distillate	2.84 4.72	111	568.1	1.5582	1.5352	1.5104	1.4802
D-3ds pot distillate	4.50 8.18	113.5	568.1	1.5842	1.5580	1.5293	1.4970

* The suffix "s" indicates subatmospheric pressure. Solutions D1, D1a, D2, D2a, D3 and D3a were not investigated at subatmospheric pressure.

** Apparent analytical error.

*** Not stable at room temperature.

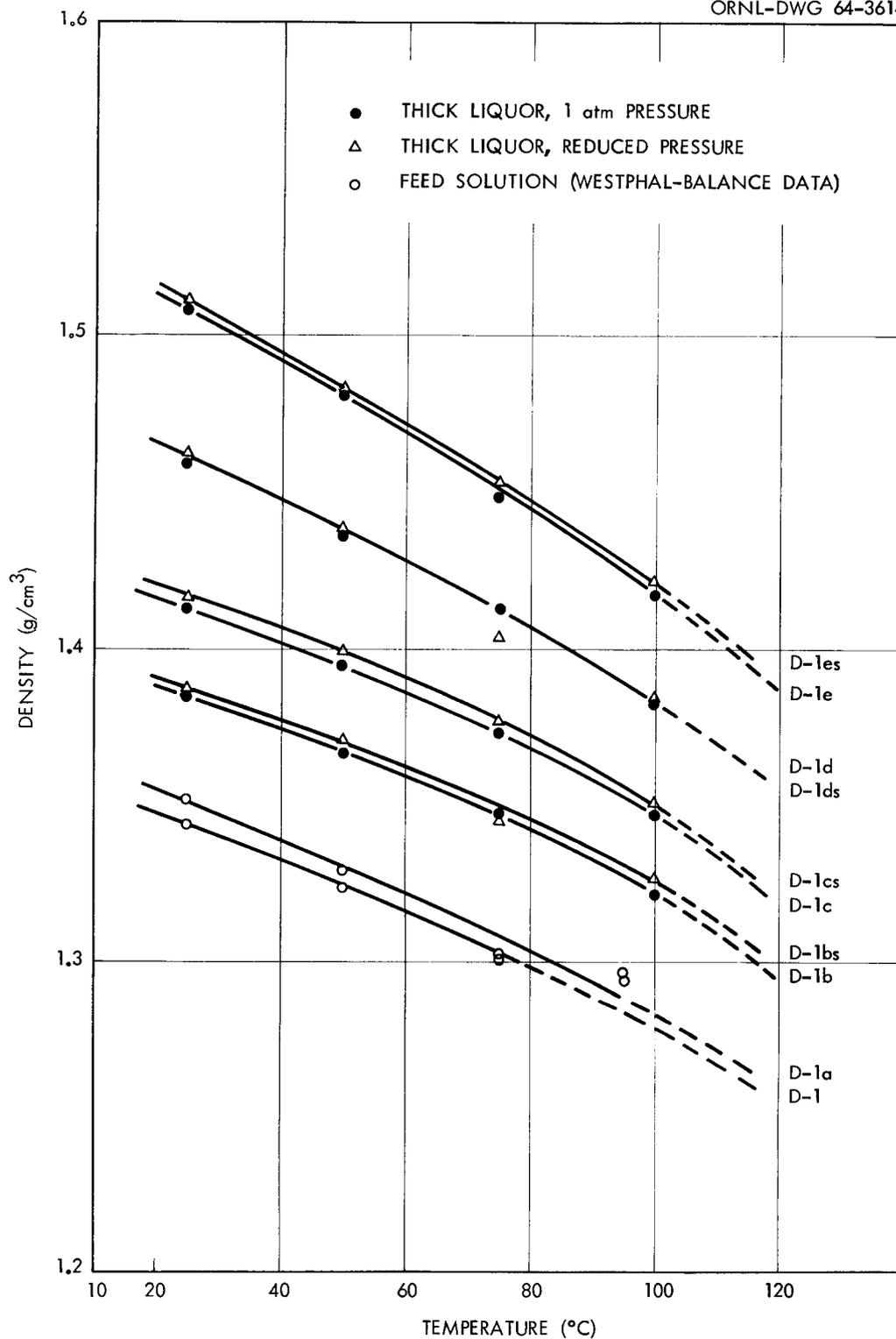


Fig. 17a. Density of Simulated Stainless Steel (Darex) Waste Solutions.
 $C_{Fe^{3+}} = 1.2-1.3 \underline{M}$; $C_{H^+} = 0.5-7.0 \underline{M}$ (data from Tables 8 and 9).

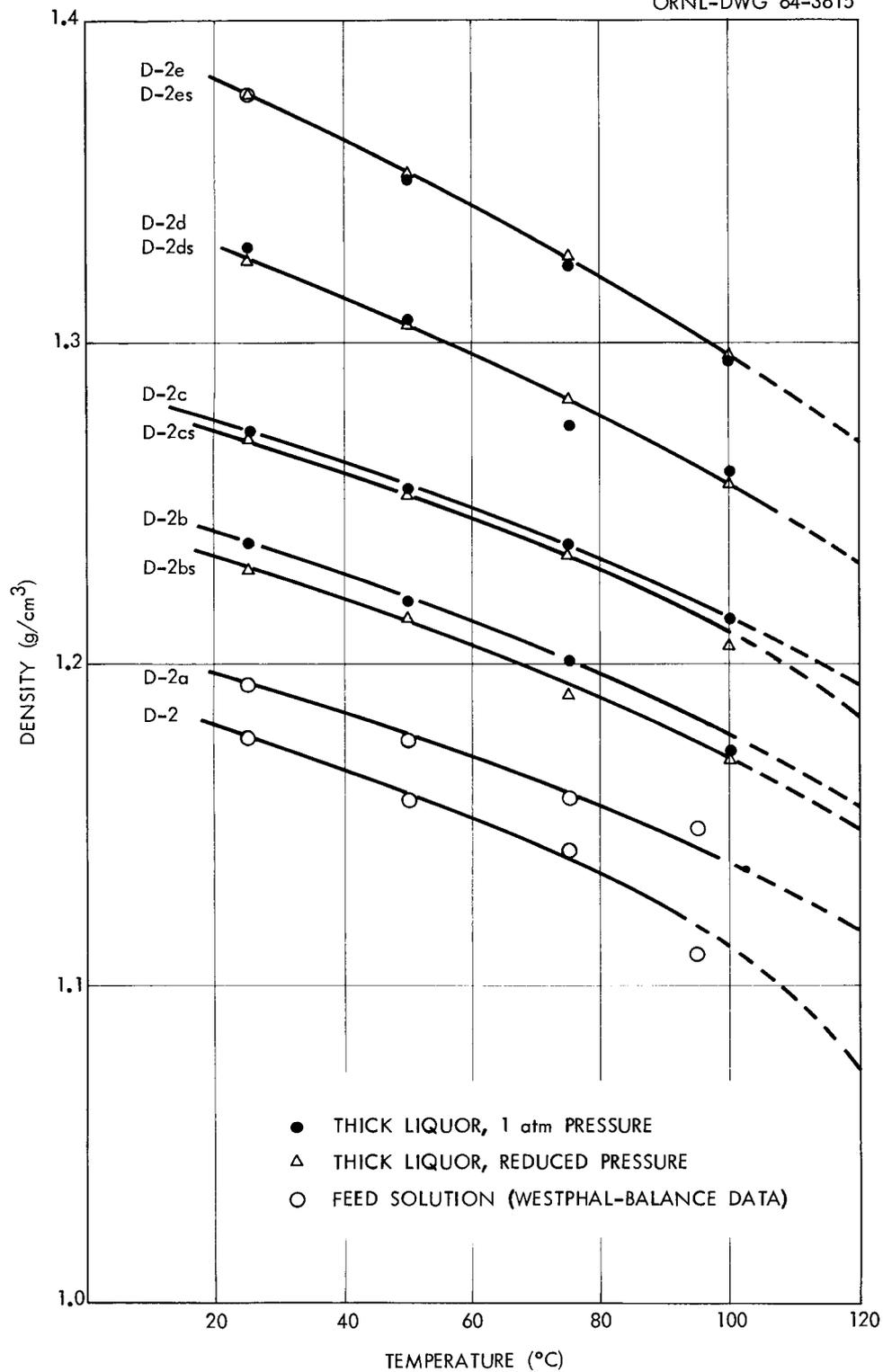


Fig. 17b. Density of Simulated Stainless Steel (Darex) Waste Solutions.
 $C_{Fe^{3+}} = 1.8-1.9 \underline{M}$; $C_{H^+} = 0.5-7.0 \underline{M}$ (data from Tables 8 and 9).

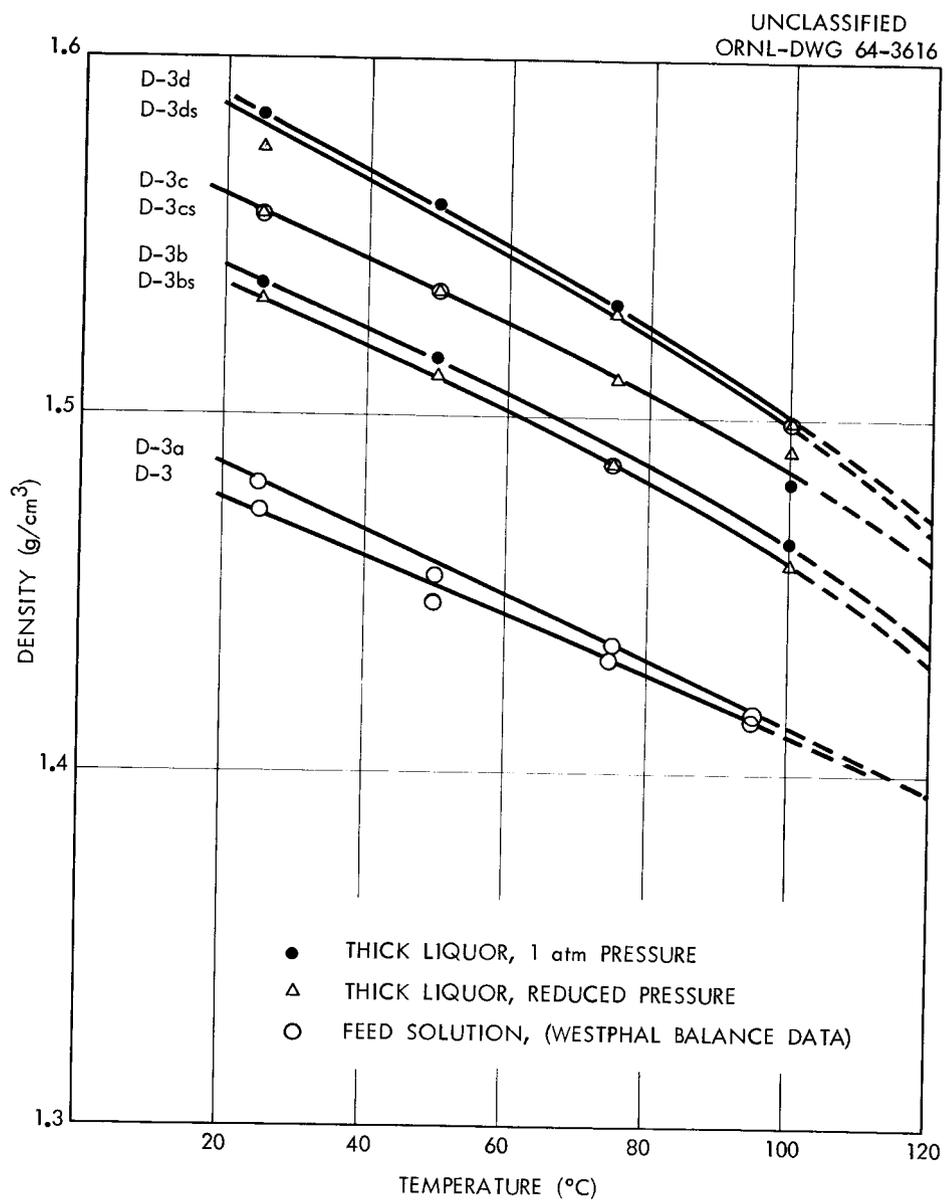


Fig. 17c. Density of Simulated Stainless Steel (Darex) Waste Solutions. $C_{Fe^{3+}} = 0.6 - 0.65 \text{ M}$; $C_{H^+} = 0.5-0.7 \text{ M}$ (data from Tables 8 and 9).

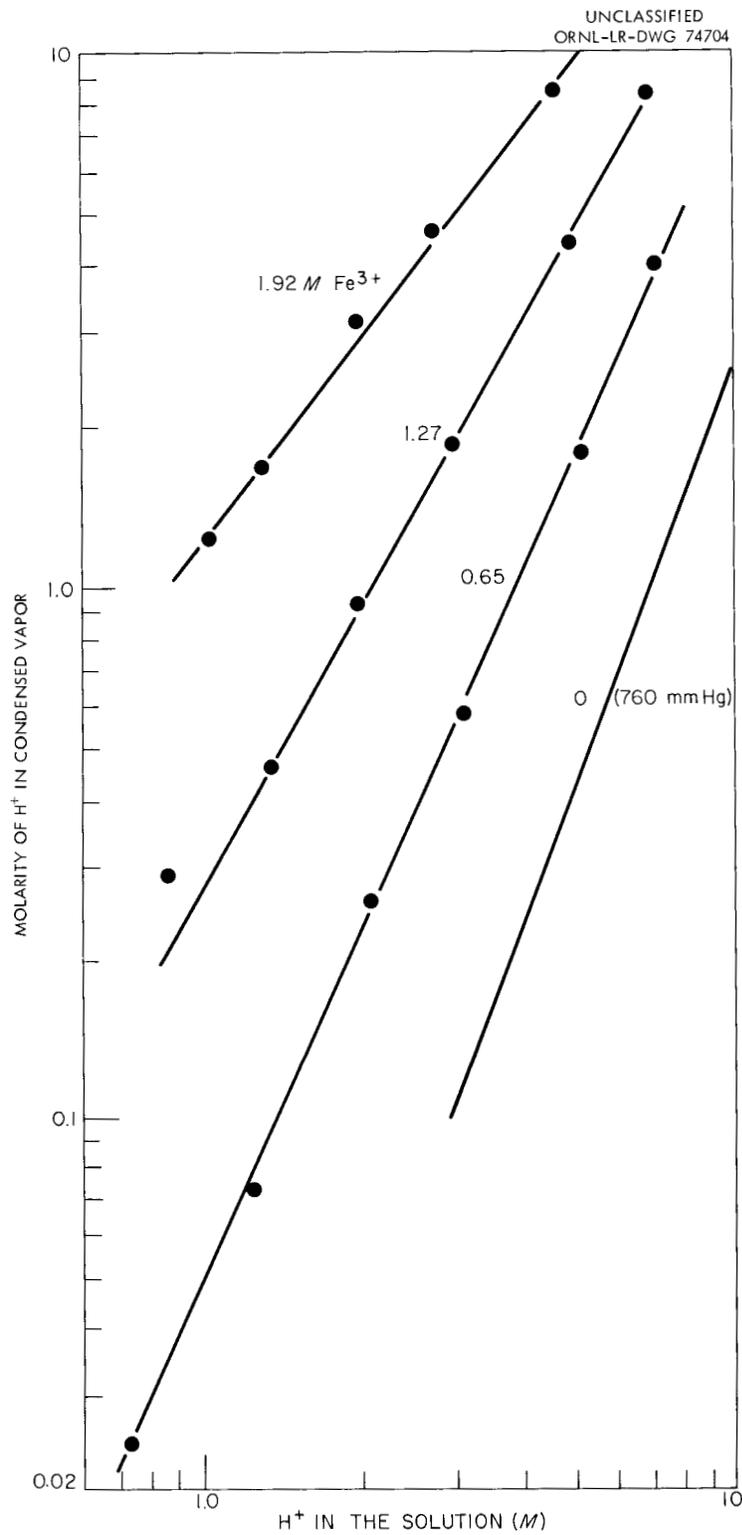


Fig. 18a. Vapor-Liquid Equilibrium in Simulated Stainless Steel (Darex) Waste Solutions at 746 to 751 mm Hg.

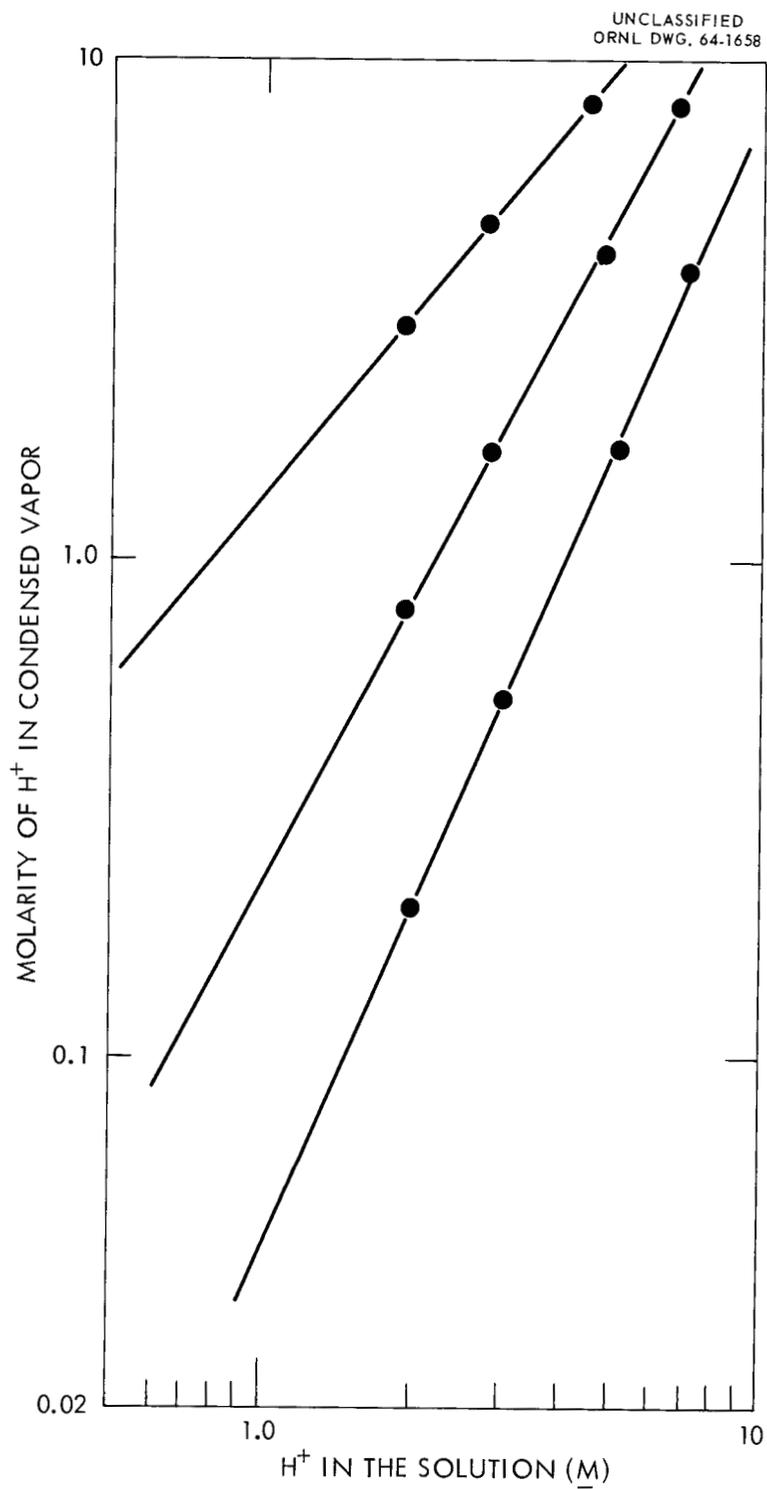


Fig. 18b. Vapor-Liquid Equilibrium in Simulated Stainless Steel (Darex) Waste at 559-569 mm Hg.

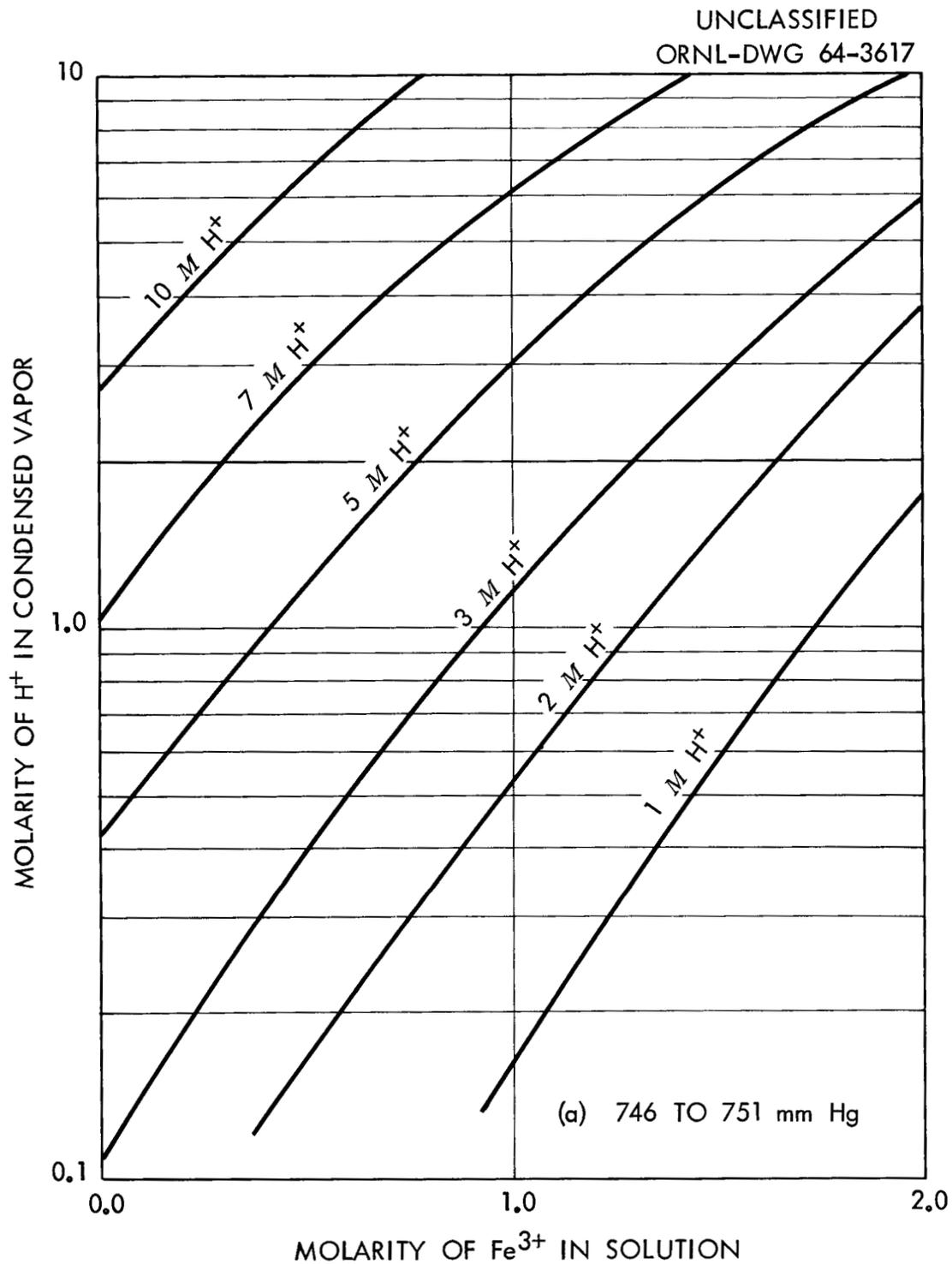


Fig. 19a. Vapor-Liquid Equilibrium in Simulated Stainless Steel (Darex) Waste Solutions.

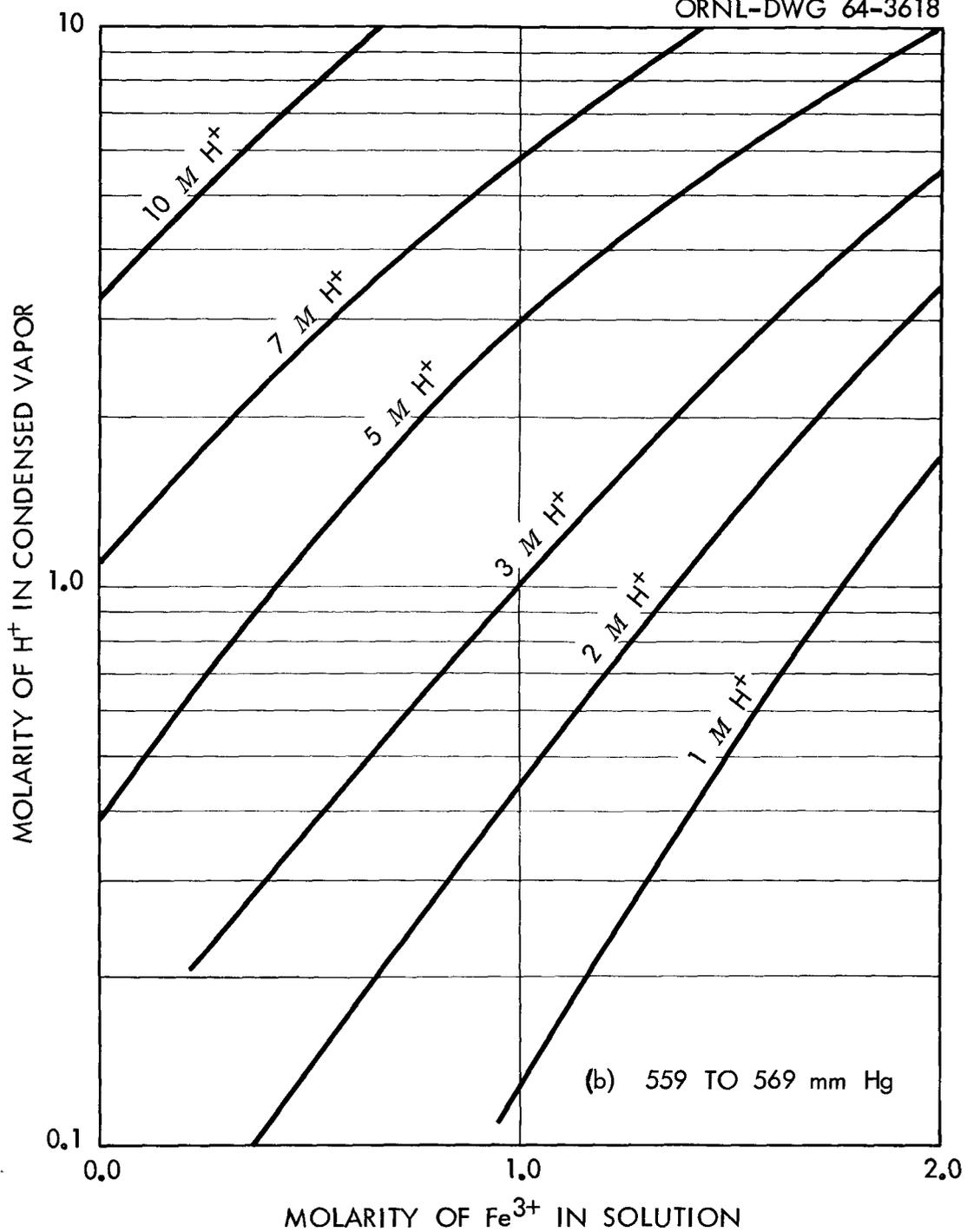
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Fig. 19b. Vapor-Liquid Equilibrium in Simulated Stainless Steel (Darex) Waste Solutions.

Table 10. Phosphate and Borophosphate Glasses Incorporating Simulated Stainless Steel (Darex) Waste Oxides.
Glasses Obtained With This Waste Type Did Not Entail Large Volume Reductions.

Darex waste composition (M): 1.25 Fe³⁺, 0.38 Cr³⁺, 0.18 Ni²⁺, 0.04 Mn²⁺, 0.75 H⁺, 6.0 NO₃⁻, 0.002 Ru with 260 ppm Cl⁻.

Melt	1	2	3	4	5	6	7	8	9	10	11	12
a. Varying wt % Waste Oxides												
Additives, moles/liter												
NaH ₂ PO ₄ ·H ₂ O	1.5	1.0	2.0	2.5	3.0	2.5	4.0					
NaH ₂ P ₂ O ₇ ·H ₂ O	2.0	2.0	2.0	2.0	2.0	2.0	2.0					
Na ₂ B ₄ O ₇ ·10H ₂ O	0.23	0.32	0.32	0.3	0.32	0.3	--					
NaOH	0.46	0.4	--	0.37	0.4	0.37	--					
Al(NO ₃) ₃ ·9H ₂ O	3.0	4.3	4.3	4.0	4.3	4.0	5.0					
Composition of melt, wt % oxides												
Al ₂ O ₃	21.3	29.1	26.0	23.1	22.9	21.1	25.2					
Fe ₂ O ₃	13.9	13.4	11.9	11.3	10.5	10.3	9.9					
Na ₂ O	19.1	16.8	17.2	19.3	19.7	20.3	18.4					
P ₂ O ₅	34.6	28.5	33.9	36.3	37.3	33.1	42.1					
B ₂ O ₃	4.8	6.1	5.4	4.8	4.8	10.4	--					
Cr ₂ O ₃	4.0	3.9	3.5	3.3	3.0	3.0	2.9					
NiO	1.9	1.8	1.6	1.5	1.4	1.4	1.3					
MnO	0.5	0.5	0.4	0.4	0.4	0.4	0.3					
RuO ₂	0.004	0.004	0.004	0.004	0.003	0.003	0.003					
Softening point, °C	850	850	800	800	800	750	800					
Bulk density, g/cc	2.74	--	2.71	2.69	2.61	2.44	2.63					
Waste oxide in melt, wt %	20.3	19.5	17.4	16.5	15.3	15.1	14.4					
Volume reduction, vol Darex/vol melt	3.8	--	3.2	3.0	2.5	2.5	2.6					
Appearance	Black glass, some segregation	Somewhat glassy, segregated	Brown glass	Black glass	Excellent black-brown glass	Brown-black glass	Deep brown glass					
b. Percent Waste Oxides Constant at 25%												
Additives, moles/liter												
NaH ₂ PO ₄ ·H ₂ O	2.8	2.8	2.8	2.8	2.4	1.34	2.8	2.8	2.8	2.8	1.8	2.2
H ₃ PO ₃					0.4	1.46					1.0	0.6
Al(NO ₃) ₃ ·9H ₂ O		0.72	1.44	2.2	1.5	3.0		1.2	1.2	1.86	1.36	0.4
B ₂ O ₃	2.0	1.5	1.0	0.51	1.1	0.6	1.7		0.38	2.0	1.5	2.1
NaOH							1.0	2.8	1.8			
Composition of melt, wt % oxides												
Al ₂ O ₃	--	6.3	12.3	18.3	13.2	25.4	--	10.1	10.1	16.2	12.0	3.5
B ₂ O ₃	24.3	18.0	12.0	6.0	13.2	7.1	19.8	--	4.5	23.4	18.0	24.9
Na ₂ O	15.4	15.4	15.4	15.4	13.2	7.1	19.8	29.5	25.0	--	9.6	11.2
P ₂ O ₅	35.3	35.3	35.3	35.3	35.3	35.3	35.3	35.3	35.3	35.3	35.3	35.3
Waste	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Softening point, °C	850	850	900	1000	850	-- *	850	1100	800	-- *	-- *	800
Bulk density, g/cc	--	2.56	2.86	--	2.65	--	--	--	--	--	--	--
Volume reduction, vol Darex/vol melt	--	4.4	4.9	--	--	--	--	--	--	--	--	--
Appearance	Green, micro-crystal-line	Good black glass	Good black glass	Gray-black, metallic sheen	Rock-like, very hard	Sintered, did not melt below 1050°C	Green crystal-line, partly glossy	Gray, metallic partly glassy	Brown-black micro-crystal-line	Brown, crumbly	Green black rock-like segregated	Gray green crystal-line

*Did not melt at or below 1050°C.

Table 11. Phosphate and Borophosphate Melts Incorporating Simulated Stainless Steel (Darex) Waste Oxides

Waste composition (M): 6.0 NO₃⁻, 0.75 H⁺, 1.25 Fe³⁺, 0.38 Cr³⁺, 0.18 Ni²⁺, 0.04 Mn²⁺, 0.003 Ru

Melt	1	2	3	4	5	6
Additives, moles/liter						
NaH ₂ PO ₂ ·H ₂ O	2.0	2.0	2.0	2.0	2.0	2.0
Na ₂ B ₄ O ₇ ·10 H ₂ O	---	0.5	0.5	1.0	---	---
B ₂ O ₃	1.0	---	---	---	1.5	---
NaOH	1.0	---	---	---	1.5	3.0
PbO	1.0	---	---	---	---	---
AlPO ₄	---	---	1.0	2.0	---	4.0
H ₃ PO ₄	---	---	---	---	---	1.0
NaAlO ₂	---	---	---	---	---	1.0
Melt composition, wt % theoretical oxides						
Al ₂ O ₃	---	---	8.9	13.9	---	23.5
Fe ₂ O ₃	14.8	22.2	17.4	13.6	20.0	9.2
Na ₂ O	13.8	20.7	16.2	8.5	21.7	17.2
P ₂ O ₅	21.1	31.5	37.2	38.7	28.4	45.9
B ₂ O ₃	10.3	15.5	12.2	19.0	20.8	---
PbO	33.1	---	---	---	---	---
Cr ₂ O ₃	4.3	6.4	5.0	3.9	5.8	2.7
NiO	2.0	3.0	2.4	1.8	2.7	1.2
MnO ₂	0.5	0.8	0.6	0.5	0.7	0.3
RuO ₂	0.01	0.01	0.01	0.004	0.01	0.003
Softening point, °C	875	850	875	900	850	900
Bulk density, g/cc	3.75	2.97	2.88	2.73	2.86	3.17
Waste oxides in melt, wt %	21.6	32.3	25.5	19.9	29.1	13.4
Vol reduction: vol Darex/vol melt	5.6	6.6	5.0	3.7	5.7	2.9
Appearance	Brown, hard, microcrystal- line	Greenish black; glassy if quenched	Greenish black; glassy if quenched	Blackish brown; flintlike product	Greenish black; flintlike product	Brown glass

Leaching tests made on one Darex glass that contained about 15 wt % waste oxides resulted in a dissolution rate of about $1.05 \times 10^{-6} \text{ g cm}^{-2} \text{ day}^{-1}$, only slightly greater than that obtained with TBP-25 glass (Fig. 9). On the other hand, a Darex ceramic material containing about 25 wt % waste oxides gave a rate which amounted to about $1.3 \times 10^{-2} \text{ g cm}^{-2} \text{ day}^{-1}$ (Figs. 8 and 20).

Pseudo phase diagrams in which the additives (sodium oxide, boron oxide, aluminum oxide and/or aluminum phosphate) are represented at the apices of the triangles, with fixed amounts of waste oxides in the waste, indicate that softening temperatures generally increase with alumina content and decrease with sodium metaphosphate content (Fig. 21). Borate also tends to lower the melting temperature particularly at low alumina contents (Fig. 22). These trends must be accepted as only very rough generalizations.

Semicontinuous, semiengineering-scale fixation in another ceramic (No. 5, part b of Table 10) gave an apparent volume reduction of 5.1. Due to an error in estimating volume reduction, the fixation experiment was prematurely shut down. On cooling from the operating temperature (1050°C) the fixation pot expanded slightly, making removal from the furnace extremely difficult. Though the pot appeared to be in excellent condition upon removal, it corroded through rapidly after it was replaced in the furnace and fixation was resumed. The failure of the pot wall itself was not discovered until after thermocouple failure necessitated shutdown, and the pot was removed from the furnace. Failure occurred at about the level reached by the melt at the time of the first shutdown. Corrosion at this point was very likely accelerated by the stress produced when the melt expanded on solidifying. Internal unheated elements (thermocouple wells, and center tube) were attacked more severely in general than the pot wall itself. The hole in the latter, though quite large (about 2 in. in diameter) was so thoroughly plugged with corrosion scale that neither melt nor gas escaped in detectable amounts.

The solid product from this fixation experiment contained numerous voids in contrast to the small-scale specimen (No. 5, part b of Table 10). Small aggregates of magnetic metal, usually spherical in shape, were suspended in the solid. Presumably the formation of these was connected with the corrosion process.



(a)



(b)

Fig. 20. Aluminum Borophosphate Glass Incorporating Simulated Stainless Steel Waste Oxides. (a) 15.3% Waste Oxides (No. 5, Table 10a); (b) 25% Waste Oxides (No. 3, Table 10b).

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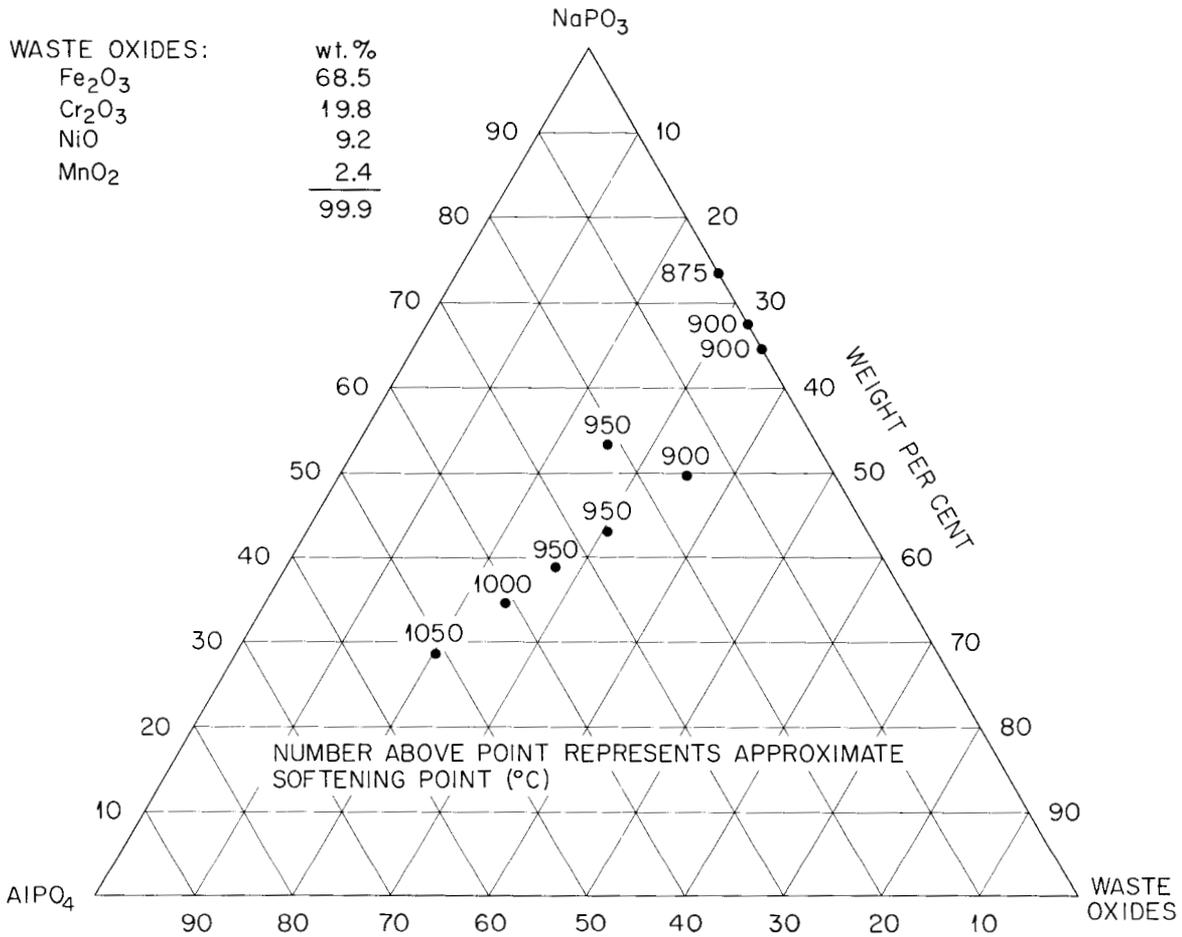


Fig. 21. Solid Phosphate Products Incorporating Stainless Steel Waste Oxides. Softening Temperatures Generally Increase with Addition of Aluminum Phosphate.

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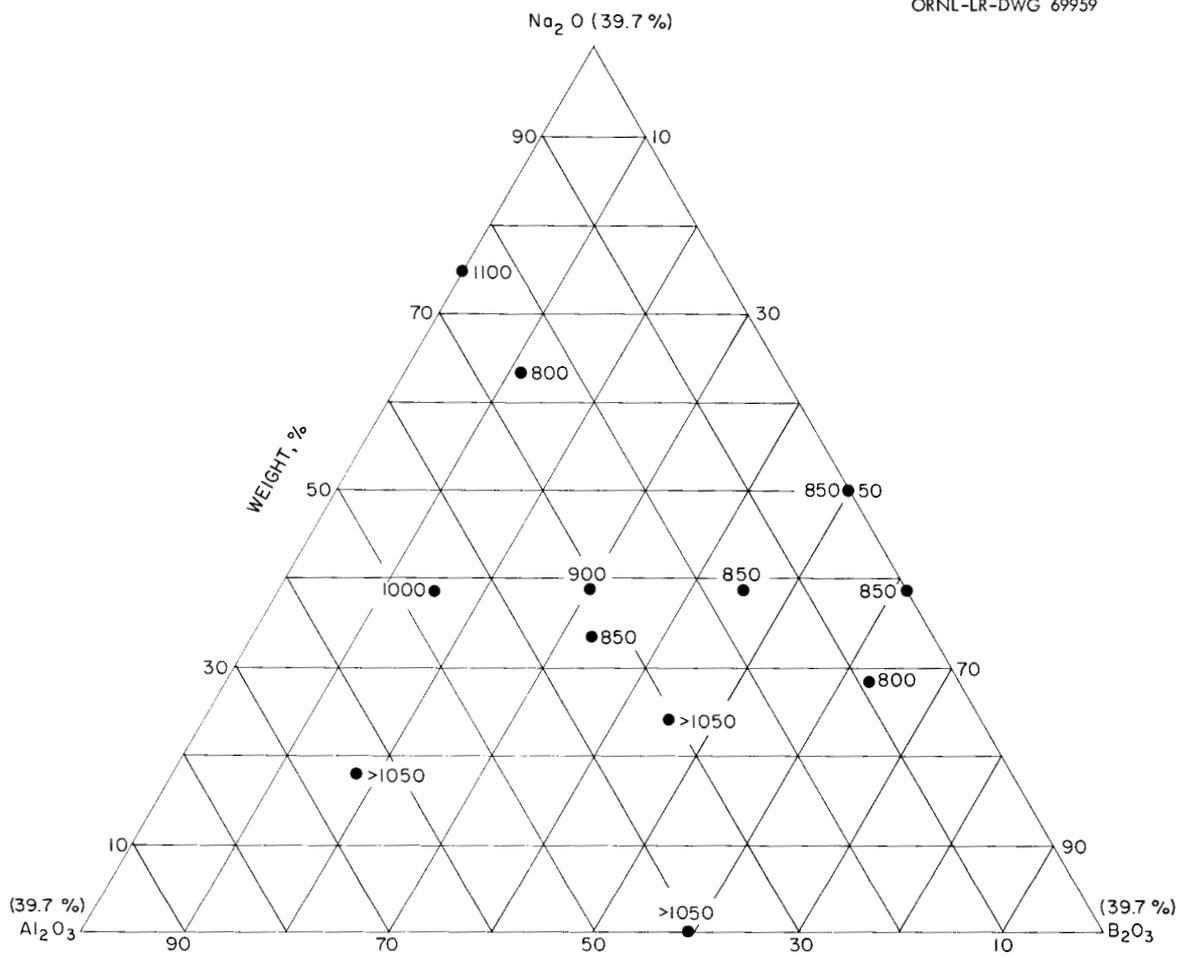


Fig. 22. Composition and Initial Softening Temperatures ($^{\circ}\text{C}$) of Solid Products Incorporating 25% Stainless Steel Waste Oxides and 35.3% P_2O_5 . Borate Addition Tends to Lower the Softening Temperature When the Al_2O_3 Content is Low.

No thermal conductivity measurements have been made on Darex glasses. Both the composition of the solid product and the method of operation for fixation of this waste type need further developmental work. No detailed corrosion studies have been made under evaporation or fixation conditions. Such studies are needed. Development of lower-melting products will help solve the corrosion problem. Results of studies of corrosion during storage of the waste in stainless steel tanks indicate the probability of intergranular attack in a stainless steel evaporator.²² The use of a titanium evaporator therefore appears desirable. Corrosion of the fixation pot can doubtless be minimized by use of an appropriately chosen mixture for glass production.

5. CONCLUSIONS

1. Successful fixation of simulated aluminum waste in lead-aluminum phosphate glass has been repeatedly demonstrated on laboratory and semiengineering (4-in.-diam pot) scales. Based on this work, the first full engineering-scale fixation attempt (8-in.-diam pot) was successful. The process can be satisfactorily contained in a stainless steel fixation pot. Corrosion of a proposed titanium off-gas system was very low. The process is ready for practical pilot plant demonstration. Further work aimed at optimization of the product and details of the process is desirable.

2. Fixation of simulated stainless-steel-type waste (from Darex or electrolytic fuel dissolution processes) in phosphate ceramics has been successfully demonstrated in the laboratory and on a semiengineering scale. Much development work is needed to optimize the nature of the product and to define the extent of corrosion of the fixation pot.

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