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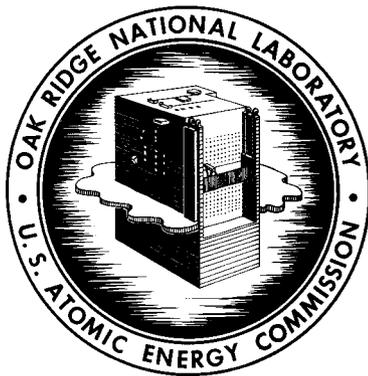
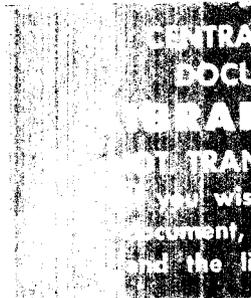


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LABORATORY DEVELOPMENT OF A
POT CALCINATION PROCESS FOR CONVERTING
LIQUID WASTES TO SOLIDS

H. W. Godbee
J. T. Roberts



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

Simulated Darex, Purex, Thorex, and TBP-25 wastes were batch-evaporated and calcined to solids. The weight of residue was decreased to $\sim 8\%$ of the original waste for Darex, to $\sim 4\%$ for Purex, to $\sim 2\%$ for Thorex, and to $\sim 7\%$ for TBP-25 by calcination to 1200°C . Semicontinuous evaporation and calcination to solids at 900°C of Darex and Purex wastes gave volume reduction factors of ~ 8 and 7-10, respectively. The nitrate contents of the residues from batch calcination to 800°C were from ~ 0.07 to 0.5 wt % while the nitrate contents of the residues from semicontinuous calcination to 900°C were from ~ 0.1 to 0.7 wt %.

Sodium, calcium, and magnesium additives to Purex waste decreased the percent of sulfate volatilized into the condensate from $\sim 30\%$ to $< 0.5\%$. Replacement of the atmosphere above the waste with NO decreased ruthenium volatility from 50-60% of that originally present in Purex waste to 0.5-3.5%.

The thermal conductivities for the calcined wastes, measured in situ, were all > 0.1 Btu/hr.ft. $^{\circ}\text{F}$ at about 400°F and increased almost linearly with increasing temperature to > 0.3 Btu/hr.ft. $^{\circ}\text{F}$ at about 1600°F in all cases studied.

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1.0 INTRODUCTION

This report describes laboratory studies of a process for converting high-activity wastes to solids by evaporation to dryness and calcination of the resulting mixture in a container, or "pot," which will also serve as the waste container during final storage. Final storage of the pot in a dry environment, such as a concrete vault, limestone cave, or salt mine, is presumed to be satisfactory. Wastes studied were synthetic TBP-25 (1), acid-deficient Thorex (2), Darex (1), and Purex (1,3).

High-activity liquid wastes from the processing of reactor fuel should be converted to the minimum practical volume of thermally stable dry solids and stored in such a way that they constitute the minimum biological hazard consistent with economics. Among the advantages of pot calcination are: (a) the relatively simple, conventional equipment required; (b) the comparative independence of feed composition, so that wastes containing low- or high-melting salts and pumpable slurries can be handled; (c) the minimum volume of noncondensable off-gas and the possibility of re-using the recovered nitric acid; and (d) the solid product, produced directly in the storage container, which is solid-phase-continuous, and would thus create fewer dusting problems in case of container failure, and which has a reasonably high thermal conductivity. Several disadvantages are a possibly lower capacity per single line of equipment than a continuous process; remote installation and removal of pots; and a possible explosion hazard during boildown of a nitrate waste containing organic materials.

The authors acknowledge technical and operational assistance from a number of persons, particularly, J. E. Davidson, P. S. Lawson, W. C. Ripka, L. L. Ennis, and G. D. Davis; and acknowledge analytical service from G. R. Wilson's and W. R. Laing's groups in the ORNL Analytical Chemistry Division.

2.0 MATERIAL BALANCE IN BATCH AND SEMICONTINUOUS EVAPORATION AND CALCINATION

The flowsheet being developed to convert high-activity wastes to thermally stable dry solids by evaporation and calcination is shown in Fig. 1. In

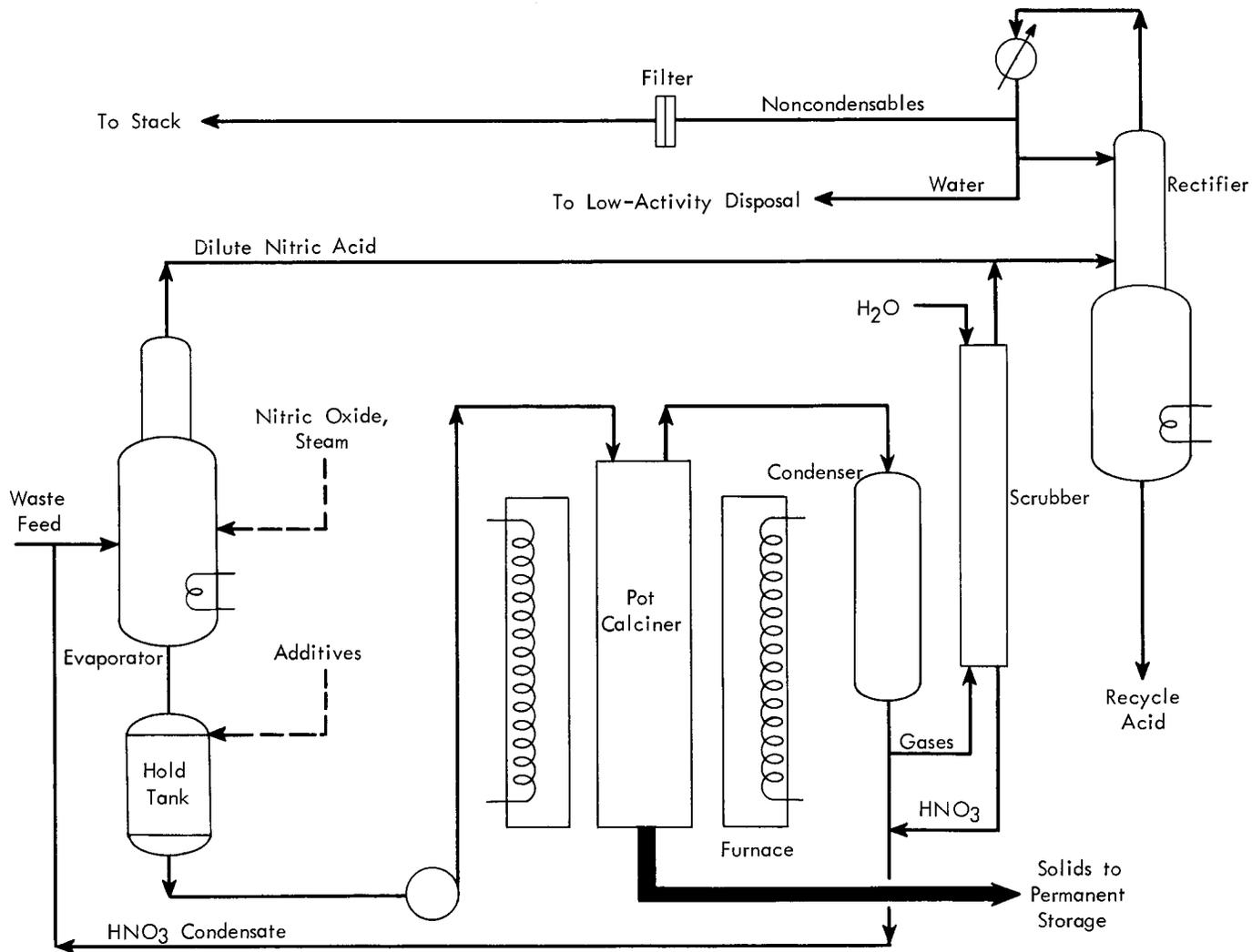


Fig. 1. Flowsheet for converting high-activity wastes to solids by pot calcination. Dotted lines indicate optional operations.

batch operation liquid waste is added to the pot, evaporated to dryness, and calcined without further addition of waste to the pot. The solids formed are porous unless melted down. In semicontinuous operation waste is fed to the pot, either intermittently or continuously, until the pot is essentially full of calcined solids. The solids are less porous for a given mixture since successive liquid feed can fill voids already formed in the pot.

In the experiments reported here the weight of residue was decreased to ~8% of the original waste for Darex, to ~4% for Purex, to ~2% for Thorex, and to ~7% for TBP-25 by calcination at 1200°C (Table 1). With the exception of Darex and Purex wastes calcined at 1200°C, in which some sintering occurred, the solids were fragile, being easily reduced to a powder by finger pressure. They were only 10-20% metal oxides or sulfates and 80-90 vol % gases. The solid phase was the continuous phase at the end of the calcination but rough handling produced a powdery product that was gas-phase-continuous. Addition of a fluxing agent, e.g. sodium sulfate, sodium

Table 1. Weight Data from Calcination to 1200°C of Residue from Evaporation and Calcination of Wastes to 400°C

Sample No.	Furnace Temp, °C	Cumulative Time in Furnace, hr				Weight of Residue, % of weight of sample processed			
		Darex	Purex	Thorex	TBP-25	Darex	Purex	Thorex	TBP-25
1	400	0	0	0	0	8.40	8.65	2.55	8.31
2	600	0.25	0.75	0.75	0.50	8.28	8.26	2.45	8.48
3	600	24.0	23.75	22.75	24.25	8.15	5.56	2.39	8.04
4	800	24.5	25.0	23.25	24.55	8.10	4.56	2.35	7.72
5	800	95.5	49.0	45.75	48.55	8.07	4.66	2.32	7.24
6	1000	96.0	50.0	46.25	49.25	8.06	4.64	2.30	7.31
7	1000	141.5	73.5	69.0	72.25	8.06	4.47	2.23	7.13
8	1200	144.0	74.25	70.3	73.75	8.06	4.55	2.24	7.02
9	1200	146.0	75.25	71.3	--	8.04	4.39	2.25	--

phosphate, sodium silicate, or sodium borate, could improve the mechanical strength, thermal conductivity, and other physical properties of the calcined product or cake. The flux need not increase the cake volume since it could fill the pores or voids of the calcined product, or even form a melt with the oxides, decreasing the volume.

2.1 Batch Evaporation and Calcination

2.1.1 Darex Waste

Batch evaporation and calcination of acidic Darex waste to 400°C yielded a porous, crumbly, dark-brown solid. The residue, which was allowed to cool to room temperature, had a bulk density of 0.85 g/ml, equivalent to a calculated porosity of 83%. The volume reduction factor was 8. The condensate volume was 99.1% of the concentrate waste volume, and it contained 91.3% of the weight (Table 2, Figs. 2 and 3).

2.1.2 Purex Waste

Batch evaporation and calcination of acidic Purex waste to 400°C yielded a porous, fairly hard, mottled brown solid. The residue, which was held at 400°C for about 20 hr, had a bulk density of 0.75 g/ml, equivalent to a calculated porosity of 80%. The volume reduction factor was 6.7. The condensate volume was 96.8% of the concentrate waste volume and contained 89.5% of the weight (Table 2, Figs. 2 and 3).

2.1.3 Thorex Waste

Batch evaporation and calcination of acid-deficient Thorex waste to 400°C yielded a porous, crumbly, off-white solid. The residue was held at this temperature about 24 hr and had a bulk density of 0.31 g/ml, equivalent to a calculated porosity of 92%. The volume reduction factor was 11.4. The condensate volume was 101% of the original waste volume, and it contained 97.5% of the weight (Table 2, Figs. 2 and 3).

2.1.4 TBP-25 Waste

Batch evaporation and calcination of acidic TBP-25 waste to 350°C yielded a porous, crumbly, off-white solid. The residue, which was not held at this temperature, had a bulk density of 0.56 g/ml, equivalent to a calculated porosity of 86%. The volume reduction factor was 3.3. The condensate volume was 95.7% of the concentrate waste volume and it contained 84.5% of the weight (Table 2, Figs. 2 and 3).

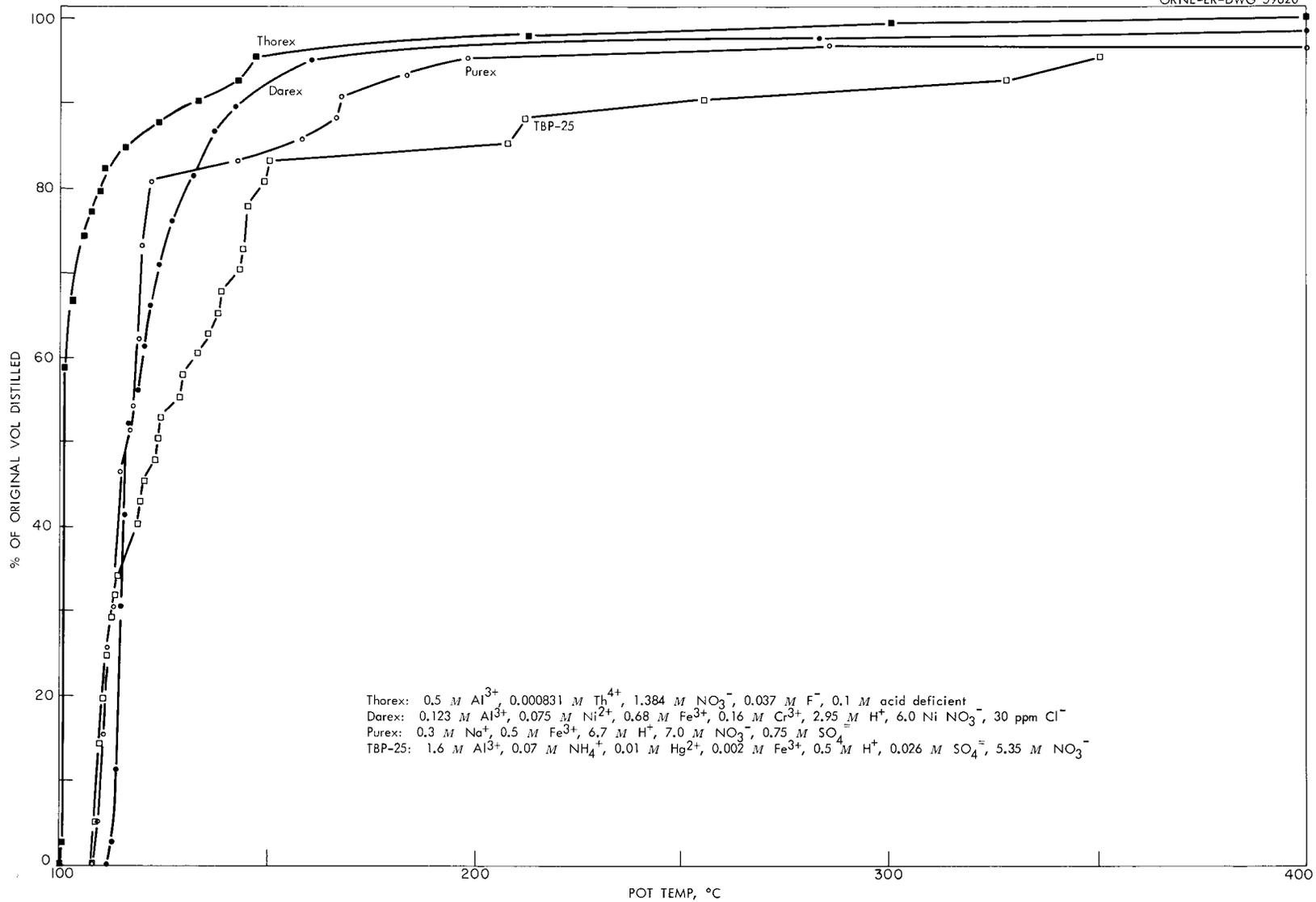


Fig. 2. Volume of waste distilled in batch evaporation and calcination of simulated high-activity fuel processing waste solutions.

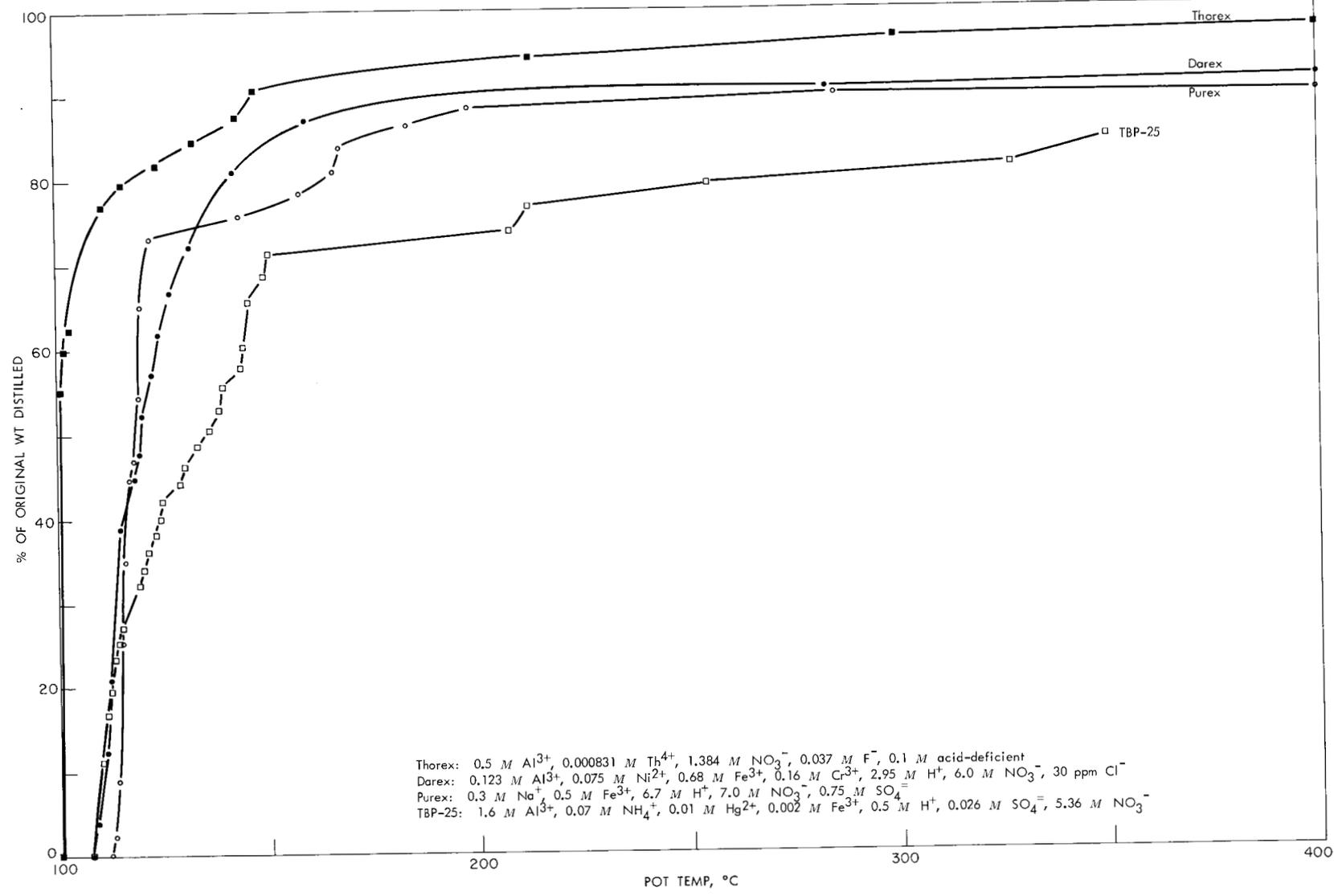


Fig. 3. Weight of waste distilled in batch evaporation and calcination of simulated high-activity fuel processing waste solutions.

Table 2. Volume and Weight Data from the Batch Evaporation and Calcination of Simulated High-activity Fuel Processing Waste Solutions

Initial waste vol: 4000 ml^a

Initial Wt, g	Calci- nation Temp, °C	Condensate		Residue				Off-Gas ^b		Wt Material Balance, %
		Vol, ml	Wt, ml	Vol, ml	Wt, g	Density (24°C), g/ml	Porosity (Calc.), %	Vol, ml	Wt, g	
Darex										
5040	400	3963	4602	500	424	0.85	83.4	31,400	69	101
Purex										
5216	400	3873	4669	600	451	0.75	80.4	730	2	98.2
Thorex										
4260	400	4025	4152	350	109	0.31	92.2	1,460	3	100
TBP-25										
5056	350	3829	4271	1200	670	0.56	85.9	23,500	52	98.8

^aAll volumes measured at 24°C, 1 atm except gases which were converted to this basis.

^bCalculated assuming stoichiometric NO₂ + 1/4 O₂ and that the perfect gas law applies.

2.1.5 Apparatus and Procedures

The experimental apparatus consisted of a glass flask, stirrer, condenser, scrubber, a polyethylene expansion bag for collecting noncondensable gases, and a gas pump (Fig. 4). Four-liter batches of simulated Darex, Purex, Thorex, and TBP-25 (Table 3) were evaporated and calcined to 400°C with continuous stirring of the liquid at about 350 rpm. The off-gas bubblers were filled with either 20% NaOH or water. The gases and vapors, principally water, nitric acid, nitrogen dioxide, oxygen, and nitrogen, from the calcination vessel passed to a downdraft condenser which liquefied most of the water and nitric acid and acted as a wetted-wall scrubber, removing nitrogen oxides and most of the volatile and entrained activity. The nitric acid could be recycled to fuel dissolution or destroyed with formaldehyde, for example. The oxides of nitrogen and other noncondensables from the condenser went to an absorber-scrubber, the acid from which could also be recycled.

The solid residues from these experiments were ground to powders, and samples were placed in ceramic boats in a muffle furnace and calcined up to 1200°C.

2.2 Semicontinuous Evaporation and Calcination

2.2.1 Darex Waste

Synthetic Darex waste concentrate was further concentrated by evaporation (Table 4) and then semicontinuously evaporated and calcined to 800°C. The volume reduction factor was 7.9, based on the volume of the original concentrated waste. The residue had a bulk density of 0.59 g/ml (Table 5), equivalent to a calculated porosity of 89%.

2.2.2 Purex Waste

In a preliminary experiment with simulated Purex waste (Table 3), white acid fumes, probably SO₃, were evolved from the calciner (Sect. 4). Consequently, in subsequent experiments additives were put into Purex waste to hold sulfate in the calciner.

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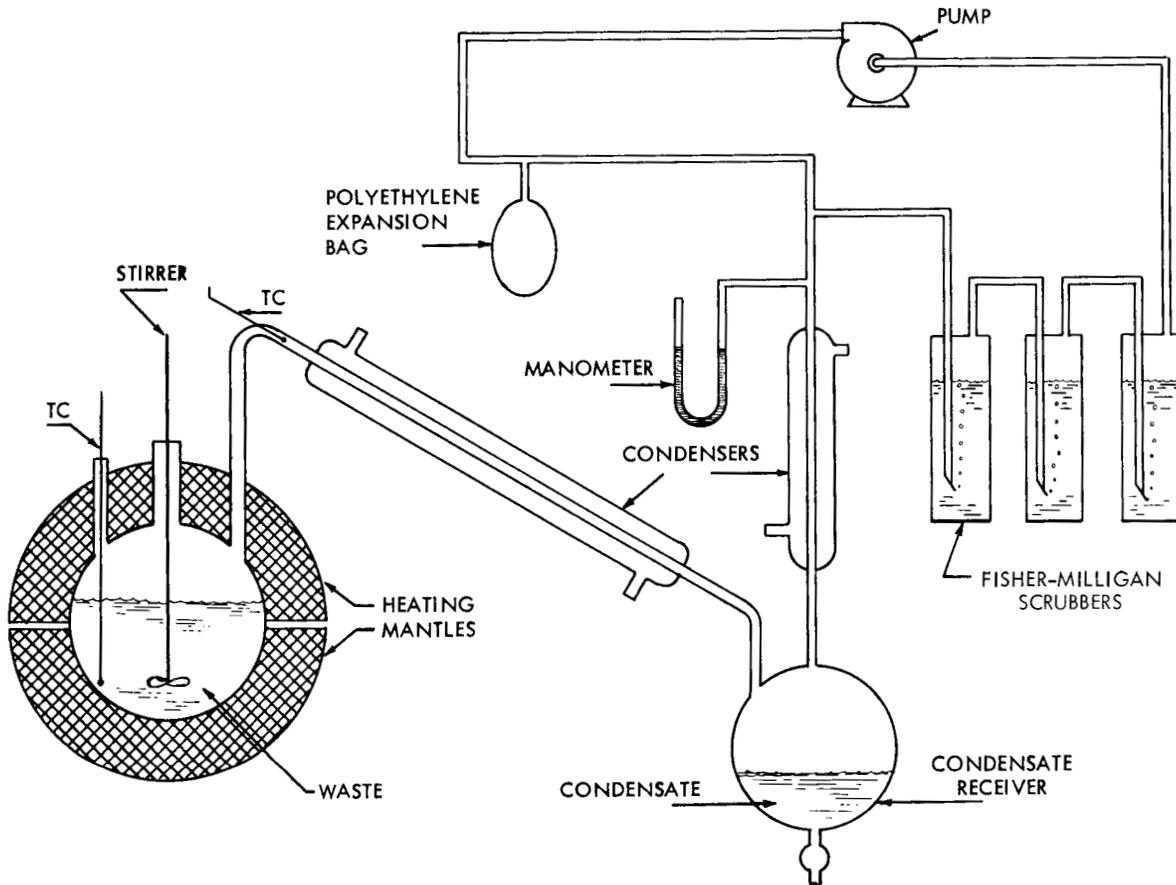


Fig. 4. Apparatus for batch evaporation and calcination of high-activity wastes.

Table 3. Composition^a of Simulated High-activity Fuel Processing Waste Solutions Used in Batch Experiments

Component	Darex	Purex	Thorex	TBP-25
Th ⁴⁺ , \underline{M}			0.00083	
Al ³⁺ , \underline{M}	0.123		0.5	1.6
Fe ³⁺ , \underline{M}	0.68	0.5		0.002
Cr ³⁺ , \underline{M}	0.16			
Hg ²⁺ , \underline{M}				0.01
Ni ²⁺ , \underline{M}	0.075			
NH ₄ ⁺ , \underline{M}			0.007	0.07
H ⁺ , \underline{M}	2.95	6.7	-0.10	0.5
Na ⁺ , \underline{M}		0.3		
Cl ⁻ , ppm	30			
F ⁻ , \underline{M}			0.037	
NO ₃ ⁻ , \underline{M}	6.10	7.0	1.38	5.35
SO ₄ ⁼ , \underline{M}		0.75		0.026
Density, g/ml	1.26	1.30	1.06	1.26

^aThe Thorex waste composition given is that of the extraction column raffinate. The other compositions are those of evaporated wastes.

Table 4. Composition of Simulated High-activity Fuel Processing Waste Solutions Used in Semicontinuous Experiments

Component	Further Concentrated ^a	
	Darex	Purex
Al ³⁺ , \underline{M}	0.17	0.1
Fe ³⁺ , \underline{M}	0.93	0.5
Cr ³⁺ , \underline{M}	0.22	0.01
Ni ²⁺ , \underline{M}	0.10	0.01
H ⁺ , \underline{M}	3.52	5.6
Na ⁺ , \underline{M}		0.6
Ru, \underline{M}		0.002
Cl ⁻ , ppm	40	
NO ₃ ⁻ , \underline{M}	7.68	6.1
SO ₄ ⁼ , \underline{M}		1.0
Density, g/ml	1.32	1.30

^aSee Sect. 2.2.3.

Table 5. Material Balances for Laboratory-scale Semicontinuous Evaporation and Calcination of Simulated High-activity Wastes

Darex concentrate: 3.52 M H⁺, 0.93 Fe³⁺, 0.22 M Cr³⁺, 0.103 M Ni²⁺, 0.169 M Al³⁺, 768 M NO₃⁻, 40 ppm Cl⁻
 Purex: 6.1 M NO₃⁻, 5.6 M H⁺, 1.0 M SO₄⁼, 0.6 M Na⁺, 0.5 M Fe³⁺, 0.1 M Al³⁺, 0.01 M Cr³⁺, 0.01 M Ni²⁺,
 0.002 M Ru

Calci- nation Temp, °C	Additive, moles/ liter	Sweep Gas	Vol Reduc- tion Factor	Residue Density, g/ml	Residue ^a	% of Original Weight			Wt Material Balance, %
						Condensate	Residue	Scrub Liquid	
Darex Concentrate									
800	--	--	7.9	0.59	Crumbly black powder, porosity 89%	86.9	7.8	2.2	96.9
Purex									
900	1.2 NaOH 0.2 Ca(OH) ₂	--	8.4	1.56	Hard brown solid, porosity 48%	85.1	13.7	0.6	99.4
900	1.2 NaOH 0.2 MgO	NO 0.48 mole/ liter	7.0	1.32	Hard brown solid, porosity 58%	85.1	13.6	1.4	100.0
900	1.2 NaOH 0.2 MgO	NO 0.39 mole/ liter	10.0	1.86	Hard brown solid, porosity 41%	86.4	13.4	0.9	100.7

^aPorosity calculated.

Sodium and Calcium Hydroxide Added. A synthetic Purex waste (Table 4)* to which 1.2 moles of NaOH and 0.2 mole of $\text{Ca}(\text{OH})_2$ per liter had been added was semicontinuously evaporated at an initial boiloff rate of 100 ml/min and calcined to 900°C . The volume reduction factor was 8.4 and the solid residue had a bulk density of 1.56 g/ml (Table 5), equivalent to a calculated porosity of 48%. Approximately 5 liters of a noncondensable off-gas, shown by gas chromatography to be essentially oxygen, was produced per liter of feed.

Sodium Hydroxide and Magnesium Oxide Added. A synthetic Purex waste (Table 4) to which 1.2 moles of NaOH and 0.2 mole of MgO per liter had been added was semicontinuously evaporated at an initial boiloff rate of 100 ml/min and calcined to 900°C . The volume reduction factor was 7.0, and the solid residue had a bulk density of 1.32 g/ml, equivalent to a calculated porosity of 58% (Table 5). Nitric oxide was added to the closed system to prevent buildup of free oxygen; ~ 0.5 mole of NO was consumed per liter of waste. The addition of NO was regulated so that the system was held at approximately atmospheric pressure. No net off-gas was produced. In a similar experiment with an initial boiloff rate of 125 ml/min, the volume reduction factor was 10, this higher value being attributed to the higher boiloff rate. The consumption of NO was ~ 0.4 mole per liter of waste. The solid residue had a bulk density of 1.86 g/ml, equivalent to a calculated porosity of 41% (Table 5).

Table 6. Nitrate Data from Batch Evaporation and Calcination of Simulated High-activity Fuel Processing Waste Solutions

Waste	Calcina- tion Temp, $^\circ\text{C}$	Nitrate, g moles				Material Balance, %
		Initial	Condensate	Residue	Off-gas	
Darex	400	24.0	22.7	0.19	1.03	98.7
Purex	400	28.0	28.37	0.035	0.024	102
Thorex	400	5.54	5.53	0.224	0.048	105
TBP-25	350	21.4	17.4	3.59	0.77	102

*The Purex waste composition given in Table 4 is believed to be more representative of a high-sulfate Purex than that given in Table 3.

2.2.3 Apparatus and Procedure

The experimental apparatus consisted of a feed system, calcination vessel, furnace, and off-gas handling system (Fig. 5). The furnace had a power rating of 5 or 9.2 kw. The calciner pot was a stainless steel vessel 18 in. long by 2 in. i.d. in the Darex work and 4 in. i.d. in the Purex (Fig. 6). The off-gas handling system included a 3.5-sq ft glass down-draft condenser, a 1-in.-i.d. by 48-in.-long glass scrubber packed with 0.16- by 0.16-in. stainless steel protruded packing, a polyethylene expansion bag, and a pump for recirculating gases to the pot. In the Darex work feed was pumped intermittently, each addition being evaporated and calcined before more was added. In the Purex work feed was pumped continuously at a rate approximately equal to the boiloff rate, dropping from 100 ml/min initially to essentially zero as the pot filled with solids in the first two experiments and from 125 to 30 ml/min in the third. The NaOH was added as 50% solution and the MgO and Ca(OH)₂ as powdered solids.

3.0 NITRATE VOLATILITY

The condensates, residues, and scrub liquids from batch semicontinuous evaporations and calcinations were analyzed for nitrate and/or total nitrogen. Results showed that the nitrate (total nitrogen expressed as nitrate) content of the residue produced by evaporation and calcination can be decreased to 0.07-0.53 wt % at 800°C, well below the 900°C scaling temperature of stainless steel waste containers. For comparison, the nitrate in the residue from a fluidized bed operated at about 500°C was 2-4.5 wt % (5). The amount of denitration depended not only on the temperature of calcination but also on the time at a temperature. The Darex waste, principally Fe(NO₃)₃-HNO₃, was more easily denitrated than TBP-25, principally Al(NO₃)₃-HNO₃, as would be expected from the Fe(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O thermograms* (Appendix, Sect. 9.1). The weight percent nitrate in the condensate, the percent of original water and of original N₂O₅ distilled as

*Prepared by W. E. Tomlin of the Chemical Technology Division.

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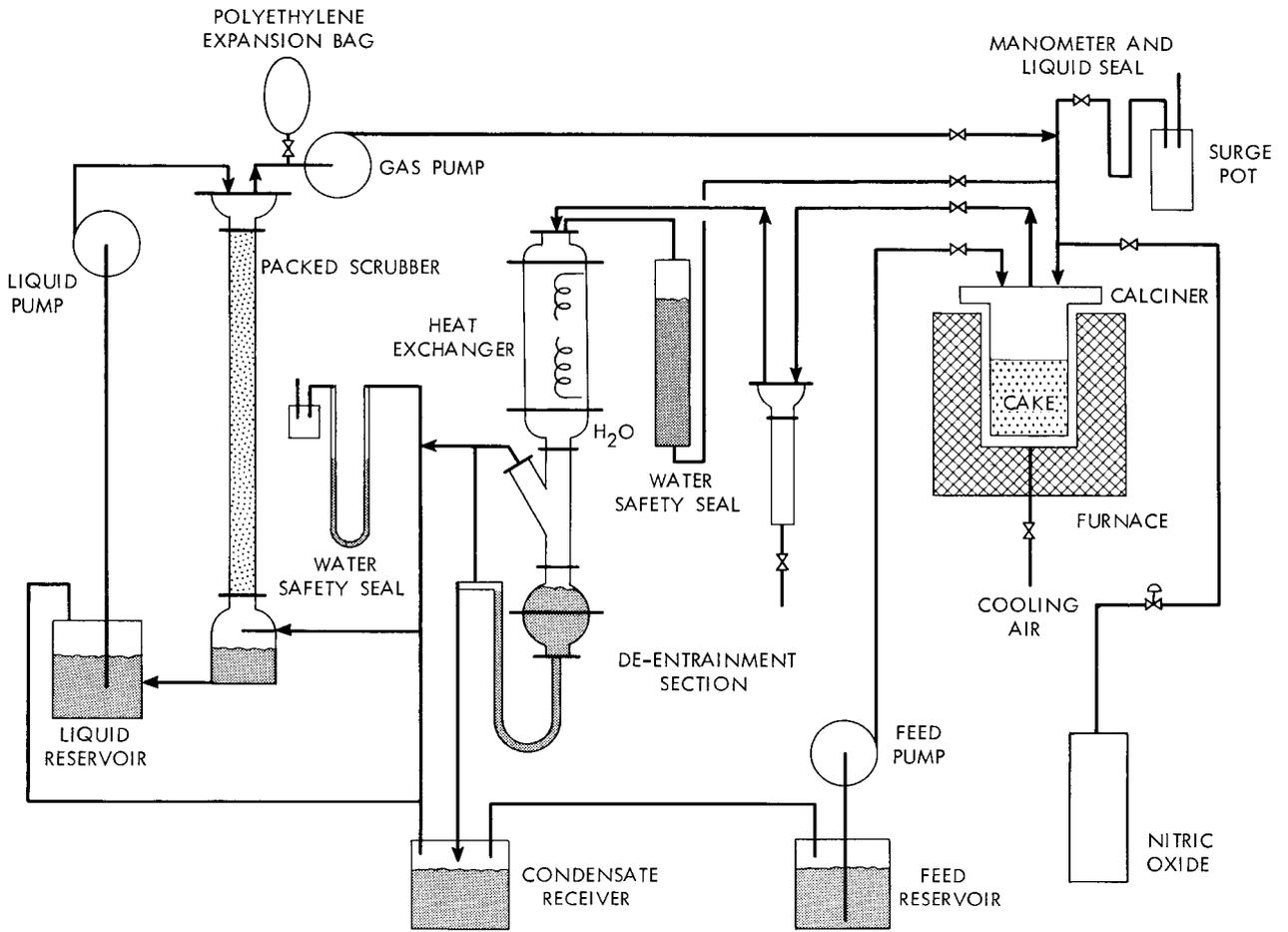


Fig. 5. Schematic of apparatus for calcining wastes and scrubbing volatile ruthenium from off-gas.

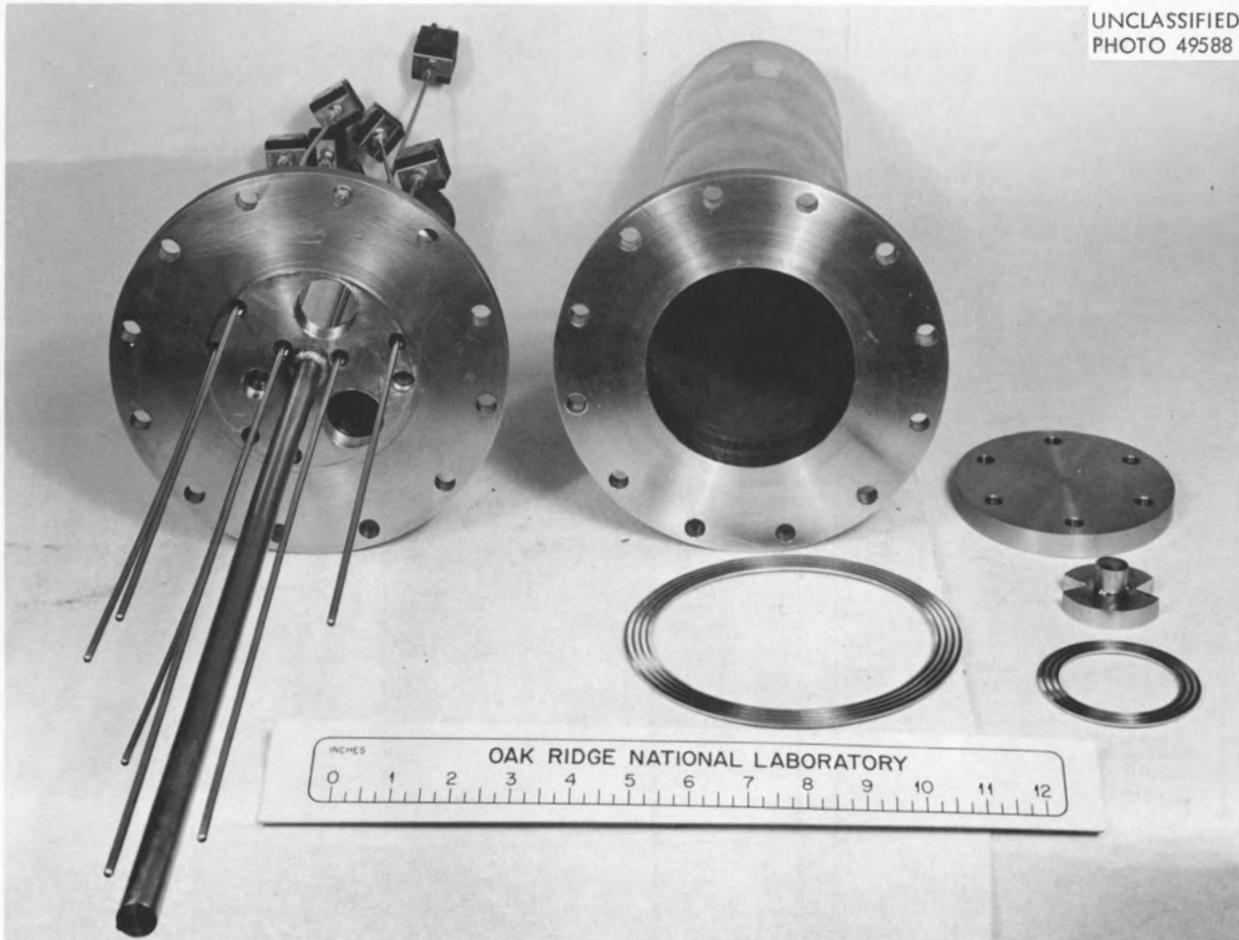


Fig. 6. Stainless steel calciner pot, disassembled.

a function of nitrate in the concentrate are given in the appendix (Sect. 9.2). The calculations were made from the experimental batch distillation data and the physical properties of nitric acid (6).

3.1 Batch Evaporation and Calcination

3.1.1 Darex Waste

Batch evaporation and calcination of acid Darex waste to 400°C yielded a condensate, residue, and scrub liquid containing 94.6, 0.81, and 4.27%, respectively, of the initial nitrate (Table 6, Fig. 7). Further calcination of the residue in a muffle furnace decreased the nitrate from 2.79 wt % at 400°C to 0.03-0.04 wt % at 1000°C and to 0.004 wt % at 1200°C (Table 7).

3.1.2 Purex Waste

Batch evaporation and calcination of acid Purex waste to 400°C yielded a condensate, residue, and scrub liquid containing 101, 0.12, and 0.09 wt %, respectively, of the initial nitrate (Table 6, Fig. 7). Further calcination of the residue in a muffle furnace decreased the nitrate from 2.60 wt % at 400°C to 0.1-0.2 wt % at 1000°C and to <0.10% at 1200°C (Table 7).

3.1.3 Thorex Waste

Batch evaporation and calcination of acid-deficient Thorex waste to 400°C yielded a condensate, residue, and scrub liquid containing 99.7, 4.04, and 0.87 wt %, respectively, of the initial nitrate (Table 6, Fig. 7). Further calcination of the residue in a muffle furnace decreased the nitrate from 5.30 wt % at 400°C to 0.2 wt % at 1000°C (Table 7).

3.1.4 TBP-25 Waste

Batch evaporation and calcination of acid TBP-25 waste yielded a condensate, residue, and scrub liquid containing 81.2, 16.8, and 3.6%, respectively, of the initial nitrate (Table 6, Fig. 7). Further calcination of the residue in a muffle furnace reduced the nitrate from 2.70 wt % at 400°C to 0.084-0.159% at 1000°C (Table 7).

3.1.5 Apparatus and Procedure

Four-liter batches of Darex, Purex, Thorex, and TBP-25 synthetic wastes (Table 3) were evaporated and calcined to 400°C in the glass equipment

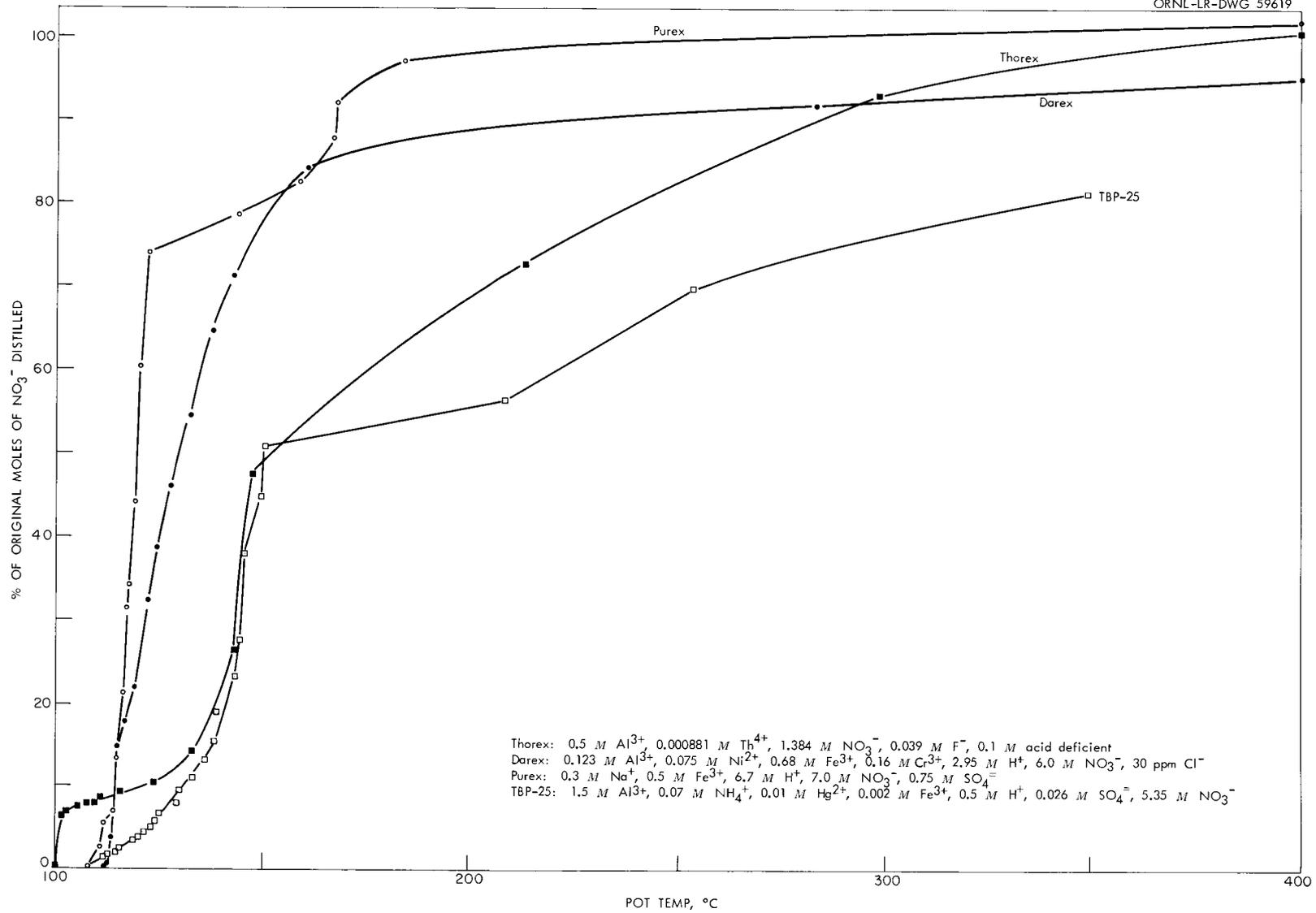


Fig. 7. Nitrate recovered in condensate from batch evaporation and calcination of simulated high-activity fuel processing waste solutions.

Table 7. Nitrate Data from Calcination to 1200°C of Residue from Batch Evaporation and Calcination of Wastes to 400°C

Sample No.	Furnace Temp, °C	Cumulative Time in Furnace, hr				Nitrate in Residue, wt %			
		Darex	Purex	Thorex	TBP-25	Darex	Purex	Thorex	TBP-25
1	400	0	0	0	0	2.79	2.60	5.30	2.70
2	600	0.25	0.75	0.75	0.50	0.27	0.30	1.30	1.77
3	600	24.0	23.75	22.75	24.25	0.12	0.10	1.30	0.84
4	800	24.5	25.0	23.25	24.55	0.08	0.40	0.50	0.62
5	800	95.5	49.0	45.75	48.55	0.07	0.20	0.20	0.53
6	1000	96.0	50.0	46.25	49.25	0.04	0.10	0.20	0.084
7	1000	141.5	73.5	69.0	72.25	0.03	0.10	0.21	0.159
8	1200	144.0	74.25	70.3	73.75	0.02	0.10	-	-
9	1200	146.0	75.25	71.3	-	0.004	0.10	-	-

described in Sect. 2.1.5 with continuous stirring of the liquid. The residues from these evaporations were crushed and ground, and the powders were further calcined in a muffle furnace up to 1200°C.

3.2 Semicontinuous Evaporation and Calcination

3.2.1 Darex

Semicontinuous evaporation and calcination of a Darex concentration (Table 4) were carried out to 800°C. The condensate, residue, and scrub liquid contained 87.5, 0.64, and 6.8%, respectively, of the feed nitrate.

3.2.2 Purex

Semicontinuous evaporation and calcinations with Purex waste included additives to prevent sulfate volatility (Sect. 4). A run with synthetic Purex waste (Table 4) to which sodium was added as 50% NaOH solution (1.2 moles NaOH/liter of waste) and calcium as $\text{Ca}(\text{OH})_2$ (0.2 mole per liter of waste) was carried to 900°C. The condensate, residue, and scrub liquid contained 98.4, 0.13, and 1.8%, respectively, of the initial nitrate in the waste. Gas chromatographic analysis showed the off-gas (about 5 liters per liter of waste) to be essentially oxygen (trace N_2O and NO_2). A run with synthetic waste to which was added sodium (1.2 moles NaOH per liter of waste) and magnesium (0.2 mole MgO per liter of waste) was carried to 900°C. The condensate, residue, and scrub liquid contained 92.5, 0.18, and 8.1%, respectively, of the original nitrate. Nitric oxide was added to the system during the experiment to prevent buildup of oxygen, and no net noncondensable off-gas was produced. The consumption of NO during the experiment was 0.48 mole per liter of waste. In a duplicate experiment the condensate, residue, and scrub liquid contained 95.2, 0.18, and 4.4%, respectively, of the initial nitrate, and consumption of NO was 0.39 mole per liter of waste.

In two additional experiments with the Purex + Na + Mg mixture above, the nitric oxide consumption was 0.43 and 0.36 mole per liter of Purex waste calcined. As in previous experiments with NO added to the system during evaporation-calcination, the net off-gas production was nil.

3.2.3 Apparatus and Procedure

The experimental apparatus consisted of the feed system, calciner pot, furnace, and off-gas handling system (Fig. 5) described in Sect. 2.2.3. Simulated waste, with or without additives, was fed to the calciner until the pot was filled to a predetermined level, usually one pot diameter from the top, with calcined solids. In four experiments a nitric oxide atmosphere, to decrease ruthenium volatility, was maintained in the system. The condensate, residue, and scrub liquid were analyzed for nitrate and/or total nitrogen. The off-gas, if any, was analyzed for O_2 , N_2 , NO , NO_2 , and N_2O .

4.0 SULFATE VOLATILITY

Sulfuric acid in the condensate could cause an additional corrosion problem for equipment, buildup in concentration on recycle sufficiently to present an additional disposal problem, and contaminate the recovered nitric acid sufficiently to preclude its re-use. An additive to minimize sulfate volatility should be stable at the temperature of calcination ($\sim 900^\circ C$) and should not increase ruthenium, sodium, cesium, chloride, or fluoride volatility or cause excessive foaming or bumping during evaporation and calcination. Thermograms for various salts (Sect. 9.1) suggest sodium, calcium, and magnesium as possible additives to hold sulfate in the calciner pot.

4.1 Batch Evaporations and Calcinations

In the second experiment with Purex waste (Table 5) containing no additives, analyses indicated that the condensate, bubblers, and residue contained 13.2, 53.8, and 34.2%, respectively, of the original sulfate. This residue value compares well with a calculated 30.0% remaining in the residue, assuming that the sodium in the feed retained a stoichiometric amount of sulfate as Na_2SO_4 . All the sodium, calcium, and magnesium compounds added (Table 8) prevented sulfate or sodium, beyond that caused by entrainment, appearing in the off-gas. However, mixtures containing calcium gave precipitates which caused severe bumping during evaporation, though no worse

Table 8. Sulfate Volatility during Batch Evaporation-Calcination of Purex Waste in Stainless Steel

Purex waste: 6.1 NO_3^- , 5.6 M H^+ , 1.0 M SO_4^- , 0.6 M Na^+ , 0.5 M Fe^{3+} ,
0.1 M Al^{3+} , 0.01 M Cr^{3+} , 0.01 M Ni^{2+} , 0.002 M Ru

No.	Chemical	moles/liter	No.	Chemical	moles/liter
1	NaNO_3	1.4	7	Ca(OH)_2	0.8
2	NaNO_3	1.2		SiO_2^c	0.8
	$\text{Ca(NO}_3)_2$	0.2	8	Na_2SiO_3	0.8
3	NaNO_3	1.6	9	Na_2SiO_3	0.6
	CaSiO_3^a	0.2		CaSiO_3^b	0.4
4	NaNO_3^b	1.6	10	Ca(OH)_2	0.8
	CaSiO_3	0.2	11	Na(OH)	1.2
5	NaNO_3^c	1.6		Ca(OH)_2	0.2
	SiO_2^c	0.4	12	NaOH	1.2
6	CaSiO_3^a	0.8		MgO	0.2

^aMicro-Cel B, a Johns-Manville synthetic calcium silicate.

^bMicro-Cel E, a Johns-Manville synthetic calcium silicate.

^cSyloid 244, a Davison Chemical Company fine sized silica.

than Purex waste containing no additives. Mixtures with calcium silicate, added as Micro-Cel which has a very large surface area, gave powdery calcined products. Sodium silicate gave inorganic gels and/or sand-like precipitates.

The apparatus used was a 1500-ml stainless steel calcination pot, a 5-kw furnace, and an off-gas handling system consisting of scrubbers containing caustic followed by water and a polyethylene expansion bag (Fig. 8). All tubings and connections before the pump were stainless steel, glass, or Teflon. In the initial experiment with Purex (composition in Table 3), the expansion bag was upstream from the gas bubblers and was destroyed by white acid fumes, probably SO_3 , evolved from the calciner at about 775°C . In subsequent experiments the bag was located downstream from the bubblers. Test mixtures were evaporated and calcined to 900°C and the solutions from the gas bubblers were analyzed for sulfate and sodium.

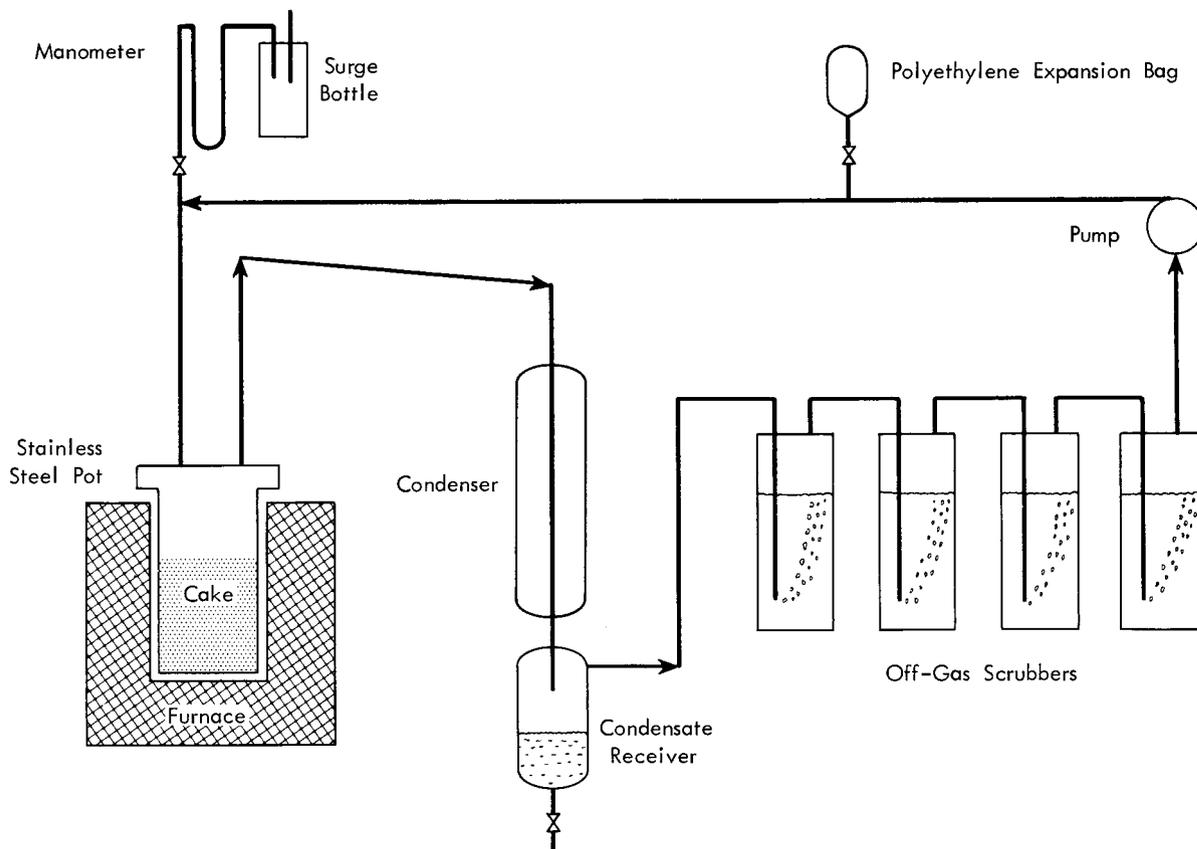


Fig. 8. Schematic of apparatus for batch evaporation-calcination of high-activity wastes in stainless steel pot.

4.2 Semicontinuous Evaporation and Calcination

The condensate, residue, and scrub liquid from the semicontinuous evaporation at an initial boiloff rate of 100 ml/min and calcination to 900°C of a Purex waste (Table 4) plus additives contained 0.24, 101.3, and 0.006%, respectively, of the original sulfate in the waste when 1.2 moles of NaOH and 0.2 mole of $\text{Ca}(\text{OH})_2$ per liter were added. In a similar experiment with 0.2 mole of MgO substituted for the $\text{Ca}(\text{OH})_2$ and an initial boiloff rate of 100 ml/min, the sulfate values were 0.28, 98.0, and 0.018%, respectively, of the sulfate originally present. In a third experiment the same as the second except for an initial boiloff rate of 125 ml/min, the condensate, residue, and scrub liquid contained 0.51, 93.6, and 0.001%, respectively, of the original sulfate.

The apparatus consisted of the feed system, calcination vessel, furnace, and off-gas handling system described in Sect. 2.2.5. Simulated Purex waste (Table 4) containing additives was fed to the calciner. The criteria for the addition of calcium (or magnesium) and additional sodium to the waste were that the equivalents of calcium or magnesium and sodium be greater than the equivalents of sulfate, to prevent sulfate volatility, and that the equivalents of sulfate be greater than the equivalents of sodium to prevent sodium or cesium volatility (Sect. 9.1). The condensate, residue, and scrub liquid were analyzed for sulfate.

5.0 RUTHENIUM VOLATILITY

The limiting radioactivity in the treatment of off-gases from evaporation and calcination of radioactive wastes is probably ruthenium, since it is volatile under oxidizing conditions even at relatively low temperatures (7). The calciner off-gases would be treated and the activity recycled (Fig. 1), but control of the ruthenium volatility would simplify the recycle system and minimize contamination of process equipment. The effectiveness of NO, TBP, DBP, and MBP in decreasing ruthenium volatility was studied.

5.1 Batch Evaporation and Calcination

5.1.1 Effect of NO

In a typical experiment NaOH (1.2 moles/liter waste) and MgO (0.2 mole/liter waste) were added to the synthetic Purex waste (Table 4) to prevent sulfate volatility (Sect. 4) and the mixture was evaporated to dryness and calcined to a residue temperature of 500°C. Before the evaporation started the system was flushed with NO gas, and during the experiment NO was added as required to keep the system volume constant at atmospheric pressure (see also Sect. 2.2.2). The individual condensate samples were analyzed for Ru-106 in a gamma scintillation counter. The first 92% of the condensate contained only 0.03% of the total Ru-106 in the feed. The remaining 8% of the condensate, which came over above 145°C, contained 1.4% of the total Ru-106. The first scrubber contained 0.60% of the total Ru-106, the second scrubber 0.16%, and the last two scrubbers were at background counting levels. The filter paper contained 0.032% of the total Ru-106. The calcined residue was removed, dissolved in refluxing HCl, and found to contain 88% of the total Ru-106. The Ru-106 material balance for this experiment was 90%, not including what may have been left on the equipment (Table 9). The experiment was repeated immediately in the same equipment after cleaning the scrubbers and changing the filter paper but without cleaning the flask and condenser. In the second experiment the residue contained 98% of the feed Ru-106, the condensate 1.6%, the bubblers 0.70%, and the filter paper 0.005%, giving a 100% material balance. The missing activity from the two experiments was recovered by evaporating and condensing 125 ml of 15 M HNO₃ in the system. The overall material balance for the two experiments was 100.5%. In comparing the second experiment with the first, the fact that the extra 10% of the Ru-106 appeared in the residue rather than in the condensate implies that the ruthenium plated on equipment was primarily in the flask rather than in the condenser. This was confirmed by the absence of any visible black RuO₂ deposit in the condenser.

Table 9. Ruthenium Volatility during Batch Evaporation of Purex Waste in Glass Equipment

Composition of Purex Waste: 6.1 M NO_3^- , 5.6 M H^+ , 1.0 M $\text{SO}_4^{=}$, 0.6 M Na^+ , 0.5 M Fe^{3+} , 0.1 M Al^{3+} , 0.01 M Cr^{3+} , 0.01 M Ni^{2+} , 0.002 M Ru with 0.1 $\mu\text{c/ml}$ Ru-106

Expt. No.	Additives to 1 liter of Waste, moles		Sweep Gas	Final Residue Temp, °C	Visible Ru Deposit	% of Original Ruthenium			Ru Material Balance, %	
						Residue	Washings	Condensate		Scrubbers
1	None		None	440	Yes	27.7	8.7	63.4	0.44	100.24
2	None		None	390	Yes	38.7	10.6	48.5	0.30	98.10
3	None		Nitric oxide	545	No	98.6	1.8	0.5	0.73	101.63
4	NaOH MgO	1.2 0.2	None	450	Yes	54.8	26.5	20.5	0.30	102.10
5	NaOH MgO	1.2 0.2	Nitric oxide	498	No	80.8	12.9	3.5	1.69	98.89
6	NaOH MgO	1.2 0.2	Nitric oxide	500	No	88.0	Not Washed	1.5	0.75	90.25
7	NaOH MgO	1.2 0.2	Nitric oxide	530	No	98.0	10.8 ^a	1.6	0.70	111.10

^aThe equipment from Expt. 6 was not washed but was used for Expt. 7 so that the equipment washing for Expt. 7 includes the ruthenium plated out in Expt. 6.

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5.1.2 Effect of Na-Ca-Mg

In an experiment similar to those above without NO, the first 89% of the condensate contained 6% of the Ru-106, and the remaining 11% of the condensate (at temperatures above 137°C) contained an additional 14% of the total Ru-106. The first bubbler contained 0.24% of the Ru-106, the second bubbler 0.038%, the third 0.012%, and the fourth 0.009%. The residue contained 55% of the total Ru-106, and a 15 M HNO₃ treatment of the equipment yielded an additional 26%, giving an overall Ru-106 balance of 102% (Table 9). A black deposit that formed in the condenser near the inlet was removed in the 15 M HNO₃ wash, indicating that part of the 26% of the Ru-106 found in the wash represented plating in the condenser as well as in the flask.

Comparison of the experiments with and without NO shows that the use of NO significantly decreased loss of ruthenium by the residue, decreased ruthenium plating in the condenser, and decreased ruthenium in the condensate but increased the ruthenium content in the bubblers.

Similar experiments in which 0.8 mole Ca(OH)₂ was added per liter of waste instead of 1.2 moles NaOH-0.2 mole MgO gave similar results.

The addition of Na-Mg-Ca to control sulfate volatility also affected the ruthenium volatility. Table 9 also shows the results of three experiments with synthetic Purex LWV without addition of sodium, magnesium, or calcium. Two of the experiments were duplicates, with no NO. The reproducibility was not so good as in the two duplicate experiments with sodium-magnesium-nitric oxide (mentioned above): 28-39% of the Ru-106 appeared in the residue, 9-11% in equipment washes, 48-63% in the condensate, 0.30-0.44% in the bubbler, for material balances of 98-100%. In a third experiment, with NO, 99% of the Ru-106 appeared in the residue, 2% in the equipment wash, 0.5% in the condensate, and 0.7% in the bubblers, giving a material balance of 102%.

The manner in which the ruthenium concentration varied during the experiments is shown in Fig. 9a. The effect of sodium-magnesium addition is a decrease of ruthenium volatility during the evaporation period, probably as a result of the decreased acidity, but an increase in ruthenium

volatility during the calcination period, possibly as a result of increased retention of bisulfate and nitrate by the residue at the end of the evaporation and the subsequent release of nitric acid by the residue during calcination.

5.1.3 Effect of TBP, DBP, and MBP

Runs similar to those above were made with TBP, DBP, and MPB added to synthetic Purex waste in amounts equal to 0.01 mole per liter of waste (Fig. 9b). The 0.01 mole TBP per liter of waste was about as effective as NO in decreasing ruthenium volatility during the evaporation but less effective during the calcination, with a total of 4.5% of the Ru-106 found in the condensate. The 0.01 mole DBP per liter LWV was less effective than NO during evaporation but about as effective during calcination, with a total of 12.9% of the Ru-106 found in the condensate. The 0.01 mole MBP per liter of waste was less effective than NO during both evaporation and calcination, with a total of 7.2% of the Ru-106 found in the condensate. In an experiment with 0.01 mole TBP plus 0.01 mole DBP per liter of waste the ruthenium in the condensate was about the same as with NO during evaporation and calcination, with a total of 0.9% of the Ru-106 found in the condensate.

The following additives were found not to be effective in suppressing ruthenium volatility: sodium nitrate, sodium sulfate, sodium phosphate, sodium silicate, calcium nitrate, calcium silicate,* and silica.**

The use of ruthenium 103-106 tracer from different sources (e.g., pure RuCl_3 in HCl solution and an alkaline solution from ORNL tank farm supernatant that had been volume-reduced by a factor of 40) gave results in agreement with each other, within normal limits of reproducibility, indicating that an equilibrium mixture of ruthenium species was obtained during evaporation and calcination.

* Added as Micro-Cel, a Johns Manville synthetic calcium silicate.

** Added as Syloid 244, a Davison Chemical Co. fine-size silica.

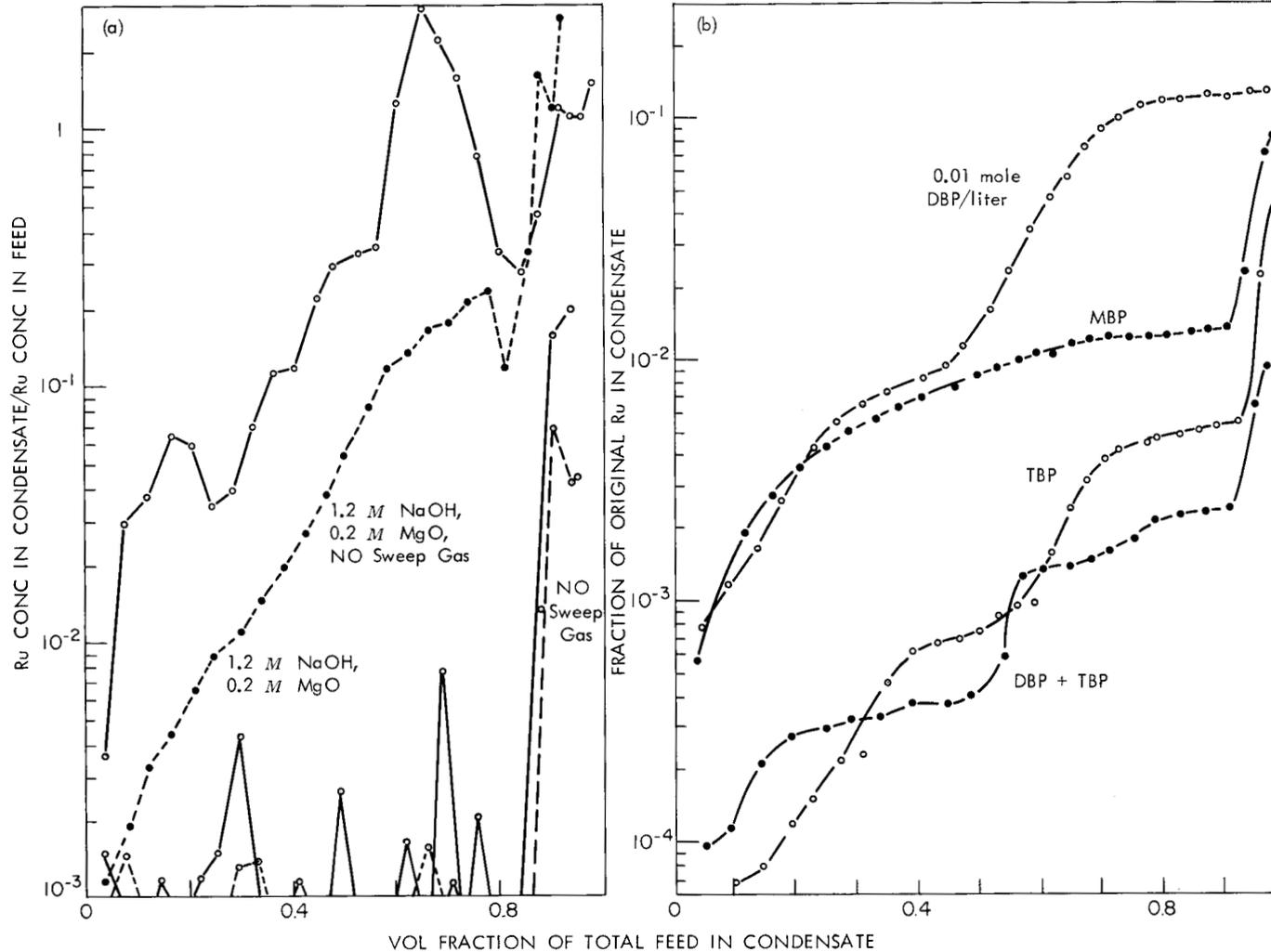


Fig. 9. Volatility of ruthenium during evaporation of Purex 1WW concentrate in glass equipment. 1WW composition: $6.1 M NO_3^-$, $5.6 M H^+$, $1.0 M SO_4^{2-}$, $0.6 M Na^+$, $0.5 M Fe^{3+}$, $0.1 M Al^{3+}$, $0.01 M Cr^{3+}$, $0.01 M Ni^{2+}$, $0.002 M Ru$ with $0.1 \mu c$ of Ru-106 per milliliter; (a) differential plot, additives as indicated; (b) integral plot, 0.01 mole additive per liter.

5.1.4 Experimental Apparatus and Procedure

The experimental apparatus consisted of a 200-ml glass flask, a glass distilling head, a glass condenser, and stainless steel-sheathed thermocouples for recording temperatures in the liquid-solid and vapor phases (Fig. 10). Experiments were performed in glass so that the boiling characteristics of the waste as well as the quality and quantity of residue could be observed. However, the foremost reason for the glass equipment was so that the plating or deposition of ruthenium (probably RuO_2) on the equipment could be observed. Experiments were performed with 125 ml of a Purex waste (Table 4) containing 0.184 g/liter (0.002 M) of stable ruthenium and 0.1 $\mu\text{c/ml}$ of Ru-106 tracer. The condensate was collected in 5-ml samples and the noncondensable off-gas was passed through four water-filled scrubbers in series and then through a Millipore AA (0.8 μ) filter. The gas was pulled through the scrubbers and filter with a Sigma-motor tubing pump and recirculated to the flask. Ruthenium in the condensate was determined by chemical analyses for stable ruthenium in some experiments and gamma counting in all experiments. The chemical and radiochemical analyses agreed sufficiently well that it was indicated that the stable and radioactive species were in equilibrium (Fig. 11).

5.2 Semicontinuous Evaporation and Calcination

5.2.1 Results and Discussion

The condensate from a semicontinuous evaporation and calcination to 900°C of a synthetic Purex waste (Table 4) plus calcium (0.2 mole Ca(OH)_2 /liter of waste) and additional sodium (1.2 moles NaOH/liter of waste) was analyzed for stable ruthenium. The results showed 26% of the total ruthenium in the condensate, which result is about half the amount found in small-scale batch experiments with the same Purex-calcium-sodium mixture. Perhaps the difference is accounted for by ruthenium plated on the stainless steel lines between the condenser and calciner.

The condensate from another semicontinuous evaporation and calcination to 900°C of a synthetic Purex waste (Table 4) containing magnesium (0.2 mole/liter waste) and sodium (1.2 moles/liter of waste) with NO added to the system was analyzed for stable ruthenium. The results showed 32% of the

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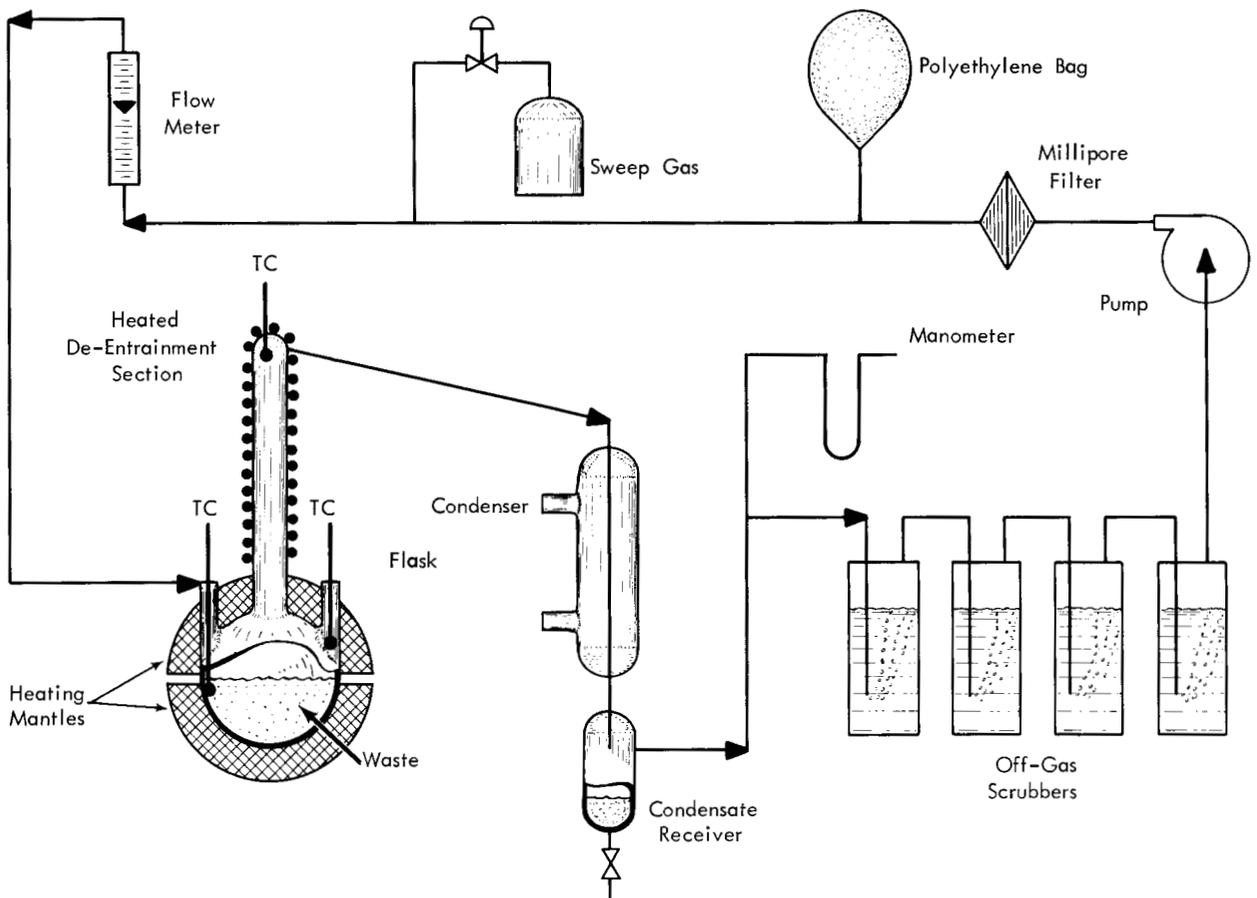


Fig. 10. Schematic of apparatus for studying ruthenium volatility during batch evaporation-calcination in glass equipment.

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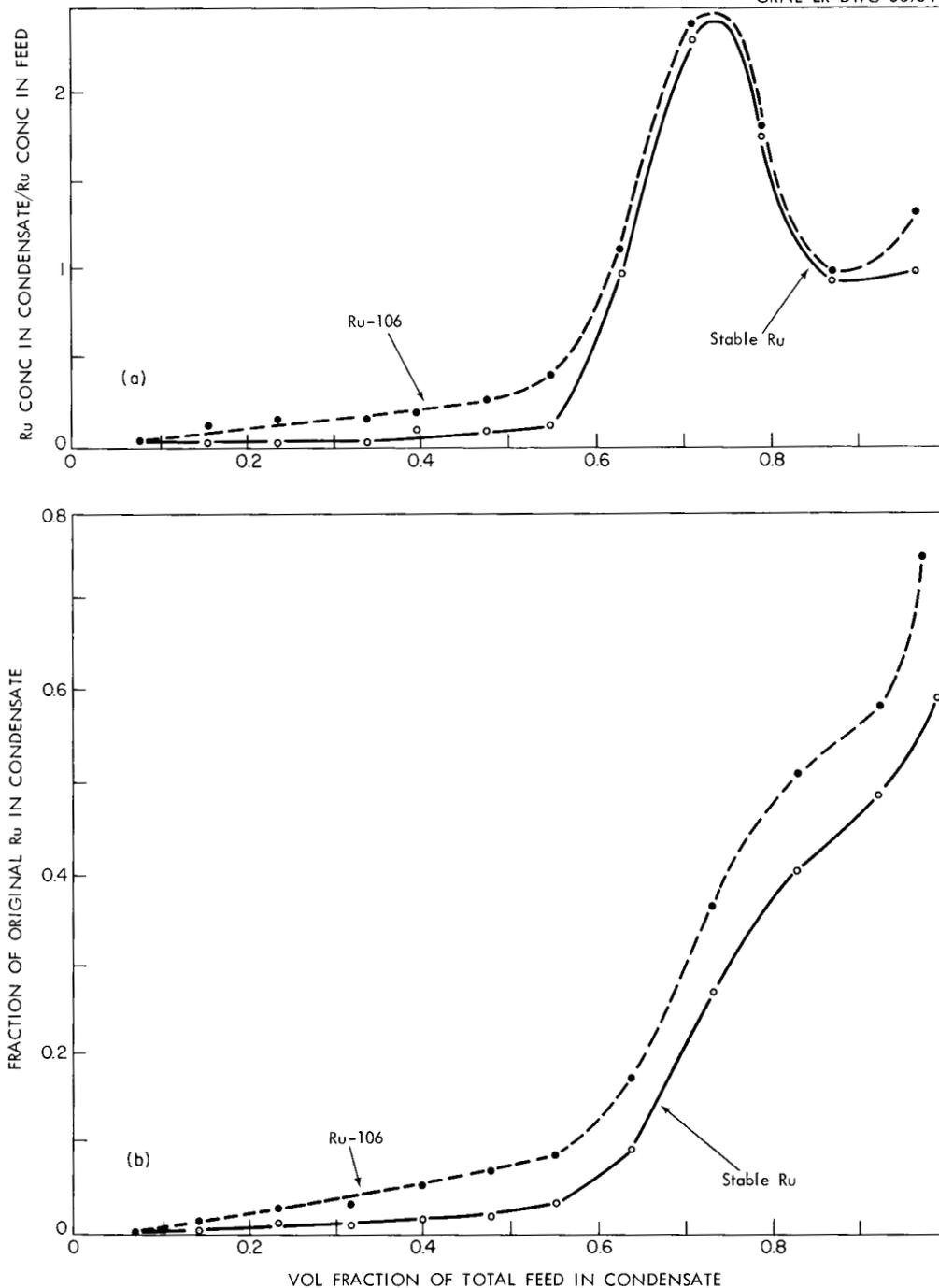


Fig. 11. Comparison between radioactive and stable ruthenium determinations during evaporation of Purex 1WW concentrate in glass equipment. Purex 1WW composition: 6.1 M NO_3^- , 5.6 M H^+ , 1.0 M $\text{SO}_4^{=}$, 0.6 M Na^+ , 0.5 M Fe^{3+} , 0.1 M Al^{3+} , 0.01 M Cr^{3+} , 0.01 M Ni^{2+} , 0.002 M Ru with 0.1 μc Ru-106 per milliliter; (a) differential plot; (b) integral plot.

original ruthenium in the condensate. This fraction of the ruthenium found in the condensate is about 20 times higher than earlier small-scale batch experiments with the same Purex-magnesium-sodium mixture (Table 10). Analysis of the condensate from a second similar experiment with the same Purex + sodium + magnesium mixture with NO added to the system showed 46% of the original ruthenium in the condensate. In a third experiment with the same Purex + sodium + magnesium and nitric oxide to the feed on the pressure side of the feed pump instead of to the vapor space of the calciner (Fig. 5), 18% of the original ruthenium was in the condensate. These results indicated that the efficiency of contacting the feed with NO made a difference in the amount of ruthenium volatilized, and in a fourth similar experiment with the above Purex + sodium + magnesium the NO feed contacting time was increased fivefold.* Analyses for stable ruthenium showed 20% of the original ruthenium in the condensate. Perhaps the method of operation, i.e., batch as opposed to semicontinuous, accounts for part of this difference. In other words, the concentrations in the calciner vessel for the quasi-steady-state conditions of semicontinuous operations are possibly at all times different from those in the pot of a simple batch operation.

5.2.2 Experimental Apparatus and Procedure

The experimental apparatus consisted of a feed system, calciner pot and furnace, and off-gas handling system (Sect. 2.2.1). Although the experimental apparatus is in a hood for experiments with feed containing radioactive ruthenium, to date the feed has contained only stable ruthenium.

6.0 ORGANIC NITRATE REACTIONS

Since TBP and uranyl nitrate can react explosively (8), it is necessary to know the conditions of temperature and pressure and the concentrations of reactants necessary for a violent or highly exothermic reaction to be initiated. Preliminary experiments indicated that an explosive reaction is not easily initiated between TBP and Purex waste, but further work is required to ensure that explosive conditions can never develop during evaporation-calcination.

* The average residence time of the NO in the feed line was increased from about 0.1 min to about 0.5 min.

In experiments with Purex waste (Table 4) plus TBP, DBP, MBP, butanol, or Amsco, only Amsco showed a reaction and then only when the Amsco and waste were allowed to stand a few hours before being heated. When heated in a test tube over a bunsen burner, evolution of brown gas occurred just before the boiling point was reached, and immediately after that a "pop." When there was no standing before heating the "pop" did not occur. In the cases of TBP, DBP, MBP, and butanol the odor of butyric acid and butyric esters was detected.

The samples of waste plus organic were heated to about 500°C in glass test tubes over an open flame or, in larger scale experiments, in a glass flask with condenser and thermocouple (Sect. 5.1). TBP was added in the amounts 3, 30, and 300 ml of TBP per liter. The experiments containing 300 ml of TBP per liter also contained 2.86 g of UO_3 per liter. In two experiments 4 ml of either MBP or DBP was added per liter of Purex.

7.0 THERMAL CONDUCTIVITY

The containment or storage of wastes from the processing of nuclear fuels must provide for the dissipation of heat generated by the radioactive decay of unstable isotopes. Conditions must preclude the attainment of a temperature detrimental to the waste, its container, or the surrounding medium. One of the most important waste characteristics affecting the temperature rise in stored solid wastes is the thermal conductivity of the solid. Calculations (9) have shown that a thermal conductivity, k , of 0.1 Btu/hr.ft.^{°F} is probably acceptable for storage of calcined wastes, though higher values would be desirable.

The physical texture of the solid is the factor that causes the greatest variation (4). Porous materials may be classified as cellular or granular. A granular material, a two-phase system in which the gas phase is continuous and the solid is dispersed, e.g. sand, has a lower thermal conductivity than a cellular one, where the solid phase is continuous and the gas dispersed, e.g. a sponge, of the same material and porosity.

7.1 Determination of Thermal Conductivity

The k values for calcined wastes, measured in situ, were all >0.1 Btu/hr.ft. $^{\circ}$ F. The values increased almost linearly with increasing temperature in all cases studied.

The thermal conductivities of both Darex and TBP-25 products after granulation were 0.1 Btu/hr.ft. $^{\circ}$ F or more. That of the Darex product crushed to pass a 1 mesh screen, density 1.14 g/ml, porosity 78%, varied from about 0.10 Btu/hr.ft. $^{\circ}$ F at 400 $^{\circ}$ F to 0.13 at 1600 $^{\circ}$ F (Fig. 12). The values for the TBP-25 product similarly crushed, density 0.43 g/ml, porosity 89%, varied from 0.08 Btu/hr.ft. $^{\circ}$ F at 400 $^{\circ}$ F to 0.13 at 1600 $^{\circ}$ F. These TBP-25 values are 1.5- to 3-fold lower than those for the in situ solid with 90% porosity. A granular alumina made in an Idaho Chemical Processing Plant fluidized-bed calciner from synthetic waste (10), 80% porosity, had a thermal conductivity of 0.12 Btu/hr.ft. $^{\circ}$ F. The k values for Ottawa sand, density 1.72 g/ml, porosity 35%, were 2.5- to 5-fold greater than those for crushed Darex or TBP-25 (Figs. 12 and 13). The variation of k, as measured in place, was from 0.23 Btu/hr.ft. $^{\circ}$ F at 400 $^{\circ}$ F to 0.38 Btu/hr.ft. $^{\circ}$ F at 1600 $^{\circ}$ F for Purex + Na + Ca (Fig. 13); and from 0.19 Btu/hr.ft. $^{\circ}$ F at 400 $^{\circ}$ F to 0.66 Btu/hr.ft. $^{\circ}$ F at 1600 $^{\circ}$ F for Purex + Na + Mg (Fig. 13). These values are about 5 to 15 times greater than the thermal conductivity of air at 1 atm (Fig. 12).

The linearity with temperature for the calcined solids is typical of a granular rather than a cellular material although the pot-calcined solids had the physical appearance of a cellular material. The products, except those containing sodium sulfate, were fragile and could be broken up by handling. It may be desirable to add some material, such as sodium sulfate, in order to improve the k and the mechanical strength of the calcined cake.

7.2 Temperature Rise of Calcined Wastes

For a single 55-gal sphere of calcined TBP-25 waste cooled 120 days ($Q = 1056$ Btu/hr.ft 3) prior to storage, the maximum temperature rise above the surroundings was calculated to be 1567 $^{\circ}$ F (Table 10). For the same waste cooled 1 year ($Q = 223$ Btu/hr.ft 3) prior to storage, the maximum

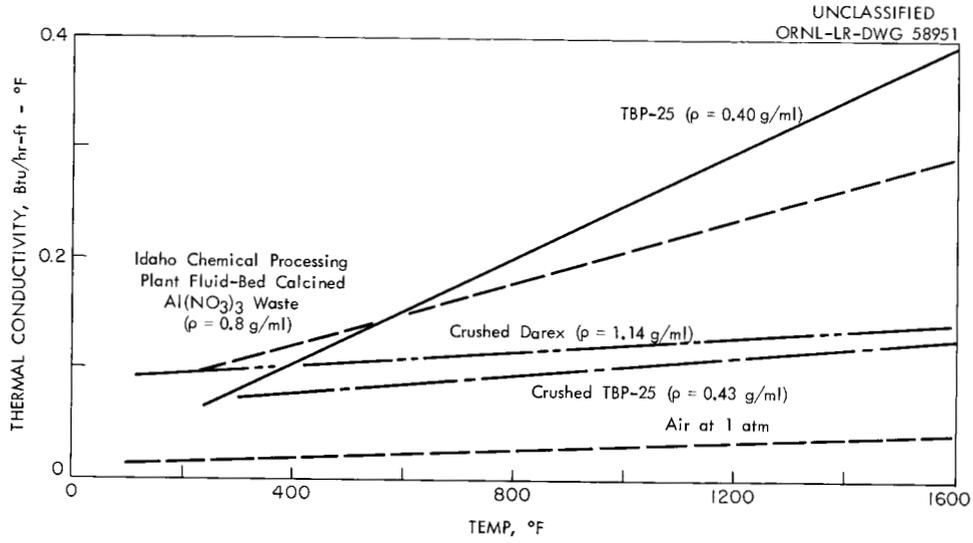


Fig. 12. Variation of thermal conductivity with temperature for calcined TBP-25 and Darex wastes.

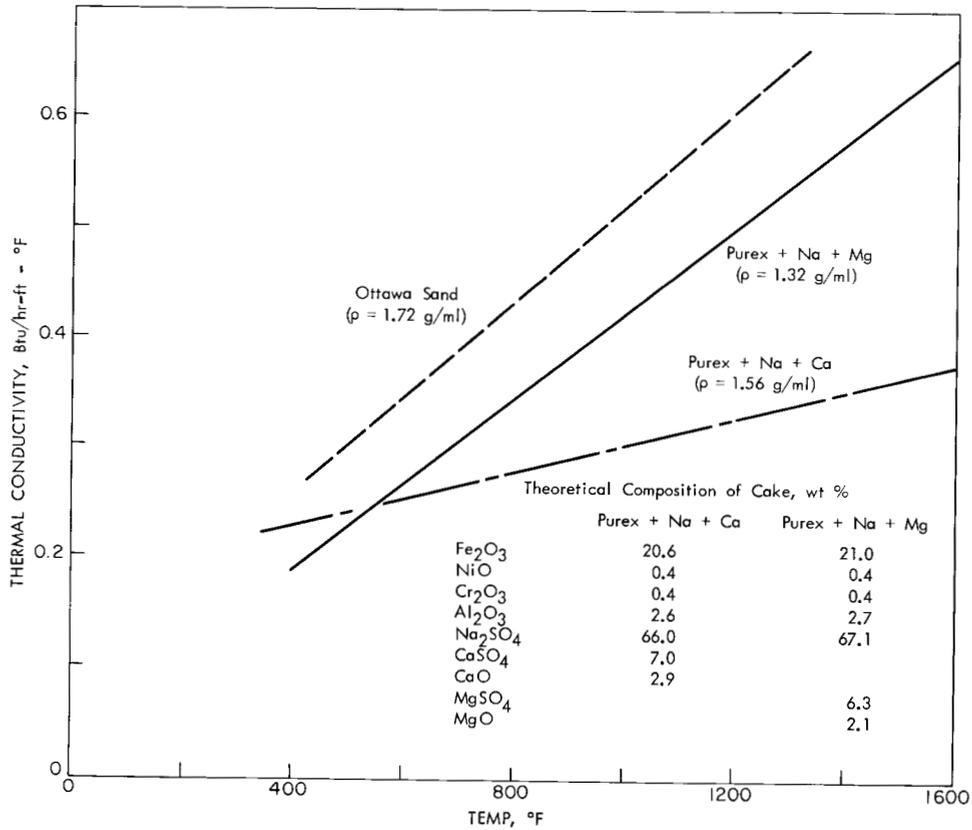


Fig. 13. Variation of thermal conductivity with temperature for calcined Purex waste.

Table 10. Estimation of Temperature Rise in Stored Calcined Wastes^a

Case A: k = 0.1 Case B: k = 2.44 x 10 ⁻⁴ T + 7.32 x 10 ⁻³ (over temperature range 235 to 1600°F) Temperature of heat sink = 70°F	Temperature Rise (T), °F			
	Decayed 120 days Prior to Storage (Q = 1056 Btu/hr.ft ³)		Decayed 120 days Prior to Storage (Q = 223 Btu/hr.ft ³)	
	Case A	Case B	Case A	Case B
Temp. rise in waste between center and surface k = constant, $T_W = QR^2/6k$	2590		544	
$k = aT + b, \Delta T_W = - \left[\frac{b}{a} + T_0 \right] + \sqrt{\left[\frac{b}{a} + T_0 \right]^2 + \frac{QR^2}{3a}}$		850		463
Temp. rise between waste and cave wall $\Delta T_S = \frac{QR}{3h} \left[1 + \left(\frac{R}{r} \right)^2 \right]$	630	630	132	132
Temp. rise at cave wall $\Delta T_C = \frac{QR^2}{3K} \left(\frac{R}{r} \right)$	87	87	18	18
Total temp. rise in waste $\Delta T_{total} = \Delta T_W + \Delta T_S + \Delta T_C$	3307	1567	694	613

- ^a Q = volumetric heat generation rate.
R = radius of waste package, 1.21 ft (55-gal sphere).
k = thermal conductivity of waste, Btu/hr.ft.°F.
T₀ = temperature of surface of waste sphere, °F.
h = surface conductance, 0.7 Btu/hr.ft.°F.
r = radius of cave or vault, 6 ft.
K = thermal conductivity of cave or vault, 1 Btu/hr.ft.°F

temperature is 613°F (Table 10). These calculations assume the surroundings, an infinite heat sink, to be at 70°F . The previous calculations (4), which indicated maximum temperature rises of 3307 and 694°F , respectively, in the 120-day- and 1-year-cooled waste (Table 10) were made with k assumed to be constant at $0.1 \text{ Btu/hr.ft.}^{\circ}\text{F}$. The linear variation of k observed here is given by

$$k = 2.44 \times 10^{-4} T + 7.32 \times 10^{-3}$$

with k in $\text{Btu/hr.ft.}^{\circ}\text{F}$ and T in degrees Fahrenheit. Expressing thermal conductivity as $k = aT + b$, the maximum temperature rise in the waste from surface to center is given by

$$\Delta T_W = - \left(\frac{b}{a} + T_0 \right) + \sqrt{\left(\frac{b}{a} + T_0 \right)^2 + \frac{QR^2}{3a}}$$

where T_0 is the temperature of the surface of the sphere, Q is the volumetric heat generation rate, and R is the radius of the sphere. The equations for the other temperature rises are given in Table 10.

When several containers are stored in the same cave or vault, they will influence each other in respect to temperature rise. "Forced" cooling, by refrigeration of the air in the vault or by blowing air through the vault, may be necessary, though less desirable than "natural" cooling. Disposal of wastes near the surface, using the atmosphere as a heat sink, may be another solution.

7.3 Experimental Apparatus and Procedure

Thermal conductivity was determined by a steady-state method using radial heat flow in a hollow cylinder (Figs. 14 and 15). The cylinder had an i.d. of 0.5 in. and o.d. of 4 in. and was 18 in. long (Fig. 6). The calcined solids were formed with a 0.5-in-dia stainless steel tube down the center and thermocouples spaced radially throughout them. The solids were formed in this way so that, after a heater was inserted down the 0.5-in. tube, k could be measured without disturbing the calcined solid. The thermal conductivity was calculated by integrating Fourier's law for heat flow

$$q = -kA \frac{dT}{dX}$$

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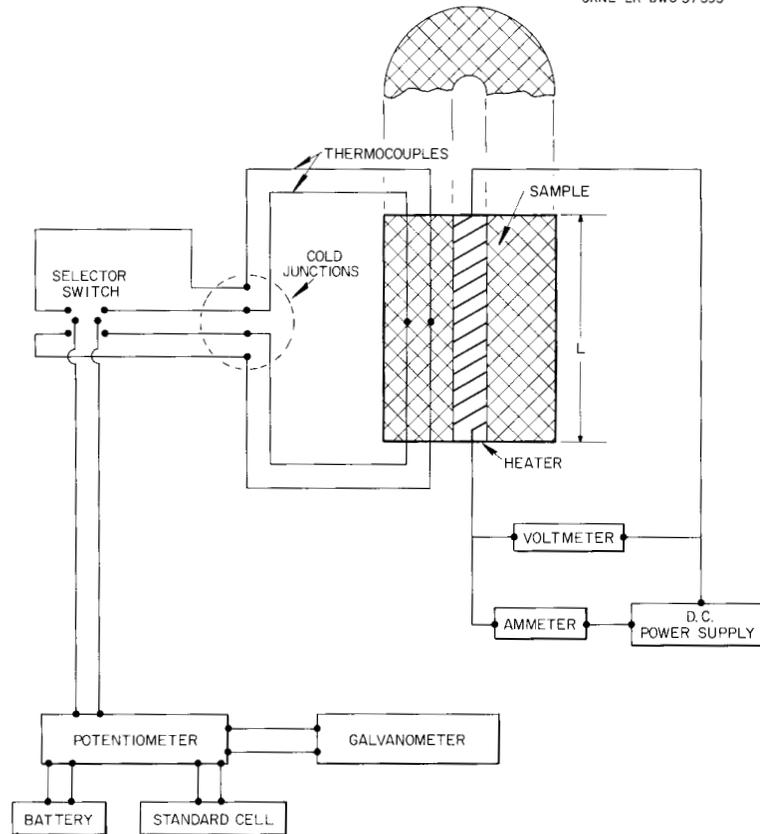


Fig. 14. Schematic of the arrangement of apparatus to measure the thermal conductivity of various solid wastes. L = length of hollow cylinder taken as test zone.

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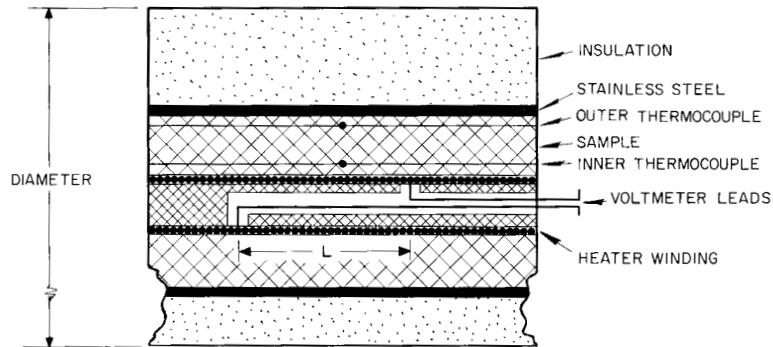


Fig. 15. Cross section of test specimen to measure the thermal conductivity of various solid wastes. L = length of test zone.

for a cylinder of length L between the limits of radius R_1 at temperature T_1 and radius R_2 at temperature T_2 to give

$$\bar{k} = \frac{q}{2\pi L (T_1 - T_2)} \ln \frac{R_2}{R_1}$$

where \bar{k} is the mean value of k over the temperature range T_1 to T_2 . The mean value of thermal conductivity is defined by

$$\bar{k} = \frac{\int_{T_1}^{T_2} k dT}{T_2 - T_1}$$

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9.0 APPENDIX

9.1 Thermograms for Various Waste Components*

Thermograms for various waste components are presented in Fig. 16.

9.2 Curves for Nitrate Volatility from Simulated High-activity Wastes

Curves for wt % nitrate in the condensate vs pot temperature are presented in Fig. 17. Curves for wt % nitrate in the condensate vs wt % nitrate in the pot are presented in Fig. 18. Curves for H_2O and N_2O_5 distilled as a function of pot temperatures are presented in Fig. 19.

*Prepared by W. E. Tomlin of the Chemical Technology Division.

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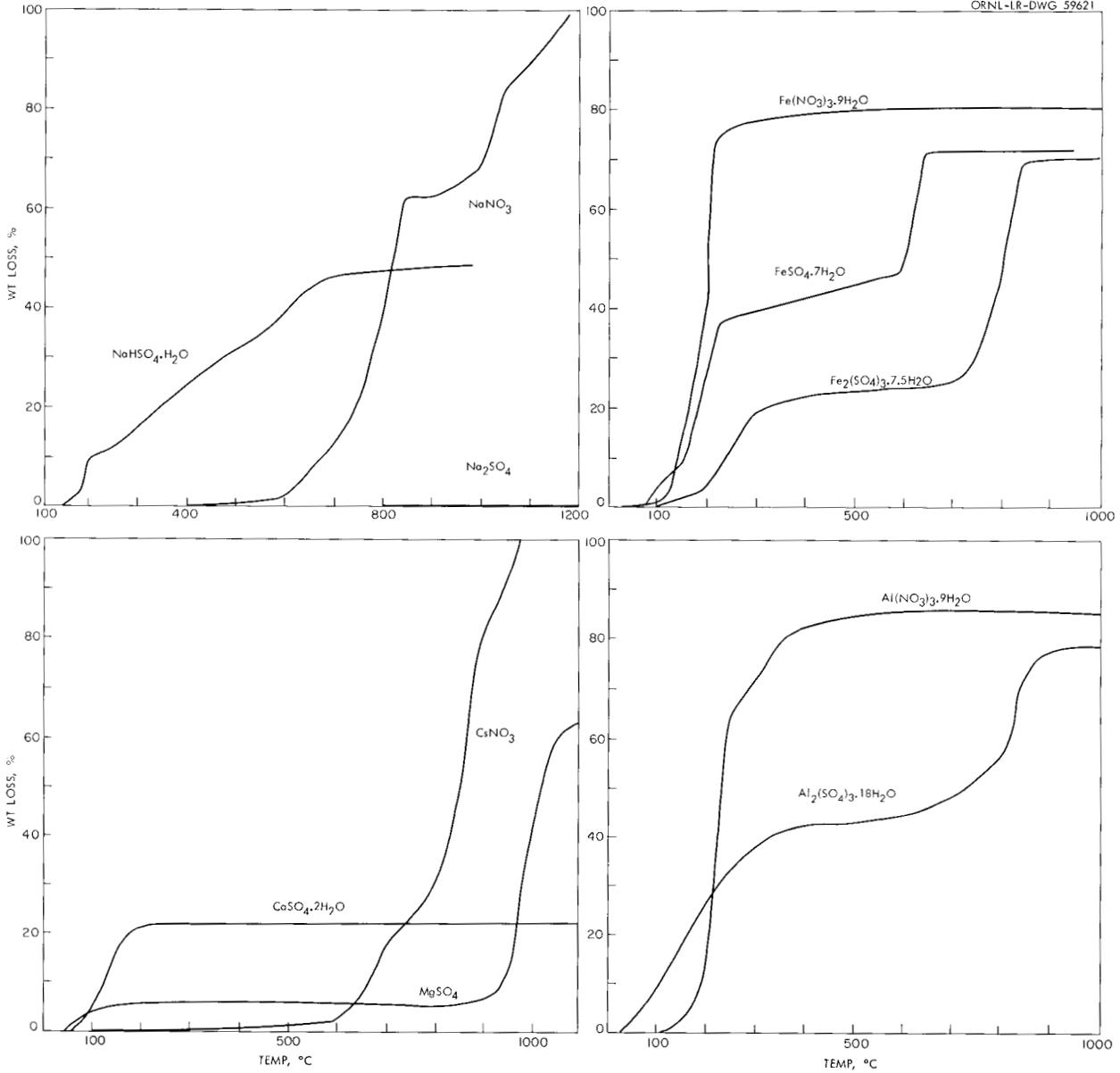


Fig. 16. Weight loss of various salts as a function of temperature.

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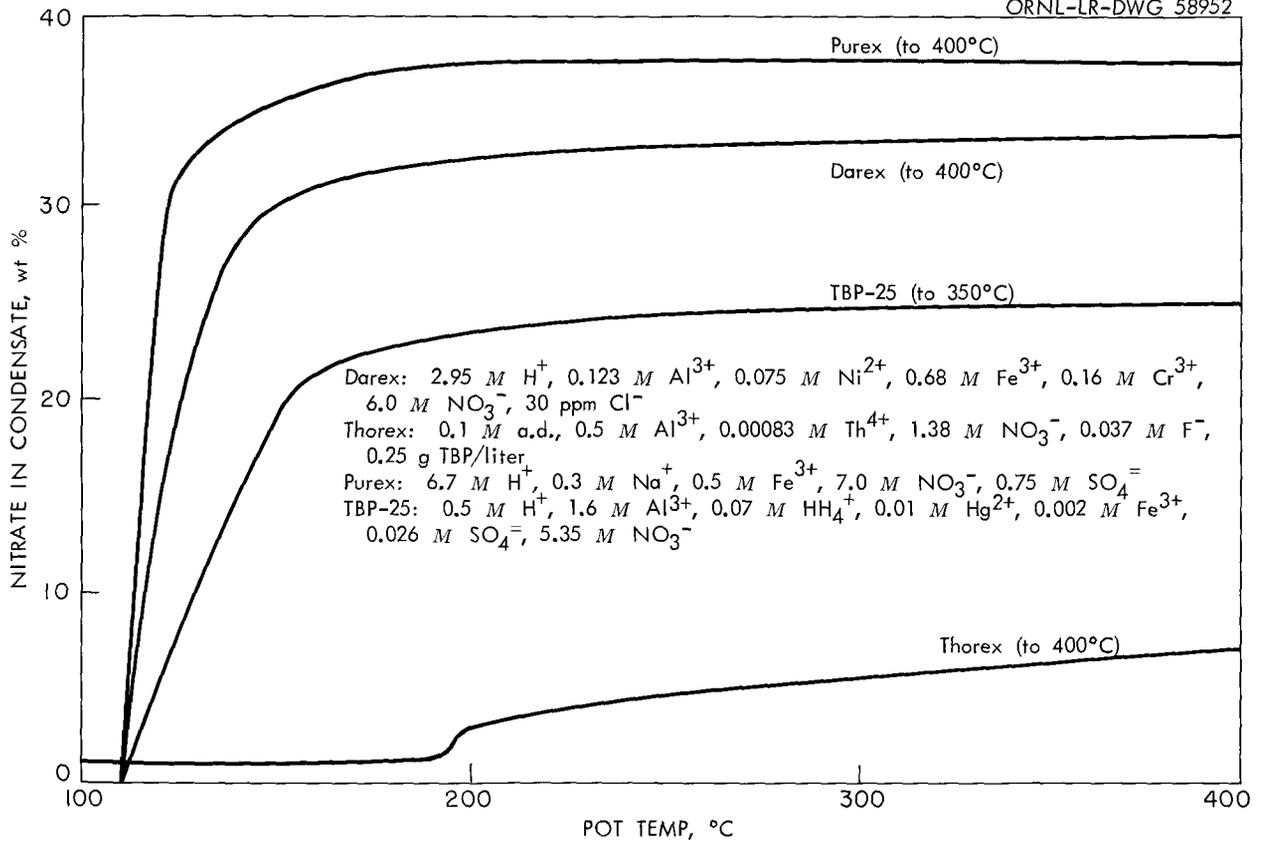


Fig. 17. Batch evaporation and calcination of acidic Purex waste to 400°C.

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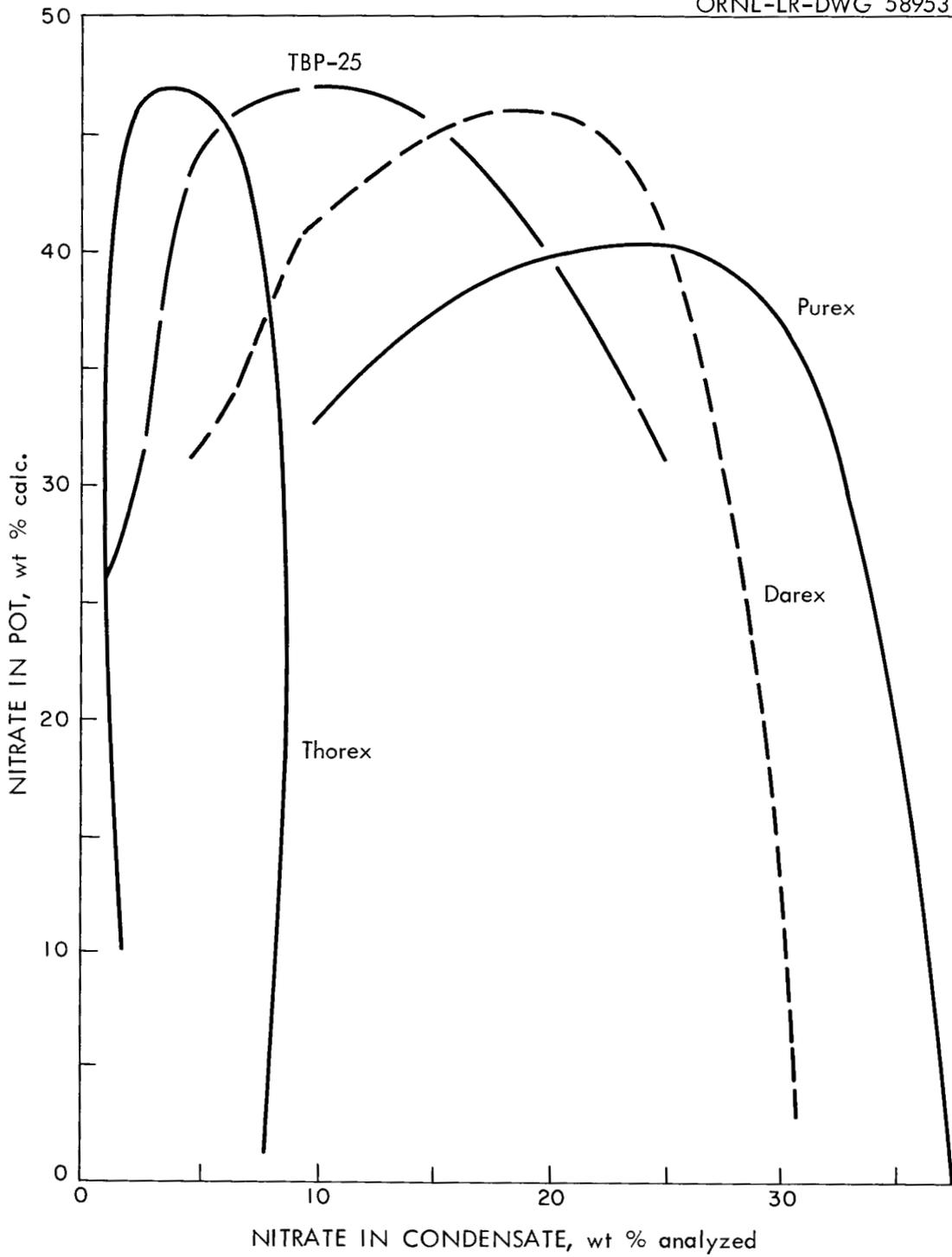


Fig. 18. Batch evaporation and calcination of acidic Darex waste to 400°C. Darex waste: 0.075 M Ni²⁺, 0.68 M Fe³⁺, 0.16 M Cr³⁺, 0.123 M Al³⁺, 2.95 M H⁺, 6.0 M NO₃⁻, 30 ppm Cl⁻.

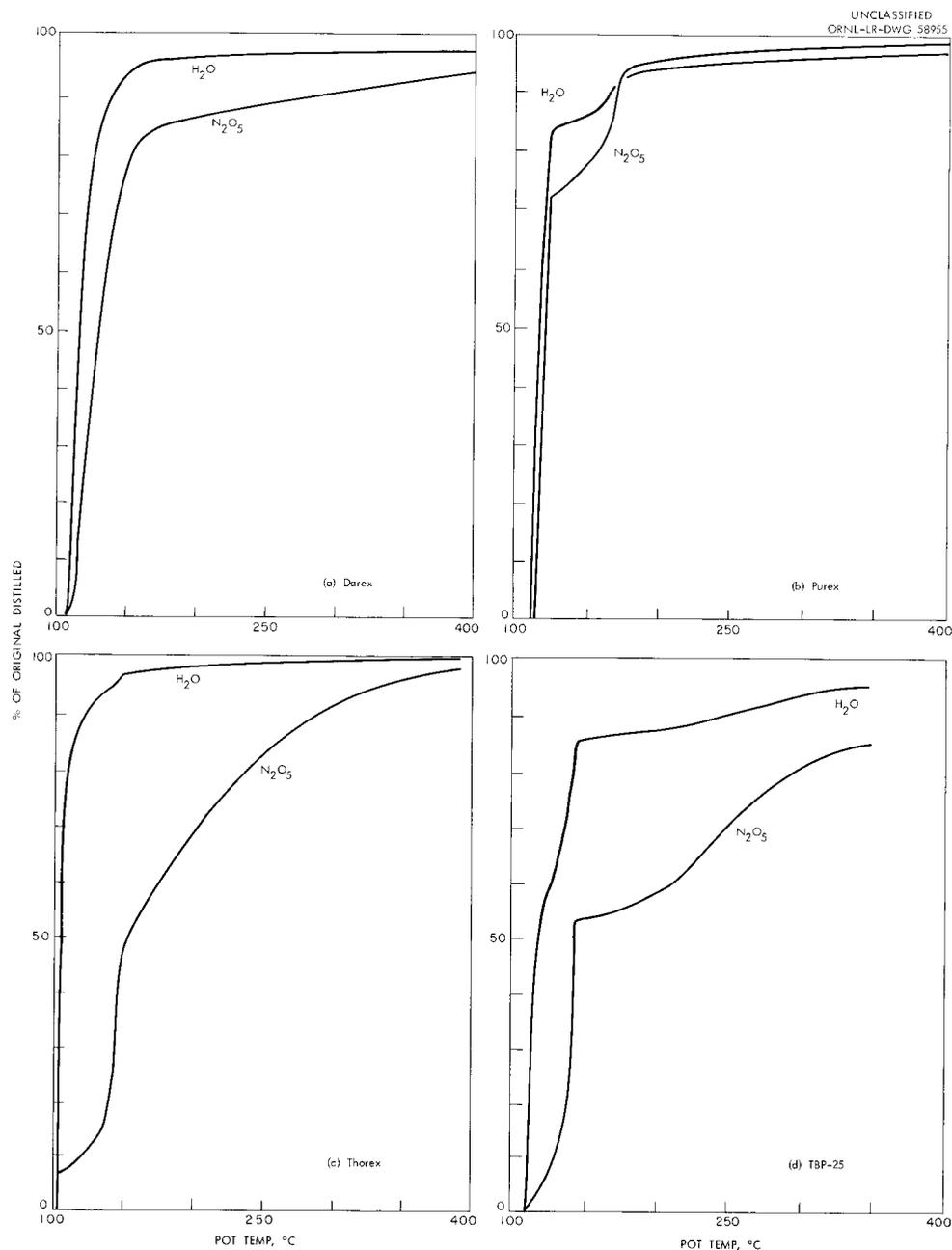
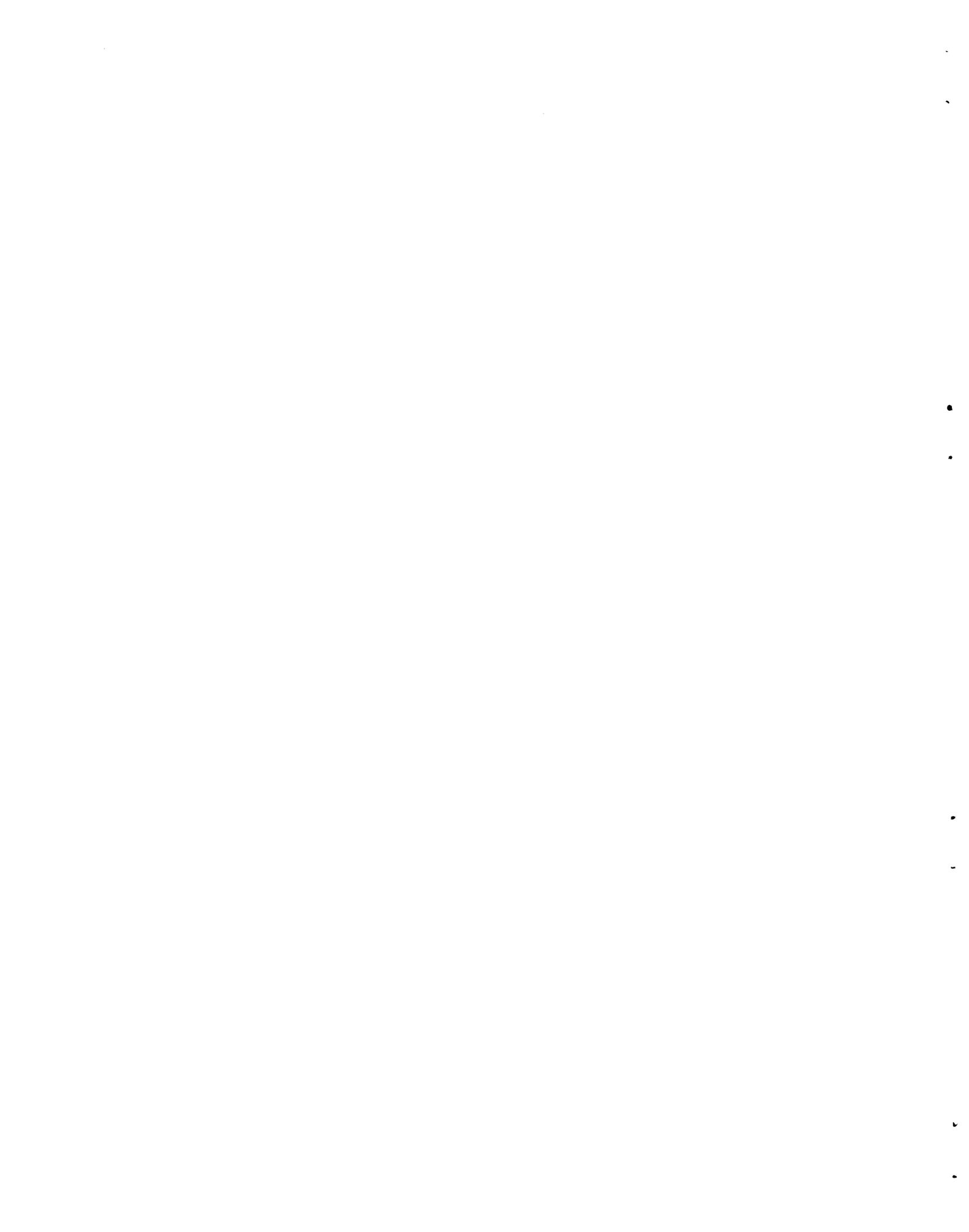


Fig. 19. Water and N_2O_5 distilled from simulated high-activity waste during batch evaporation and calcination. (a) Darex waste: 0.075 M Ni^{2+} , 0.68 M Fe^{3+} , 0.16 M Cr^{3+} , 0.123 M Al^{3+} , 2.95 M H^+ , 6.0 M NO_3^- , 30 ppm Cl^- , 68.0 wt % H_2O , 25.9 wt % N_2O_5 ; (b) Purex waste: 0.3 M Na^+ , 0.5 M Fe^{3+} , 6.7 M H^+ , 7.0 M NO_3^- , 0.75 M SO_4^{--} , 62.0 wt % H_2O , 29.4 wt % N_2O_5 ; (c) Thorex waste: 0.5 M Al^{3+} , 0.00083 M Th^{4+} , 0.007 M NH_4^+ , 1.384 M NO_3^- , 0.037 M F^- , 0.1 M acid deficient, 89.9 wt % H_2O , 7.2 wt % N_2O_5 ; (d) TBP-25 waste: 1.6 M Al^{3+} , 0.07 M NH_4^+ , 0.01 M Hg^{2+} , 0.002 M Fe^{3+} , 0.5 M H^+ , 0.026 M SO_4^{--} , 5.35 M NO_3^- , 70.1 wt % H_2O , 22.9 wt % N_2O_5 .



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