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WASTE TREATMENT AND DISPOSAL PROGRESS REPORT
FOR APRIL-MAY 1962

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ORNL-TM- 376

CHEMICAL TECHNOLOGY DIVISION
AND
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT
FOR APRIL-MAY 1962

R. E. Blanco and E. G. Struxness

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

High-Level Waste Calcination. Chemical and material balance flowsheets were prepared for the pot calciner pilot plant, which is to be installed at Hanford. As part of the mechanical testing program, it was demonstrated that already designed pots can be satisfactorily sealed by welding. A test rack was designed for testing calciner feed pumps, and a design study indicated the practicability of installing radioactive hot cell equipment for evaporation-calcination tests in an existing facility originally intended for self-sintering experiments with high-activity wastes.

In two engineering-scale runs, simulated high-activity waste was satisfactorily evaporated and pot-calcined. In the first run a large fraction of the mercury volatilized from the calcination pot and was returned to the evaporator. A mercury trap in the primary off-gas line, in the second run collected only 19% of the mercury.

Type 304L stainless steel coupled to titanium was corroded at an apparently uniform rate of 77 mils/mo during the final 2 hr of a TBP-25 evaporation-glass fixation cycle (900°C) compared with an estimated 61 mils/mo when exposed alone; the titanium was corroded at a rate of 31 mils/mo.

Aluminum borophosphate glasses were prepared which incorporated up to 17 wt % Darex waste oxides, gave volume reductions of 2.5 to 3.8 and had bulk densities between 2.44 and 2.74 g/ml and initial softening points of 750 to 850°C. Incorporation of 25 wt % Darex waste oxides in similar glasses resulted in products which became devitrified to give crystalline or segregated glassy materials. A semicontinuous fixation of TBP-25 waste in phosphate-lead glass resulted in volatilization of about 16% of the ruthenium; physical entrainment of the Pm-147 present was only about 0.1%. Operation with a rising liquid level and a minimum inventory of unmelted solid appears to be advantageous for ruthenium control. A container of a similar glass held 4 weeks at 900°C developed a vacuum which eventually reached 27 in. H₂O.

Low-Level Waste Treatment. Three pilot plant demonstration runs were completed. The presence of phosphates in the plant feed caused a premature resin column fission product breakthrough during one of the runs after 1022 bed volumes had been treated. Run HR-10 was successfully made with decontamination factors for Sr-90 and Cs-137 of 2880 and 181, respectively, after 1500 resin bed volumes, representing <1% of MPC_w for both isotopes.

Recirculation of 5-10% of the clarifier solids to a laboratory scale flash mixer lowered the total hardness of the clarifier effluent (caustic-copperas treatment) to 8-14 ppm (as CaCO₃). Addition of copperas to the flocculator instead of the flash mixer lowered the clarifier effluent hardness to 5.2 ppm. The presence of 1.7 to 2.4 ppm Turco 4324 in tests with ORNL tap water had no effect on total hardness of the effluent, but 3.2 ppm increased flash mixer and clarifier effluent hardness to 44 and 37 ppm, respectively.

BO-4 grade vermiculite was inferior to CS-100 resin in terms of flow rate, pressure drop, and decontamination factor. With vermiculite and a feed flow rate of $0.25 \text{ ml/cm}^2 \cdot \text{min}$, 50% Cs breakthrough occurred at 1000 bed volumes and the Sr d.f. was ~ 1000 at 1500 bed volumes. Decontamination decreased with increasing flow rate. With CS-100 resin at a flow rate of $5 \text{ ml/cm}^2 \cdot \text{min}$, the d.f.'s for Sr and Cs were 1100 and 1800, respectively, at 1500 bed volumes.

Engineering, Economics, and Hazards Evaluations. A cost study of the shipment of calcined solids in 6, 12, and 24-in.-dia cylinders was completed. Costs were lowest for shipment in the largest casks considered manageable, 60 in. i.d. and containing four 24-in.-dia, nine 12-in. dia, or thirty-six 6-in.-dia cylinders. Some wastes would have to be aged before shipping to allow heat generating fission products to decay. The longest decay time required was 11 years for acidic Purex waste in 24-in.-dia cylinders.

Weights and costs of casks at minimum ages were about 100 tons and \$50,000 for iron casks, 80 tons and \$120,000 for lead casks, and 65 tons and \$650,000 for depleted uranium casks. Shipping costs were lowest in all cases for lead casks, and ranged from $0.70 \times 10^{-3} \text{ mil/kwh}_e$ for acidic Purex in 24-in.-dia cylinders for a 1000-mile round trip to $32 \times 10^{-3} \text{ mill/kwh}_e$ for reacidified Thorex in smaller cylinders for a 3000-mile round trip.

Disposal in Deep Wells. The low-activity wastes being considered for disposal by deep-well injection require containment for about 200 years. Intermediate-activity wastes, requiring containment for 450 years, may be considered for disposal by this method if low-activity wastes can be handled satisfactorily. It is unlikely that high-activity wastes resulting from chemical processing of spent reactor fuel elements will be released to the ground without first immobilizing the fission products.

Strontium-90, the major contributor to the hazard of the waste, will move only 1 - 10% as fast as the transporting water because of ion exchange. Precipitation reactions will provide additional restrictions to radiostrontium movement. Cesium-137 is expected to move much more slowly than Sr-90 because of highly selective exchange reactions. Ruthenium-106 movement is not likely to be hazard-controlling.

Disposal in Natural Salt Formations. Salt samples from the Carey Salt Mine at Hutchinson, Kansas, fractured at about 250°C and released trapped moisture totaling 0.106 - 0.293% of the weight of the salt. Salt from the Carey Mine at Lyons with a moisture content of 0.048% to 0.100% broke up at about 215°C .

Clinch River Study. The Subcommittee on Bottom Sediments, Clinch River Study, met on May 10, 1962 to compile and evaluate all available data pertaining to deposition of and radioactivity associated with bottom sediments of the Clinch and Tennessee Rivers. A draft of the evaluation is in preparation for review in early July 1962.

A contract was awarded to Sprague and Henwood, Inc., Scranton, Pa., to collect bottom sediment cores in 14 sections of Clinch River from Miles 1.3 to 32.5, in two sections of Emory River, and in one section of Poplar Creek. The distribution of radioactivity, particle size, and mineralogy of the bottom sediment are to be studied.

A piston core sampler was developed and tested in 12.5-ft-deep water for use in coring of fine sediments. Core recoveries were 73 and 81% for bottom sediments 5.5 ft and 4.3 ft deep.

Fundamental Studies of Minerals. A highly selective sorbent for strontium was prepared by heating gibbsite ($\text{Al}(\text{OH})_3$) above its decomposition temperature of 150°C . Aluminum oxides with high surface area ($>200 \text{ m}^2/\text{g}$) were formed, in contrast to the low surface area ($\sim 0.3 \text{ m}^2/\text{g}$) for the original gibbsite. Distribution coefficient (K_d) ranged from 4000 to 40,000 when the solid/solution ratio was increased from 0.001g/50 ml to 0.05 g/50 ml. A raw aluminum ore (bauxite from Arkansas) containing 40% gibbsite showed good strontium-sorbing properties when the gibbsite component was decomposed by heating.

White Oak Creek Study. Ruthenium-106 determinatives on a series of soil samples taken within the bed of former White Oak Lake indicated that (1) as of February 1962, there was approximately 1200 curies of Ru-106 in the bed; (2) Ru-106 concentrations are highest in the top 2 in. of soil; (3) about 75% of the activity in the lake bed is associated with the first 2 ft of soil; (4) and, although Ru-106 is being transported by ground water through the lake bed soil, a relatively small amount of it reaches the creek in this way. The activity flows onto the bed from two streams that drain the intermediate-activity waste pit area.

Foam Separation. In continuous tests with ORNL tap water and low-activity waste, the total dissolved hardness was reduced to <2 ppm, as calcium, by precipitation with 0.005 M each of NaOH and Na_2CO_3 , coagulation with ~ 2 ppm Fe^{3+} , and filtration in a sludge column clarifier. Suspended hardness was <0.2 ppm. Beaker tests showed that Turco 4234, Fab, sodium hexametaphosphate, and sodium pyrophosphate all had more deleterious effects on water softening with 0.01 M NaOH than on softening with NaOH- Na_2CO_3 .

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1.0 INTRODUCTION

This report is the seventh in a series* of bimonthly reports on progress in the ORNL development program, the objective of which is to develop and demonstrate, on a pilot plant scale, integrated processes for treatment and ultimate disposal of radioactive wastes resulting from reactor operations and reactor fuel processing in the forthcoming nuclear power industry. The wastes of concern include those of high, intermediate, and low levels of radioactivity in liquid, solid, or gaseous states.

Principal current emphasis is on high- and low-activity liquid wastes. Under the integrated plan, low-activity wastes, consisting of very dilute salt solutions such as cooling water and canal water, would be treated by scavenging and ion exchange processes to remove radioactive constituents and the water discharged to the environment. The retained waste solids or slurries would be combined with the high-activity wastes. Alternatively, the retained solids or the untreated waste could be discharged to the environment in deep geologic formations. The high-activity wastes would be stored at their sites of origin for economic periods to allow for radioactive decay and artificial cooling.

Two methods are being investigated for permanent disposal of high-activity wastes. One approach is conversion of the liquids to solids by high-temperature "pot" calcination or fixation in the final storage container (pot) itself and storage in a permanently dry environment such as a salt mine. This is undoubtedly the safest method since complete control of radioactivity can be ensured within present technology during treatment, shipping, and storage. Another approach is disposal of the liquid directly into sealed or vented salt cavities. Research and development work is planned to determine the relative feasibility, safety, and economics of these methods, although the major effort will be placed on conversion to and final storage as solids.

Tank storage or high-temperature calcination of intermediate-activity wastes may be unattractive because of their large volumes, and other disposal methods will be studied. One method, e.g., addition of solidifying agents prior to direct disposal into impermeable shale by hydrofracturing, is under investigation. Particular attention is being given to the engineering design and construction of an experimental fracturing plant to dispose of ORNL intermediate-activity wastes by this method if proved feasible.

Environmental research on the Clinch River, motivated by the need for safe and realistic permissible limits of waste releases, is included in this program. The objective is to obtain a detailed characterization of fission product distribution, transport, and accumulation in the physical, chemical, and biological segments of the environment.

* ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, ORNL-TM-169 and ORNL-TM-252.

2.0 HIGH-LEVEL WASTE CALCINATION

The pot calcination process for converting high-activity-level wastes to solids is being studied on both a laboratory and engineering scale to provide design information for construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes. The first phase of the program is concerned with direct calcination processes where melting does not occur and little or no additives are combined with the wastes. In the second phase, enough additives are used to induce melting to form a glasslike material in which the fission products are fixed.

2.1 Pilot Plant (J. M. Holmes, E. J. Frederick, J. O. Blomeke)

The AEC has decided to transfer the hot waste pilot plant from the ICPP to Hanford, and initial discussions with Hanford representatives were held at ORNL on May 1, 1962. The intent is to locate the pot calciner process in the proposed new Fuels Recycle Pilot Plant Building, possibly integrating its operation with that of the Hanford spray calciner. The present schedule calls for hot operation of this plant to start during the first quarter of 1965.

Flowsheets. An optimized process flowsheet for the pot calciner process was prepared and forwarded to Hanford for study. Batch- and continuous-operation material balance flowsheets for the calcination of TBP-25, Purex (high sulfate), and Darex wastes were transmitted to Hanford. Material balance flowsheet preparation is now completed.

Mechanical Test Program. The decision to relocate the hot waste pilot plant will not affect the mechanical testing program under way at Georgia Nuclear Laboratories (1). Bids were received for fabrication of the filling station and the calcination pots, both critical items in the test program. None of the vendors could meet the required delivery date, and these items are being fabricated at ORNL. The current schedule (Table 2.1) reflects progress to date as well as the projected sequence in which the program is to proceed.

The results of automatic welding tests made on simulated calciner pot closures to develop welding procedures for in-cell operation are reported in Lockheed Report EL-5690 and are summarized as follows:

1. Sound crackfree welds can be made with the two joint designs (Fig. 2.1) as determined by visual and penetrant inspection. Radiography showed the first sample to be free of internal flaws such as cracks and porosity. The remaining samples will be radiographed for internal defects after completion of the pressure and temperature cycling tests at GNL. These welds will also be sectioned to determine the depth of penetration.
2. The electrode must be accurately positioned over the weld joint to obtain complete fusion of the bottom edges of the joint.

Table 2.1. 1962 Schedule for Pot Calciner Mechanical Testing Program

	Project Completed						
	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.
Weld Specimens							
Leak tests (completed)		XXX					
X-ray welds		XXXXXXXXXXXXXXXX					
Section and metallographic burst tests (completed)							
Grayloc Seal Test							
Leak test	XX						
Report, Tasks I and II			XXX				
Pot Calciner Mockup in Cell							
Dolly-furnace installation (completed)							
Controls	X	X					
Rigging		XX					
Instrumentation		X		X		X	
Proposed Filling Station Item 1							
Installation				X			
Proposed Alternative Head Item 2							
Installation						X	
Welding Station			XX	XXXXXXXXXXXXXXXX			
Demonstrations							
Cycling				XXXXXXXXXX			
Welded closures					XXXXX		
Mechanical closures						XXXX	
Disassemble and Ship							XX
Report							XXXX

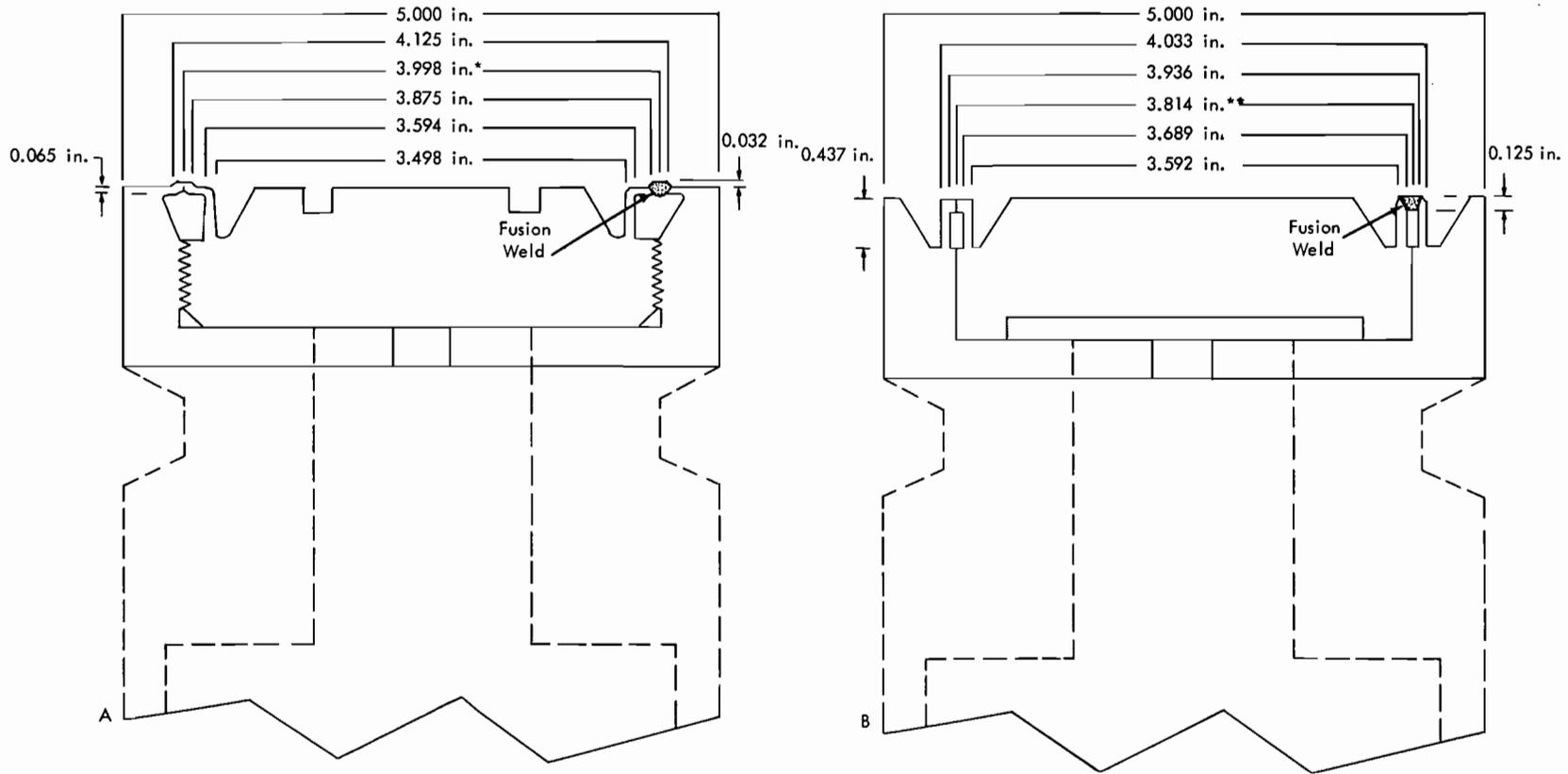


Fig. 2.1. Cross section of weld joint designs A and B. Solid lines show simulated weld test sample, broken lines, its orientation to the calcining pot neck. *Joint clearance for assembly is 0.001 in. **Male dimension shown; female dimension 3.811 in. for shrink fit.

3. "Arc blow" was present during the welding of all samples. In all cases, the arc was deflected in a direction radially away from the center of rotation of the test piece.
4. The cover for the shrink fit closure tends to cock and jam during assembly of the cover into the preheated body.
5. No detrimental pressure buildup occurred in the closed vessel attached to the test pieces.
6. The NO gas present had no apparent effect on the stability of the welding arc.

Design of Pump Test Loop. Equipment was designed and instrumentation specified for testing pumps for suitability as calciner feed pumps in the hot pilot plant. The test loop (Fig. 2.2) will permit four pumps to be tested simultaneously under simulated process conditions.

Pot Calciner Temperature Program. Internal heat generation in pot-calcined solids will decrease the time required for the calcination step but will also permit the cake temperatures to rise above the desired calcination temperature if the pot wall temperature is not properly controlled. Calcination temperatures above 1832°F (1000°C) are undesirable because of excessive sulfate, sodium, and fission product volatilization and excessive corrosion of the pot wall. Perona (2) has shown that an entire cake with an internal heat generation rate of 5000 Btu/hr·ft³ in a 1-ft-dia pot would exceed 1650°F after 15 min of calcination if the wall was maintained at 1650°F. The maximum temperature in the cake would be about 2300°F (1260°C) after 15 min and about 2500°F (1370°C) at thermal equilibrium.

In a study to determine a program for controlling the pot calciner wall temperature upon completion of feeding to ensure calcination of the entire cake at 1650°F (900°C) (3), a finite difference solution obtained with an analog computer showed that a linear approximation to a wall temperature program would permit calcination of the entire cake in a temperature range 1650-1832°F. A program (Fig. 2.3) involves heating the pot wall at 1650°F for 0.8 hours and then cooling to the required equilibrium wall temperature in 1.1 hr assuming a cake thermal conductivity of 0.2 Btu/hr·ft·°F and an internal heat generation rate of 4000 Btu/hr·ft³. The wall temperature is designated as W_0 while the surface temperature of the internal cavity of the cake is taken as W_5 and intermediate temperatures are spaced at equal increments of radius. Locations of these radii plus the initial and equilibrium temperature curves for solids having thermal conductivities of 0.2 and 0.1 Btu/hr·ft·°F are shown in Fig. 2.4. The equilibrium temperature profiles were determined from the cake thicknesses, thermal conductivities, and internal heat generation rates assuming 1650°F temperature at the surface of the interior cavity. For solids of the same heat generation rate but a conductivity of 0.1 Btu/hr·ft·°F, a heating time of 0.8 hr and cooling time of 2.5 hr to the equilibrium wall temperature is indicated (Fig. 2.5).

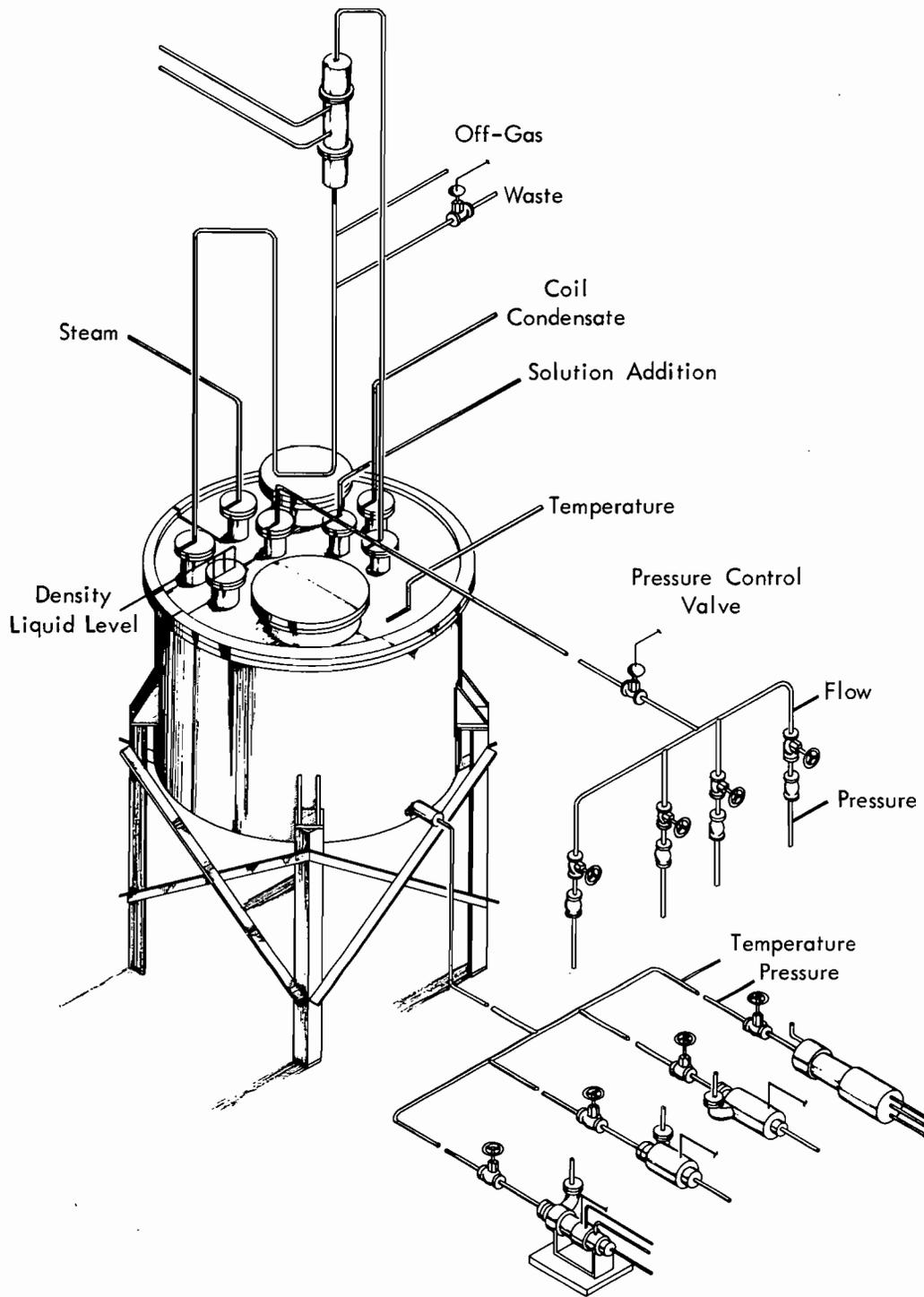


Fig. 2.2. Pump test loop.

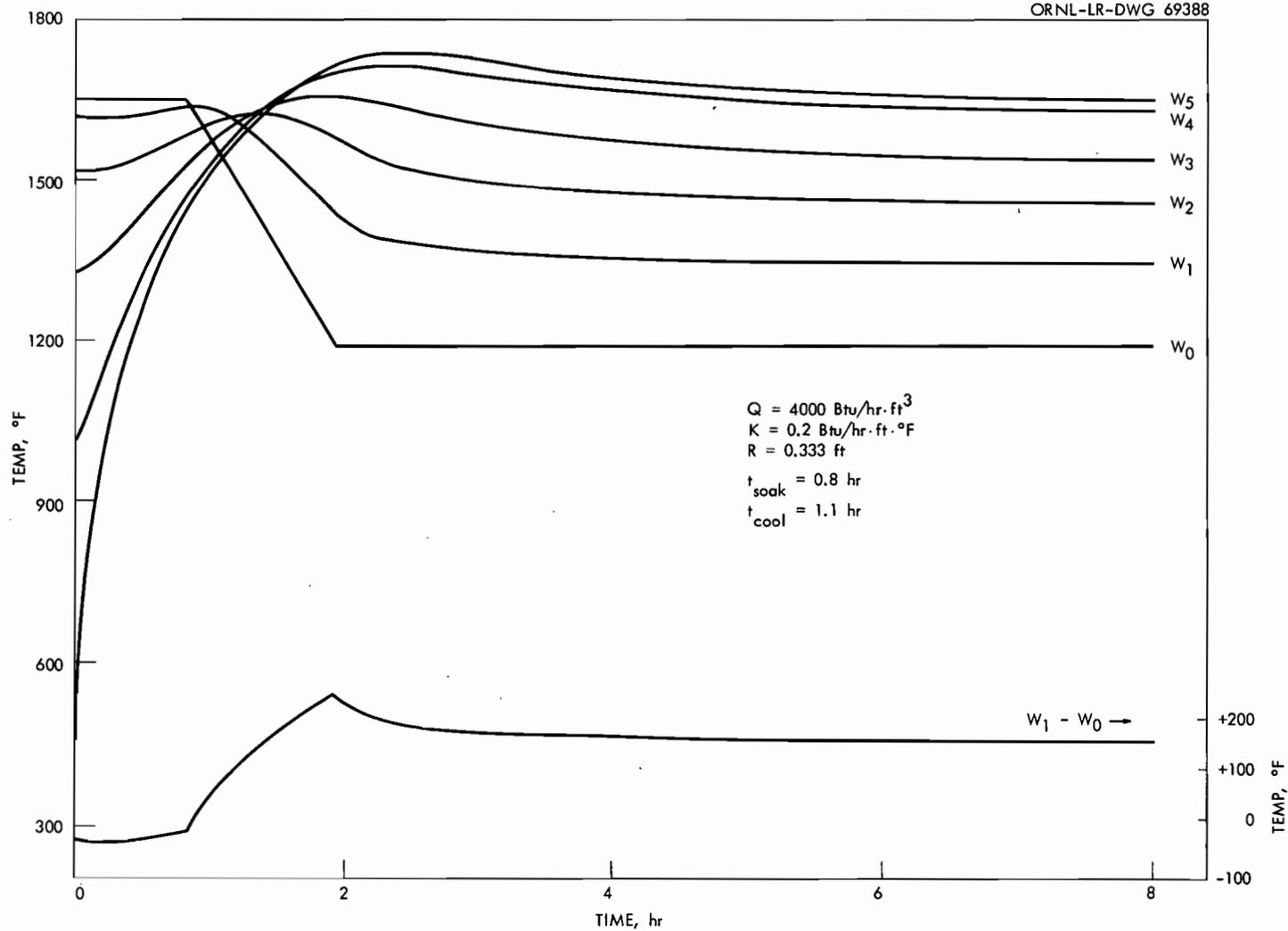


Fig. 2.3. Calcination cooling program.

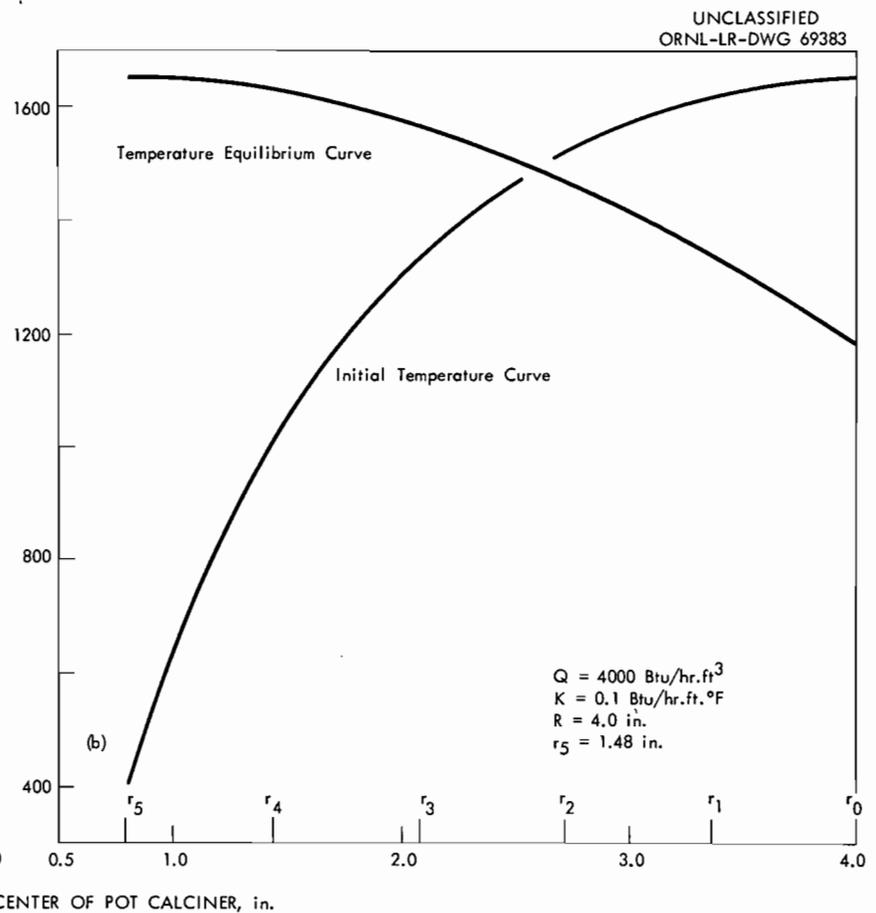
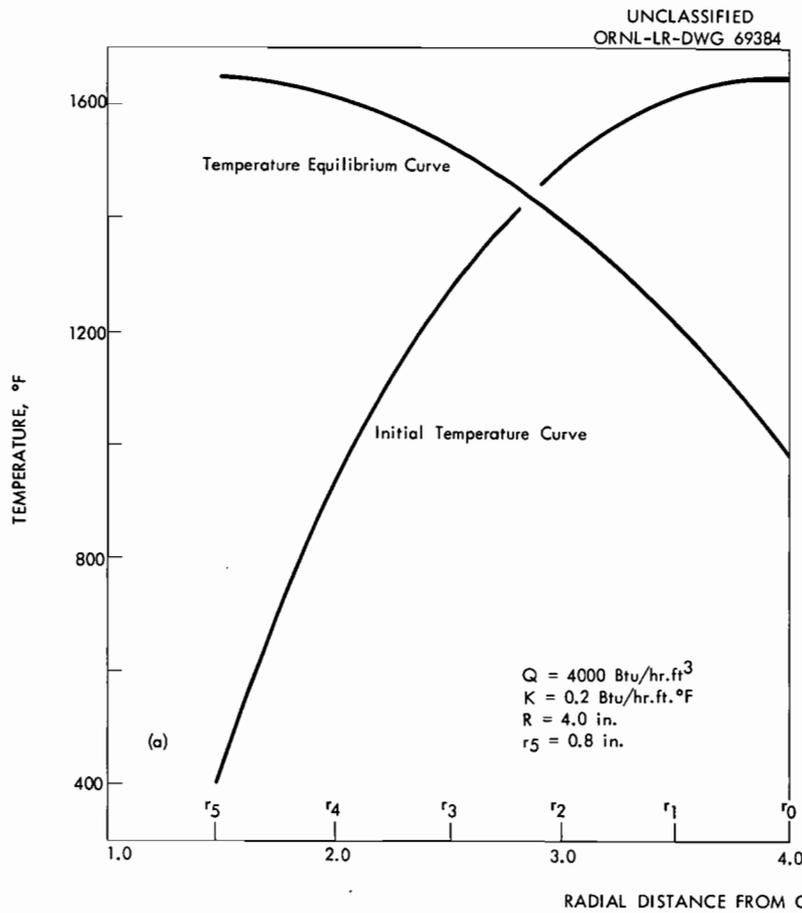


Fig. 2.4. Initial and final temperature conditions for calciner cooling program for solids with thermal conductivities of (a) 0.2 Btu/hr.ft.°F and (b) 0.1 Btu/hr.ft.°F.

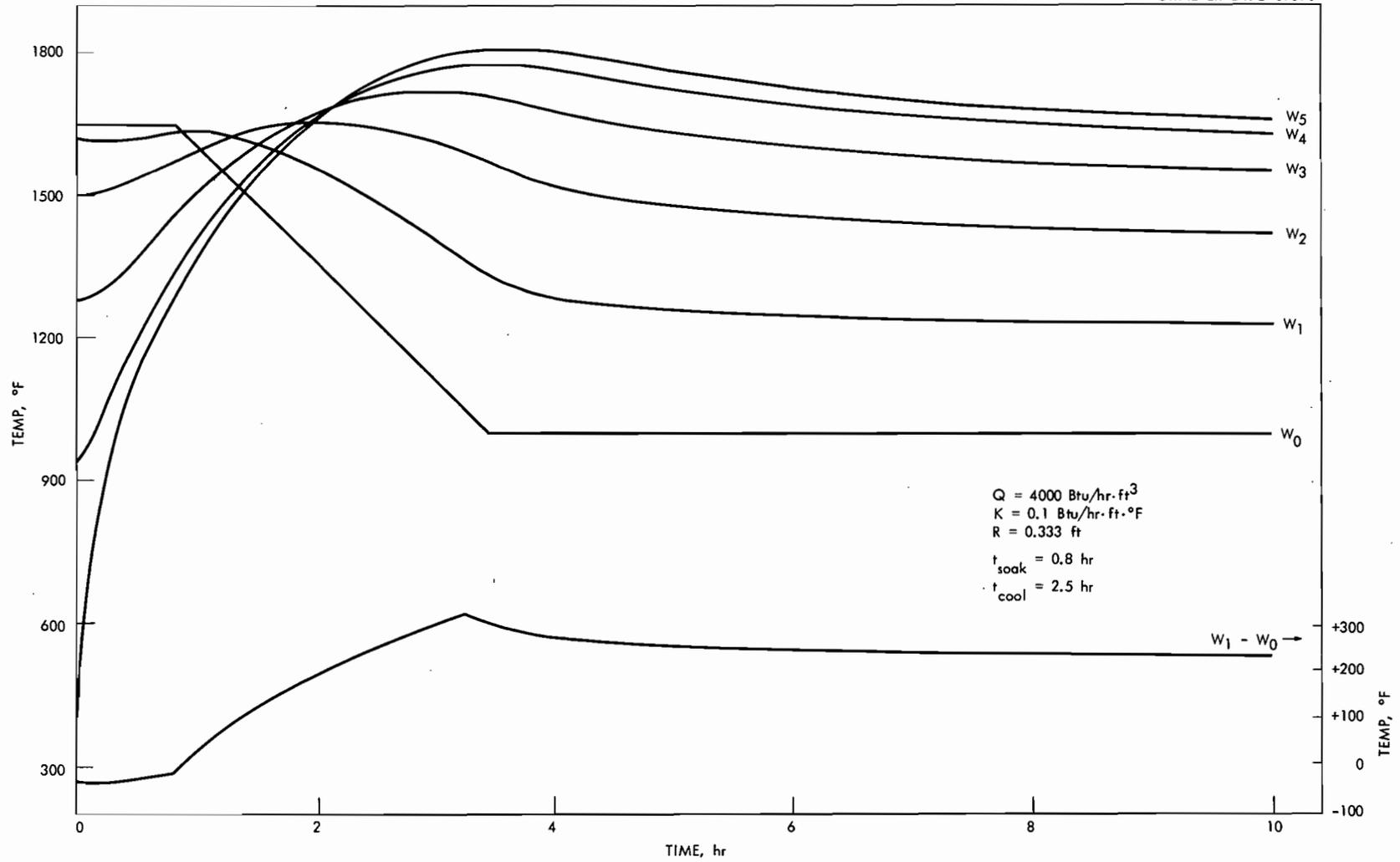


Fig. 2.5. Calcination cooling program.

A study of the time required to heat the pot wall at 1650°F if it is necessary to recalcine a pot full of cake with no center cavity showed that heating a cake with an internal heat generation rate of 4000 Btu/hr.ft³ and a conductivity of 0.1 Btu/hr.ft.°F for 1.87 hr and then cooling the wall rapidly to 300°F would completely recalcine the cake in the range 1610-1820°F (Fig. 2.6).

2.2 Design of Radioactive Cell Equipment (B. B. Klima and J. O. Blomeke)

The uncertainty that cell 1 in Bldg. 4507 will be available as scheduled for the hot evaporation and calcination tests necessitates considering alternative locations. Studies on the feasibility of using self-sintering pilot pit facilities for carrying out these tests indicated that an additional cost of \$45,000 will be required for process equipment modifications and installation; however, this installation would provide for storage and observation of calcined solid residues, which could not be done in Bldg. 4507.

2.3 Engineering-scale Nonradioactive Tests (J. C. Suddath, C. W. Hancher)

Two engineering-scale calcinations were made with simulated TBP-25 waste containing no radioactive elements.

Test R-65. The purpose of test R-65 was to determine the distribution in the system of mercury volatilized from the calcination pot. It was found to be 42% back in the evaporator, 8% in the primary off-gas line, and 20% in the calciner pot top, with 9% remaining in the solid. Mercury deposited between the top of the solid and the baffle, which could not be sampled, would probably account for the missing 20%. From the top of the baffle in the calcination pot to above the flanged section where the primary off-gas line decreases its diameter to 1 in., the temperature was 180-200°C, and in the primary off-gas line, 180-470°C. Steam introduced into the secondary off-gas line at a rate of 1.5-2.0 liters of water per hour kept it free of mercury deposits.

Conductivity measurements for use in maintaining the evaporator acidity low enough to prevent ruthenium volatilization were made satisfactorily by a vapor sampler on the evaporator condensate. However, the sampling rate was sensitive to the boilup rate and decreased to 15-20 cc/min during the latter part of the test. This is much too slow considering the conductivity cell holdup of 400 cc, and the control had to be switched to the conductivity cell downstream of the evaporator condenser, which operates on the totally condensed evaporator condensate.

The run was continuous, with 470 liters of simulated waste fed to the system in 23 hr at an average rate of 20.6 liters/hr and a feed/water ratio of 3.1/1. The nitrate balance was 102% and the aluminum balance, 95% (Table 2.2). The wet test meter used to measure the off-gas was not in operation, but the off-gas volume did not appear excessive. The solid product had a bulk density of 0.68 g/cc, and the composition was 47 wt % Al, 0.94 wt % Fe, 0.58 wt % Hg, and 0.07 wt % NO₃⁻. The mercury concentration at the top of the solid was 1%.

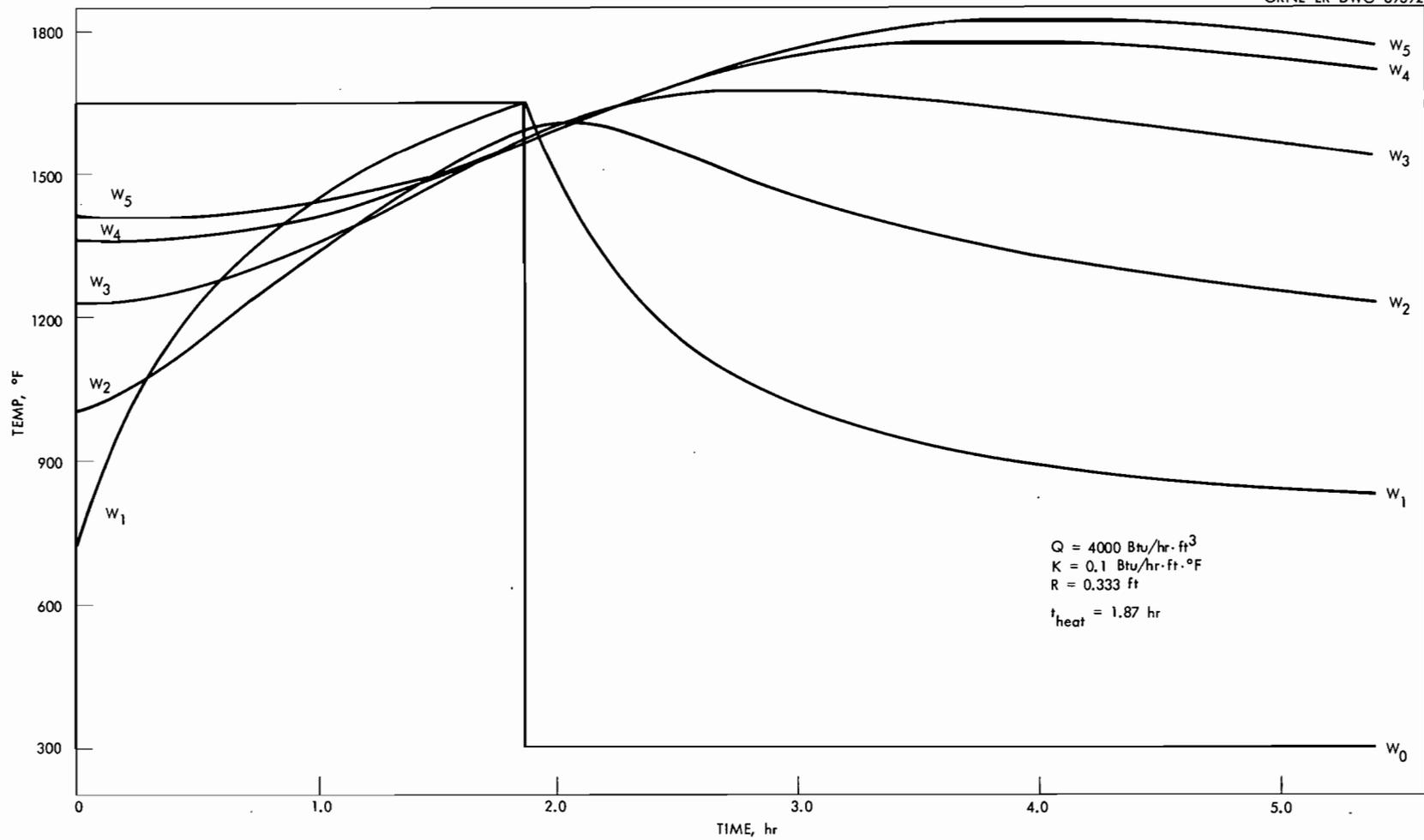


Fig. 2.6. Pot reheating study.

Table 2.2 Material Balances in TBP-25 Simulated Waste Calcination Tests
Runs 65 and 66

Stream	NO ₃		Al		Fe		Hg	
	g	%	g	%	g	%	g	%
Run R-65								
Feed	195,636	100	22,276	100	111.2	100	2,380	100
Evaporator	16,050	8.2	2,050	9.2	30.0	26.3	1,000	42
Condensate	183,812	94	5.05	-	1.8	1.6	640 ^a	28
Solid	283	-	19,035	85.5	405	352 ^b	240	10
		102		95		380		80
Run R-66								
Feed	192,172	100	21,283	100	89.8	100	1,877	100
Evaporator	8,322	4.3	0.087	5.1	12.0	13.6	1,188	63.3 ^c
Condensate	162,154	84.5	7.8	-	4.49	4.9	32.4	1.7
Solid	15.2	-	18,837	88.7	214	235 ^b	624	33.2
		89		94		243		98

^aOff-gas.

^bHigh value probably due to corrosion product.

^c29.3% in evaporator, 19.0% in mercury trap, 15.2% in off-gas line and calciner top.

Temperature data for the calciner furnace, the calciner outer surface, and the temperatures of the interior of the calciner pot, obtained by the automatic data logger and processed by a computer (Fig. 2.7), show the solid depositing radially from the wall of the calciner toward the center. The thermal conductivity of the radially depositing solids varied randomly from hour to hour (Table 2.3) but averaged 0.92 Btu hr⁻¹ ft⁻¹ °F⁻¹.

The control limits for the run and the hourly system variables and parameters are shown in Tables 2.4 and 2.5.

Test R-66. In test R-66 a mercury trap (Fig. 2.8) was inserted in the primary off-gas line and steam was blown through the secondary off-gas line in an attempt to collect volatilized mercury. The trap retained 19% of the mercury in the system, while 15% plated out in the calciner top and off-gas line and 29% went back into the evaporator;

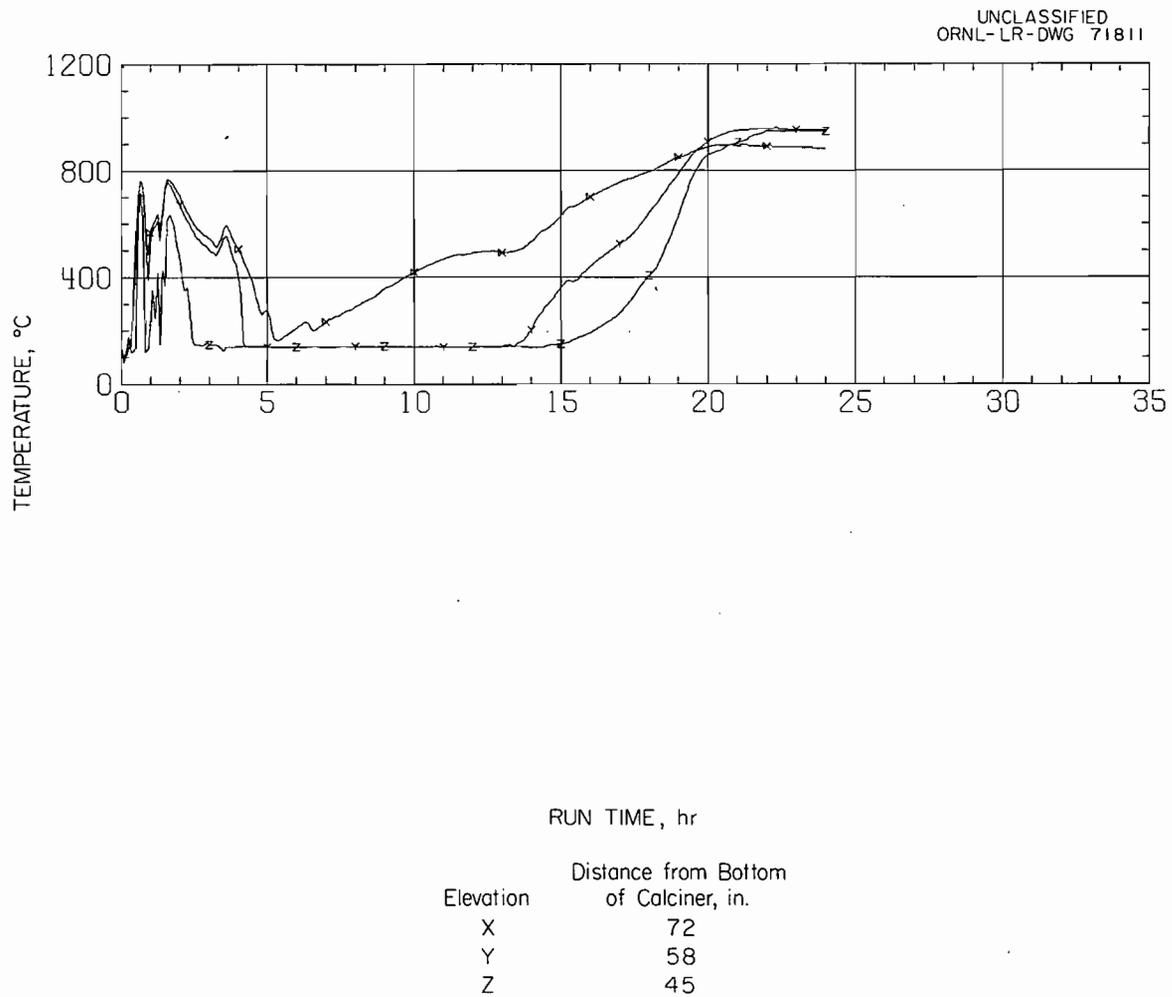
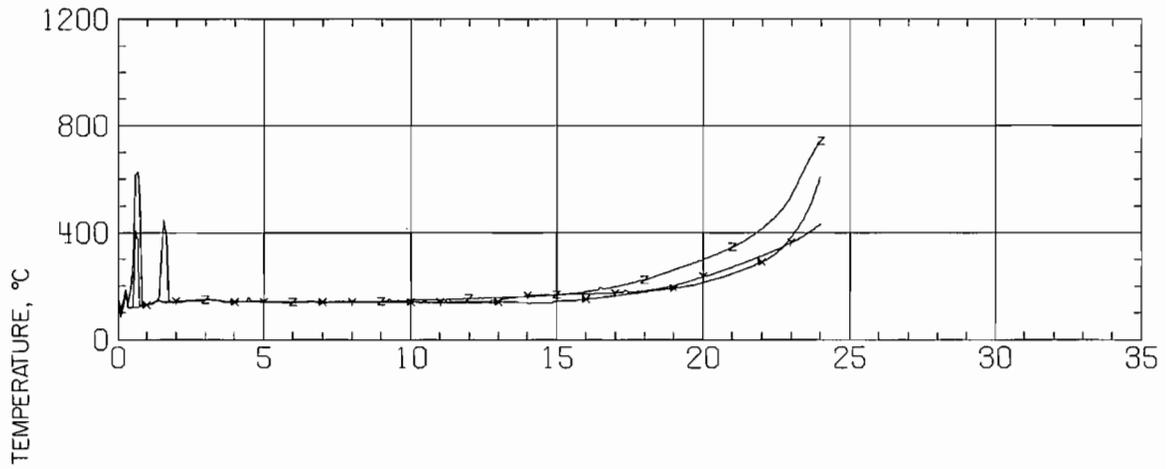


Fig. 2.7 Calciner center line zone temperatures R-65.

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RUN TIME, hr	
Elevation	Distance from Bottom of Calciner, in.
X	32
Y	19
Z	6

Fig. 2.7 (a) Calciner center line zone temperatures R-65.

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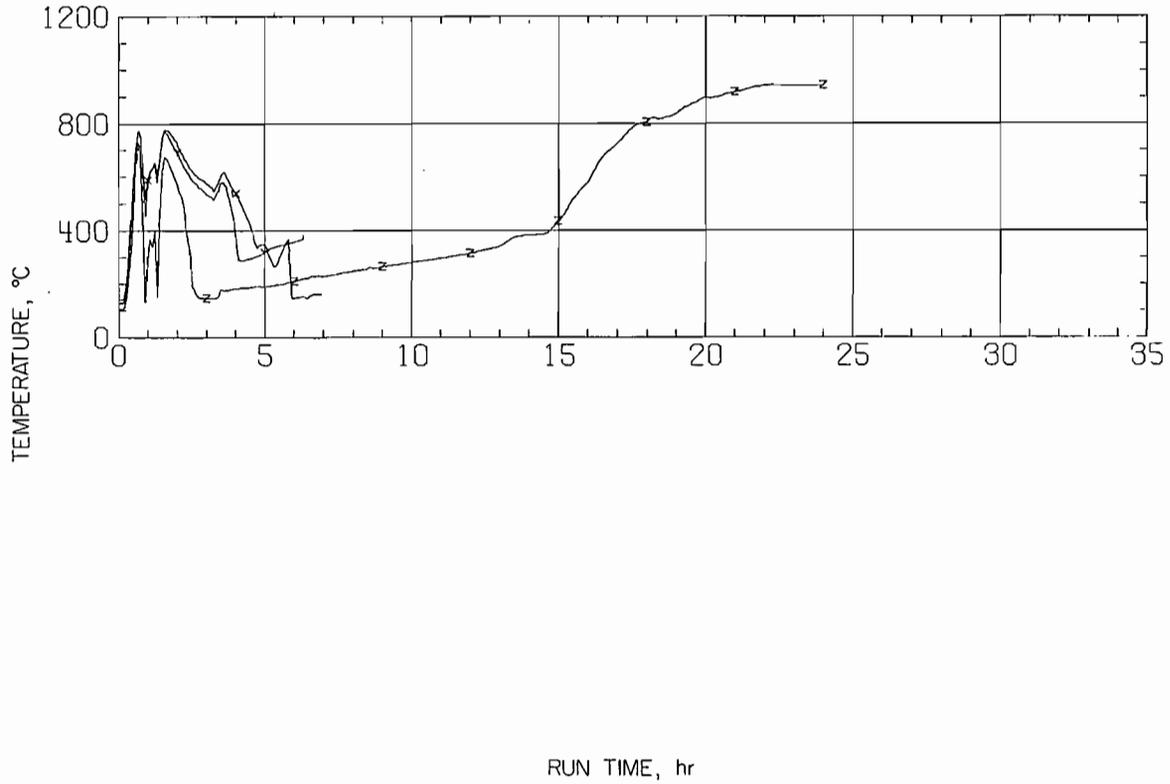
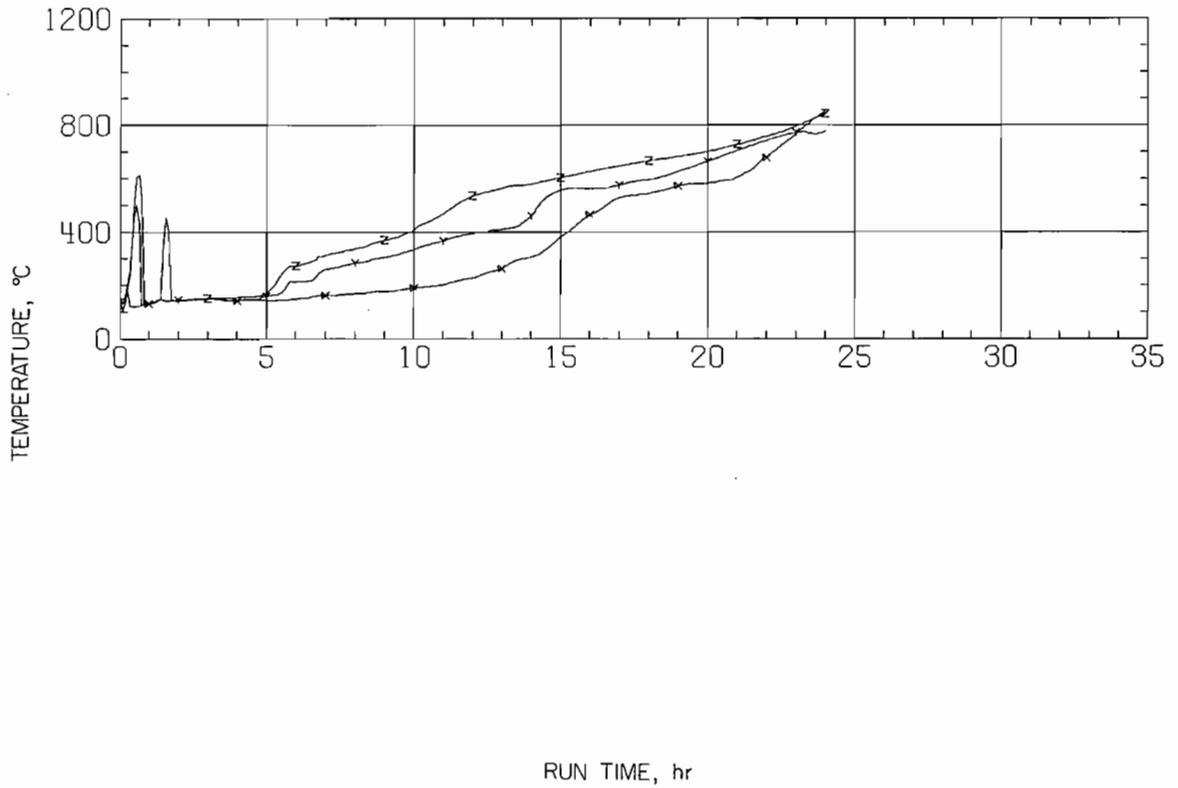


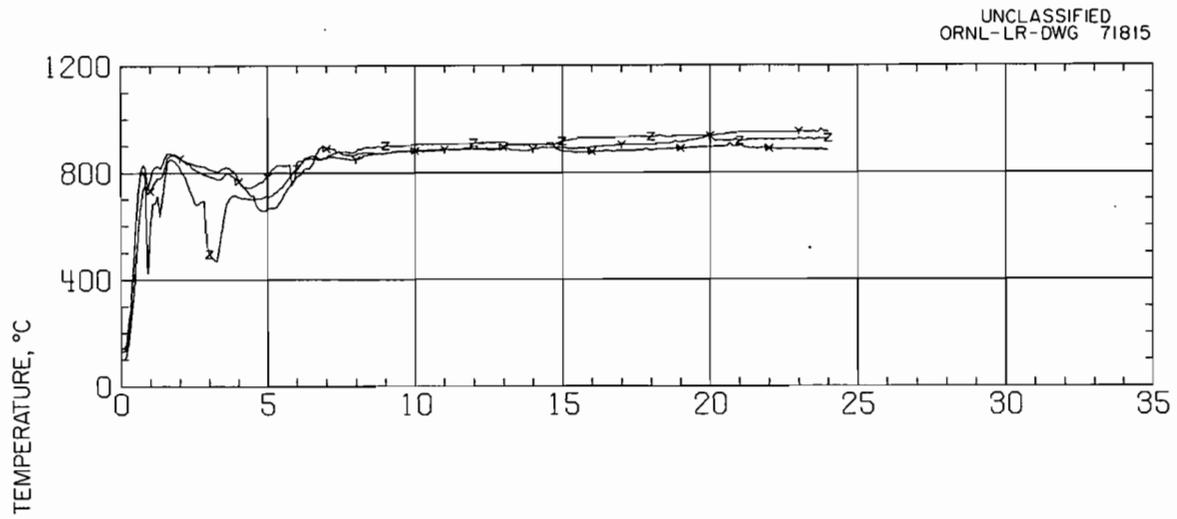
Fig. 2.7 (b) Calciner inside near wall zone temperatures R-65.

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Elevation	Distance from Bottom of Calciner, in.
X	32
Y	19
Z	6

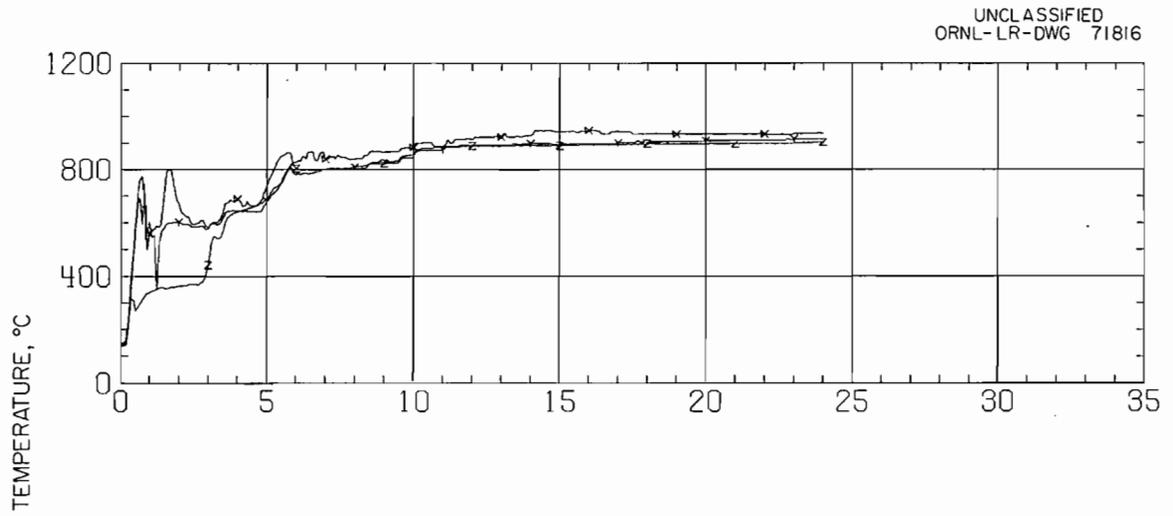
Fig. 2.7 (c) Calciner inside near wall zone temperatures R-65.



RUN TIME, hr

Elevation	Distance from Bottom of Calciner, in.
X	72
Y	58
Z	45

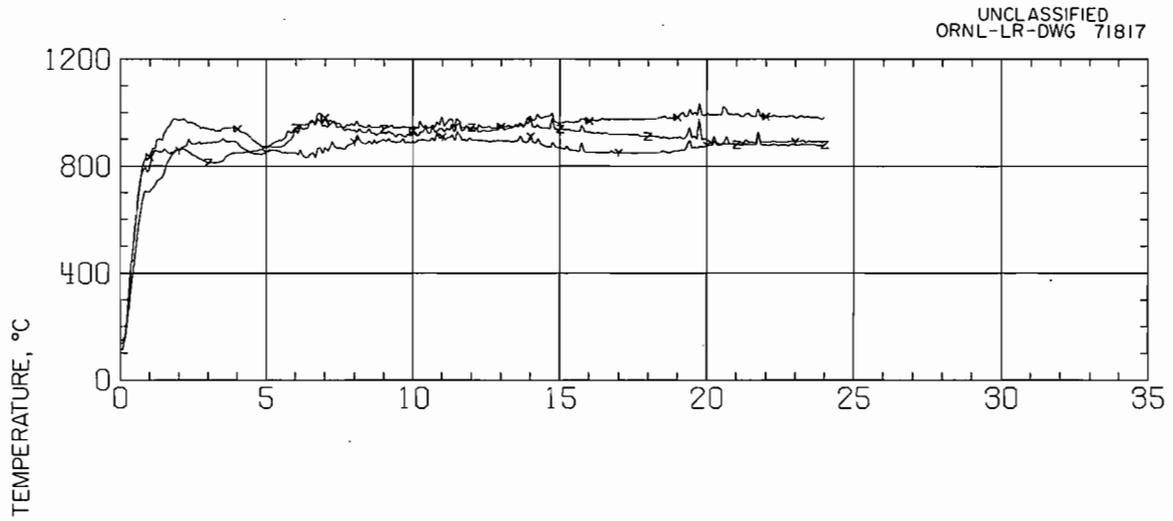
Fig. 2.7 (d) Calciner surface zone temperatures R-65.



RUN TIME, hr

Elevation	Distance from Bottom of Calciner, in.
X	32
Y	19
Z	6

Fig. 2.7 (e) Calciner surface zone temperatures R-65.



RUN TIME, hr	
Elevation	Distance from Bottom of Calciner, in.
X	72
Y	58
Z	45

Fig. 2.7 (f) Calciner furnace zone temperatures R-65.

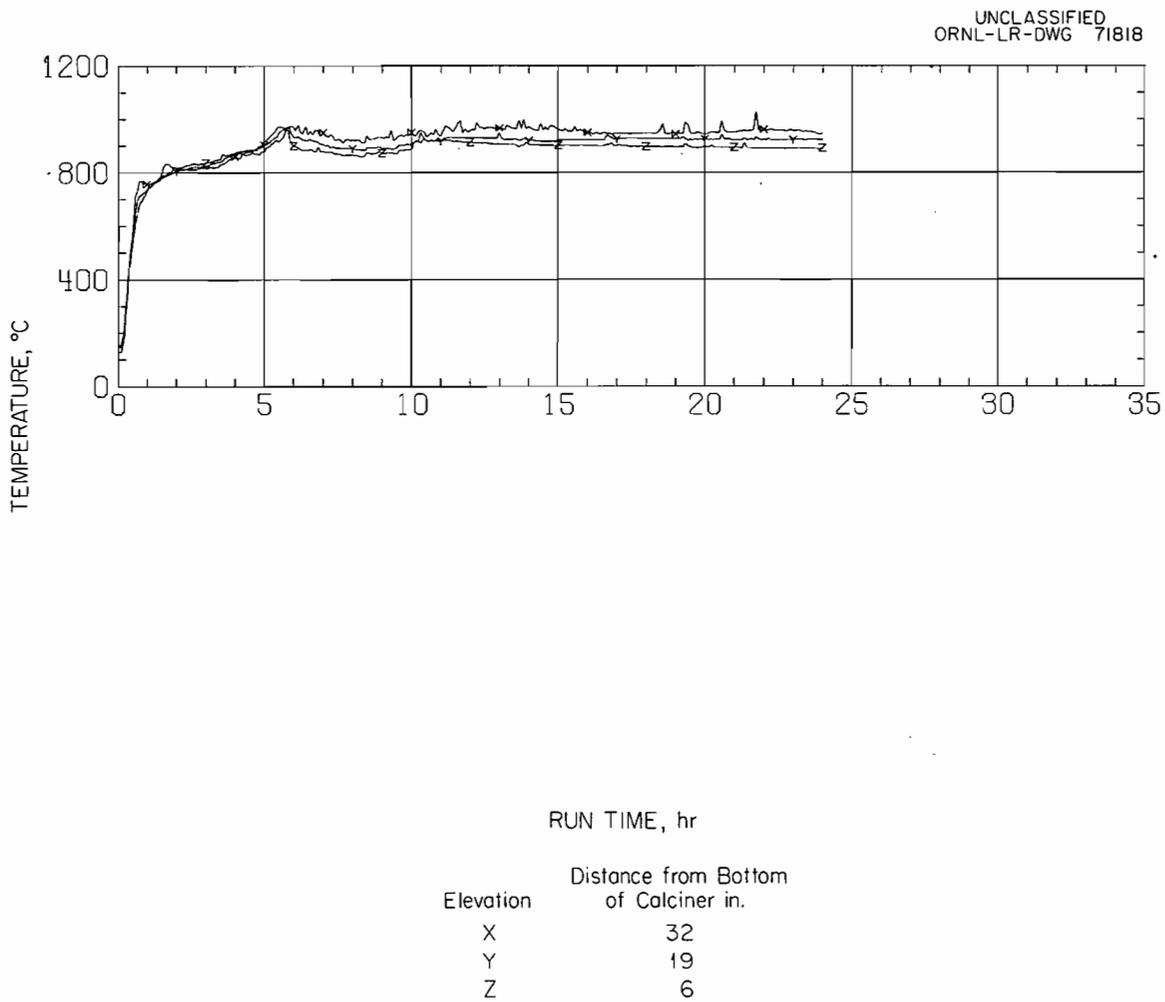


Fig. 2.7 (g) Calciner furnace zone temperatures R-65.

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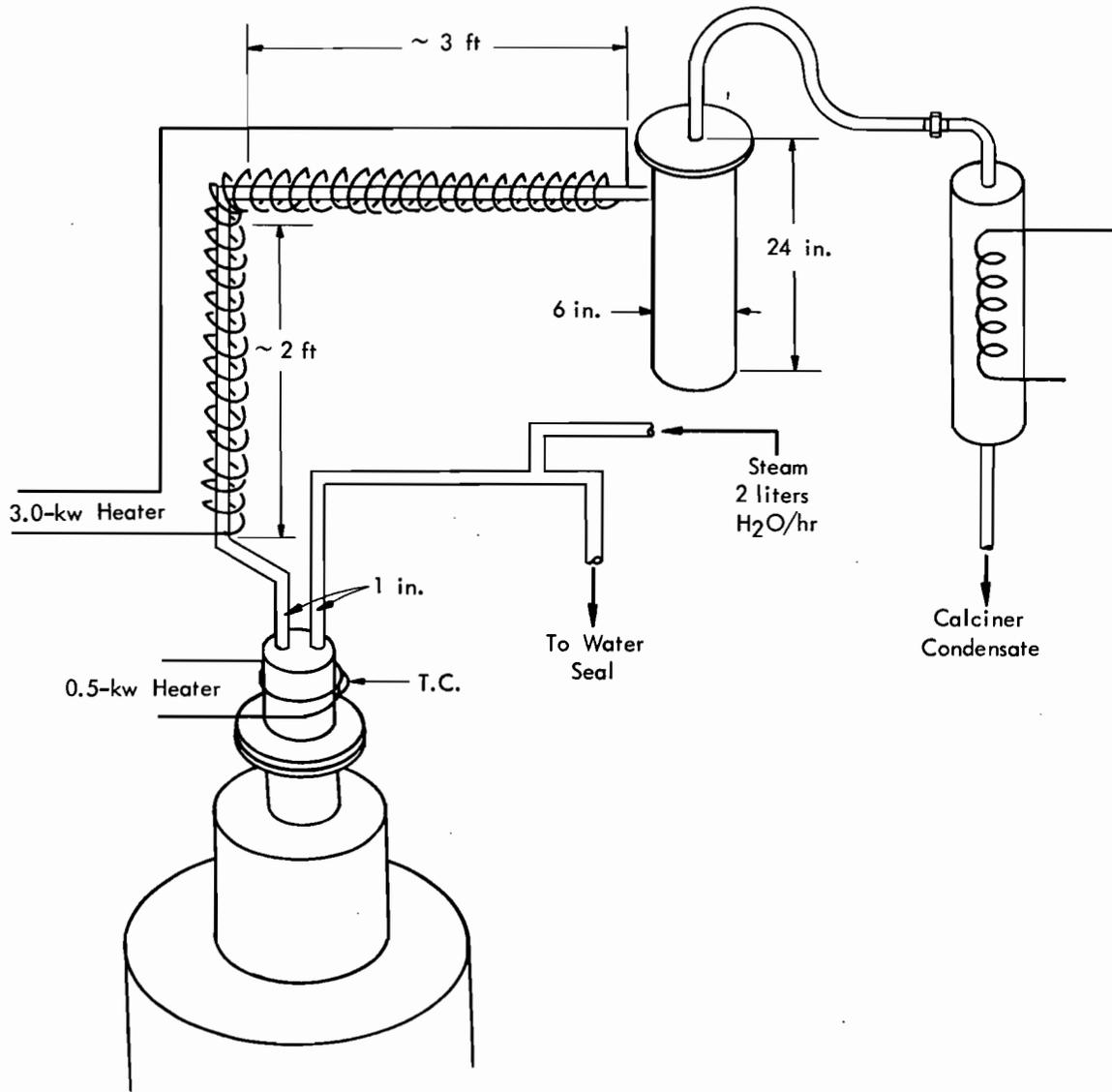


Fig. 2.8. Mercury trap in waste calcination runs R-65 and 66.

Table 2.3 Thermal Conductivity of Calcination Cake in Test R-65
during Operation

Test, hr	K, Btu hr ⁻¹ ft ⁻¹ °F ⁻¹		Cake Vol, liters
	From Skin to Center	From Skin to Edge	
1	0.212	0.215	4.118
2	0.632	0.680	9.325
3	1.023	1.063	14.961
4	1.095	1.121	20.878
5	1.082	1.235	26.043
6	0.888	1.054	30.181
7	0.705	0.808	33.152
8	0.912	1.055	36.396
9	0.945	0.978	39.349
10	0.863	0.813	41.779
11	1.008	0.882	44.287
12	0.880	0.739	46.283
13	0.657	0.548	47.682
14	0.627	0.578	48.879
15	0.886	0.741	50.320
16	0.859	0.843	51.555
17	0.495	0.627	52.172
18	1.183	1.605	53.367
19	0.547	0.740	53.777
20	1.511	1.869	54.572
21	0.799	1.362	54.982
Avg.		0.92	

33% remained in the calcined solids. No mercury deposited in the secondary off-gas line when steam was added at a rate of 1-2 liters/hr, but the primary off-gas line was plugged with mercury oxide at the junction of the 3-in.-dia top of the flanged section with the 1-in.-dia off-gas line, although there was little pressure drop. The calciner top was operated at 400°C and the off-gas line at 450°C. The calcined solids had a bulk density of 0.65 g/cc.

The mercury trap had a large cool surface for the mercury oxide to condense on in a vessel that could be flooded with nitric acid. The off-gas lines to the mercury trap were maintained at a temperature above the condensation temperature of the mercury oxide-nitrate, which appears to be 450-500°C from laboratory calcination tests and mercury trap experiments. The temperature of the off-gas line between the calciner top and the mercury trap averaged 430°C instead of the desired 450°C, and electrical heating tape of 1.0 kw capacity kept the calciner top temperature at 350-425°C.

Table 2.4. Control Limits and Operating Conditions for Tests R-65 and R-66

Control	Control Scale	Set Point, % of Scale	Proportional Band, %	Reset Time, min	Over Limits		Under Limits		% of time out of control	Total Control Time, hr	Control Limits, % of scale
					No. of times	% of time	No. of times	% of time			
Test R-65											
Calciner liquid level	58-62 liters	60	200	240	1	3	2	1.5	5	16	95-20
Evaporator density	1.0-2.0 g/cc	35	100	10	1	53	0	0	53	24	±5
Liquid level	22-27 liters	50	50	10	0	0	0	0	0	24	±20
Acidity	1.2-2.0 <u>M</u>	50	200	10	2	0.6	6	5.5	6	24	±15
Vapor pressure	-5 to +5 psig	40	20	1.0	0	0	1	1	1	24	±2
Test R-66											
Calciner liquid level	58-62 liters	60	200	150	0	16	0	16	9	18	95-20
Evaporator density	1.0-2.0 g/cc	35	100	10	1	8	1	9	1	38	±5
Liquid level	22-27 liters	50	50	10	0	0	0	0	0	28	±2
Acidity	1.2-2.0 <u>M</u>	50	200	10	0	4	0	4	2	28	±15
Vapor pressure	-5 to +5 psig	40	20	1	1	0.3	2	1	2	38	±2

Table 2.5. Hourly system variables and parameters

TEST NO R-65		FEED TYPE - TBP-25			OPERATION MODE - CONTINUOUS					
RUN TIME	FEED	WATER	CALCINER ADDITIVE	EVAP. COND.	CALCINER FURNACE	CALCINER COND.	EVAP. COND.	SYSTEM OFF-GAS	EVAP. DENSITY	
HOURS	LITERS	LITERS	LITERS	LITERS	(HUNDRED-THOUSANDS OF BTUS)			CU FT	GM/CC	
1	59.	0.	-0.	54.	1.37	0.96	1.83	-0.	1.34	
2	110.	0.	-0.	223.	2.94	2.16	3.61	-0.	1.39	
3	153.	125.	-0.	445.	4.44	3.47	6.41	-0.	1.38	
4	196.	303.	-0.	677.	6.01	4.84	10.94	-0.	1.34	
5	252.	477.	-0.	908.	7.51	6.04	17.09	-0.	1.31	
6	295.	655.	-0.	1070.	8.95	6.99	22.24	-0.	1.35	
7	341.	769.	-0.	1213.	10.04	7.68	25.87	-0.	1.38	
8	368.	882.	-0.	1323.	10.86	8.44	28.78	-0.	1.40	
9	390.	969.	-0.	1398.	11.47	9.12	31.04	-0.	1.40	
10	410.	1022.	-0.	1473.	12.29	9.69	32.58	-0.	1.41	
11	426.	1079.	-0.	1546.	12.91	10.27	33.97	-0.	1.41	
12	440.	1136.	-0.	1617.	13.52	10.74	35.22	-0.	1.42	
13	453.	1193.	-0.	1675.	14.07	11.07	36.45	-0.	1.42	
14	453.	1250.	-0.	1705.	14.62	11.35	37.48	-0.	1.42	
15	453.	1280.	-0.	1762.	15.09	11.68	37.85	-0.	1.42	
16	453.	1337.	-0.	1762.	15.44	11.97	38.28	-0.	1.44	
17	453.	1337.	-0.	1788.	15.85	12.11	38.49	-0.	1.44	
18	453.	1363.	-0.	1794.	16.26	12.39	38.91	-0.	1.45	
19	459.	1363.	-0.	1824.	16.60	12.49	39.12	-0.	1.45	
20	459.	1393.	-0.	1824.	16.87	12.68	39.33	-0.	1.48	
21	459.	1393.	-0.	1858.	17.21	12.77	39.54	-0.	1.52	
22	467.	1419.	-0.	1867.	17.35	12.86	39.74	-0.	1.53	
23	476.	1419.	-0.	1867.	17.48	13.01	39.96	-0.	1.56	

RUN TIME	EVAP. LIQUID H+	EVAP. MAJOR CATION FE OR AL	CALCINER COND. H+	EVAP. COND. H+	EVAP. COND. MAJOR ION FE OR AL	EVAP. COND. RU	EVAP. LIQUID TEMP.	EVAP. VAPOR TEMP.	CALCINER FEED TEMP.	CALCINER OFF-GAS TEMP.
HOURS	MOLAR	GM/LITER	MOLAR	MOLAR	GM/LITER	GM/LITER	DEG.C	DEG.C	DEG.C	DEG.C
1	1.70	58.8	5.20	1.90	0.003	-0.	111.	110.	104.	350.
2	1.18	72.0	5.00	1.54	0.003	-0.	112.	114.	108.	470.
3	1.94	66.6	7.00	2.34	0.003	-0.	112.	114.	107.	365.
4	1.67	58.2	6.06	1.52	0.002	-0.	109.	112.	104.	345.
5	2.09	51.4	6.77	1.16	0.003	-0.	108.	110.	104.	226.
6	1.47	63.0	7.15	1.37	0.003	-0.	110.	112.	105.	215.
7	1.17	70.4	7.79	1.54	0.003	-0.	112.	114.	106.	202.
8	0.97	75.6	8.02	1.66	0.002	-0.	114.	116.	108.	186.
9	0.70	76.0	6.95	1.66	0.002	-0.	115.	116.	106.	182.
10	0.62	78.9	6.89	1.65	0.003	-0.	116.	116.	107.	192.
11	1.19	79.9	6.70	1.68	0.004	-0.	116.	116.	107.	193.
12	0.58	80.6	7.20	1.64	0.002	-0.	117.	116.	106.	192.
13	0.64	82.4	7.61	1.82	0.004	-0.	116.	116.	106.	180.
14	0.49	83.1	9.64	1.62	0.002	-0.	117.	116.	106.	222.
15	0.39	84.9	8.85	1.50	0.003	-0.	118.	115.	106.	225.
16	0.38	68.5	9.32	1.59	0.002	-0.	118.	110.	107.	240.
17	0.61	83.4	7.30	1.54	0.003	-0.	118.	110.	106.	242.
18	0.78	87.0	7.75	1.74	0.003	-0.	118.	110.	107.	202.
19	0.65	89.7	5.15	1.92	0.003	-0.	119.	110.	107.	229.
20	0.47	88.8	4.51	1.86	0.003	-0.	120.	110.	107.	198.
21	0.24	95.7	3.26	1.93	0.003	-0.	121.	110.	109.	206.
22	0.05	98.9	2.35	1.41	0.003	-0.	123.	110.	108.	198.
23	0.	108.0	2.02	1.66	0.003	-0.	126.	112.	109.	181.

The run was continuous, with 449 liters of solution containing 47 g of aluminum and 428 g of nitrate per liter fed in 22 hr at an average rate of 16.5 liters/hr (max. 55 liters/hr). The water/feed volume ratio was very high, 6.4, because of the amount of water used in steam sweeping the off-gas lines and the low nitric acid concentration maintained in the evaporator condensate. This concentration was 1.5-1.8 M during the entire test except for the last 10 hr, during which it decreased to less than 0.2 M. Material balances were very good: nitrate 88%, aluminum 95%, and mercury 98%. The iron balance was 200%, probably because of pot corrosion. The thermal conductivity of the cake varied from a high of $2.4 \text{ Btu hr}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$ to a low of 0.27, averaging 1.3.

The control limits for the run and the hourly system variables and parameters are shown in Tables 2.4 and 2.6.

2.4 Fixation in Glass (W. E. Clark, H. W. Godbee, F. R. Clayton)

Aluminum borophosphate glasses were prepared which contained up to 20 wt % Darex waste oxides and did not become visibly devitrified on overnight annealing. Volume reductions were 2.5 to 3.8, initial softening temperatures varied from 750 to 850°C, and bulk densities varied from 2.44 to 2.74 g/ml (Fig. 2.9a, Table 2.7).

Glassy products containing up to 25 wt % waste oxides and 35.3 wt % P_2O_5 normally became devitrified on annealing or showed segregation. The solids showed a wide range of properties, from crystalline materials that softened at as low as 800°C, through "glasses," to calcined solids that showed no sign of melting at 1050°C (Table 2.9, Fig. 2.10). Two of these products (Nos. 2 and 3 Table 2.8, Fig. 2.9b) appeared to be true glasses, but became devitrified to some degree when prepared in larger batches which allowed more complete annealing. Volume reductions were 4.4 and 4.9, and bulk densities were 2.56 and 2.86 g/ml, respectively.

Specimens of two Darex products (No. 5 Table 2.7 and No. 3 Table 2.8) were spiked with Cs-137 and leached with a stream of distilled water as previously described (4). After 168 hr exposure the cumulative leaching rates were 1.7×10^{-7} and $8.7 \times 10^{-3} \text{ g/cm}^2\cdot\text{day}$, respectively. The tests are continuing.

Ruthenium Volatilization in Semicontinuous Glass Formation. The addition of extra phosphite did not prevent volatilization of ruthenium from the hot walls of the container during glass formation from simulated TBP-25 waste containing 0.3 μC of Ru-106 and 2 μC of Pm-147 per milliliter. The additives were 2.25 M NaH_2PO_2 and 0.25 M PbO ; 16.2% of the total ruthenium, but less than 0.11% of the promethium, went into the condensate and off-gas in a semicontinuous evaporation, calcination, and fusion, ruthenium by volatilization and promethium by physical entrainment. The experiments were carried out essentially like those reported previously (5), where 2.0 M NaH_2PO_2 was added and 12.5% ruthenium volatilized. In order to follow the volatilization of the ruthenium with time, the condensate was siphoned through a tube which passed directly above the counting crystal of a gamma

Table 2.6. Hourly system variables and parameters, Part A

TEST NO R-66		FEED TYPE - TBP-25			OPERATION MODE - CONTINUOUS				
RUN TIME	FEED	WATER	CALCINER ADDITIVE	EVAP. COND.	CALCINER FURNACE	CALCINER COND.	EVAP. COND.	SYSTEM OFF-GAS	EVAP. DENSITY
HOURS	LITERS	LITERS	LITERS	LITERS	(HUNDRED-THOUSANDS OF BTUS)			CU FT	GM/CC
1	55.	26.	-0.	68.	0.27	0.20	0.37	-0.	1.35
2	96.	26.	-0.	137.	1.78	1.42	1.44	-0.	1.35
3	136.	53.	-0.	288.	3.28	2.53	3.70	-0.	1.35
4	175.	163.	-0.	502.	4.64	4.09	9.17	-0.	1.29
5	209.	340.	-0.	835.	6.15	5.23	14.94	-0.	1.26
6	245.	635.	-0.	1007.	7.79	6.40	21.42	-0.	1.31
7	292.	757.	-0.	1126.	8.95	7.31	25.03	-0.	1.42
8	329.	837.	-0.	1234.	10.18	8.11	27.62	-0.	1.39
9	352.	920.	-0.	1276.	11.00	8.71	29.23	-0.	1.38
10	365.	946.	-0.	1337.	11.68	9.34	30.25	-0.	1.36
11	372.	1000.	-0.	1388.	12.36	9.81	31.01	-0.	1.36
12	394.	1026.	-0.	1417.	12.77	10.39	31.82	-0.	1.37
13	394.	1052.	-0.	1458.	13.52	10.80	32.63	-0.	1.36
14	407.	1079.	-0.	1467.	13.86	11.21	33.44	-0.	1.36
15	414.	1079.	-0.	1507.	14.55	11.56	34.28	-0.	1.36
16	421.	1109.	-0.	1551.	15.03	12.00	34.69	-0.	1.36
17	436.	1136.	-0.	1552.	15.50	12.44	35.10	-0.	1.35
18	436.	1136.	-0.	1588.	15.91	12.72	35.73	-0.	1.34
19	443.	1162.	-0.	1590.	16.46	13.12	36.16	-0.	1.36
20	443.	1162.	-0.	1626.	16.87	13.48	36.36	-0.	1.36
21	449.	1189.	-0.	1629.	17.21	13.76	36.78	-0.	1.34
22	449.	1189.	-0.	1630.	17.48	13.95	37.19	-0.	1.34
23	449.	1189.	-0.	1657.	17.96	14.16	37.38	-0.	1.34
24	449.	1215.	-0.	1684.	18.17	14.32	37.59	-0.	1.33
25	449.	1242.	-0.	1684.	18.65	14.56	37.78	-0.	1.34
26	449.	1242.	-0.	1684.	18.92	14.76	37.97	-0.	1.34
27	449.	1242.	-0.	1714.	19.40	14.88	38.16	-0.	1.32
28	449.	1272.	-0.	1787.	19.47	15.06	38.34	-0.	1.30
29	449.	1345.	-0.	1949.	20.01	15.17	38.34	-0.	1.32
30	449.	1506.	-0.	2116.	20.15	15.27	38.34	-0.	1.32
31	449.	1673.	-0.	2222.	20.56	15.35	38.34	-0.	1.33
32	449.	1779.	-0.	2422.	20.63	15.51	38.34	-0.	1.31
33	449.	1779.	-0.	2592.	21.10	15.57	38.34	-0.	1.31
34	449.	2149.	-0.	2762.	21.17	15.66	38.34	-0.	-0.
35	449.	2319.	-0.	2932.	21.58	15.75	38.34	-0.	-0.
36	449.	2489.	-0.	3129.	21.65	15.84	38.34	-0.	-0.
37	449.	2686.	-0.	3299.	21.99	15.96	38.34	-0.	-0.

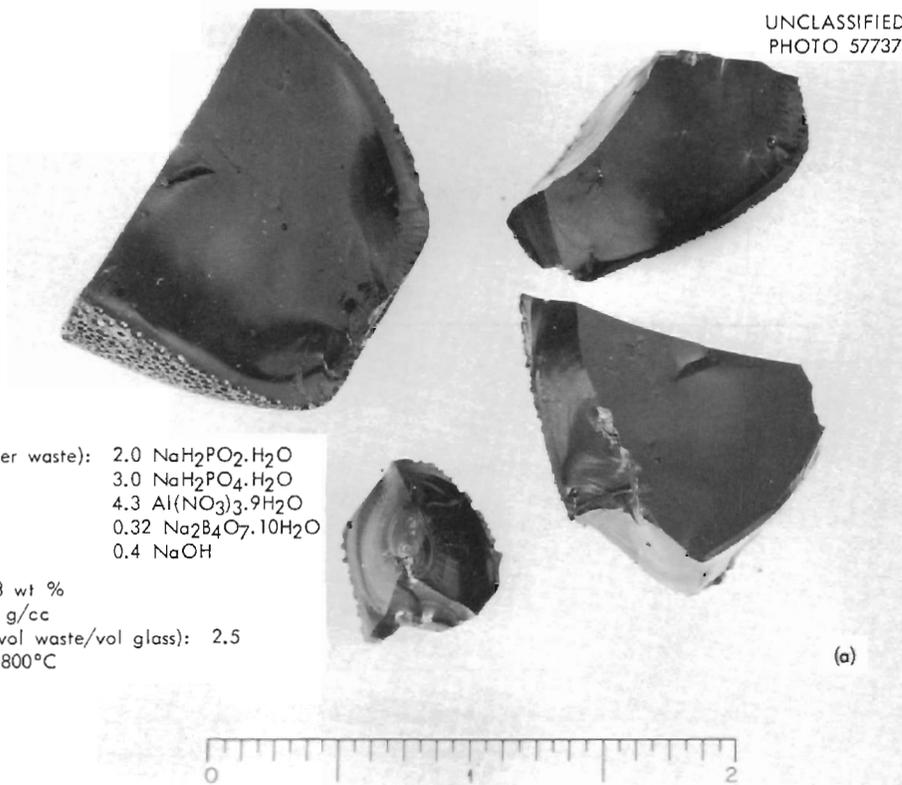
Table 2.6. Part B

TEST NO R-66		FEED TYPE - TBP-25			OPERATION MODE - CONTINUOUS					
RUN TIME	EVAP. LIQUID H+	EVAP. MAJOR CATION FE OR AL	CALCINER COND. H+	EVAP. COND. H+	EVAP. COND. MAJOR ION FE OR AL	EVAP. COND. RU	EVAP. LIQUID TEMP.	EVAP. VAPOR TEMP.	CALCINER FEED TEMP.	CALCINER OFF-GAS TEMP.
HOURS	MOLAR	GM/LITER	MOLAR	MOLAR	GM/LITER	GM/LITER	DEG.C	DEG.C	DEG.C	DEG.C
1	0.36	64.8	1.67	0.52	0.002	-0.	111.	104.	99.	150.
2	1.74	60.3	2.38	1.56	0.002	-0.	111.	110.	105.	370.
3	2.76	47.2	5.20	1.94	0.002	-0.	110.	110.	104.	290.
4	2.64	45.2	5.99	1.37	0.002	-0.	109.	110.	104.	292.
5	3.04	38.8	7.85	0.90	0.002	-0.	110.	109.	102.	295.
6	1.60	51.8	6.21	0.92	0.003	-0.	108.	110.	103.	294.
7	0.86	74.4	6.71	1.70	0.003	-0.	116.	116.	110.	345.
8	1.30	69.0	6.26	1.86	0.003	-0.	112.	114.	132.	323.
9	1.41	65.4	6.26	1.72	0.002	-0.	112.	113.	109.	348.
10	1.90	60.8	5.63	1.86	0.003	-0.	111.	113.	108.	348.
11	1.90	59.9	4.86	1.75	0.002	-0.	111.	112.	123.	355.
12	1.83	61.3	5.20	1.82	0.003	-0.	111.	112.	124.	360.
13	1.86	62.2	4.47	1.70	0.001	-0.	111.	108.	107.	370.
14	1.90	62.0	4.69	1.93	0.002	-0.	111.	108.	122.	370.
15	1.86	62.0	4.84	1.72	0.002	-0.	110.	109.	108.	375.
16	1.94	56.9	4.70	1.84	0.002	-0.	110.	109.	108.	380.
17	2.40	58.4	4.60	1.90	0.002	-0.	110.	110.	108.	380.
18	2.53	56.1	4.29	1.99	0.002	-0.	110.	110.	108.	380.
19	2.40	56.6	3.25	1.82	0.002	-0.	110.	109.	107.	380.
20	2.74	56.1	4.54	1.95	0.001	-0.	110.	110.	108.	395.
21	1.96	58.2	3.78	1.46	0.002	-0.	110.	108.	106.	415.
22	2.34	57.5	4.84	1.74	0.002	-0.	110.	109.	107.	420.
23	2.70	54.2	4.79	1.90	0.002	-0.	111.	109.	107.	410.
24	2.98	52.2	5.42	2.00	0.002	-0.	110.	109.	106.	415.
25	2.38	54.2	6.00	1.53	0.002	-0.	109.	108.	106.	420.
26	2.87	52.7	5.97	1.76	0.002	-0.	110.	109.	106.	420.
27	3.18	48.7	4.20	1.74	0.002	-0.	110.	109.	107.	415.
28	3.28	43.5	5.25	1.86	0.003	-0.	110.	109.	106.	425.
29	2.71	43.5	5.65	0.34	0.003	-0.	114.	-0.	-0.	430.
30	2.58	42.3	6.20	0.20	0.003	-0.	103.	-0.	-0.	420.
31	2.62	42.9	6.04	0.15	0.002	-0.	103.	-0.	-0.	420.
32	2.10	43.4	4.73	0.11	0.002	-0.	112.	-0.	-0.	440.
33	1.36	44.4	3.55	0.08	0.002	-0.	102.	-0.	-0.	410.
34	1.04	44.7	2.73	0.70	0.002	-0.	101.	-0.	-0.	420.
35	0.78	45.6	1.65	0.60	0.003	-0.	101.	-0.	-0.	430.
36	0.73	45.0	1.54	0.04	0.002	-0.	101.	-0.	-0.	420.
37	0.56	45.0	0.84	0.03	0.003	-0.	100.	-0.	-0.	420.

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Additives (moles/liter waste):
2.0 $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$
3.0 $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
4.3 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
0.32 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
0.4 NaOH

Waste oxides: 15.3 wt %
Bulk density: 2.61 g/cc
Volume reduction (vol waste/vol glass): 2.5
Softening point: $\sim 800^\circ\text{C}$



Additives (moles/liter waste):
2.8 $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$
1.0 B_2O_3
1.44 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Waste oxides: 25.0 wt %
Bulk density: 2.86 g/cc
Volume reduction (vol waste/vol glass): 4.9
Softening point: $\sim 900^\circ\text{C}$

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Fig. 2.9. Batch-formed glass incorporating (a) 15.3 and (b) 25 wt % Darex waste oxides

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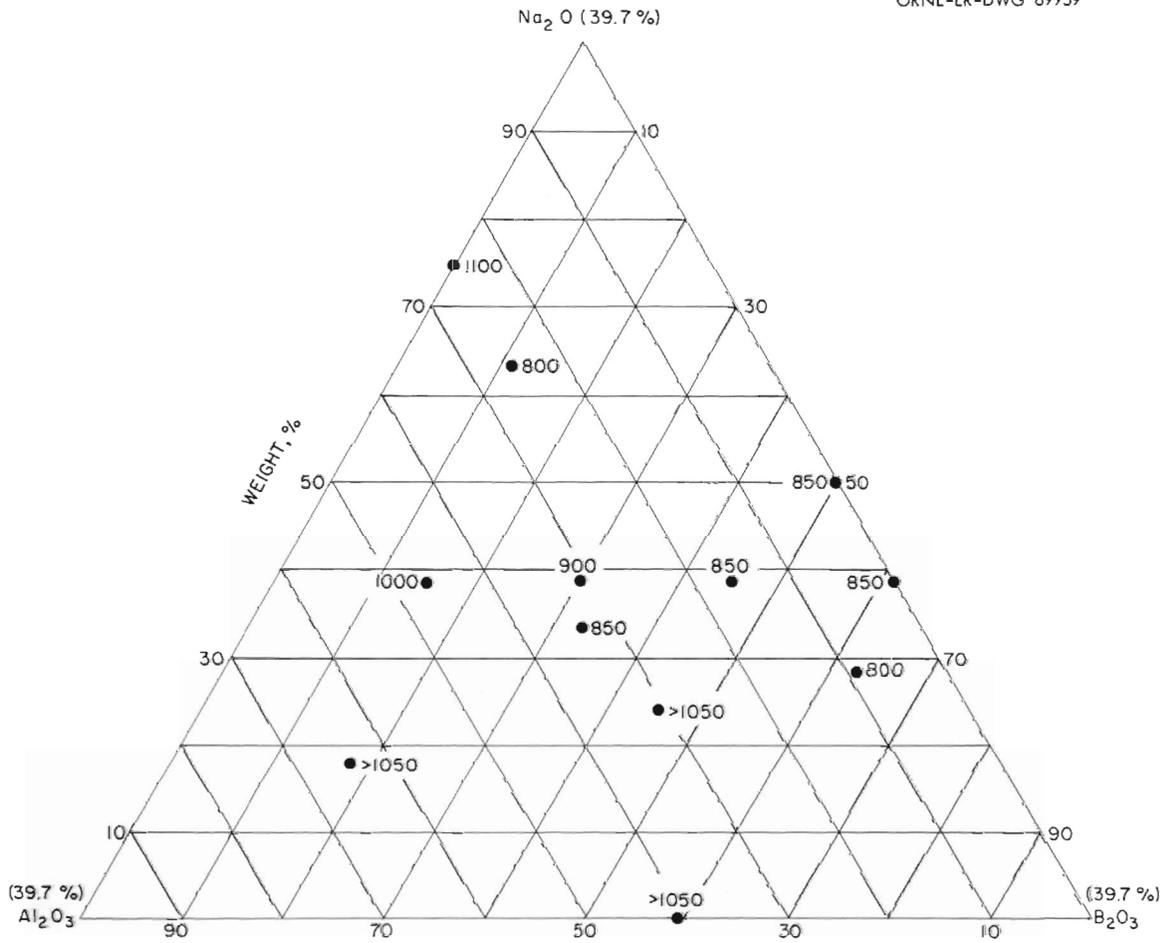


Fig. 2.10. Composition and initial softening temperatures ($^{\circ}\text{C}$) of solid products incorporating 25% Darex waste oxides and 35.3% P_2O_5 .

Table 2.7. Phosphate and Borophosphate Melts Incorporating Darex Waste Oxides

	Melt 1	Melt 2	Melt 3	Melt 4	Melt 5	Melt 6	Melt 7
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 PO ₂ ·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
Oxides, wt % theoretical							
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 oxides in melt, wt %	20.3	19.5	17.4	16.5	15.3	15.1	14.4
Vol reduction (waste sol'n to melt)	3.8	---	3.2	3.0	2.5	2.5	2.6
Appearance	Black glass, some seg- rega- tion	Some- what glassy, segre- gated	Brown glass	Black glass	Excel- lent black- brown glass	Brown- black glass	Deep brown glass

Table 2.8. Fixation Products Containing 25% Darex Waste Oxides and 35.3% P₂O₅
Darex waste, M: 6.0 NO₃⁻, 0.75 H⁺, 1.25 Fe³⁺, 0.38 Cr³⁺, 0.18 Ni⁺⁺, 0.04 Mn⁺⁺, 0.002 Ru

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11	No. 12
Additives, moles/liter												
NaH ₂ PO ₂ ·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	---	---	---
Oxides, wt % theoretical												
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	---	---	---	---	---	---	---
Vol reduction (waste sol'n to melt)	---	4.4	4.9	---	---	---	---	---	---	---	---	---
Appearance	Green, micro- crystal- line	Good black glass	Good black glass	Gray- black, metal- lic sheen	Rock- like very hard	Sinter- ed, did not melt below 1050°C	Green crystal- line, partly glassy	Gray, metallic, partly glassy	Brown- black, micro- crystal- line	Brown, crumbly, did not melt be- low 1050°C	Green- black, rock- like, segre- gated, did not melt be- low 1050°C	Gray- green, crys- talline

scintillation counter. Because of considerable difficulty with gas lock in the siphon due to accumulation of oxides of nitrogen, the trace of activity vs time (Fig. 2.11) is only approximate. Comparison of the plot of the Ru-106 activity vs time with plots of temperature vs time for the thermocouples in the fixation pot indicated that the larger increases in activity corresponded to times at which sudden meltdown occurred in the fixation pot after the inventory of unmelted solid had been allowed to build up to an abnormal depth.

Table 2.9. Volatilization of Ru-106 and Entrainment of Pm-147 during Semicontinuous Fixation of TBP-25 Waste in a Phosphate-Lead Glass

Simulated waste composition: 1.3 M H^+ , 6.6 M NO_3^- , 1.72 M Al^{3+} , 0.003 M Fe^{3+} , 0.02 M Hg^{++} , 0.0003 M Ru^{3+} . Fixation additives: 2.25 M NaH_2PO_2 , 0.25 M PbO .

	Vol, ml	dpm/ml	% of original
Ru-106			
Feed	2.7×10^4	6.15×10^5	
Condensate	2.68×10^4	1.0×10^5	16.1
Secondary off-gas	2.15×10^3	700	0.009
Jet pot liquid	5.4×10^3	140	0.005
Recycle liquid	2.4×10^4	720	0.1
			16.2
Pm-147			
Feed	2.7×10^4	1.87×10^6	
Condensate	2.68×10^4	$< 2 \times 10^3$	< 0.106
Secondary off-gas	2.15×10^3	< 100	$< 4 \times 10^{-4}$
Jet pot liquid	5.4×10^3	< 100	$< 1 \times 10^{-3}$
Recycle liquid	2.4×10^4	< 100	$< 5 \times 10^{-4}$
			< 0.11

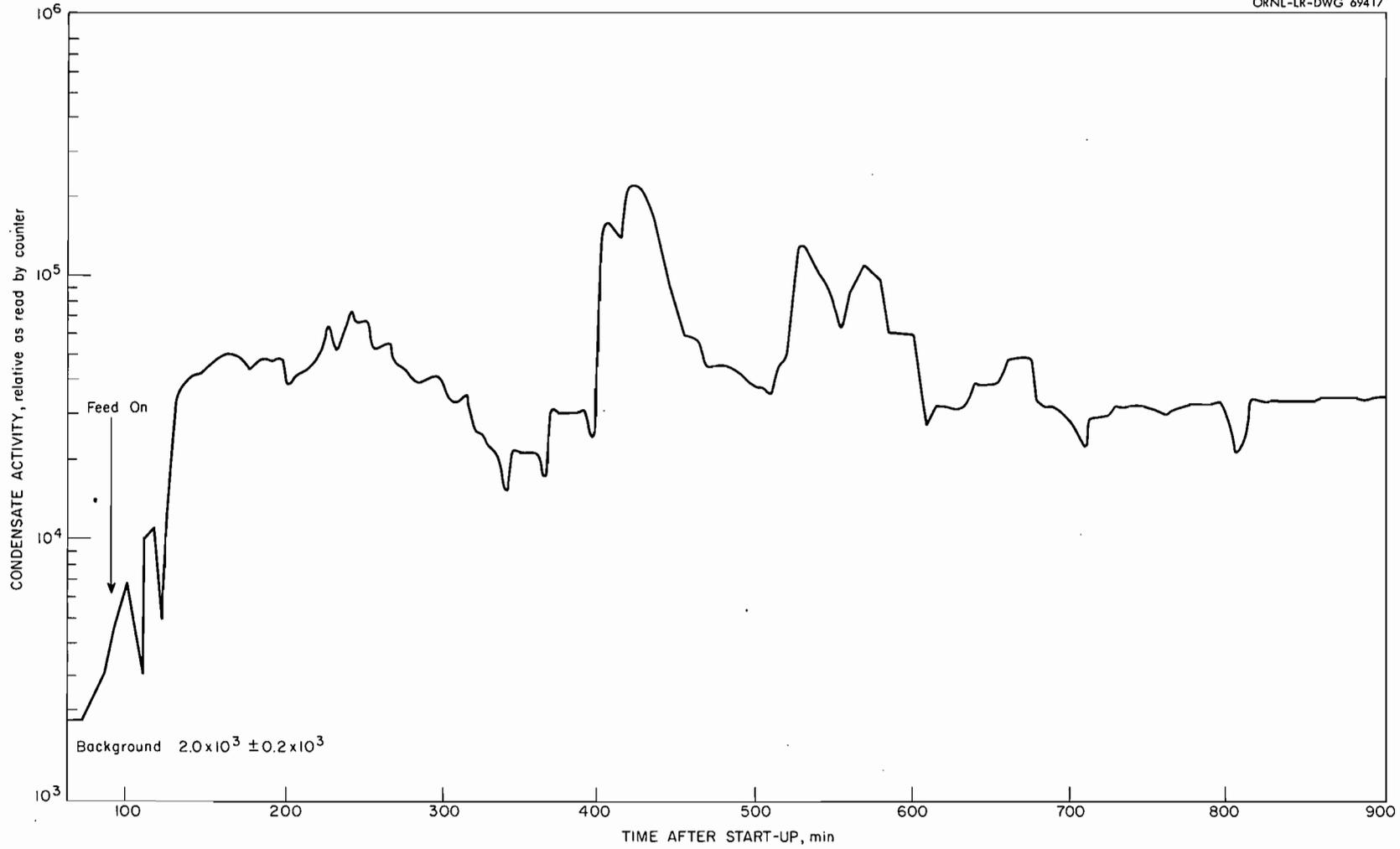


Fig. 2.11. Variation of volatile ruthenium activity with time during semicontinuous fixation of TBP-25 waste in phosphate-lead glass.

The mechanism of ruthenium volatilization under these circumstances is unknown; the liquid condensate does not show the colors usually associated with ruthenium distilled from nitrate solutions. It is believed that the amount of ruthenium volatilized can, however, be considerably decreased by controlling the method of operation so as to keep the inventory of unmelted solid product always at a minimum, thus minimizing the amount of dry solid which will be exposed on the walls at any given time.

Pressure Buildup from Glass. The results of 30 days' heating of a glass prepared similarly to the above indicated that there will not be an appreciable buildup of pressure in storage. A batch of glass prepared as above was heated to 900°C in a leak-tested stainless steel container, the container being vented to a gas train consisting of a condensate receiver, a drying tube, a gas sample bottle, a liquid trap, and a caustic bubbler (Fig. 2.12). When the internal temperature of the container became constant at 900°C, the gas train was shut off and its internal pressure was measured and continuously recorded. A weight gain of 0.5 g was registered by the desiccant in the drying tube during the heating. When the container reached 900°C and was closed off, it developed a vacuum which increased slowly to about 27 in. H₂O, at which point the valve separating the container from the gas train developed a leak and the pressure rose to 12 in. vacuum (Fig. 2.13). After the leak was corrected the pressure decreased again to about 24 in. H₂O vacuum after a total of 30 days at 900°C. It is postulated that the vacuum is caused by reaction of the oxygen in the air space above the glass with the stainless steel container. Any water which may diffuse out of the molten glass must also react with the stainless steel to give oxide and hydrogen. The latter would diffuse out through the metal walls and apparently "leak-tight" seals to maintain the vacuum.

The prolonged exposure of the glass in the stainless steel container resulted in the glass acquiring a browner coloration than the original product, due to diffusion of corrosion product oxides through the fluid melt. Metallic lead was also present in much larger aggregates than was observed in the original glass, probably owing to reduction of lead oxide by the stainless steel. The outside wall of the container did not appear to have suffered extensive corrosion as a result of the long high-temperature exposure; the inner tube (Fig. 2.14) developed a leak during production of the glass and became filled with glass which had to be drilled out to allow insertion of a heater for use in measuring the thermal conductivity of the product (6). This drilling damaged the tube considerably, resulting in an apparently badly corroded tube.

2.5 Corrosion (W. E. Clark, Chemical Technology Division; L. Rice and D. N. Hess, Reactor Chemistry Division)

Coupling of type 304L stainless steel calcination pots and/or pot head assemblies to titanium appears to present no particular corrosion problem. Calculated corrosion rates, assuming that all corrosion occurs during the 2 hr exposure at 900°C (6) were 77 and 31 mils/mo for type 304L and titanium specimens, respectively, coupled to each other. There was no visual evidence of serious localized attack on either specimen. The rate for stainless steel is slightly in excess of the 61 mils/mo for stainless steel alone calculated from the 5.1 mil/mo rate for 24 hr exposure, but considering the assumptions made, these results probably agree within experimental error.

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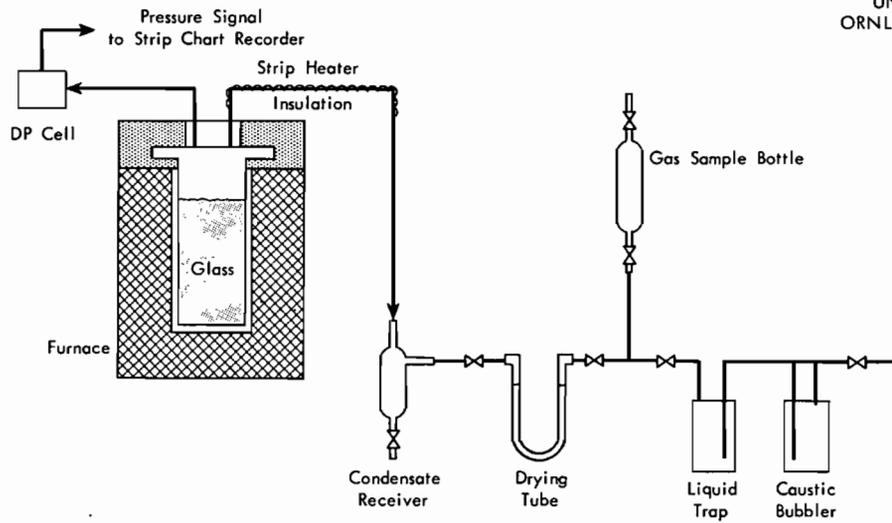


Fig. 2.12. Apparatus to measure pressure in sealed waste can during prolonged heating.

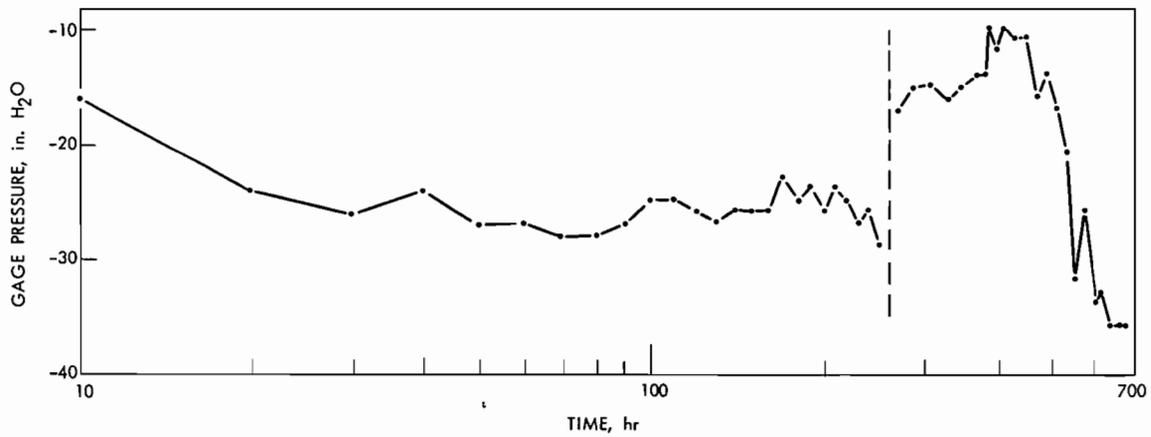


Fig. 2.13. Pressure in sealed waste can during prolonged heating of phosphate-lead glass to 900°C.

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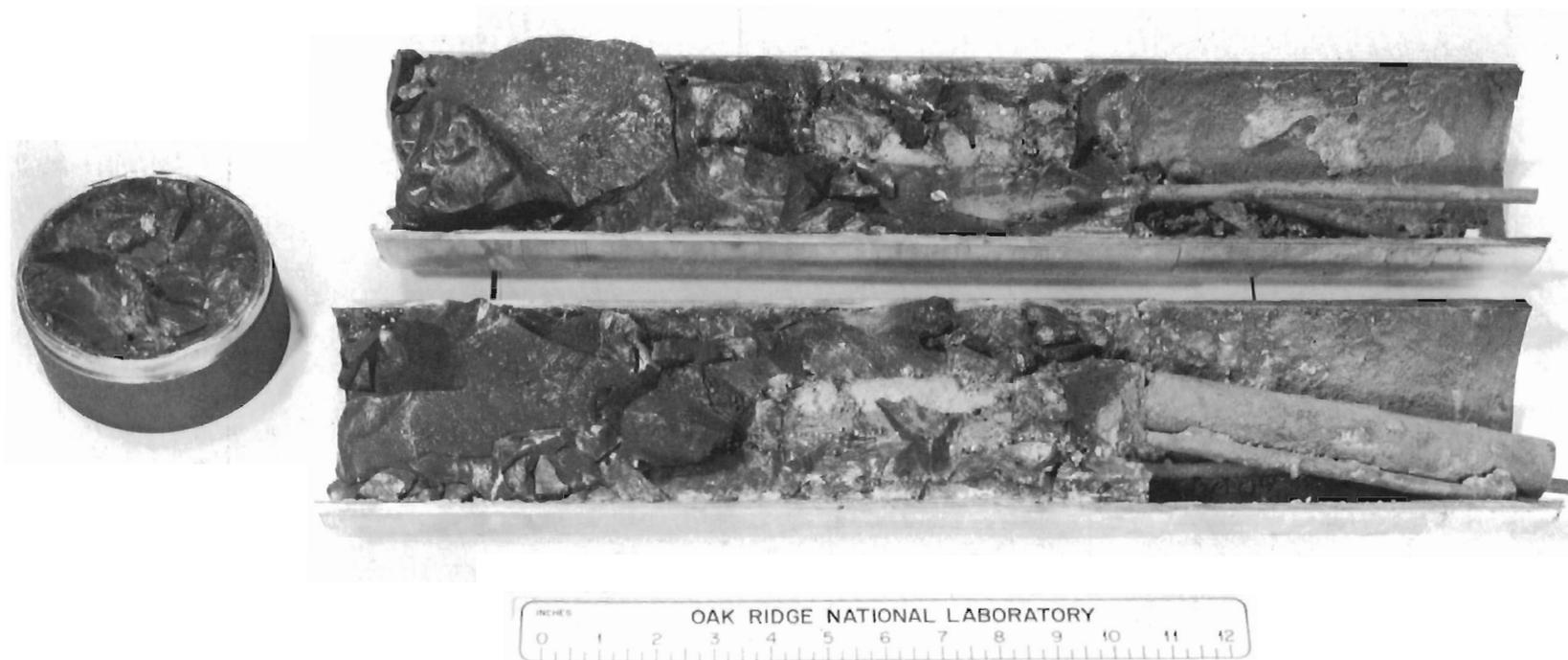


Fig. 2.14. Phosphate-lead glass incorporating simulated TBP-25 waste oxides after 30 days heating to 900°C in a stainless steel fixation pot.

It seems likely that coupling of 304L to titanium will result in no serious corrosion problems in the TBP-25 waste. The test was made in the modified calcination equipment (top flange and condenser tubing constructed from titanium). A titanium-45A specimen, coupled to type 304L stainless steel, was exposed to simulated TBP-25 waste solution during evaporation (3.5 hr at 265°C or less) and at the fixation temperature of ~900°C for 2 hr (Table 2.10).

Table 2.10. Distillate Collected during Evaporation and Fixation of TBP-25 Waste Solutions*

Time After Startup, hr	Average Temperature, °C	Vol of Constituents Collected over This Time Interval, ml
1-1/2	180	14
2	190	8
2-1/2	200	20
3	210	35
3-1/2	265	23
5-1/2	910	4

* Solution contained 1.3 M H^+ , 6.6 M NO_3^- , 1.72 M Al^{3+} , 0.16 g/l Fe^{3+} , 4.0 g/l Hg^{++} , 0.027 g/l Ru^{3+} , 26.5 g/l $NaH_2PO_2 \cdot H_2O$, and 7.0 g/l PbO . Original volume was 125 ml.

In a similar test in Purex waste, an uncoupled type 304L stainless steel specimen had a calculated overall corrosion rate in excess of 1300 mils/mo (6).

Previous tests (6) in which the corrosion of types 347 and 304L stainless steel were briefly compared were favorable to the latter. Visual observation of the stainless steel container used in the semicontinuous fixation of TBP wastes in glass (1) showed that the heaviest corrosion was associated with the type 347 stainless steel "spider" used to position the thermocouples in the pot (Fig. 2.15). At points of maximum corrosion the corrosion product was magnetic. Examination of the material by microscopy and by electron and x-ray diffraction indicated rather aggressive intergranular attack, particularly at the corners. The corrosion products included Fe_3O_4 and Cr_2O_3 . The Fe_3O_4 present was not sufficient to account for the high degree of magnetism found; the chromium appears to have been preferentially leached from the steel, leaving a magnetic layer of Fe-Ni (7). The inside of the can itself was slightly magnetic at certain points, but at no point did the attack appear to approach that on the spider.

The most aggressive attack on the pot walls is expected during the final stages of Purex glass fixation when the pot walls will be under tension at fixation temperatures.

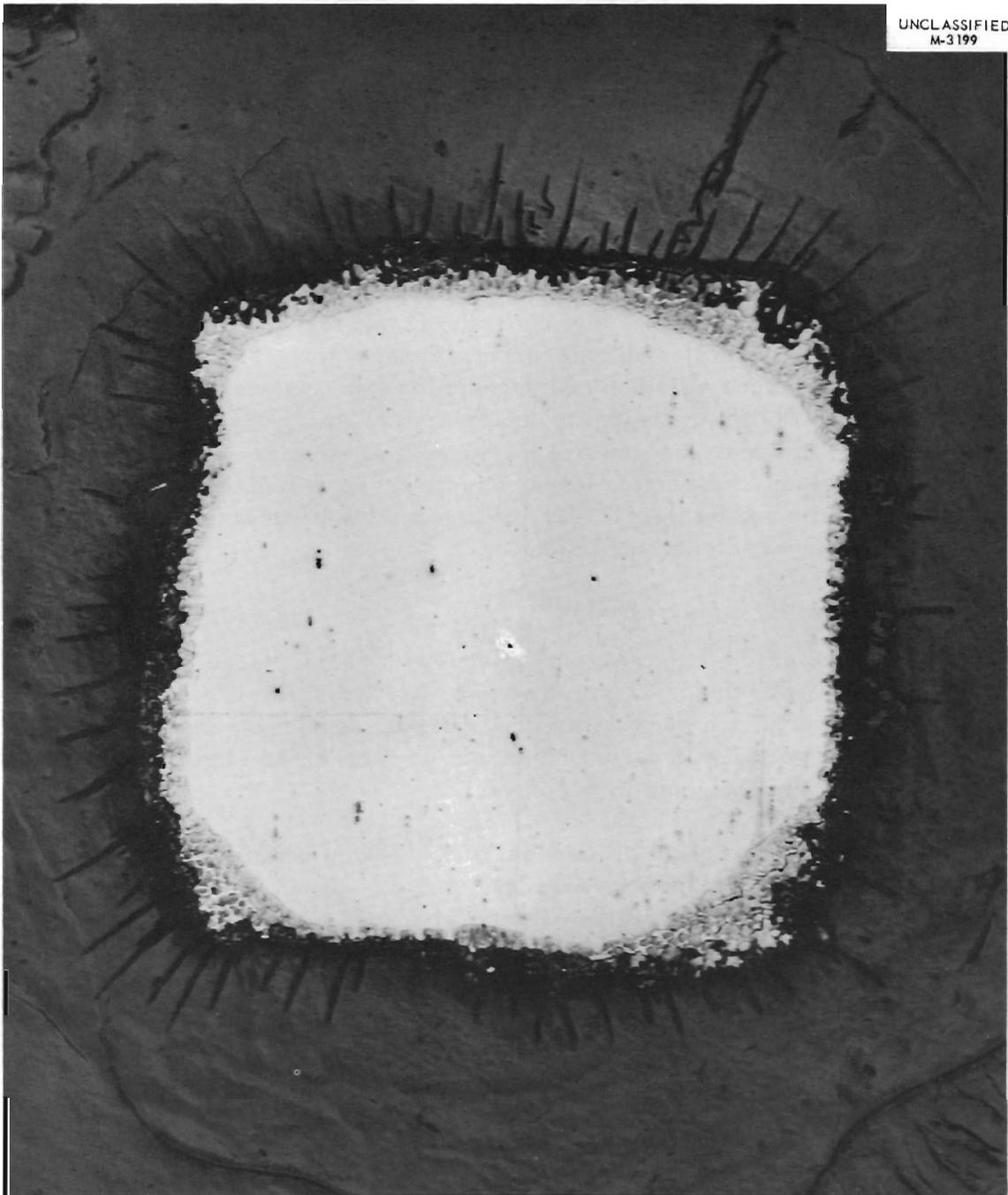


Fig. 2.15. Corrosion of 347 stainless steel "spider" in pot during formation of TBP glass. 20X. Reduced 16%.

Tests are being started in which small type 304L pots will be exposed to a Purex evaporation-glass fixation cycle, ending with prolonged heating at 1050°C while the pot is subjected to a tensile stress of 150 lb/in.² After a week's exposure at 1050°C, the specimen will be sectioned and examined.

3.0 LOW-LEVEL WASTE TREATMENT

A scavenging-ion exchange process (8,9) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations with ORNL low-activity-level waste as a medium for study. The process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; the Cs/Na separation factor is 160 for phenolic groups and 1.5 for sulfonic groups. Other cations, e.g., strontium and rare earths, are also sorbed efficiently. Inorganic ion exchange media, such as vermiculite and clinoptilolite, are being studied as alternatives. The waste solution must be clarified prior to ion exchange since these media do not remove colloidal materials efficiently. Water clarification techniques are being developed for both the ion exchange processes and for the ORNL lime-soda process waste water treatment plant, in both development and pilot plant programs.

3.1 Pilot Plant (R. E. Brooksbank)

Three demonstration runs were completed with ORNL process wastes, with volumes ranging from 49,000 to 55,000 gal. Two runs, HR-10 and HR-12, were made with all process equipment. Run HR-11 was made with the flocculation-precipitation equipment only in an attempt to decrease the total hardness of the clarifier effluent and to study the effect of phosphate in the process.

Operation. Throughout all previous runs, the total hardness of the clarifier effluent has averaged 59 ppm (as CaCO₃). Decrease of this value would significantly increase the on-stream life of the polishing filters and the resin column. For this reason, run HR-10 was made with 12.5 to 25 ppm of slaked lime as an additive to the flash mixer. Neither this treatment nor increasing the temperature of the feed stream from 18 to 24°C significantly decreased the effluent hardness. Radiochemical analysis of process streams indicated Sr-90 and Cs-137 decontamination factors of 2880 and 181, respectively, after 1500 bed volumes of process waste had been treated. The Cs-137 removal was 95% (compared to 99% in previous runs); however, plant effluent activity was < 1% of MPC_w for both Cs-137 and Sr-90 for a 168-hr week.

Run HR-11 was made to further test the addition of lime and the operability of the polishing filters after fresh anthracite was charged to the units. A total of 18,000 bed volumes was transferred through the replaced anthracite at a rate of 3.2 gal/min·ft². The need for frequent backwashing and decreased filter efficiency made the charge necessary.

Run HR-12 was started with standard flowsheet conditions (10 gpm of feed, 0.01 M NaOH, 5 ppm of Fe coagulant) but was terminated after 1500 bed volumes because of premature Sr-90 breakthrough ($C/C_0 = 25\%$, representing 500% of the MPC_w) due to phosphate in the feed solutions. The source of this contaminant (1-3 ppm) was traced to the periods when the BNL carrier was being decontaminated at the ORNL facility. The major contributor, Turco 4324, is known (10) to impede precipitation of calcium carbonate from water, thereby increasing the residual hardness of the polishing filter and clarifier effluents. Increased calcium loading of the resin bed would be expected under these conditions. At the end of this run, the total hardness of the plant effluent was 13 ppm, a factor of 13 higher than normal. Radiation γ scans of the resin bed indicated that displacement of Cs-137 from the bottom of the column started after 1022 bed volumes had been treated.

Process Material Balance. One objective of run HR-12 was to measure the distribution and behavior of major process chemicals. Back-washed solids from the polishing and sludge filters were packaged and weighed or dissolved with dilute nitric acid and the resultant solutions analyzed. During previous runs, it had been noted that the polishing filters, designed for turbidity removal, also decreased the residual total hardness, from 70 to 10 ppm, in the absence of phosphate. A material balance run, made to check the reliability of in-plant analyses used for process control, showed only 0.69% of the hardness unaccounted for:

	<u>Hardness Removal, % of feed</u>
Precipitation-clarification	32.90
Anthracite filtration	45.10
Ion exchange	21.40
	<hr/>
	99.30
Effluent	<u>0.01</u>
	99.31
Unaccounted for	0.69

3.2 Laboratory Studies (R. R. Holcomb)

Recirculation of clarifier solids to the flash mixer in the laboratory scale model (5) decreased effluent hardness by a factor of 2-3. ORNL tap water containing ~100 ppm total hardness as $CaCO_3$ was treated in a flash mixer, sized for a 30-min holdup, at 250 ml/min with the standard caustic (0.01 M NaOH)-copperas (5 ppm Fe) process. The hardness of the water leaving the mixer decreased from 65-70 to 40-45 ppm as the vessel became coated with $CaCO_3$ deposit. The flash mixer was then coupled to the laboratory model clarifier (5), which affords 1-2 min flocculation and 10 min sludge blanket clarification. Sludge was recycled from the bottom of the sludge blanket to the flash mixer at 5-10% of the treatment rate to furnish preformed solids for seeding new precipitate. The total hardness of the water leaving the flash mixer

and clarifier averaged 40 and 8-14 ppm as CaCO_3 , respectively. Changing the copperas addition from the flash mixer to the flocculator decreased the hardnesses to 15 and 5.2 ppm, respectively. When ORNL low-activity waste was treated by the standard process above, the hardnesses were 56 and 54, respectively. The increase was attributed to the presence of hexametaphosphate (11), a constituent of detergents and decontaminating solutions such as Turco 4324.

The addition of excess sodium carbonate decreased the total residual hardness in the presence of Turco 4324. The clarification system was then operated with tap water with Turco 4324 added to simulate low-activity waste. Starting with tap water, the hardness of the flash mixer effluent and clarifier overflow remained constant at 15 and 5.6 ppm, respectively, for 72 hr. The addition of 1.7 ppm of Turco had no effect in 24 hr continuous operation. The Turco addition was then increased to 2.5 ppm, where it remained for 2 hr (four volume changes in the flash mixer), with no effect. Increasing the Turco concentration to 3.2 ppm caused an increase in hardness in the flash mixer effluent and clarifier overflow to 44 and 37 ppm, respectively, after 24 hr. The addition of 53 ppm (0.005 M) of Na_2CO_3 to the flash mixer decreased the residual hardnesses to 15 and 5.6 ppm within 16 hr.

These data indicate a threshold level of contaminant that will not interfere with the standard caustic-copperas treatment of low-activity waste. When this level is exceeded, the addition of sodium carbonate to the standard treatment will overcome the detrimental effect. The exact sodium carbonate requirement as a function of contaminant concentration and the effect of the increased sodium ion concentration on the ion exchange treatment will be defined in future experiments. A demonstration with actual waste is also required.

A complete water analysis for samples of tap and low-activity waste water showed most constituents constant or nearly so. Noteworthy variations were:

Constituent	Concentration, ppm	
	Tap Water	Waste Water
Total hardness (as CaCO_3)	87	94
Dissolved CO_2	1.8	10.6
Total solids	84.2	183
Na	3	30
U	<0.003	0.01
PO_4	<0.02	3.3
F	1	7
Cl	1.1	4.9

Vermiculite was definitely inferior to CS-100 resin for removing cesium and strontium from the caustic-copperas clarifier effluent. Sufficient results are now available from the small (7/8 in. i.d. by 6 in.) BO-4 grade vermiculite columns to determine the feasibility of using vermiculite as the ion exchange medium of the scavenging-ion exchange process. Four columns were operated on the actual waste stream at 1, 5, 15, and 50 ml/min, respectively. Breakthrough or leakage of cesium and strontium of at least 1% of the feed concentration and as high as 50% occurred at or prior to 1500 bed volumes in all columns except the first. The first column, 0.25 ml/min·cm², showed cesium in the effluent, ~50% breakthrough,* at 1000 bed volumes, but the d.f. for strontium was ~1000 up to 1500 bed volumes. This compares to cesium and strontium d. f. 's of 1100 and 1800, respectively, at 1500 bed volumes at a flow rate of 5 ml/min·cm² for CS-100 resin in a control run made at the same time. These results, together with the serious mechanical pressure drop problem encountered with the very fine vermiculite, indicate vermiculite to be a poor exchanger for use with the high-caustic head-end treatment.

4.0 ENGINEERING, ECONOMICS, AND HAZARDS EVALUATION

4.1 Shipment of Calcined Solids (J. O. Blomeke, R. L. Bradshaw, J. J. Perona)

Subject to the heat transfer limitations presented in the previous issue of this report, costs were calculated to be minimum for the largest casks considered manageable because the ratio of cask volume per pound of shielding weight increases as the cask size increases. These casks, 60 in. dia, can contain four, 24-in.-dia., nine, 12-in.-dia, or thirty-six, 6-in.-dia cylinders of calcined waste and weigh up to 100 tons. Shielding thicknesses of lead to give 10 mrem/hr at 3 meters at minimum shipping ages ranged from 21 to 25 cm for the various waste types. Iron shielding thicknesses were higher by a factor of 1.7 and uranium thicknesses lower by a factor of 0.56 than those of lead. Weights and costs for these casks at minimum ages were about 100 tons and \$50,000 for iron casks, 80 tons and \$120,000 for lead casks, and 65 tons and \$650,000 for uranium casks. Cask costs were amortized over 10 years at 4% interest.

Rail freight costs of \$44, \$82, and \$120 per ton were assumed for round-trip distances of 1000, 2000, and 3000 miles. Handling costs were assumed to be \$360 per trip plus \$13,000 per year amortization of a 100 ton bridge crane. Shipping costs were lowest in all cases for lead casks, but in some cases the use of lead casks required longer minimum ages. At 1000 miles the use of iron casks cost less than uranium casks, but at 3000 miles the cost of uranium casks is less than of iron and approaches the cost of lead. Costs in lead casks ranged from 0.70×10^{-3} mill/kwh_e for acidic Purex waste residue in four, 24-in.-dia cylinders per cask at 1000 miles to 32.3×10^{-3} mill/kwh_e for the shipment of reacidified Thorex in smaller cylinders at 3000 miles (Figs. 4.1 and 4.2).

*Based on a feed concentration which varied from 23 to 191 d/m·ml and an effluent concentration of 36.7 d/m·ml for cesium at 1000 bed volumes.

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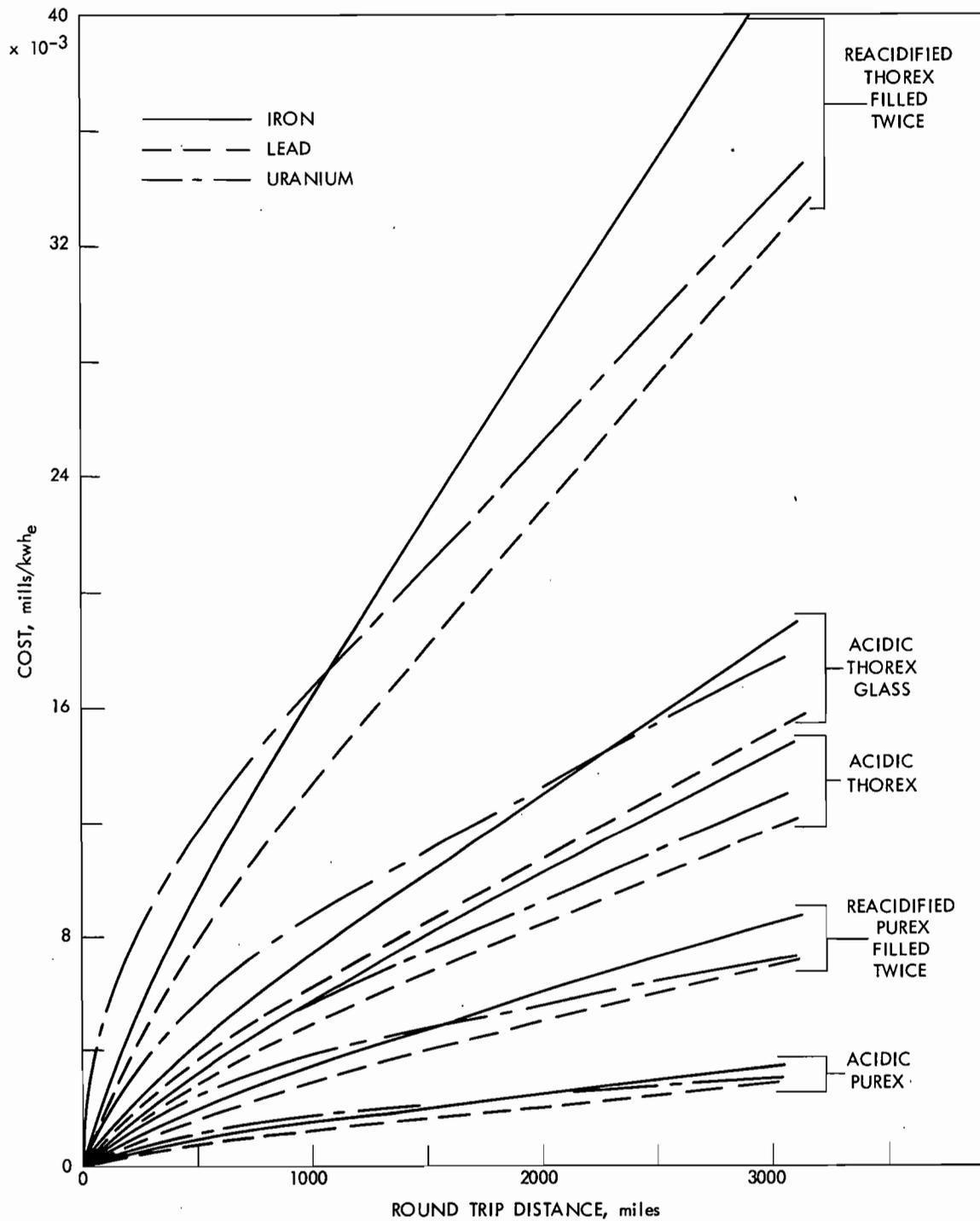


Fig. 4.1. Shipping costs for carriers containing thirty-six 6-in. dia cylinders or nine 12-in. dia cylinders.

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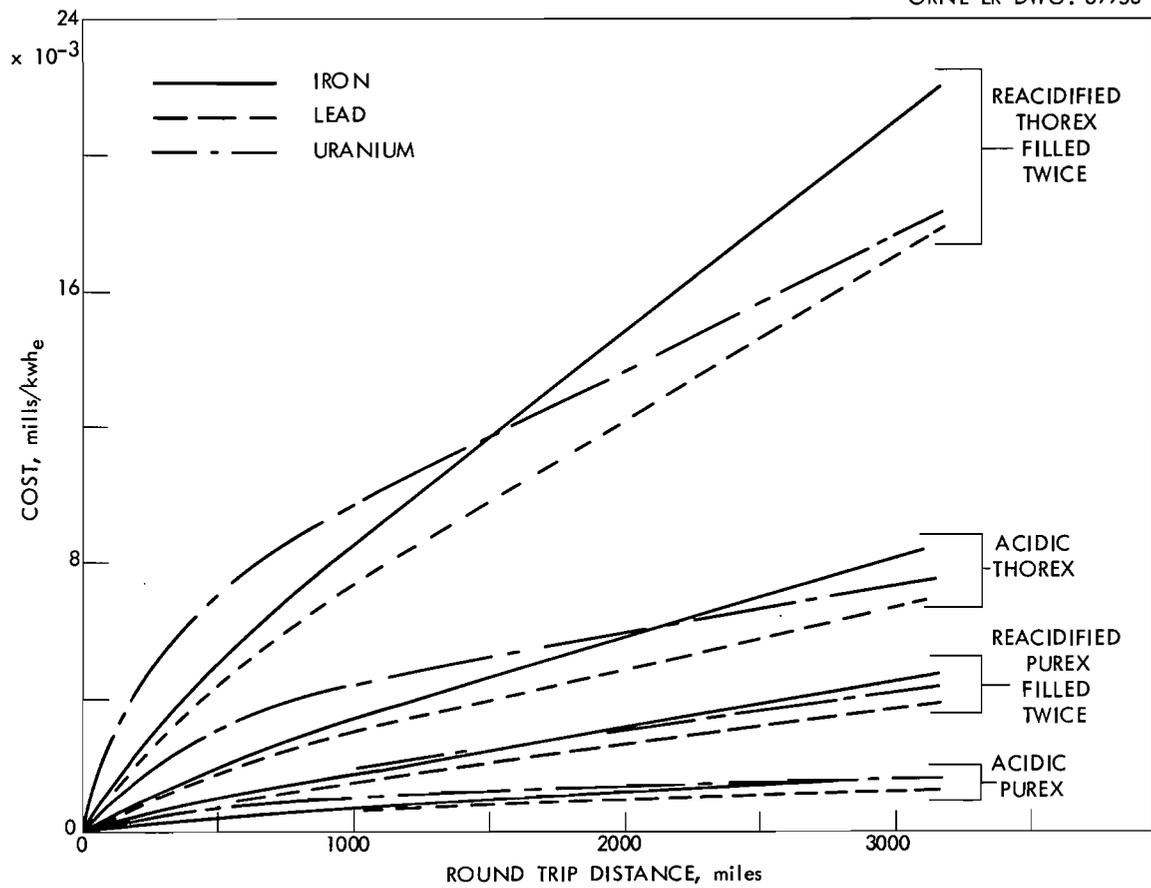


Fig. 4.2. Shipping costs for carriers containing four 24-in.-dia cylinders.

5.0 DEEP-WELL INJECTION OF RADIOACTIVE WASTES

D. G. Jacobs and O. M. Sealand

When radioactive liquids are discharged to the ground, the primary means of transport of activity is by movement of water through the formation. The radionuclides follow the same paths as the water but move at a slower velocity due to the sorptive properties of, primarily, the clay minerals in the formation. Although the sands constituting good aquifers are fairly clean, enough clay is present to give them a significant exchange capacity. Kaufmann et al. (12) found exchange capacities of several California oil sands to range from 0.48 to 20 meq/100 g with a mean value of ~5 meq/100 g.

5.1 Nature of the Wastes Considered for Deep-well Disposal

It seems most likely that initial application of deep-well techniques will be for disposal of the high-volume low-activity process waste water streams, ~400,000 gal of which is generated daily at ORNL (13). Its stable-chemical composition is essentially the same as local tap water, and Sr-90 is the only radionuclide present in concentration consistently above the permissible concentration for drinking water (Table 5.1). This waste stream is now treated by a modified water softening plant for removal of calcium and Sr-90 (~80%), and clay is added to remove ~85% of the Cs-137 (Sect. 3.0). The 200 years required for Sr-90 to decay to the permissible drinking-water concentration indicates the containment time required for safe disposal.

If deep well disposal proves satisfactory for low-level wastes, disposal of intermediate-level wastes could follow. The ORNL intermediate-level waste (13), which is produced at a daily rate of ~10,000 gal, has a high salt content (Table 5.1). Excess caustic (NaOH) is added to precipitate most of the calcium, Sr-90, and rare earths, and the supernate is discharged to the ground in near-surface trenches. Although most of the Sr-90 is removed during neutralization, it remains the hazard-controlling radionuclide in the supernate, its concentration being ~100,000 times the permissible drinking water concentration, and 450 years would be required for its decay to this concentration. Cesium-137 and Ru-106 are also above the permissible concentration levels in this waste stream.

Ion Exchange by Clays. Ion exchange by the clay minerals is caused primarily by charge deficiencies within the crystal lattice. The rigid structure of the lattice does not permit ions of opposite charge to reach the seat of the charge, and an electric double layer is established at the clay lattice surface. Unless specific steric effects are operative, ions of opposite charge to the surface (counterions) are held in a loosely bound state at the surface and can be stoichiometrically replaced by other ions of the same sign of charge. Ions of the same sign of charge as the surface (co-ions) are repelled rather than attracted by the surface. In temperate regions the electric charge on the clays is predominantly negative, giving rise to a cation-exchange capacity. Anions are not actively adsorbed by these clays except when islands of positive surface charge exist or when special sorptive processes are operative.

Table 5.1 Compositions of ORNL Process Waste Water and Intermediate-Activity Waste

Component	MPC _w * μc/ml	Half-life, years	Process Waste Water ^{14, 15}				Intermediate Activity Waste			
			Avg Conc, μc/ml	Avg Conc, ÷ MPC _w	Time to Decay to MPC _w , years	Stable Ion Avg Conc, M	Avg Conc, μc/ml	Avg Conc, ÷ MPC _w	Time to Decay to MPC _w , years	Stable Ion Avg Conc, M
Sr-90	10 ⁻⁶	28	1.4x10 ⁻⁴	140	200		0.1	10 ⁵	450	
Cs-137	2x10 ⁻⁴	27	1.6x10 ⁻⁴	0.80			2	10 ⁴	360	
Ru-106	10 ⁻⁴	1	1.4x10 ⁻⁵	0.14			0.5	5x10 ³	12	
Ca ⁺⁺						0.00086				
Mg ⁺⁺						0.00041				
Na ⁺						0.0012				0.615
NH ₄ ⁺										0.025
Al ³⁺										0.022
OH ⁻										0.022
NO ₃ ⁻										0.41
SO ₄ ⁼										0.037
Cl ⁻										0.006

* Continuous occupational exposure value (168-hr week) for critical organ from "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," NBS Handbook 69 (1959).

In most cases, unless the ion exchange process has modified the crystal structure of the clay, the exchange of ions is stoichiometrically reversible and is subject to the laws of mass action. Departures from mass-action laws are usually more significant from a theoretical than from a practical viewpoint.

When a liquid waste of a different composition than the native water is discharged into an aquifer, numerous changes occur. Radioactive cations are removed from solution by ion exchange and are deterred in their movement and stable ions in the waste are exchanged with those previously on the exchanger. If the total electrolyte concentration is greatly different, the zeta potential of the charged clay surface may change, resulting in dispersion (in systems with lower electrolyte concentration) or flocculation (in systems of higher electrolyte concentration) of the clays, and anion retardation may result from passive uptake (negative sorption) of them within the aqueous shear zone of the clay particle. At the leading edge of the waste solution invasion, the solution composition is altered until it comes into equilibrium with the ions on the exchanger, while near the point of injection, the ions at the exchanger surface come to equilibrium with the ionic composition of the waste solution. Between these boundaries is a transition zone where the ionic composition of the solution and the exchanger surface is at an intermediate state of equilibrium. The extent of the transition zone depends on the nonhomogeneity of the formation, the kinetics of the various exchange reactions, and the efficiency of contact between the solution and the exchanger.

Other chemical phenomena that may be important in altering the chemical and physical environment of the formation are precipitation, changes in oxidation-reduction potentials, and changes in pH. In fact, these changes may be of more importance than simple ion exchange in restricting movement of some of the radionuclides.

Fission-Product Movement in the Ground. The effect of ion exchange on the velocity of movement of a radionuclide compared to that of the transporting water can best be shown by sample calculations for the ORNL low- and intermediate-level waste streams and the exchange properties of Richfield sand (Table 5.2) which has a porosity of 35%, and exchange capacity Q of 6.86 meq/100 g, and a bulk density of 1.25 g/ml in our loosely packed columns.

Strontium. For a first approximation, we can assume that all the stable divalent ions behave similarly, and this is verified by experimental data. Sodium competes with the divalent ions for the exchange sites:



The selectivity coefficient for this exchange reaction for divalent ions compared to sodium, g/ml, is given by

$$K_{\text{Na}}^{\text{M}} = \left(\frac{q_{\text{M}}}{c_{\text{M}}} \right) \left(\frac{c_{\text{Na}}}{q_{\text{Na}}} \right)^2$$

Table 5.2. Calcium-Sodium-Strontium Exchange Properties of Richfield Sand

Ca^{++} meg/ml	Na^+ , meg/ml	Q meg/100 g	$K_{\text{Ca}}^{\text{Sr}}$	$K_{\text{Na}}^{\text{Ca}}$, g/ml	$K_{\text{Na}}^{\text{Sr}}$, g/ml
0.00	0.50	6.87	---	---	326
0.01	0.00	6.59	1.06	---	---
0.01	0.10	6.64	1.10	25.6	28.2
0.01	0.20	7.22	1.32	21.2	27.7
0.01	0.30	6.86	1.32	26.1	34.5
0.01	0.40	7.04	1.39	23.4	32.6
0.01	0.50	6.77	1.29	28.6	36.9
Avg		6.86	1.25	25.0	

where q_{Na} , q_{M} are the partial exchange capacities for sodium and divalent ions, meq/g, and c_{Na} and c_{M} are the equilibrium concentrations of sodium and divalent ions in solution, meq/ml, the total exchange capacity, $Q = 0.0686$ meq/g, is equal to the sum of the partial exchange capacities. Substitution of the concentrations of the ORNL low-activity waste stream in this expression ($K_{\text{Na}}^{\text{M}} = 25$ g/ml, $c_{\text{M}} = 0.00254$ meq/ml, and $c_{\text{Na}} = 0.0012$ meq/ml) indicates a partial divalent cation capacity of 6.73 meq/100 g.

Because the concentration of strontium is so much lower than that of the total divalent ions, the strontium will not affect the partial divalent ion capacity. The selectivity of strontium to calcium on the exchanger can be expressed by

$$K_{\text{Ca}}^{\text{Sr}} = 1.25 = \left(\frac{q_{\text{Sr}}}{c_{\text{Sr}}} \right) \left(\frac{c_{\text{Ca}}}{q_{\text{Ca}}} \right).$$

A useful term in describing ion movement in a continuous exchange system or ion distribution in an equilibrium system is K_{d} . K_{d} is defined as the ratio of the concentration of an ion sorbed per unit weight of exchanger to the concentration of unsorbed ion per unit volume of solution, or $K_{\text{d}} = q/c$ for a given ion. With the units for measuring concentration described above, K_{d} has dimensions of milliliters per gram.

From the expression of Sr-divalent ion exchange, K_{d} for strontium is given by

$$(K_d)_{Sr} = K_{Ca}^{Sr} \left(\frac{q_{Ca}}{c_{Ca}} \right) = 1.25 \left(\frac{0.0673 \text{ meq/g}}{0.00254 \text{ meq/ml}} \right) = 33.1 \text{ ml/g}$$

We further note from this expression and from the expression for monovalent-divalent exchange that strontium sorption is favored by systems having a high selectivity for strontium compared to other divalent cations, a high exchange capacity, a high ratio of monovalent to divalent cations, and a low total salt concentration.

The mean velocity of the radiostrontium compared to that of the transporting water is given by

$$\frac{\bar{v}_{Sr}}{\bar{v}_{H_2O}} = \frac{1}{1 + \frac{(K_d)_{Sr} \rho_b}{f}} = \frac{1}{1 + \frac{(33)(1.25)}{(0.35)}} = \frac{1}{119}$$

where ρ_b is the bulk density of the formation, and f is the fraction pore space. Thus, for this waste stream, ion exchange will cause the strontium to move less than 1% as rapidly as water in the formation.

At the high pH of the ORNL intermediate-activity waste stream, the aluminum would behave as AlO_2^- and the remaining cations, which are monovalent, would have a total concentration of $\sim 0.64 \text{ M}$. In the absence of stable divalent cations, the selectivity of strontium to sodium was determined to be 326 g/ml for Richfield sand in 0.5 M NaCl. Since the chemical concentration of the radiostrontium is negligible compared to the total cation concentration, $q_{Sr} \ll q_{Na}$, $q_{Na} \approx Q$ (the total exchange capacity), and

$$(K_d)_{Sr} = \left(K_{Na}^{Sr} \right) \left(\frac{q_{Na}}{c_{Na}} \right)^2 = (326 \text{ g/ml}) \frac{(0.0686 \text{ meq/g})^2}{(0.64 \text{ meq/ml})^2} = 3.75 \text{ ml/g.}$$

If ion exchange should be the only process operating to retard the movement of strontium in this waste stream, the strontium would move less than 10% as fast as the water in the formation. However, in a high pH system the precipitation of slightly soluble calcium-strontium salts is likely, resulting in much slower movement of strontium than predicted from simple ion exchange in a neutral pH system (see Sect. 8).

Cesium. The basal surface of the plate-like layer lattice clay minerals is composed of open hexagonal networks of oxygen atoms. The openings in this surface are of a size such that the easily dehydrated potassium and cesium ions can partially penetrate the surface and come much closer to the seat of the lattice charge than the more completely hydrated alkali metal and alkaline earth cations. Thus cesium is ordinarily very strongly sorbed by most clay minerals from waste solutions composed primarily of sodium or calcium salts.

Sample calculations from laboratory data of the relative affinities of various clay minerals for cesium compared to sodium, the cesium K_d for the above-described aquifer (assuming that all the exchange capacity, 0.0686 meq/g, is due to a single type clay mineral), and the velocity of water compared to cesium (Table 5.3) have been qualitatively verified by field experience. In the ground, especially when illitic clays are predominant, cesium ordinarily moves much more slowly than strontium.

Table 5.3. Predicted Behavior of Cesium on Injection of ORNL Low- or Intermediate-Activity Waste into Richfield Sand

Clay Mineral	K_{Na}^{Cs}	Low-Activity Waste		Intermediate-Activity Waste	
		$(K_d) C_{sr}$ ml/g	$\bar{v}_{H_2O}/\bar{v}_{Cs}$	$(K_d) C_{sr}$ ml/g	$\bar{v}_{H_2O}/\bar{v}_{Cs}$
Illite	13,000	13,390	47,800	1393	4975
Vermiculite	130	134	479	14	51
Kaolinite	130	134	479	14	51
Arizona bentonite	56	58	208	6.0	22
Wyoming bentonite	38	39	140	4.1	15

Ruthenium. The behavior of ruthenium in the ground is more complicated than that of either strontium or cesium because of its tendency to form complex ions and the effect of pH and oxidation-reduction potentials on its behavior. Much of the ruthenium in the ORNL low-activity waste stream probably exists in noncomplexed forms and would be deterred from movement in the soil by ion exchange of cationic species and by a combination of surface precipitation and filtration of Ru(III) and Ru(IV) oxides and hydroxides. However, in the intermediate-activity wastes, which originate as nitric acid, the tendency for formation of nitroso-nitrato complexes is much more pronounced. These complexes resist changes in oxidation state and are removed slowly in the ground.

The behavior of ruthenium in the ground is difficult to predict. However, in the ground disposal of ORNL intermediate-activity wastes, it is the first radionuclide to reach monitoring wells, but 80 to 90% of it is removed from solution while passing through less than 100 ft of shale. Only about 50% of the remaining radioruthenium is removed before the water reaches the surface.

Movement of ruthenium in the ground from the disposal of low-activity waste would pose no problem as the Ru-106 concentration of this waste is initially below the

MPC_w. In the disposal of intermediate-activity wastes, ruthenium could become hazard-controlling if precipitation of slightly soluble calcium-strontium salts slowed the movement of Sr-90.

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

6.1 High-Temperature Experiments (R. L. Bradshaw and F. M. Empson)

Design of the high-temperature array, to be operated in the floor of the Carey Mine at Hutchinson, was described earlier (7). Preparation for this experiment has continued, and operation is planned for mid-July.

Holes have been drilled for high temperature cylinders II and III, one in the floor about 75 ft from the array and the other in the adjacent wall. The arrangement duplicates the first high-temperature experiment (high-temperature cylinder I), except that the hole containing the heater is 10 rather than 8 in. dia. It is planned to start these tests before those on the high-temperature array but to operate them concurrently.

6.2 Trapped Moisture in Natural Salt Formations (H. Kubota)

Salt samples in the form of core drillings and chunks are being tested for shattering temperature and for moisture content. Samples tested thus far shattered with an initially large breakup at temperatures between 215 and $250^{\circ}\text{C} \pm 15^{\circ}\text{C}$, followed by a series of minor breakups at higher temperatures. The resultant salt particles vary in size from powdery material to chunks nearly 2 in. across.

Salt samples from the Carey Mine at Hutchinson, Kansas, began to disintegrate at about 250°C . The moisture contents ranged from 0.106 to 0.293% for both core drillings and mine-run chunks. A specimen of clear salt, in which liquid inclusions were clearly visible, contained 1.08% moisture.

Samples from the Carey Mine at Lyons, Kansas, first disintegrated at about 215°C . The moisture content was lower, 0.0448-0.100%.

7.0 CLINCH RIVER STUDY

7.1 Bottom Sediments (R. J. Pickering* and P. H. Carrigan*)

The Subcommittee on Bottom Sediments, Clinch River Study, met May 10, 1962, to compile and evaluate all available data pertaining to bottom sediments of the Clinch and Tennessee Rivers. Data on sediment deposition has been collected by TVA on these rivers; data on radiation levels and concentrations of radionuclides in the sediments has been collected by the USPHS, Applied Health Physics Section, ORNL, Waste Disposal Research Section, ORNL, and the USGS; and data on physicochemical properties of the

*U. S. Geological Survey

sediments has been collected by the USPHS, USGS, and Waste Disposal Research Section, ORNL. The members of the subcommittee are preparing a draft of this evaluation for review by July 1962.

A contract has been awarded to Sprague and Henwood, Inc., Scranton, Pa., to collect sediment cores by a Swedish foil sampler in the Clinch River study reach for geochemical study at ORNL. Cores will be collected in 14 sections of the Clinch River from Mile 1.3 to Mile 32.6 in two sections of Emory River, and in one section of Poplar Creek. Downstream from about Mile 14 on the Clinch River, ten cores per section will be collected; upstream, the fine sediments do not extend the full river width and five cores per section will be collected by the contractor. Samples of coarse material in these upstream sections will be taken by personnel of ORNL-USGS with Eckman dredges and/or a TVA volumetric silt sampler.

A piston core sampler developed and tested for obtaining fine sediments consists of a steel tube with plastic liner, and 1-3/4 in. i.d. Core barrels of 1-1/2, 5, and 7 ft are available. The sampler is equipped with a tapered, sharp-edged shoe and a spring finger core catcher at the lower end. At the upper end are stabilizing fins and a mounting flange for one to four 42-lb drive weights. The piston is made of hard rubber. The sampler is driven into the sediment by dropping it from the water surface. Prior to driving, the length of cable attached to the top of the piston is adjusted so that the piston will remain at the sediment surface during the operation.

The sampler was tested in water 12-1/2 ft deep. In two tests, the core recoveries were 73 and 81%, in sediment depths of 5.5 and 4.3 ft, respectively. In both tests the driving weight was 136 lb.

7.2 Water Sample Analyses (S. Helf*)

A laboratory study of the volatility of Ru-106 in environmental water samples was completed. Concentration of river water containing Ru-106 did not result in loss of this radionuclide from volatilization even in the presence of nitric acid when samples were concentrated by boiling.

The experiments were made on three 1000-ml samples of water collected at White Oak Dam. Two samples were concentrated by gentle boiling to a volume less than 200 ml, and 900 ml of the third was similarly evaporated after addition of 100 ml of 70% nitric acid. The concentrate volumes were adjusted to 200 ml, and the ruthenium concentration of each was determined by a gamma spectrometer and compared to the concentration in an untreated 200-ml sample. The results showed the concentration is 4 and 8% higher in ruthenium concentration after boiling without nitric acid and 3% higher with nitric acid than an untreated sample. These increases in activity are due to the formation of a thin layer of sediment in boiling.

*U. S. Army, Picatinny Arsenal

8.0 FUNDAMENTAL STUDIES OF MINERALS

T. Tamura

Reagent-grade aluminum oxide powder has been shown (16,17) to selectively remove strontium from waste solutions. Hydrus aluminum oxide minerals, which occur commonly in soils, were more effective (Table 8.1) than the pure oxide after being decomposed to the oxide by heating. The experiments were made with "Arkansas bauxite," obtained from Reynolds Metal Company, Louisville, Ky., which contains 40% gibbsite ($\text{Al}(\text{OH})_3$) and 60% kaolinite ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$). That the gibbsite was the active substance was indicated with samples of aluminum hydroxide, obtained from Fisher Chemical Company and identified by x-ray examination as gibbsite, and kaolinite from Georgia. The aluminum hydroxide as received removed only 2% of the strontium from a simulated waste solution, but after being heated to 450°C, removed nearly 100%. The strontium absorption capacity of the kaolinite was low, and was even lower when the kaolinite had been heated to 600°C. The kaolinite had been heated for another purpose, and the heating temperature is thus not really comparable with that of the other samples. The theoretical weight loss of pure aluminum hydroxide on heating, $2 \text{ Al}(\text{OH})_3 \xrightarrow{\text{heat}} \text{Al}_2\text{O}_3 + 3 \text{ H}_2\text{O}$, is 34.64%, and gibbsite heated to 800°C lost 34.22% of its weight.

In order to determine whether the surface area developed by the heating was the important factor in strontium absorption, samples of gibbsite were heated to different temperatures and the surface areas measured. Gibbsite decomposes at 150-300°C (18), and the surface area was increased 1000-fold by heating to 200°C (Table 8.2). However, the strontium capacity was greater for the material heated to 400°C to an equilibrium weight loss (Table 8.3). The pH was not adjusted after the start of the experiment, and the low strontium absorption in 24 hr contact is believed due to a gradual decrease in pH. Material heated to 450°C for 3 hr in the earlier experiments was slightly less effective than the 400°C material.

In further experiments with a sample of gibbsite heated to 400°C for 3 hr, the distribution coefficient, K_d , increased with increasing amount of material (Table 8.4). A similar effect in illite-cesium reactions (19) was explained by assuming the presence of a few sites very selective for the radionuclide. If highly selective sites are present in heated aluminum hydroxide, this material might be considered as a final scrubber for strontium. Activated alumina of high surface area is widely used and is available commercially. Work is being continued on this material to obtain a better understanding of the reaction.

Table 8.1. Strontium Removal from Simulated Waste Solution by Aluminum Oxide Minerals

Waste solution: 0.1 M NaNO₃ containing 1 mg of Sr per liter
25 ml of solution contacted with mineral and system maintained
at pH 10

Mineral	Wt of Mineral Used in Contact, g	Strontium Removed, %		
		1 hr Contact	4 hr Contact	24 hr Contact
Pure Al ₂ O ₃	0.2500	79.3	86.0	9.16
Arkansas bauxite*				
Unheated	0.2500	42.4	46.4	49.6
Heated to 350°C	0.1667	96.6	98.6	99.3
Al(OH) ₃				
Unheated	0.2500	2.44	4.40	3.44
Heated to 450°C	0.2500	99.8	99.9	99.9
Kaolinite				
Unheated	0.2500	17.3	38.2	46.4
Heated to 600°C	0.2150	15.2	18.5	23.7

* 40% Al(OH)₃

Table 8.2. Effect of Temperature of Heating of Aluminum Hydroxide on Surface Area*
Samples heated to weight loss equilibrium.

Heating Temperature, °C	Heating Time, hr:min	Weight Loss, %	Surface Area, m ² /g
100	15:00	0.00	0.3
200	173:20	25.00	303
300	23:20	29.71	---
400	17:25	31.33	280
500	6:35	33.37	202
800	25:50	34.22	74

*Surface area of Al₂O₃ ignited powder (Allied Chemical Co.): 6.6 m²/g.

Table 8.3. Strontium Removal by Heat-treated Aluminum Hydroxide

Waste solution: 25 ml of 0.1 M NaNO₃ containing 1 mg of Sr per liter contacted initially at pH 10 and not adjusted later

Amount of mineral used: ≈ 0.01 g of 800°C heated aluminum hydroxide

Heating Temperature, °C	Strontium Removal, %			pH of Waste Solution after 50 hr Contact with Mineral Sample
	1 hr Contact	3 hr Contact	24 hr Contact	
Equilibrium				
100	0.13	1.45	1.86	7.34
200	67.5	72.1	72.1	7.90
400	78.8	81.0	78.5	8.08
500	73.9	74.1	66.0	7.90
800	42.0	38.8	37.4	7.74
3 hr heating				
450	73.5	74.7	71.6	8.54

Table 8.4. Strontium Removal from Simulated Waste by Aluminum Oxide Prepared by Heating Aluminum Hydroxide to 500°C for 3 hr

50 ml of waste used in each test

Wt of Oxide, g	1 hr Contact		4 hr Contact		24 hr Contact	
	Sr Re-moved, %	K _d	Sr Re-moved, %	K _d	Sr Re-moved, %	K _d
0.001	8.17	4,450	7.25	3,900	8.33	4,550
0.005	28.75	4,030	32.49	4,810	34.47	5,260
0.101	52.42	5,500	59.20	7,250	60.75	10,400
0.020	80.84	10,600	87.38	23,100	86.90	15,800
0.030	90.54	16,000	94.10	26,000	93.78	25,200
0.050	94.53	17,300	97.29	35,900	97.50	39,000

9.0 WHITE OAK CREEK BASIN STUDY*

9.1 Distribution and Transport of Radionuclides in the Bed of Former White Oak Lake (T. F. Lomenick)

Several thousand curies of Ru-106 per year flow onto the bed of former White Oak Lake from the intermediate-level waste pits, but less than half the material goes into White Oak Creek. Waste from the seepage pits is transported to the lake bed by two surface streams (Fig. 9.1). During the dry summer months these streams recharge the ground water in the lake bed and thus allow little, if any, Ru-106 to travel over the land surface to White Oak Creek. However, in the wet winter months, most of the water flows over the surface of the lake bed into the creek. A series of soil samples were taken from the lake bed in February, 1962.

The cores were obtained with a 2-in.-dia thin-walled tube, the Shelby tube sampler, which was driven into the earth and recovered manually. A total of 54 boreholes was completed for this investigation. The cores, varying in depth from 24 to 60 in., were taken approximately 50 ft apart along lines at right angles to the surface flow of waste over the lake bed (Fig. 9.1). The samples were sliced and segmented into increments of 0-2 in., 2-6 in., 6-12 in., 12-18 in., 18-24 in., 24-36 in., 36-48 in., and 48-60 in. Approximately 4 g of the oven-dried sample from each increment was scanned for Ru-106 with a single-channel γ analyzer. Counting results from the samples were plotted on cross sections through the soil to indicate the vertical and lateral distribution of the activity.

Cross section B-B' (Fig. 9.2) indicates highest activity concentrations in the top few inches of soil near boreholes 2 and 3. This condition is as expected, since the surface flow of waste at this cross section is largely confined to this zone. However, there was relatively little contamination of the soil below 2 ft. Near borehole 5 more activity was detected at depths of 0.5 and 2 ft than at the land surface.

At cross section D-D' (Fig. 9.3), the maximum concentrations are centered around boreholes 2, 3, and 5. Surface water flow, which is divided into two prongs at this point, coincides with these zones of maximum concentration. Thus, the ruthenium does not enter the lake bed soil over the full length of the cross section but is limited to two zones of seepage. The activity in boreholes 1, 6, and 7 illustrates the lateral and vertical migration of the ruthenium from the points of initial entry into the soil. Comparing cross sections B-B' and D-D' shows that the contamination zone is wider at the latter than at the former, and maximum concentrations are greater at cross section B-B',

*This project, entitled "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin," (AEC Activity 060501000) is supported by the U. S. Atomic Energy Commission's Division of Biology and Medicine. All other projects covered in this report are supported by the Division of Reactor Development (AEC Activity 04640011).

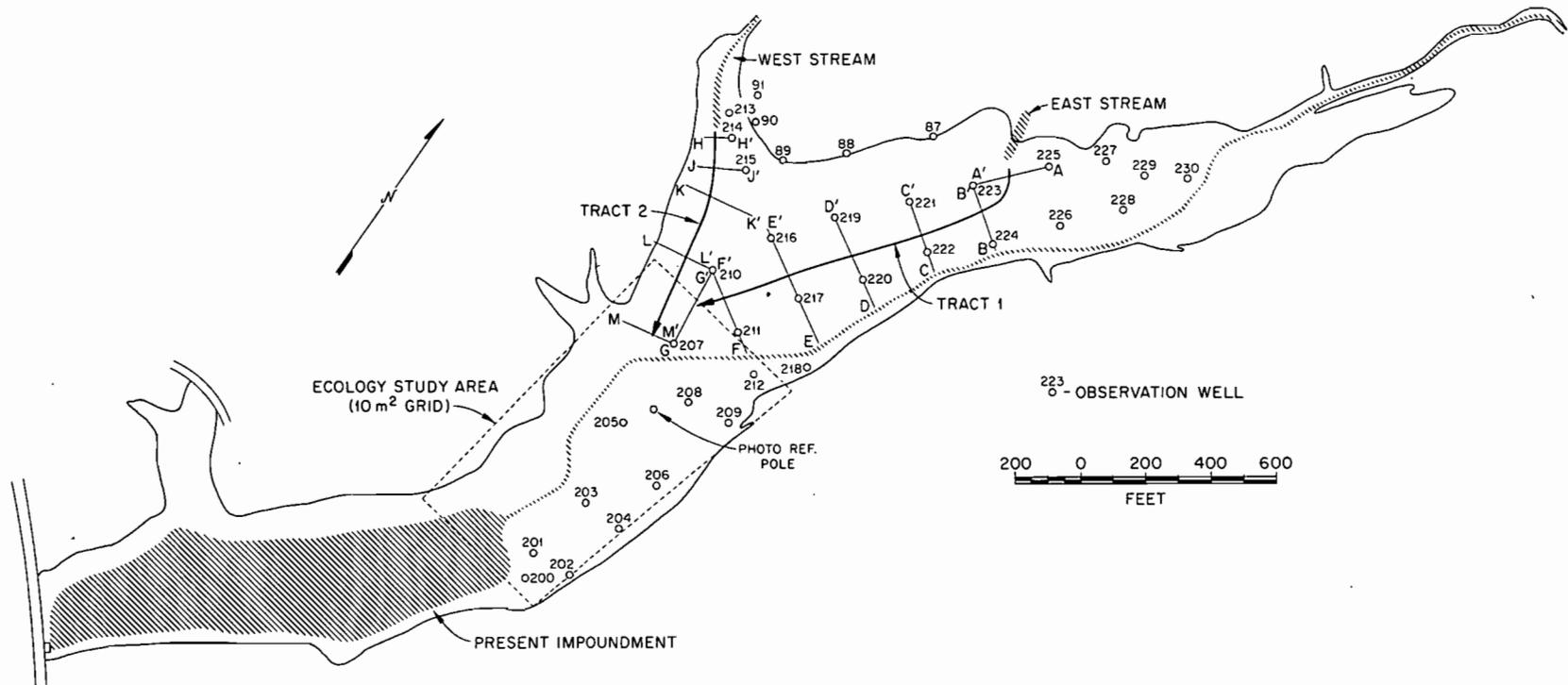


Fig. 9.1 Map of White Oak Lake bed showing transverse lines of bore holes along tracts of ruthenium seepage.

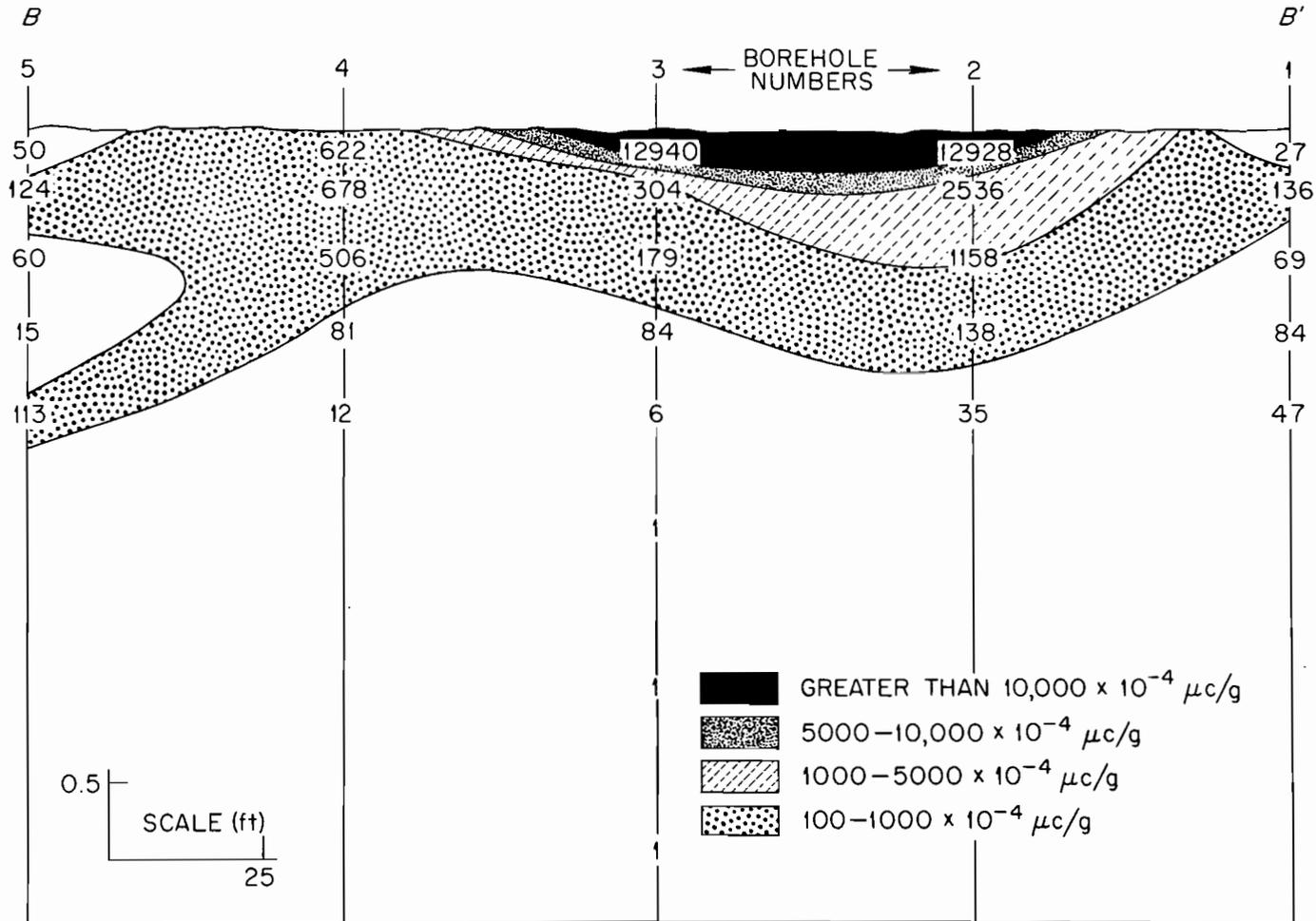


Fig. 9.2 Cross section B-B' in White Oak Lake bed showing ruthenium concentrations.

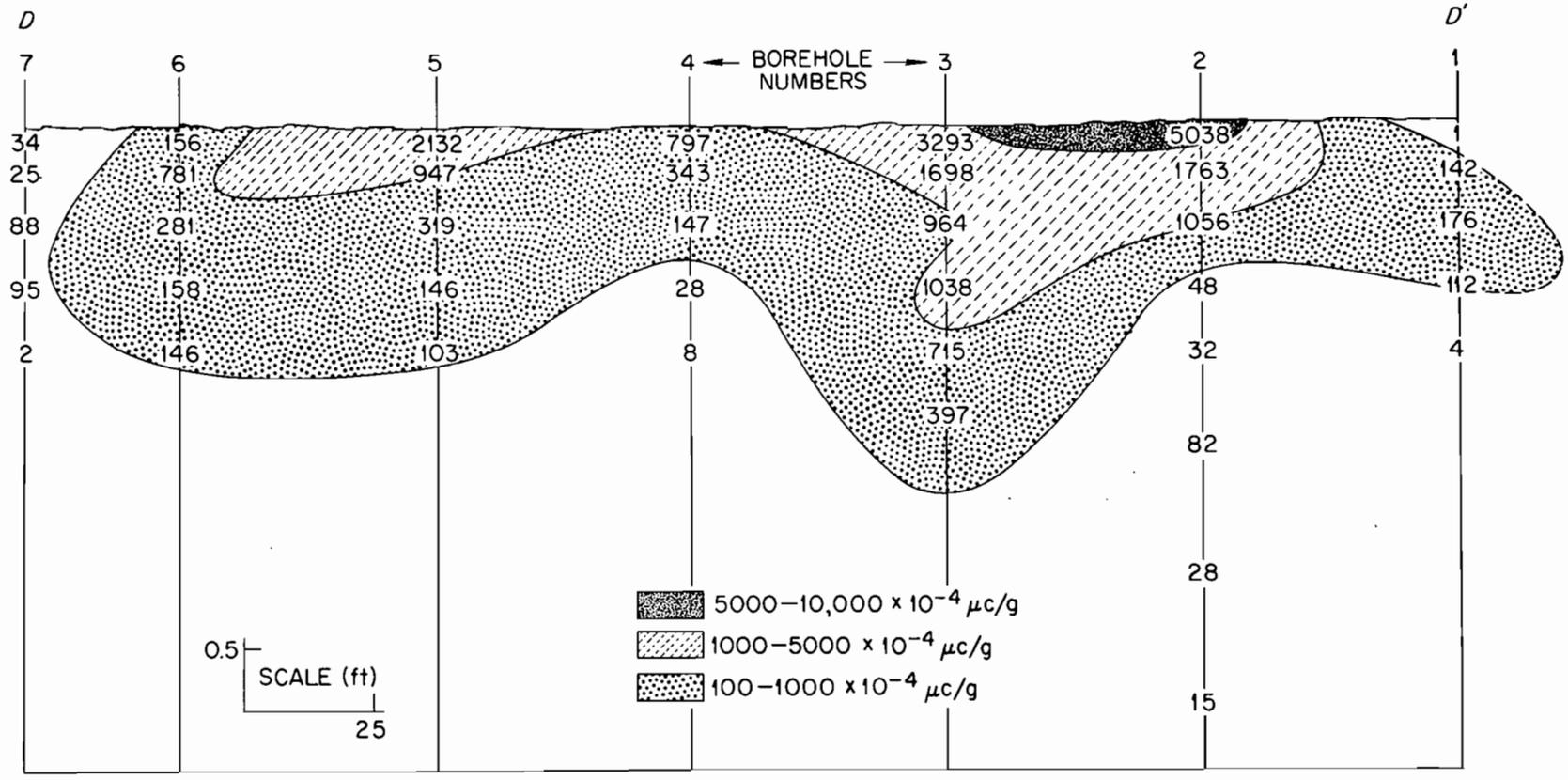


Fig. 9.3 Cross section D-D' in White Oak Lake bed showing ruthenium concentrations.

which is about 400 ft nearer the source of contamination. The somewhat deeper penetration of activity at section D-D' is probably due to a slightly more permeable soil at that point.

The pattern of Ru-106 distribution at cross section J-J' (Fig. 9.4) along Tract 2 is generally the same as in cross sections B-B' and D-D' along Tract 1. However, the contamination zone is not nearly so widespread.

The curies of Ru-106 in each cross section were calculated and the results summed to yield the total Ru-106 in each tract. As of February, 1962, the lake bed contained approximately 1200 curies of Ru-106 (Table 9.1) with 85% of the Ru-106 along Tract 1. This is due in part to the larger percentage of ruthenium transport onto the lake bed from the east stream (85% of the total in 1960 and 62% in 1961) and to the greater distance to the creek along Tract 1.

The amount of Ru-106 in the lake bed probably will vary greatly throughout the year. The amount of activity leaving the waste pits is largely dependent on the concentration and total volume of Ru-106 pumped to the system (20) and large changes in the volume and concentration of waste transported to the waste pits will measurably affect the amount of Ru-106 that flows onto the lake bed. In addition, less ruthenium is removed from the waste flow during the wet winter months when most of the water flows over the surface of the bed into the creek than during the dry summer months when the waste streams recharge the ground water in the area. Finally, the short half-life of the isotope (1 year) will cause the budget in the area to change measurably in a relatively short period of time.

The bed contained 1200 curies of Ru-106, the concentration being highest in the top 2 in. of soil and about 75% associated with the first 2 ft. Ruthenium is transported by ground water through the lake soil, but a relatively small amount of it reaches the creek in this way.

10.0 FOAM SEPARATION

E. Schonfeld, W. Davis, Jr., P. A. Haas

Strontium may be removed from solutions similar to low-activity process wastes, e.g. tap water, by the foam separation technique, the process being greatly facilitated if the calcium concentration is decreased to 1-2 ppm.

Continuous Operation Tests with ORNL Tap Water. Concentrations of calcium and magnesium in ORNL tap water were decreased from 25 to 1-2 ppm, as Ca, in laboratory-scale tests with a gently agitated sludge chamber. Precipitation was with 5×10^{-3} M each of NaOH and Na_2CO_3 and coagulation with 1 or 2 ppm Fe^{3+} ; retention times in the sludge bed were 35 min and flow rates $\sim 8 \text{ gal hr}^{-1} \text{ ft}^{-2}$. The resulting solution contained only 0.2 ppm Ca + Mg as suspended solids. Decontamination factors were 20-200

Table 9.1. Distribution of Ru-106 in the Bed of Former White Oak Lake

Cross Section	Ru-106, curies						Total
	0-2 in. from Surface	2-6 in. from Surface	6-12 in. from Surface	12-18 in. from Surface	18-24 in. from Surface	24-60 in. from Surface	
AA'-BB'	62	35	17	3	1	5	122
BB'-CC'	54	32	28	6	4	43	167
CC'-DD'	35	47	39	20	15	99	255
DD'-EE'	27	38	27	19	14	82	207
EE'-FF'	17	28	24	14	6	54	146
FF'-GG'	21	29	27	17	10	37	140
	<u>216</u>	<u>209</u>	<u>162</u>	<u>79</u>	<u>50</u>	<u>320</u>	<u>1036</u>
HH'-JJ'	5	2	2	4	<1	3	13
JJ'-KK'	13	8	7	2	1	5	34
KK'-LL'	20	19	16	6	1	3	65
LL'-MM'	<u>14</u>	<u>16</u>	<u>12</u>	<u>5</u>	<u>1</u>	<u>11</u>	<u>59</u>
	52	45	37	13	3	22	172
Totals	268	254	199	92	53	342	1208

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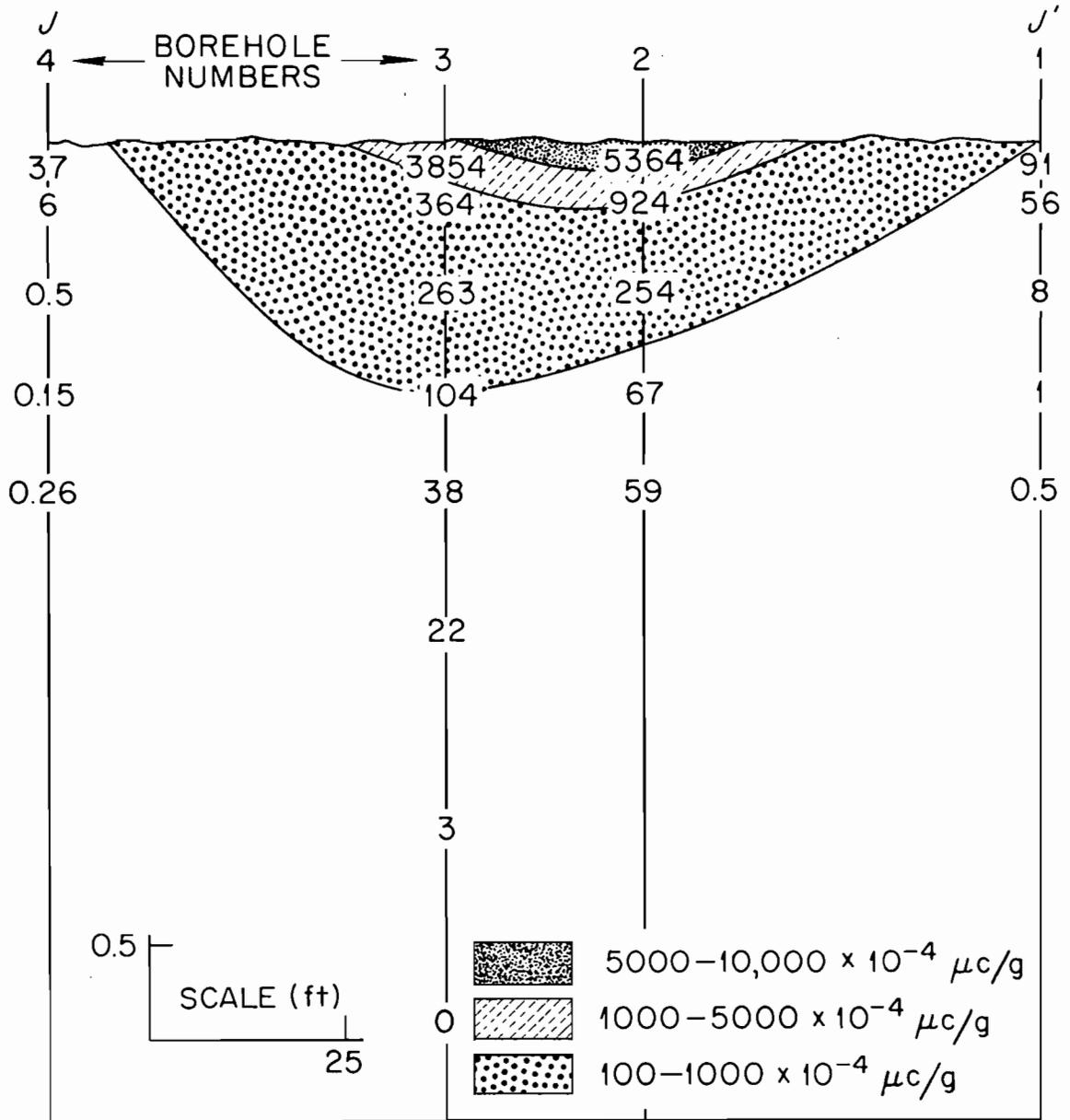


Fig. 9.4 Cross section J-J' in White Oak Lake bed showing ruthenium concentrations.

from Sr and 10-40 from Cs. Addition of grundite clay to the alkali chamber in ~0.5-g amounts at ~12-hr intervals over a 2-day run, to an average of ~0.5 lb/1000 gal, gave a further d.f. from Cs of >10. Passage of 4000 column volumes of the solution plus suspended solids from the sludge column through a column of the cheap ion-exchange mineral Decalso did not improve the d.f. from Cs but increased that from Sr by a factor of ~50. Cesium broke through to 1% at ~5000 column volumes and to 10% at ~6500 column volumes.

Continuous Operation Tests with ORNL Low Activity Waste. In a 100-hr continuous run with ORNL low activity waste, the above-described Na_2CO_3 -NaOH process decreased the average hardness to 1.9 ppm, as Ca, or <5 ppm as CaCO_3 , as contrasted with corresponding values of 1.2 and 3 ppm for tap water. The average strontium decontamination factor during the run was 10. Low-activity waste, containing materials such as hexametaphosphate from Turco 4234, was softened nearly as well as tap water; the strontium decontamination factor was lower by a factor of 2-20, but is still considered very good for such a process.

The waste was fed at the rate of 11.5 cc/min, equivalent to ~9.4 gal $\text{ft}^{-2}\text{hr}^{-1}$, into the bottom of a gently agitated 2-in.-dia sludge column, or clarifier. Sodium carbonate and NaOH solutions to make the product 5×10^{-3} M in each were added at the same point. Ferric nitrate was added to the sludge bed to make the concentration 2 ppm Fe^{3+} . During each day of operation the waste feed was obtained fresh after its discharge from the equilization basin. Large quantities of Turco 4234 were added to the waste in this 5-day interval as a result of washing two high-activity waste shipping containers (21).

Water Softening Tests. Materials in low-activity waste that might interfere with precipitation of Ca and Mg by NaOH or Na_2CO_3 -NaOH are Turco 4234, Fab, and components of these proprietary formulations, such as sodium dodecylbenzene sulfonate, sodium hexametaphosphate, sodium tripolyphosphate, and sodium pyrophosphate. At concentrations of 1.5 to 3 ppm in water, Turco 4234, Fab, sodium hexametaphosphate, and sodium pyrophosphate all had a more deleterious effect with NaOH softening than with Na_2CO_3 -NaOH softening (Table 10.1). Sodium dodecylbenzene sulfonate and sodium tripolyphosphate had only small effects on either softening process. With three samples of ORNL low-activity waste used in the continuous softening tests described above, the effect was much greater on the NaOH softening process than on the Na_2CO_3 -NaOH process. In a single test with 5×10^{-3} M NaOH, 60 ppm of orthophosphate softener, pH 11.3, the final hardness was 5.1, indicating that orthophosphate not only does not seriously interfere with water softening in this concentration range, but is the best precipitant in the presence of interferences such as Turco 4234 and Fab soap. The tests were made in beakers. The solution plus additive was agitated for 2 hr; $\text{Fe}(\text{NO}_3)_3$ was added to a level of 2 ppm Fe^{3+} and agitated for an additional 15 min; then the solution was sampled, centrifuged and finally analyzed for dissolved Ca + Mg, i.e., total hardness. With 10^{-2} M NaOH the pH was 11.7; with 5×10^{-3} M each Na_2CO_3 and NaOH, it was 11.3.

Table 10.1. Comparison of Effects of Cleaning Agent Components and Origin of Alkalinity on ORNL Tap Water and Low Level Waste

Solution agitated 2 hr at the indicated alkalinity; then 2 ppm Fe^{3+} added, followed by 15 min additional agitation; solution hardness determined after centrifugation

Solution Tested	Conc. Added to ORNL Tap Water, ppm	Final Hardness, as ppm CaCO_3 , after Alkalizing to		
		0.005 M Na_2CO_3 + 0.005 M NaOH	0.01 M NaOH	0.005 M NaOH + 60 ppm PO_4^{-3}
ORNL tap water	---	5.9	3.5	---
Turco 4234	3	7.2	28	---
Fab	3	11.0	35.3	---
Sodium dodecylbenzene sulfonate	2	7.7	4.5	---
Sodium hexametaphosphate	1.5	11.5	21	---
Sodium tripolyphosphate	1.5	7.5	8.5	---
Tetra sodium pyrophosphate	1.5	10	16	---
Low-activity waste 1*	---	17.4	49	---
Low-activity waste 2*	---	13.1	56	---
Low-activity waste 3*	---	16.1	36	5.1
pH		11.3	11.7	11.3

*These were three of the five batches of low-activity waste, obtained just downstream from the equalization basin, that were used in continuous sludge column tests of the Na_2CO_3 - NaOH water softening process.

Engineering Studies. Some of the variables of countercurrent foam column operation are being studied in a 6-in.-dia column. A 0.4-in. dia cyclone tested as a foam breaker had a feed capacity of 14 liters/min for an inlet/outlet pressure ratio of 4. The uncondensed foam volume varied from <0.2% for dry foam to 4% of the feed foam volume for wet foam. Foam densities initially were as much as six times the steady-state values for the same conditions with recycle of the condensed foam. Bubble sizes from the spinnerette gas distributor showed little variation for gas velocities of up to 500 cm/sec in the 50- or 80- μ -dia holes, but increased as the hole gas velocities increased above this value. The bubble size distribution from the spinnerette with 50- μ -dia holes was well represented by normal distributions (avg dia 0.53 mm, $\sigma = 0.08$ mm) for hole gas velocities below 500 cm/sec. The spinnerettes at higher gas velocities and the porous metal or fritted glass gas spargers at all velocities gave size distributions with a tail of large bubbles which did not fit a normal curve. HTU values at higher column throughputs were 0.8-1.1 in. at $120 \text{ gal hr}^{-1} \text{ft}^{-2}$ and 1.4 in. for one run at $160 \text{ gal hr}^{-1} \text{ft}^{-2}$ for stripping of Sr-89 with $7 \times 10^{-4} \text{ M}$ dodecylbenzenesulfonate.

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