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ORNL-TM-133

WASTE TREATMENT AND DISPOSAL

PROGRESS REPORT

FOR OCTOBER AND NOVEMBER 1961

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ORNL-TM-133

CHEMICAL TECHNOLOGY DIVISION

AND

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR OCTOBER AND NOVEMBER 1961

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ABSTRACT

High-Level Waste Calcination. Chemical flowsheets for TBP-25 process waste were completed for the ICPP Pot Calciner Pilot Plant, and Darex and Purex flowsheets are under preparation. Design is nearly complete of the test pieces and equipment for the mechanical development program for the radioactive pilot plant, which will include heliarc welding and mechanical closure tests, remote mechanical equipment tests, and a demonstration of a remote welding machine if the welded seal appears promising.

Preliminary engineering flowsheets and cell layouts were prepared for radioactive cell studies of evaporation and calcination of actual high-activity wastes. Design of several vessels was completed and fabrication started.

Both the 600-liter batch and 25-liter continuous evaporation-calcination equipment operated satisfactorily in evaporation calcination tests with simulated Purex and TBP-25 process wastes.

Volatilization of cesium during evaporation and meltdown of a phosphate-lead glass (maximum temperature 1000°C) containing simulated TBP-25 waste oxides was $\leqslant$ 0.3%. In a similar test ruthenium was 59.8-0.67% volatilized in the presence of 0-2 moles of H_3PO_3 when the experiment was performed in a quartz pot vs 47.2-0.11% in a stainless steel pot. In vapor-liquid equilibrium studies with 0.5-10 M HNO_3 at 748 mm Hg, the relation between the logarithms of the distillation factors of ruthenium and nitric acid was linear. In the presence of 1.7 M $Al(NO_3)_3$, the relation was approximately linear up to 1 M HNO_3, but ruthenium volatility increased at higher acidities. At distillation pressures of 565 and 444 mm Hg, ruthenium volatility from 1.7 M $Al(NO_3)_3$-4 M HNO_3 was decreased by factors of ~ 11 and 17, respectively. Addition of 0.1 M H_3PO_3 decreased the ruthenium volatility from 12 M HNO_3 and from 1.7 M $Al(NO_3)_3$-2 M HNO_3 by factors of 420 and 208, respectively.

A glass made by evaporating and melting simulated TBP-25 waste solution 2 M in NaH_2PO_2 and 0.25 M in PbO was leached at rates which decreased from 2.1×10^{-6} to 2.5×10^{-7} g/cm^2/day at the end of the first and fifth weeks, respectively.

In a semicontinuous evaporation and calcination to 1000°C, a glass was formed with a density of 2.9 g/ml, 1 vol of glass representing 8 vol of waste. About 90% of the mercury and 24% of the ruthenium were volatilized, the latter believed due to equipment malfunction.

Low-Level Waste Treatment. After equipment operability and operator training phases of the low-level waste treatment pilot plant were completed, three demonstration runs were made, for a total of 234 hr operation, on 134,000 gal of ORNL tap water. In a run with ORNL process waste water, a total of 44,425 gal

(representing 1564 bed volumes) of waste was treated in 72 hr of continuous processing. The major contaminants, strontium and cesium, were removed from the feed by factors of 2956 and 287, respectively. Analysis of plant effluent samples indicated a product that was 0.9 and 0.009% of current MPC_w values for Sr-90 and Cs-137 for a 168-hr week.

A new titration procedure for determination of total hardness was developed with a sensitivity of 1 ppm vs 20 ppm for the procedure formerly used. Comparison of the coagulation-flocculation steps of the lime-soda and phenolic resin processes showed equilibrium hardness values of 49 and 9.9 ppm, respectively, after settling. Varying the iron added as scavenger from 0 to 10 ppm increased the decontamination factor for ruthenium from 9.4 to 10.8, but there was no further increase between 10 and 20 ppm of added iron.

Engineering, Economic, and Hazards Evaluation. The amounts of floor area to be mined for the storage of calcined solid wastes in rooms in salt deposits were calculated for storage of Purex and Thorex wastes from a 15,000 MW_e (70,000 MW_t) nuclear economy. Criteria for storage were that the calcined solids in cylindrical vessels must not exceed 1650°F (the maximum calcination temperature) and that the salt surface must not exceed 400°F. For storage in 6-in.-dia vessels, the minimum decay time from reactor discharge to storage in salt for acidic Purex waste is about 1.1 years, but reacidified Purex, acidic Thorex, reacidified Thorex, and acidic Thorex glass could be stored immediately after processing (120 days after reactor discharge). For storage in 24-in.-dia vessels, minimum decay times varied from 0.63 year for reacidified Thorex to 8.3 years for acidic Purex waste. Mined space requirements varied from 14.8 acres/year with 0.33 year's decay time to 2.25 acres/year with 30 years' decay time, a factor of 2.3 less than for storage of liquid wastes.

Disposal in Deep Wells. The first fracturing experiment showed that the method used was capable of developing an essentially conformable fracture in the shale under the conditions of the experiment, and that the fracture tended to follow the bedding plane into which it was injected despite a moderately complex structure of open folds, small drag folds, and minor faults. It also showed that the test method was capable of giving a clear picture of the location and extent of the fracture, limited only, for practical purposes, by the number of test wells drilled to locate the grout.

Test drilling at the site of the second fracture experiment is nearly completed and the lateral extent of the grout sheets appears to be sufficiently defined. However, the well now being drilled is encountering the several key horizons and the upper grout sheet at depths so much shallower than did the two immediately adjacent wells that at least one and perhaps all of

these holes must depart considerably from the vertical. Until these and the other test holes are surveyed the conclusion that the injection well was, by chance, drilled into a down-folded or down-faulted block is unwarranted. It now appears that both the structure of the rock and the shape of the two grout sheets is much more regular than at first believed.

A Laboratory subcontract to develop waste-cement-clay mixtures for disposal by hydrofracturing has been signed with Westco Research, a subsidiary of The Western Company of Fort Worth. Initially, Westco proposed to study set-time and set-strength characteristics of various cement-simulated waste mixes and to search for gel-additives that will give a pumpable slurry, and that will aid in retaining radiostrontium and radiocesium.

Disposal in Natural Salt Formations. It has been found that rock salt samples shatter rather violently when heated in a muffle furnace to temperature of 250-300°C. If this shattering occurs in salt in situ, it may place an upper limit on the allowable salt temperature rise in a pot-calcined waste storage facility. A test in the Hutchinson mine, with a 5-ft-long 6-in.-dia cylindrical heat source buried in a drilled hole 8 in. dia and 10 ft deep, is planned to investigate this effect.

A computer program was written to determine the gamma radiation dose in the floor, walls, and ceiling of rooms in which packaged solid wastes are buried in the floor. Results for 6-in. dia cans containing 2-year-cooled pot-calcined acid Purex waste, spaced at 5-ft centers, indicate that the total cumulative dose in salt at the centerline between cans will be of the order of 3×10^6 rad. The program is being modified to determine the total dose in salt immediately surrounding the cans. Salt near the cans will be irradiated to doses greater than 1×10^8 r, and some decrease in structural strength is anticipated; however, the bulk of the salt in the floor will not be affected.

Clinch River Study. Core samples of bottom sediments taken at 10 equally spaced intervals along five cross-sections, CRM 4.7, 7.6, 11.9, 15.3, and 19.2, were submitted to the U.S. Geological Survey for mineralogic and exchange capacity determinations. The results indicate that the vermiculite, kaolinite, and interstratified vermiculite-mica contents are about the same in the clay-size fraction of bottom sediments in the study reach. Quartz is the most abundant mineral in these sediments. The micaceous clay content is greater downstream from CRM 15.3 than at this or the next upstream section. The exchangeable magnesium content and the determined exchange capacity of the bottom sediments are nearly constant through the study reach, but the exchangeable calcium content is greatest near the mid sections.

The Steering Committee held an information meeting in Oak Ridge on October 27 and heard reports on water sampling and analysis, bottom sediments sampling and analysis, hydrologic measurements, and ecological studies. These reports will be summarized in Status Report No. 3 on the Clinch River study. Another meeting of the Steering Committee was held in Oak Ridge on November 21, to define criteria for evaluation of the safety of present disposal practices and to organize a subcommittee charged with the responsibility to conduct this evaluation.

Fundamental Studies of Minerals. Four sulfide minerals—pyrite (FeS_2), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), and stibnite (Sb_2S_3)—were investigated for sorption of ruthenium. Sorption was quite high for all minerals from synthetic waste solution tagged with Ru-106 Cl_3 but low from the untreated seep solution of operating waste pits. Sorption was increased when $Na_2S_2O_4$ was used to reduce the ruthenium in an alkaline medium. Ruthenium removal from solution was optimum in the pH range 6 to 11, where polymeric ruthenium dioxide is at a maximum.

White Oak Creek Study. Temporary water sampling stations have been installed along White Oak Creek and its tributary streams to assess the release of radionuclides to the drainage basin and to describe their accumulation and transport in the physical and chemical environment.

A study of the strontium in the creek at these stations indicates: (1) in general, the total amount of strontium in the creek varies with stream discharge; (2) the amount of sorbed strontium varies between 0.5 and 17% of the total present; (3) there is a relation between the percentage of sorbed strontium and the concentration of suspended solids in the creek water; and (4) less than 5% of the strontium detected at the station in the plant area is due to fallout.

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1.0 INTRODUCTION

This report is the fourth 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-level 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 solids and final storage as solids.

Tank storage or high-temperature calcination of intermediate-activity wastes may be unattractive because of their large volumes. Consequently, 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 at present. Particular attention is 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.

*Previous: ORNL-CF-61-7-3, ORNL-TM-15, and ORNL-TM-49.

2.0 HIGH-LEVEL WASTE CALCINATION

The pot calcination process for converting high-activity-level wastes to solids is being studied on both an engineering and laboratory scale to provide design information for construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes containing millicurie amounts of ruthenium but has not been demonstrated on actual high-activity-level wastes. A general flowsheet was shown previously (1). The chief effort reported here was on TBP-25 waste.

2.1 Pilot Plant Design

2.1.1 Chemical Flowsheets (J. O. Blomeke, R. M. Beckers, E. J. Frederick, J. M. Holmes)

Flowsheets for TBP-25 waste were completed for the ICPP Waste Calcination Pilot Plant, and Darex and high-sulfate Purex flowsheets are being prepared. Maximum feed, solids, acid product, and condensate volumes and maximum system flow rates have been specified for all three flowsheets to provide a basis for vessel sizing. Major equipment items and maximum flow rates and liquid volumes for the ICPP Pilot Plant are shown in Fig. 2.1.

2.1.2 Mechanical Development (J. O. Blomeke, R. M. Beckers, J. M. Holmes)

The mechanical development program will be carried out in three phases at the Lockheed Nuclear Products facility at Georgia Nuclear Laboratories: (1) heliarc welding and mechanical closure tests to develop a permanent seal for the pots; (2) remote mechanical equipment tests to demonstrate positioning of the pot and connecting it to its off-gas line; and (3) demonstration of a remote welding machine if the welded seal developed in phase 1 appears promising.

Phase 1. The seal weld will be made after thorough purging of the assembly with argon and insertion of the screwed cap. The lips of the seal will be fused by automatic heliarc welding with a nonconsumable electrode and no additional filler metal. During welding, the assembly (similar to the one shown in Fig. 2.2) will be turned automatically by a turntable and the electrode will be clamped in a stationary position. The weld will be pressure tested at the maximum temperature and pressure expected during pot storage. In the assembly shown, the threads were designed to take most of the stresses resulting from pressure buildup off the seal weld. Another assembly has been designed without the threads but with heavier weld lips to test the strength of the weld alone.

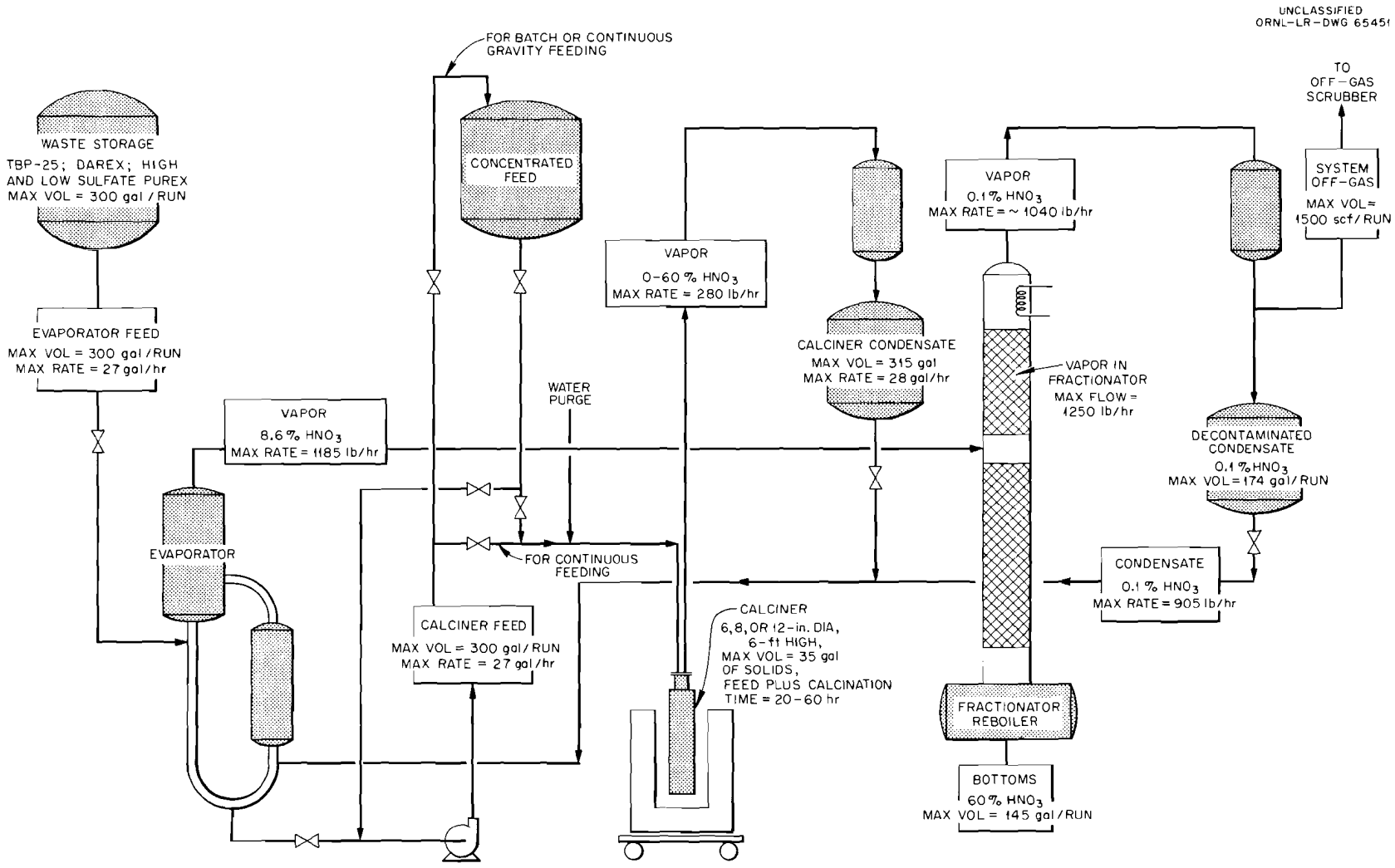

Fig. 2.1. ICPP Pot Calcination Pilot Plant. Maximum flow rates and liquid volumes based on use of a 12-in.-dia pot.

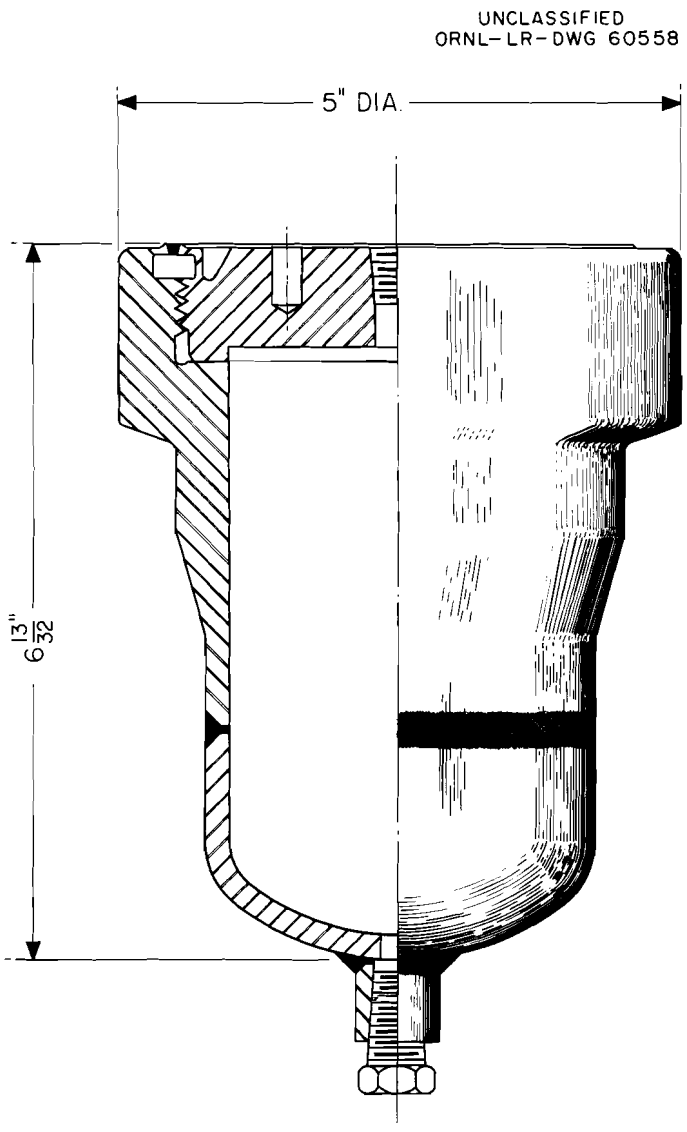

Fig. 2.2. Test Assembly for Seal-Welding of Calciner Pots.

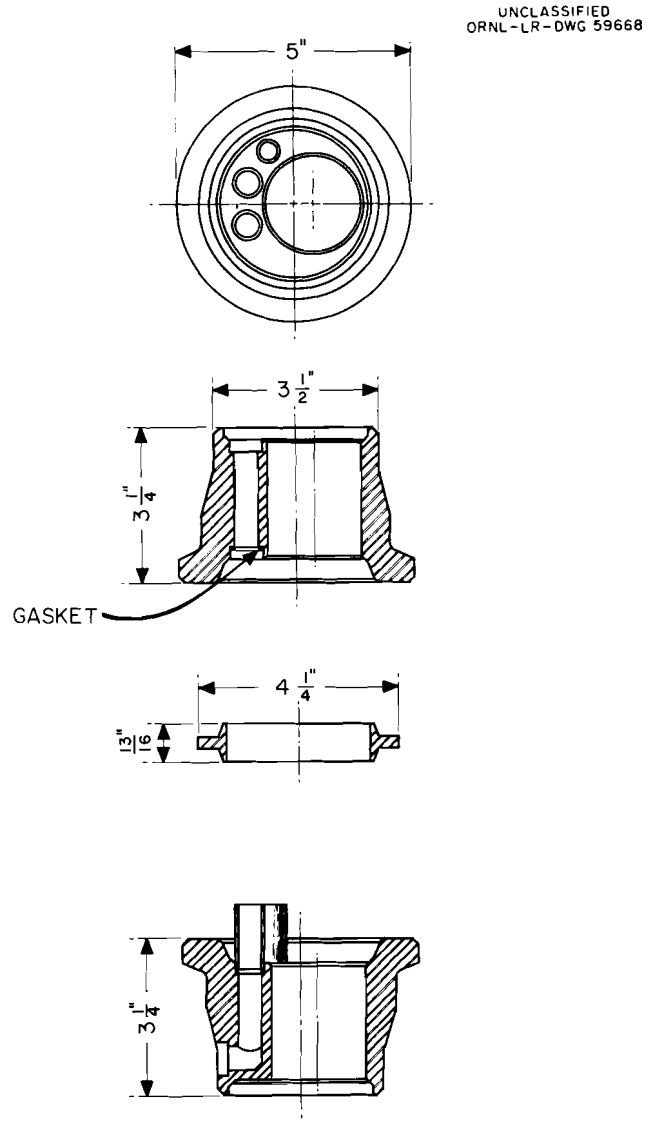

Fig. 2.3. Grayloc Connector for Mechanical Closure of Calciner Pots.

Phase 1 will also include permanent-storage leak tests of mechanical seals such as a Grayloc (Fig. 2.3). This connector permits sealing of the pot to its off-gas line during calciner pot filling by means of a tapered metal ring seal; the feed probe line will be sealed with the small gaskets as indicated. For permanent storage, the Grayloc will have a blank mating hub inserted at the sealing station and a screwed clamp applied for permanent sealing. Thermal cycling will be used in the leak tests to simulate heating and cooling of the clamp during permanent storage.

Phase 2. A cell mockup will demonstrate the positioning of a pot calciner plus connecting it to and disconnecting it from its off-gas line. The pot will be lowered into the furnace mounted on a dolly (Fig. 2.4), positioned beneath its filling cap, lifted along with the furnace by jacks mounted on the dolly, and clamped to its off-gas line by a screw clamp operated remotely or by a shaft extending through the cell wall. A gasketed connector (Fig. 2.5) will seal the vapor, feed, and probe lines from each other and the environment. It incorporates the weld design tested in phase 1 for permanent sealing of the pots. The Grayloc connector (Fig. 2.3) will also be demonstrated.

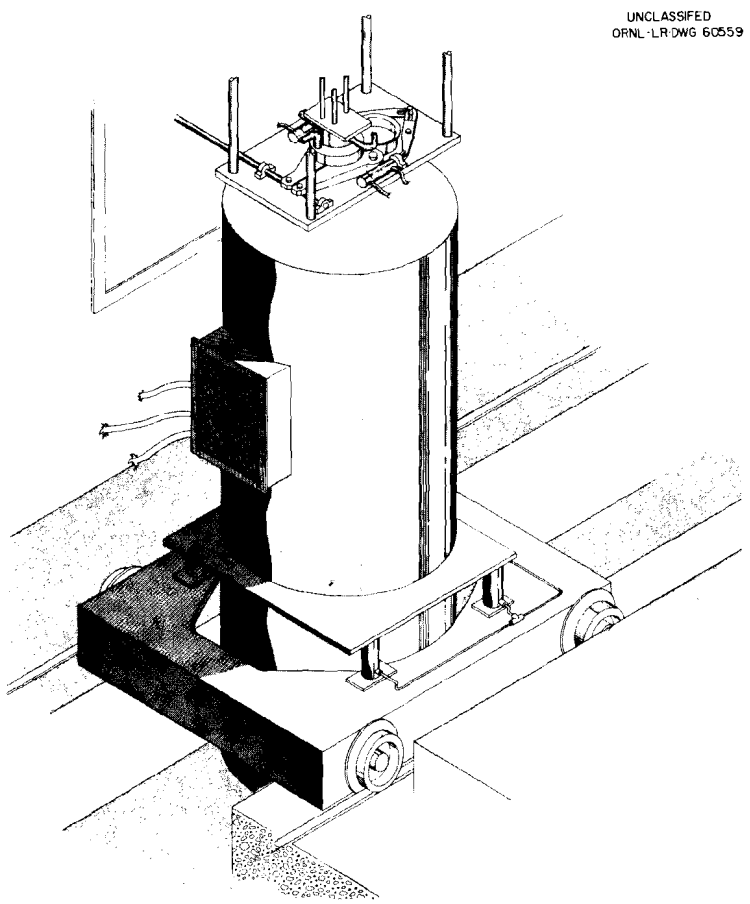

Fig. 2.4. Radioactive Pilot Plant Pot Calciner Arrangement.

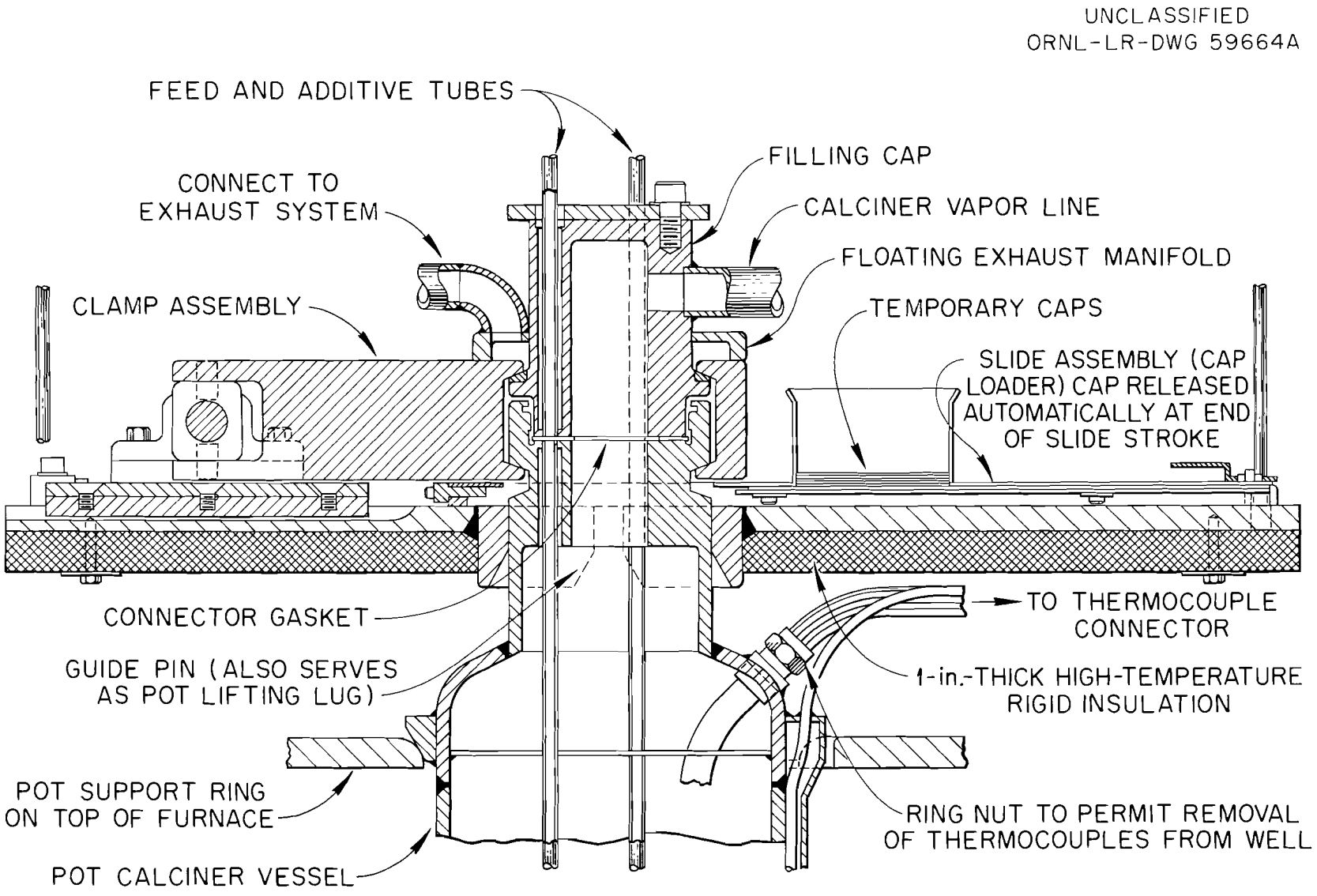

Fig. 2.5. Gasketed Connector Assembly for Calciner Pots.

After the pot has been filled, the clamp will be opened and the pot and furnace lowered slightly. During this operation air from exhaust ports in the connector assembly will sweep across the seal face to prevent cell contamination. A temporary metal plate cap will be dropped on top of the pot connector by means of the slide mechanism. The pot and furnace will then be lowered to the mobile position and moved to the sealing station, where a permanent seal will be attached. The connector in Fig. 2.5, which incorporates the welded cap design for permanent closure shown in Fig. 2.2, will also be modified to permit installation and testing of a permanent gasketed seal. After being sealed in the radioactive pilot plant, the pots will be removed from the furnace and stored for observation of pressure and temperature buildup. A vent on the caps will permit relief of any excess pressure that may build up.

2.2 Design of Radioactive-Cell Equipment (H. O. Weeren and J. O. Blomeke)

Equipment will be installed in a hot cell to study fission product volatility during evaporation and calcination of actual high-activity wastes from the Idaho Chemical Processing Plant and Hanford. The installation (2,3) is expected to yield information pertinent to radioactive pilot plant design and operation which cannot be obtained with synthetic wastes.

Preliminary engineering flowsheets and layout were prepared. Designs of the transfer tank, feed tank, condensate catch tank, seal pot, and scrub liquor catch tank were completed, and construction of some of these vessels and of the shell of the calciner furnace was started.

Waste solutions will be transferred by air lifts. Liquid seals will be used to isolate the calciner pot, condenser, and scrubber from the rest of the system so that these vessels can be kept under a nitric oxide gas blanket during operation, if desired. Since the feed rate to the calciner pot is below the capacity of even the smallest air lift, provision is being made to use two air lifts, one working against the other so that the difference in capacities will flow to the pot.

2.3 Engineering-Scale Studies (J. C. Suddath, C. W. Hancher, L. J. King)

Tests, reported in preliminary form previously, on simulated Purex and TBP-25 waste were made in the large (600 liter) batch evaporator-calciner system and in the small (25 liter) continuous system (Table 2.1). Control of both systems was good except for feed line plugging at high concentrations. The boil-up rate of the continuous evaporator was insufficient at the peak rate for the Purex flowsheet, but this has been corrected. With prolonged feeding time average feed rates decreased, but the bulk density of the calcined solids increased. An economic stopping point may be

Table 2.1 Engineering-Scale Pot Calcination Tests Conditions and Results

Feed Composition

Purex				TBP-25			
Fe^{3+}	0.5 M	Al^{3+}	0.1 M	Al^{3+}	1.7 M	Na^{+}	0.05 M
$SO_4^{=}$	1.0 M	Na^{+}	0.6 M	Hg^{++}	0.02 M	NO_3^{-}	5.8 M
Cr^{3+}	0.01 M	NO_3^{-}	6.1 M	Fe^{3+}	0.008 M	H^{+}	1.2 M
Ni^{3+}	0.01 M	H^{+}	5.6 M				

Test No.	Feed Type	System[a]	Concentration Factor	Water to Feed Ratio (liters/liter)	Off-gas to Feed Ratio (ft^3/liter)	Nitrate in Calcined Solids (wt %)	Bulk Density of Calcined Solids (g/cm^3)	Av. System Feed Rate (liters/hr)
43[b]	Purex	Continuous	1.3 - 2.2	Leak	Leak	0.008 - 0.9	1.28	50.0
44[b]			1.3 - 3.8	7.8	2.02	0.06 - 0.14	1.14	40.9
45		Batch	0.98- 1.35	3.9	2.20	0.01 - 4.7	1.17	25.2
46			0.98- 1.27	4.1	3.50	0.01 - 3.7	1.55	25.8
47	TBP-25	Continuous	1.2 - 2.3	3.4	1.90	0.36 - 6.0	0.57	30.6
48			0.93- 1.6	2.8	3.50	0.10 - 6.0	0.77	15.0
49			0.8 - 1.25	2.6	1.90	0.36 - 6.0	0.83	17.6
50[c]			0.8 - 1.47	2.4	2.40	0.08 - 4.1	0.52	11.5
51[c]		Batch	1.18- 1.38	2.5	3.20	0.08 - 6.0	0.59	7.0
52[c]			1.09- 1.44	2.3	2.40	0.06 - 0.18	0.44	9.8

a. Batch system of 600 liters capacity, continuous of 25 liters.
b. Stable Ru added to feed.
c. MBP and DBP added to feed.

determined by balancing operating time against basic fixed cost. Ruthenium volatilization was negligible. In five tests in which stable ruthenium was added to the feed, ruthenium in the evaporator condensate was below analytical detection except during minor upsets at the start of each test.

Data from Hanford (4) indicate a phosphate concentration of the order of 0.01 M in their IWW waste, and as much as 120 ppm of TBP and organic diluent in their tank farm condensates (5). The addition of 1 ml of MBP and DBP per liter of waste to the evaporation-calcination feed caused severe foaming and entrainment, resulting in lower average feed rates (Table 2.1). In laboratory-scale tests, both SAG-470 and Dow-Corning Anti-Foam A silicon additive broke the foam satisfactorily at or near the solution boiling temperature, but volatilized as the solution was concentrated to about one-third its original volume. Other anti-foaming agents will be tried.

Severe forming may not be encountered in calcination of ICPP TBP-25 waste. A 15-ml sample of waste from their tank WM-185, examined at ICPP, showed no appreciable foaming when evaporated to dryness in a 50-ml graduate although simulated TBP-25 waste doctored with DBP produced considerable amounts of foam.

2.4 Laboratory-Scale Fixation in Glasses (W. E. Clark, H. W. Godbee)

All the laboratory studies were made with simulated TBP-25 process waste solution: 1.72 M Al^{3+}, 0.003 M Fe^{3+}, 0.02 M Hg^{2+}, 0.05 M NH_4^+, 0.1 M Na^+, 1.26 M H^+, 6.6 M NO_3^-. Glasses were formed by evaporation of liquid from the solution followed by calcination to 1000°C.

2.4.1 Cesium Volatility

Cesium volatility probably will not be a problem in formation of a glass from waste containing sufficient acid oxides such as P_2O_5. Gamma scintillation counting showed the presence of 0.03% or less (background counting level) of the original Cs-137 in the evaporator condensate and 100.2% in an aqua regia solution of the solid product and stainless steel container dissolved in toto. In these experiments simulated waste containing 0.1 μc of Cs-137 tracer per milliliter was evaporated and calcined in small quartz equipment (Fig. 2.9 in ref. 1) with a 100-ml stainless steel beaker for a pot and a furnace instead of heating mantle. As glass-forming and fluxing agents, 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO were added per liter of waste.

2.4.2 Ruthenium Volatility

Operation in the presence of relatively small concentrations of phosphite and at low nitric acid concentrations and decreased pressure should minimize ruthenium volatility during evaporation-calcination. In a series of evaporation-fixation experiments in

which 0-2 moles of H_3PO_3 per liter was added to the waste, ruthenium in the condensate varied from 59.8 to 0.67% of the original when a quartz pot was used and from 47.2 to 0.11% when a stainless steel pot was used. At fixed phosphorous acid addition, the ruthenium in the condensate was a factor of 1.3-6.3 less with the stainless steel pot than with the quartz (Fig. 2.6), probably because of

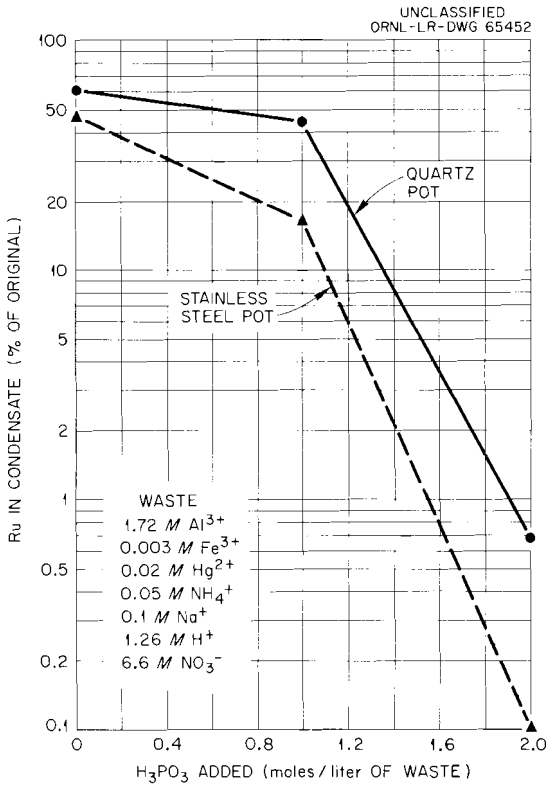

Fig. 2.6. Volatilization of Ruthenium During Evaporation-Calcination of Simulated TBP-25 Process Waste as a Function of Amount of ~~Phosphoric~~ Acid Added.
Phosphorous

plating out of ruthenium on the stainless steel. Small quartz equipment was used (Fig. 2.9 in ref. 1) with a 200-ml stainless steel or quartz pot and a furnace instead of heating mantle. The simulated waste contained 0.184 mg/ml of stable ruthenium and 0.1 μc/ml of Ru-106 tracer. The condensate was analyzed for Ru-106 by gamma scintillation counting. In previous studies to about 500°C the ruthenium in the residue dissolved in HCl, but that in the 1000°C residue has resisted dissolution by bases and non-oxidizing acids. The greater difficulty in dissolving ruthenium deposited at higher temperatures has also been observed at Hanford (6).

In Gillespie still studies ruthenium volatility from 0.5-10 M HNO_3 solutions containing only 0.002 M $RuCl_3$ ($3.7\text{-}4.0 \times 10^5$ c/m/ml Ru-106 tracer, equivalent to 1 μc/ml) was a function of the nitric acid volatility (Fig. 2.7, Table 2.2). At atmospheric pressure (744-752 mm Hg) the ruthenium volatility was described fairly accurately by the empirical equation

$$\log \frac{\text{M Ru in distillate}}{\text{M Ru in solution}} = 1.04 \log \text{M } HNO_3 \text{ in distilate} - 2.23$$

Activities in the distillate varied from 9 c/m/ml at 0.5 M original acid to 1.21×10^5 c/m/ml at 10 M original acid. However, from 12 M HNO_3, ruthenium volatility abruptly increased, in general agreement with Idaho's results (7), and two layers formed in the undisturbed distillate, the upper one orange colored with 9.1×10^5 c/m/ml of Ru-106 and the lower dark with 1.5×10^5 c/m/ml.

Ruthenium volatility from 1.7 M $Al(NO_3)_3$ containing nitric acid was similar to that from plain nitric acid solutions at added acid concentrations up to ~ 1.0 M but increased rapidly at higher acidities (Fig. 2.7). The greater volatility may be due to the higher boiling points of the concentrated salt solutions, since lowering the equilibrium distillation temperature of 1.7 M $Al(NO_3)_3$ — 4 M HNO_3 from 115°C to 108 and 101.5°C, by decreasing the pressure from atmospheric to 565 and 444 mm Hg, respectively, decreased the ruthenium volatility from 4.97×10^4 c/m/ml to 4.53×10^3 and 2.96×10^3 c/m/ml.

The relation between ruthenium and nitric acid volatilities (Figs. 2.8 and 2.9) indicates the advantage of operation at low acidity, although there is no apparent threshold for ruthenium volatility from solutions that yield distillates between about 0.1 and 8 M in HNO_3. Separation of nitric acid from ruthenium increases rapidly when the feed acidity is < 2 M (Fig. 2.10), but the concentration of nitric acid distilled decreases rapidly in this range and will be 1 M or less from solutions 1.7 M in $Al(NO_3)_3$ (Table 2.2).

The addition of 0.1 M phosphorous acid to 12 M HNO_3 18 hr prior to distillation lowered the ruthenium volatility from 2.78×10^5 to 662 c/m/ml and the nitric acid in the distillate from 8.65 to 7.68 M. A similar addition to 1.7 M $Al(NO_3)_3$ — 2 M HNO_3 immediately prior to distillation lowered the ruthenium in the distillate from 1.77×10^4 to 85 c/m/ml.

2.4.3 Cesium Leaching

From the phosphate-lead glass containing TBP-25, the leaching rate of the glass decreased from 2.1×10^{-6} g/cm^2/day at the end of the first week to 2.5×10^{-7} g/cm^2/day at the end of

Table 2.2. Volatilization of Ruthenium from Nitric Acid Solutions

(All feed solutions 0.002 M in Ru, ~1 μc Ru-106/ml;[a] feed vol 130 ml; distillate vol 9 ml)

HNO_3 in Feed (M)	$Al(NO_3)_3$ in Feed (M)	HNO_3 in Vapor (M)	HNO_3 in Liquid (M)	HNO_3 Distillation Factor, $HNO_3(V)/HNO_3(L)$	Ru-106 in Feed (10^5 counts/min.ml)	Ru-106 in Vapor (c/min.ml)	Ru-106 in Liquid (10^5 c/min.ml)	Ru Distillation Factor, Ru(V)/Ru(L)	Ratio of Distillation Factors $\frac{HNO_3(V)}{HNO_3(L)} / \frac{Ru(V)}{Ru(L)}$	Temperature (°C) Equilibrium (Still Head)	Temperature (°C) Still Pot	Pressur (mm H
0.5	0	0.005	0.54	9.31×10^{-3}	3.70	9	3.97	2.27×10^{-5}	410	100	101	~74
1	0	0.022	2.15	1.02×10^{-2}	3.94	48	4.23	1.13×10^{-4}	90.3	102	103	~74
4	0	0.23	4.30	5.35×10^{-2}	3.85	570	4.14	1.38×10^{-3}	38.8	104.5	105.5	~74
6	0	0.79	6.39	0.124	3.88	1.67×10^{3}	4.04	4.14×10^{-3}	30.7	107.5	109	~74
8	0	2.51	8.41	0.298	3.87	6.67×10^{3}	4.15	1.61×10^{-2}	18.5	111.5	113	~74
10	0	4.74	10.4	0.456	3.86	1.21×10^{4}	4.18	2.90×10^{-2}	15.7	116.5	115	~74
12	0	8.65	12.3	0.706	3.70	2.78×10^{5}	3.77	7.38×10^{-1}	0.956	117	119	~74
0.24[b]	1.7	0.023	0.34[b]	6.8×10^{-2}	3.57	48	3.84	1.25×10^{-4}	544	106	107.5	~74
0.5	1.7	0.13	0.527	0.247	3.80	292	4.08	7.16×10^{-4}	345	107.5	108.5	~74
1	1.7	0.31	1.05	0.295	3.78	1.11×10^{3}	4.06	2.74×10^{-3}	107.7	109	110	~74
1.5	1.7	0.58	1.57	0.369	3.58	4.42×10^{3}	3.84	1.15×10^{-2}	29.0	110	111.5	74
2	1.7	1.03	2.07	0.495	3.69	1.77×10^{4}	3.95	4.48×10^{-2}	110.5	111	112.5	~74
4	1.7	3.41	4.04	0.844	3.73	4.97×10^{4}	3.97	1.25×10^{-1}	6.75	115	116.5	~74
6	1.7	7.30	5.90	1.24	3.93	8.58×10^{4}	4.16	2.18×10^{-1}	5.67	118	119.5	
0.5	1.7	0.096	0.53	0.181	3.49	139	3.75	3.71×10^{-4}	488	100	102	57
1	1.7	0.27	1.055	0.256	3.58	633	3.84	1.65×10^{-3}	155	101	102.5	572
2	1.7	0.92	2.08	0.442	3.51	2.69×10^{3}	3.77	7.14×10^{-3}	61.9	104	105	57
4	1.7	3.27	4.06	0.806	3.63	4.53×10^{3}	3.90	1.16×10^{-2}	61.5	108	109.5	569
6	1.7	7.10	5.17	1.373	3.85	2.01×10^{4}	4.12	4.88×10^{-2}	28.1	110.5	112	567
4	1.7	3.28	4.05	0.810	3.57	2.96×10^{3}	3.83	7.74×10^{-3}	104.6	101.5	103	443
12[c]	0	7.68	12.3	0.624	3.73	662	4.005	1.65×10^{-3}	3.78×10^{2}	117.5	119	~748
2[c]	1.7	0.94	2.08	0.452	3.59	85	3.86	2.2×10^{-4}	2.06×10^{3}	111	113	747

[a] 1 μcurie of Ru-106 gave 3.7×10^5 c/m.ml on the counter used.

[b] From pH measurement of $Al(NO_3)_3$ solution at room temperature, no added acid.

[c] Contained 0.1 M H_3PO_3.

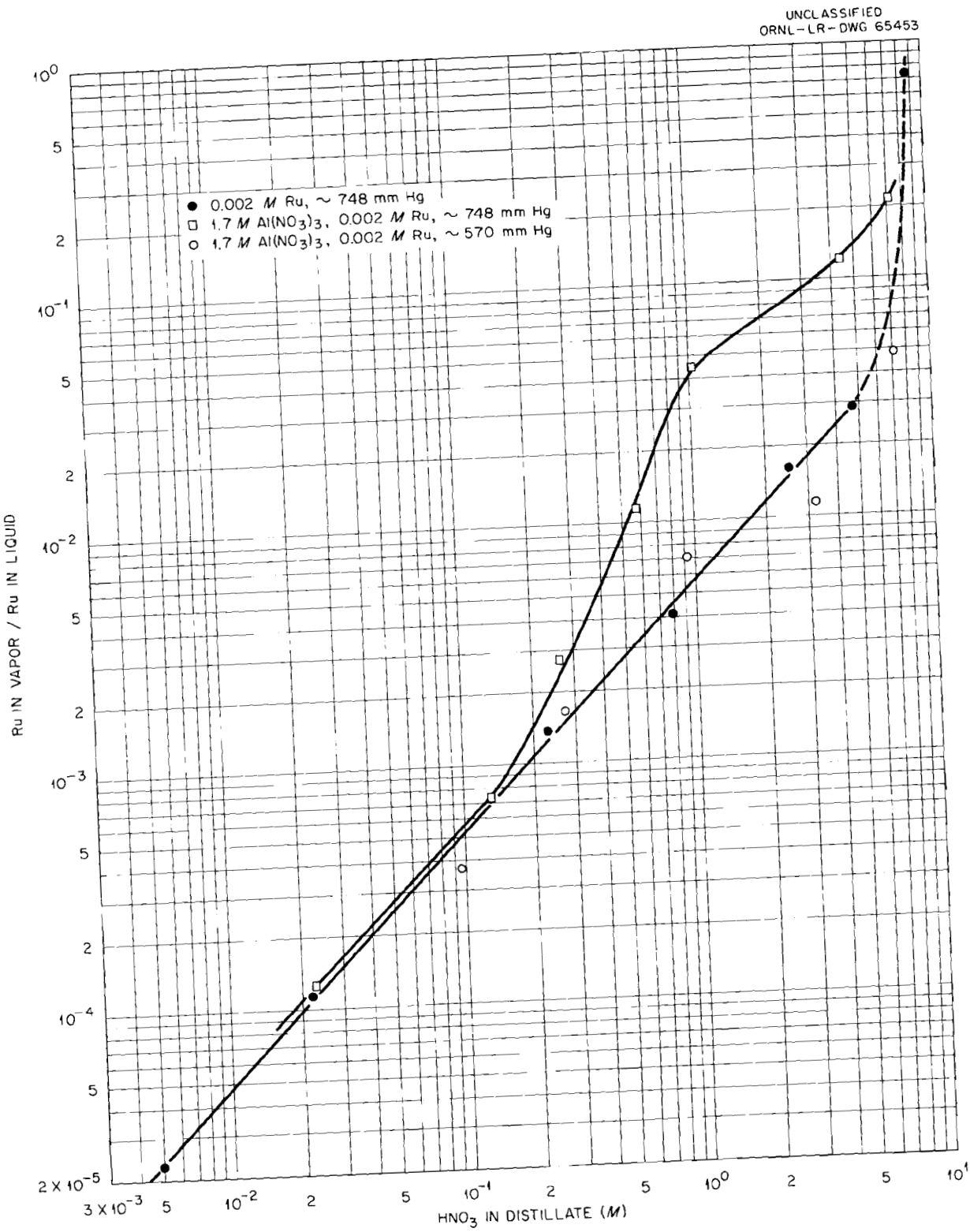

Fig. 2.7. Volatilization of Ruthenium from Acid Nitrate Solutions as a Function of Nitric Acid Volatility.

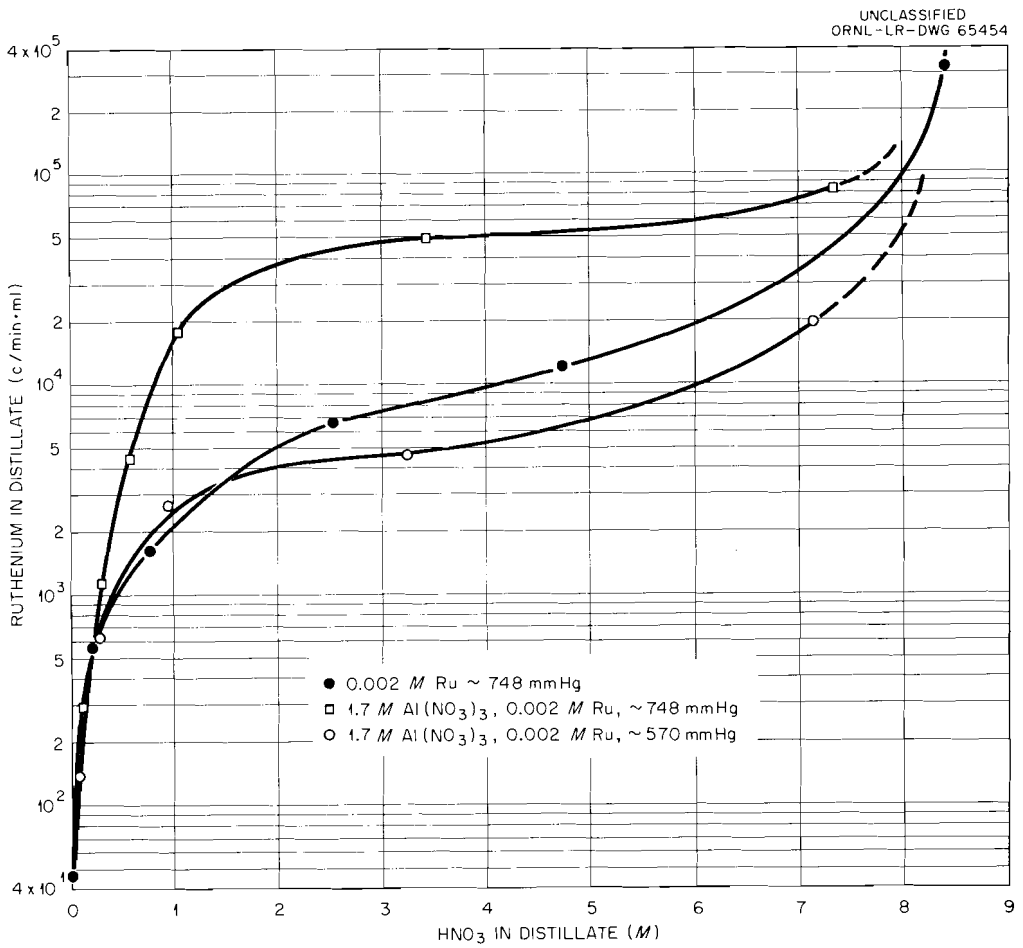

Fig. 2.8. Volatilization of Ruthenium from Nitric Acid Solution as a Function of Nitric Acid Concentration (9 ml of Distillate per 130 ml of Feed).

the fifth week. This corresponds to 4.9×10^{-4} and 5.5×10^{-5} of the original Cs-137 leached in the first and fifth weeks, respectively. These results compare favorably with those obtained at Harwell (8) with silicate-borate glasses containing approximately the same percentage of oxides from waste but are about one order of magnitude higher than the results at Chalk River (9) with nepheline syenite-lime glasses containing about one-third this amount of waste oxides.

The glass was made from 500 ml of waste solution containing 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO per liter and 0.082 μc of Cs-137 per milliliter of waste. The mixture was evaporated to dryness, heated to about 1000°C, and cooled slowly to room temperature. A 73.5-g sample of the glass, density 2.84 g/ml, containing 26 wt % waste oxides including 0.23 μc of Cs-137 per gram, was used. Its surface area, calculated from external dimensions, was 61 cm^2.

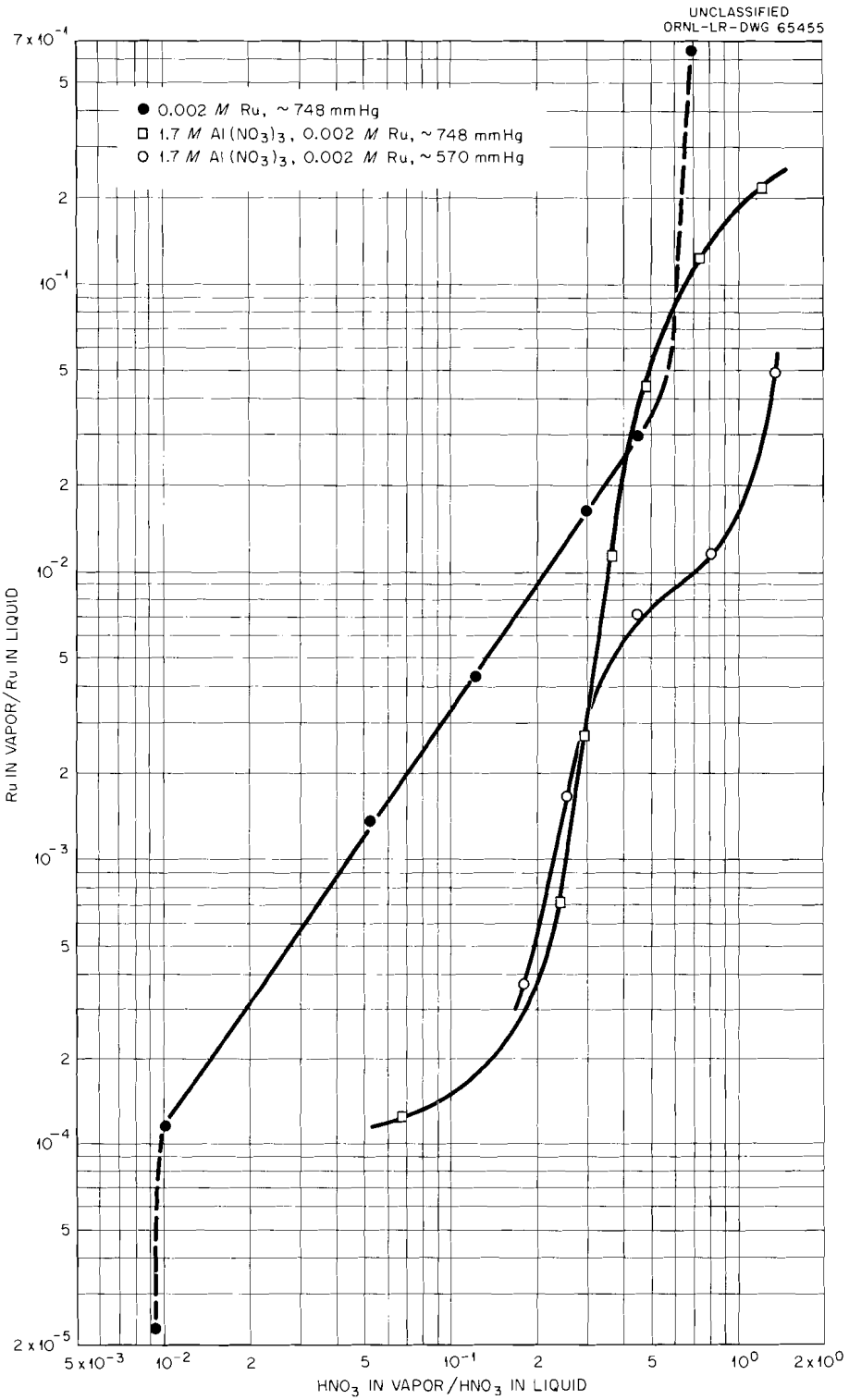

Fig. 2.9. Relation Between Ruthenium and Nitric Acid Distillation Factors. Distillation factor = the ratio CV/CL, where CV and CL are the concentrations of one component in the vapor (distillate) and thick liquor, respectively.

The sample was leached in a polyethylene cell containing 500 ml of distilled water, which was circulated through the system at 100 ml/min volumetric (1.5 cm/min linear) flow rate. The water was completely replaced each week. In calculating leaching rates, it was assumed that the activity is uniformly distributed throughout the glass.

2.4.4 Semicontinuous Glass Formation

Glass was produced by semicontinuous evaporation, calcination, and heating to 1000°C of a simulated TBP-25 waste solution to which 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO per liter had been added (Fig. 2.11). The product, with a density of ~ 2.9 g/cm^3, 1 vol of

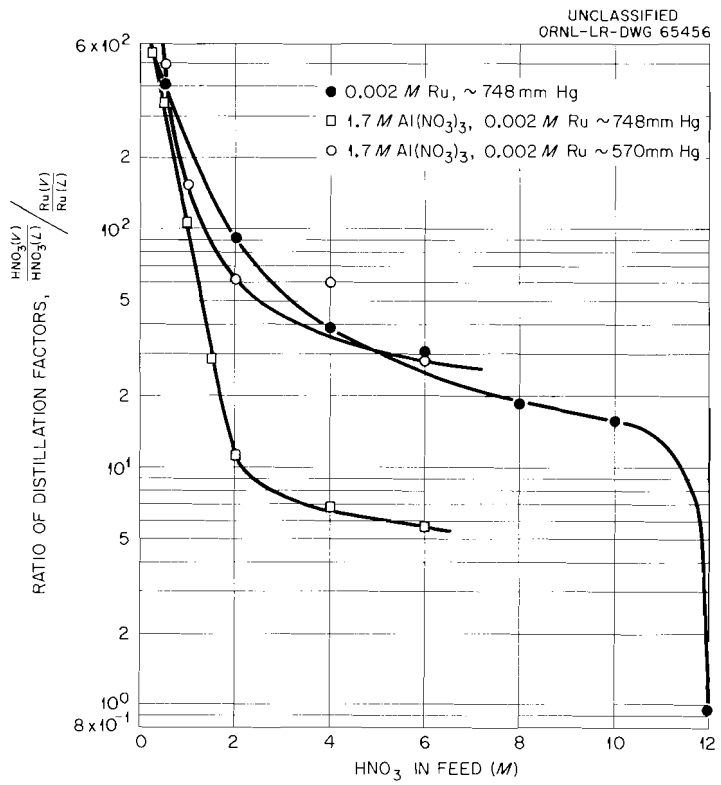

Fig. 2.10. Ratio Between Nitric Acid and Ruthenium Distillation Factors as a Function of Nitric Acid Concentration in Feed.

glass representing 8 vol of waste, compares favorably with the product of a batch experiment, which had a density of 2.84 g/cm^3, 1 vol of glass representing 8.1 vol of waste. However, as shown by neutron activation analyses, 22.7, 1.4, and 0.3% of the original ruthenium appeared in the condensate, the liquid from the packed absorber, and the liquid in the gas recirculation jet, while in the batch experiment only 0.68% of the original ruthenium was in the condensate and 0.03% or less in the off-gas scrub liquid. Further work on ruthenium volatility is planned.

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Fig. 2.11. Phosphate-Lead Glass Incorporating Simulated TBP-25 Waste Oxides. Additives: 2.0 moles of NaH_2PO_2 and 0.25 mole of PbO per liter of waste.

The experiment was performed in previously decribed equipment (Fig. 6.2 in ref. 10) consisting of a 21 x 4-in.-dia stainless steel pot in a 9-kw furnace, a downdraft condenser, packed absorber column, polyethylene expansion bag, and gas recirculation jet. Feed was pumped in at a rate of about 45 ml/min with the liquid level in the pot gradually rising from about 6 in. above the bottom to about 4 in. from the top during the feeding.

The high ruthenium volatility may be explained, at least in part, by leaks that developed when the thread lubricant in the fittings screwed on the top of the pot burned out at high temperatures; welded connections will be used in the next experiment. Since the pot was operated under vacuum (about 4 in. H_2O), air was sucked into the pot and could have formed the volatile ruthenium tetroxide at temperatures about 600° (11). Mercury in the condensate, liquid from the packed absorber, and liquid from the gas recirculation jet amounted to 78.9, 10.2, and 1.5%, respectively, of the original mercury.

3.0 LOW-LEVEL WASTE TREATMENT

A scavenging-ion exchange process (12-14) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations, with ORNL low-activity waste as the medium for study. Phenolic cation exchange resins, which have a Cs/Na separation factor of up to 160 compared to 1.5 for sulfonic and which also sorb strontium, are used in the column. The solutions are clarified prior to ion exchange since ion exchange resins do not remove colloidal materials efficiently.

3.1 Pilot Plant (R. E. Brooksbank, J. O. Blomeke, W. T. McDuffee, J. M. Holmes, W. R. Whitson)

Construction of a 10-gpm pilot plant for the scavenging-ion exchange process was completed (Figs.3.1-3.3). The major equipment items are the flash mixer, flocculator, clarifier, sludge filter, and ion exchange columns. Three shakedown runs were made for a total of 234 hr operation, with 134,000 gal of ORNL tap water, and a 73-hr continuous full-scale run was made in which a total of 44,425 gal of ORNL process waste, representing 1564 bed volumes, was treated. The chief constituents, strontium and cesium, were removed from the feed by factors of 2956 and 287, respectively.

Cold Operability Tests. Repeated plugging of the NaOH pump by foreign material in the commercial 19 M caustic was eliminated by using rayon-grade caustic and diluting it in the pump head tank.

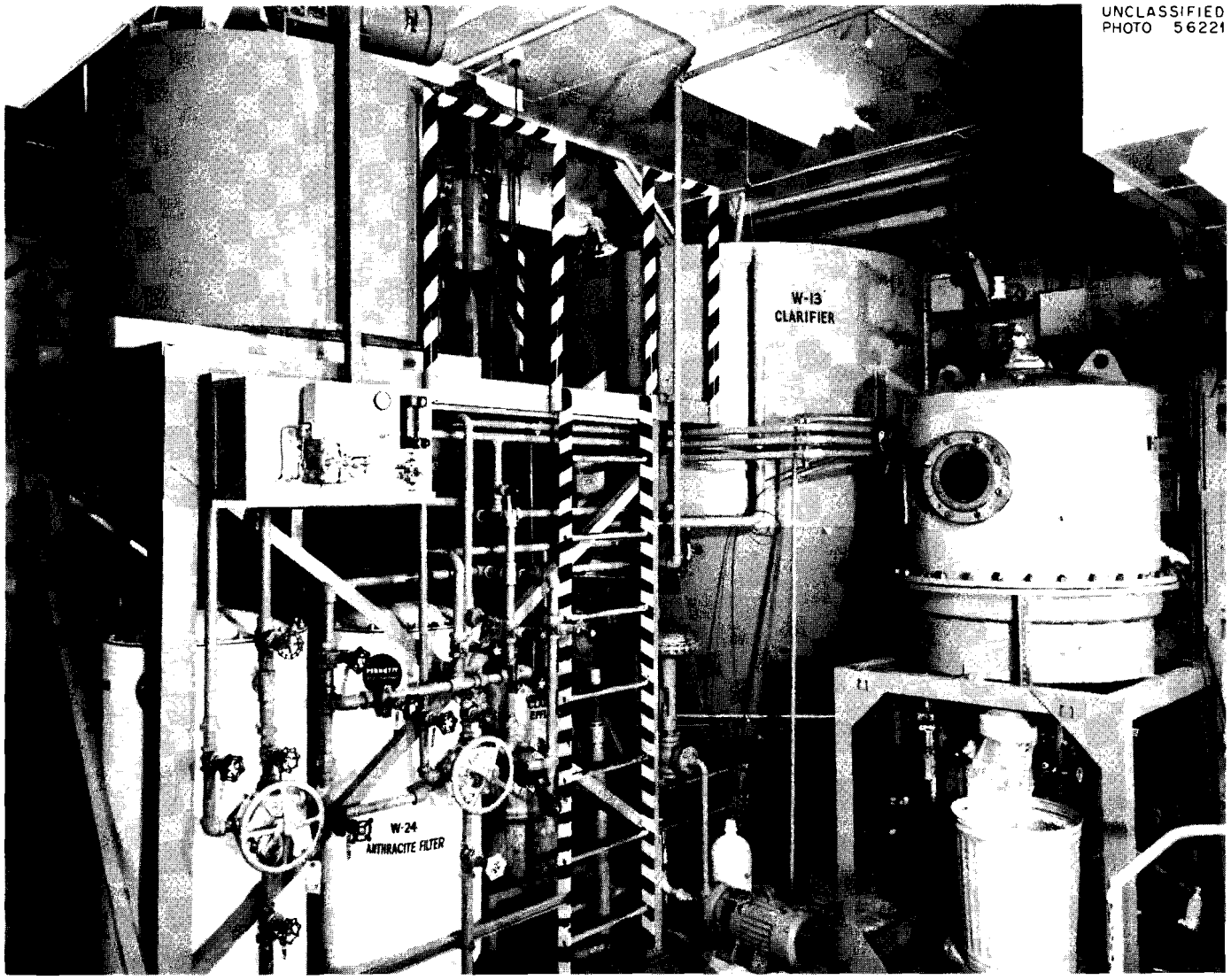

Fig. 3.1. Flocculation, Clarification, and Filtration Equipment for Low-Level Pilot Plant.

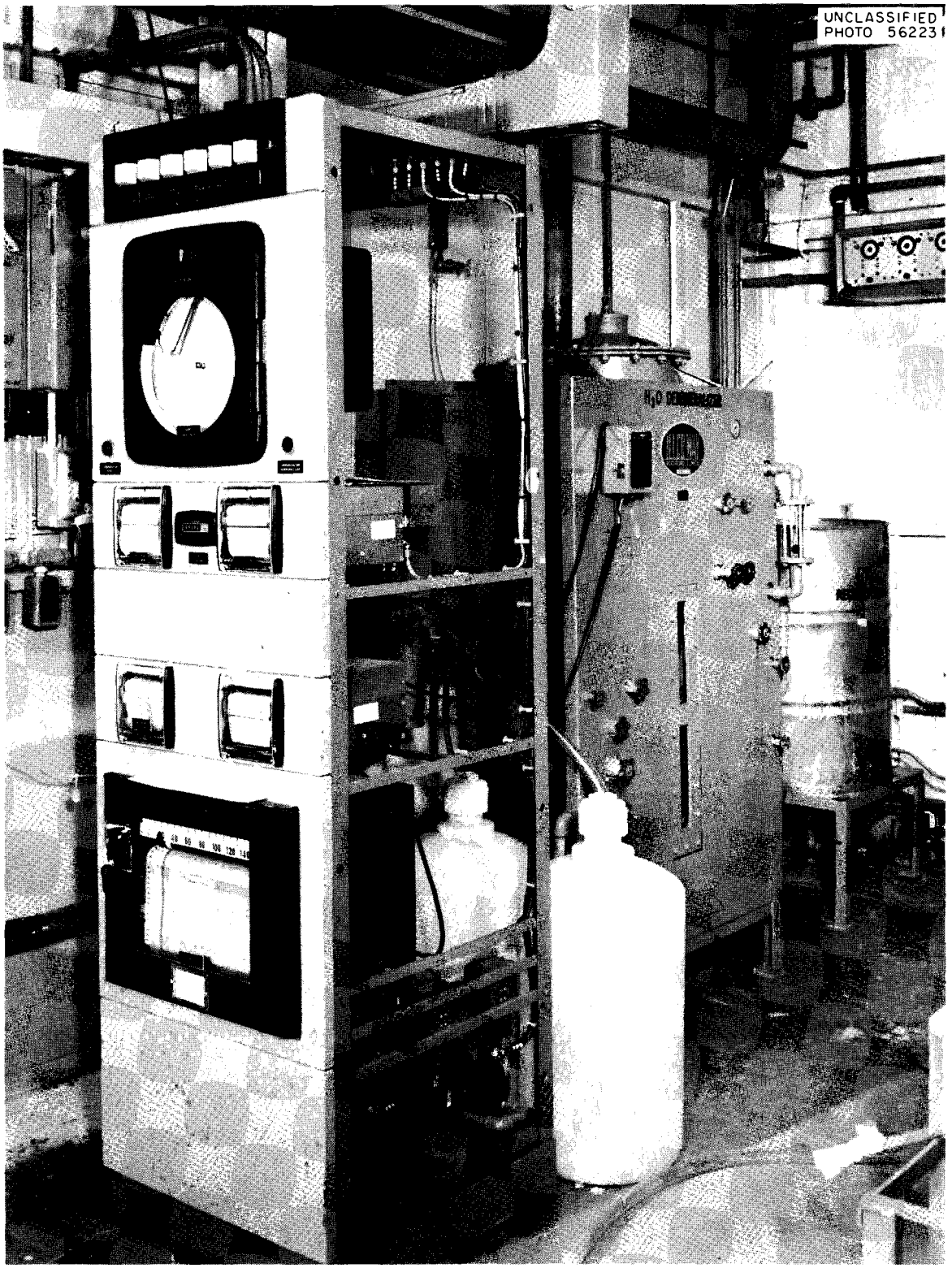

Fig. 3.2. Control Panel for Low-Level Pilot Plant.

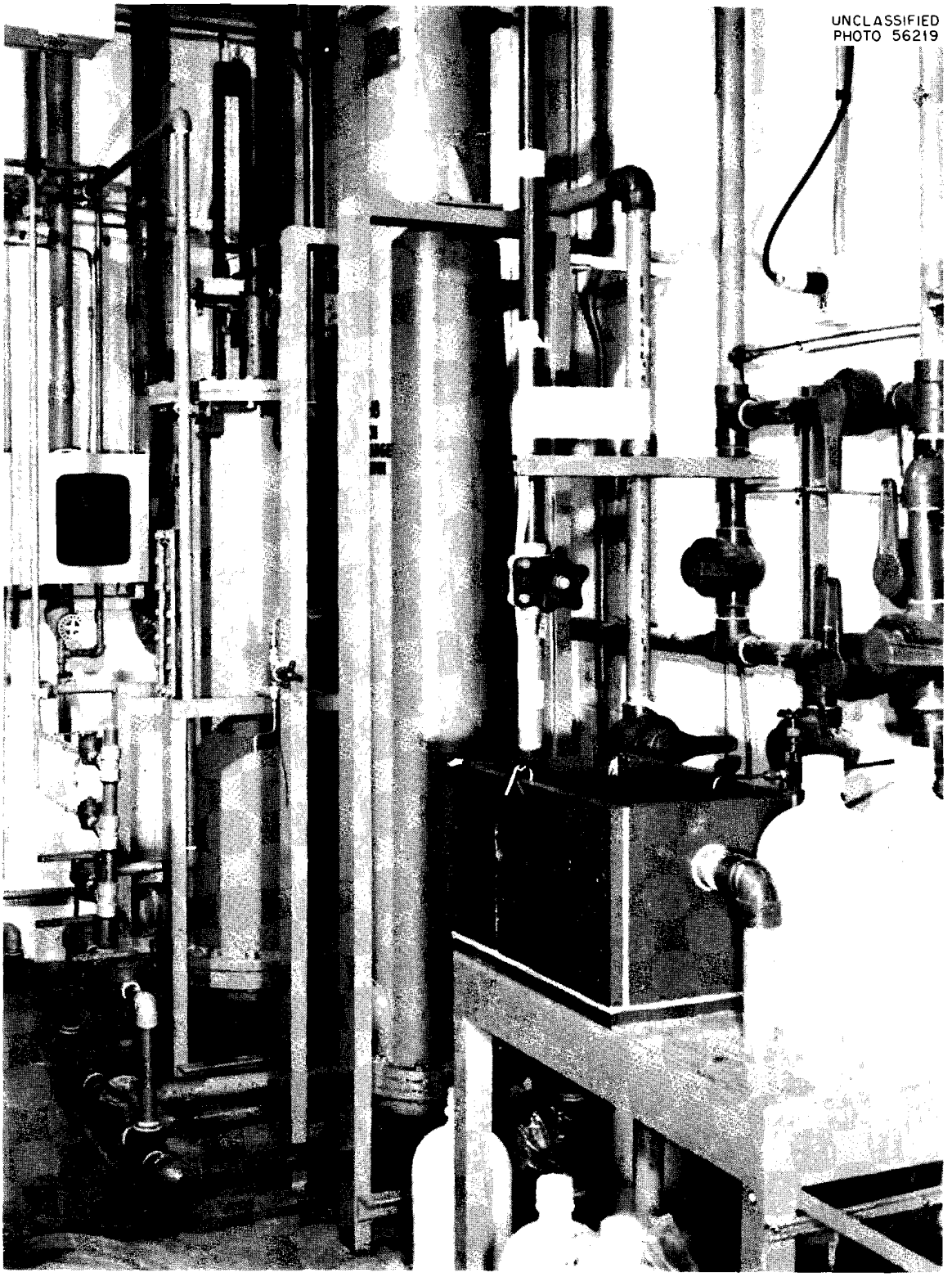

Fig. 3.3. Ion Exchange Equipment for Low-Level Pilot Plant.

The clarifier was operated at flows of 5-12 gpm. An inner cone that had been installed proved impractical compared to the flow-diverting baffle as originally designed. With the cone, hardness and turbidity of the effluent overflowing the clarifier were both a factor of 5 higher than with unrestricted sludge, and an adequate sludge blanket could not be maintained even at half the design flow rate. The 1.5-in. Sch 40 steel pipe between the flocculator and clarifier was replaced with a 2-in.-i.d. caustic-resistant steel-reinforced rubber hose to decrease line resistance and prevent the floc from breaking into smaller particles.

Initial tests with the Permutit sand- and anthracite-filled polishing pressure filters indicated that filtration times of 40-72 hr can be expected before excessive pressure drops will necessitate backwashing of these units. The anthracite filter performed suitably, although the turbidity of the effluent from it was 2 ppm as opposed to 0.3 ppm for the sand filter during one test period.

Of three methods tested for filtering the contaminated sludge from the bottom of the clarifier vessel, pressure filtration with an Eimco leaf filter was the easiest to operate. However, vacuum filtration with an Oliver rotary drum unit (Fig. 3.4) was selected for radioactive operation because of the health hazard involved in direct handling of the sludge with the leaf filter. Decantation with three 55-gal drums in series was used during transient operation.

The rotary drum filter performed sporadically during both cold testing and hot operation, but satisfactorily for 24 hr during the latter part of the cold testing. The failure during the hot runs was probably the result of the scraper blade being loose and pushed slightly away from the precoated surface, permitting an impervious 1/16-in.-thick layer of sludge to form on the precoating material. This was discovered on inspection of the apparatus after the hot runs. The average sludge withdrawal rate from the clarifier was 2.1 gpm, which produced 0.5 lb per hour of sludge cake containing 75 wt % water. This was only 25% of the theoretical sludge formation rate; however, the level of the sludge blanket remained fairly constant in the clarifier.

No major difficulties were encountered with either the 10-in.-dia 8-ft-high or 18-in.-dia 32-in.-high resin columns during cold testing. Flowing stream hardness titrations indicated no calcium breakthrough.

ORNL Process Waste. From ORNL waste water, the major contaminants, strontium and cesium, were removed by factors of 2956 and 287, respectively, > 99% of each. Analysis of plant effluent samples indicated product activities of 0.9 and 0.009%, respectively, of current MPC_w values for Sr-89-90 and Cs-137 for a 168-hr week. About 63% of the

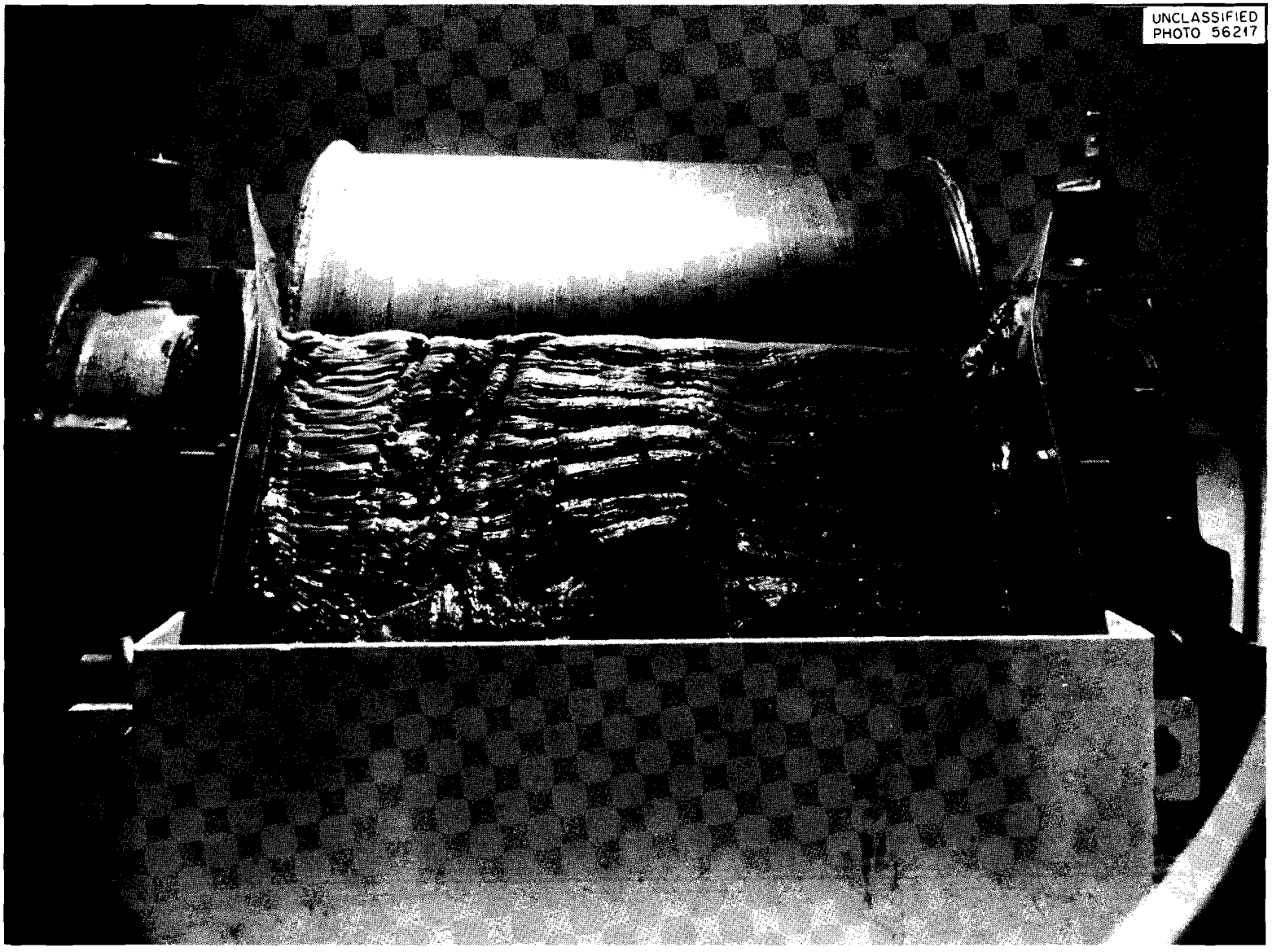

Fig. 3.4. Removal of Radioactive Sludge with Rotary Drum Filter.

Sr-89-90 was removed by the sludge blanket in the clarifier and the remainder by the resin, but essentially all the cesium was removed by ion exchange (Table 3.1).

Table 3.1 Removal of Activity from ORNL Low-Activity Process Waste (Run HR-2)

Activity	Clarification-Filtration DF	Clarification-Filtration % Removed	Across Ion Exchange DF	Across Ion Exchange % of Remaining Removed	Overall DF	Overall % Removed
Gross β	4.8	79.2	6.4	84.0	30.0	96.7
Gross γ	4.4	77.1	10.1	90.1	44.2	97.7
Sr-90, Sr-89	2.7	63.1	1090	99.9	> 2956	> 99.9
Cs-137	1	0	288	99.5	287	99.5
Co-60	19.1	92.1	1.3	22.6	16.3	93.9
TRE	3.5	77.1	1.0	1.8	3.5	71.6

Effluent from the 10-in.-dia by 8-ft-high resin bed contained no detectable hardness but contained 2 ppm turbidity from leaching of resin coloring matter. Sorbed material was eluted from the resin with 10 vol of 0.5 M HNO_3 (Fig. 3.5), and the resin was rinsed with demineralized water and converted to the Na^+ form by 20 vol of 0.1 M NaOH.

In a preliminary run, a total of 58,380 gal of process waste water was processed over a 97-hr period to displace nonradioactive sludge blanket formed earlier with the use of only the flash mixer, flocculator, and clarifier. Approximately 24 hr after startup the feed solution hardness increased from 114 ppm (expressed as $CaCO_3$) to 144 ppm, causing the clarifier effluent hardness to increase from 18 to 50 ppm. An attempt to decrease the hardness by pumping 40-80 ppm of Na_2CO_3 to the flash mixer, to make up for apparent carbonate deficiency in the feed, was unsuccessful.

3.2 Process Development (W. E. Clark, R. R. Holcomb)

The Milton-Roy Chemalyzer used for continuous total hardness measurements on the ion exchange column effluent in the pilot plant did not function properly because of the high pH (11.9-12.0) of the stream. A laboratory study showed that the instrument would indicate a hardness breakthrough but would not give quantitative results. Attempts to compensate the Chemalyzer for the constant 0.01 M NaOH concentration in the plant effluent stream by acidifying the reagent solution have been unsuccessful in restoring quantitative accuracy. However, the study has produced a new manual hardness titration procedure with sensitivity to 1 ppm or less.

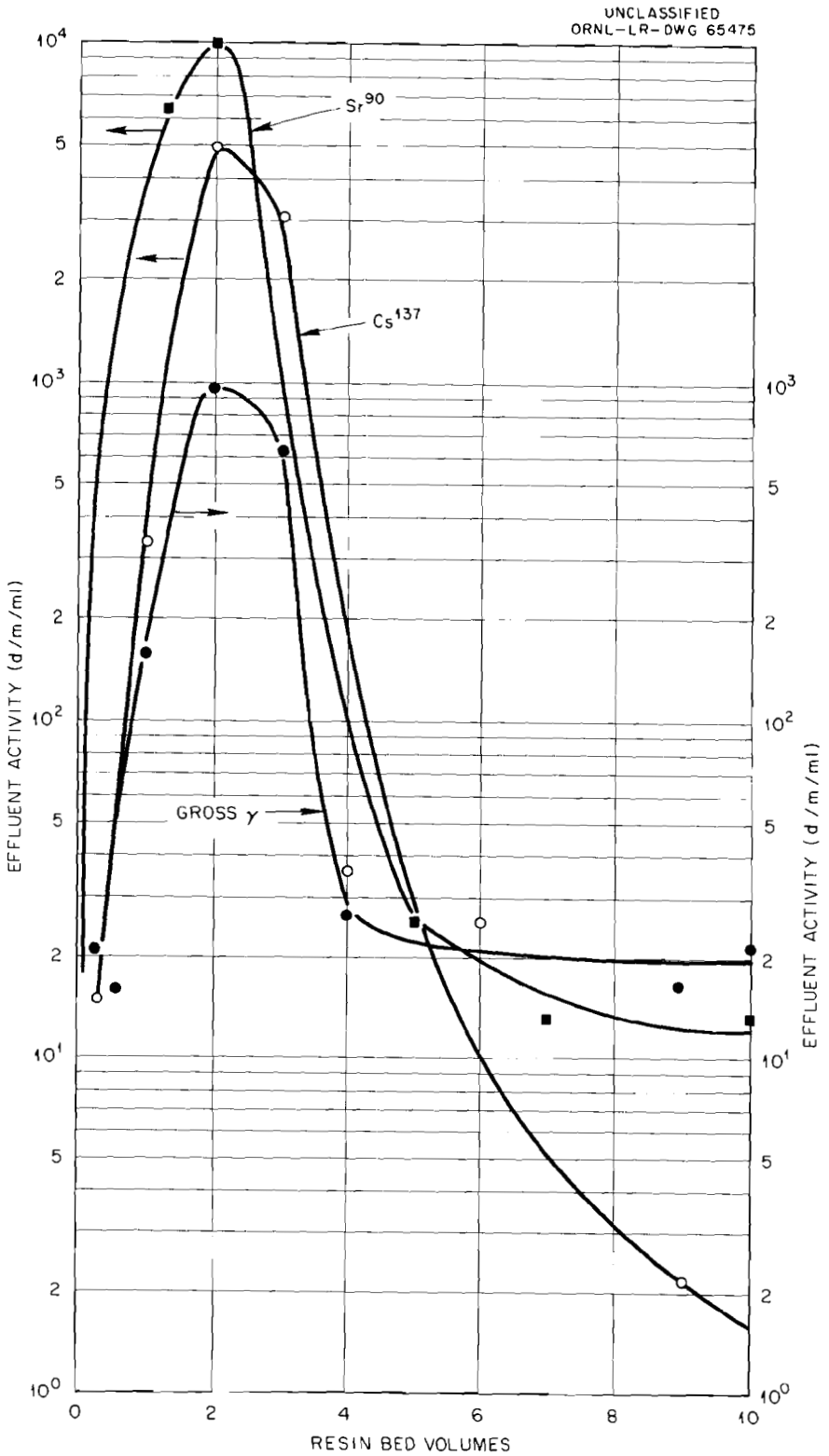

Fig. 3.5. Removal of Gross γ, Cs-137, and Sr-90 from Duolite CS-100 Resin with 0.5 M HNO_3.

The head-end treatment of the scavenging-ion exchange process with caustic and copperas ($FeSO_4.7H_2O$) should produce higher decontamination factors than can be obtained with the cold lime-soda process now in use. ORNL tap water, which contains 110-116 ppm of total hardness (EDTA) (15) as $CaCO_3$ and 88-95 ppm total alkalinity (no phenolphthalein alkalinity) as $CaCO_3$, was treated with lime soda in one case and caustic-copperas in the other in standard jar tests. After flocculation the total hardness values were 55 and 47 ppm, respectively, and after overnight settling, 49 and 9.9 ppm.

Although the ruthenium concentration in ORNL process waste water is below the 10% MPC_w discharge level, and little or no specific ruthenium treatment is required, improvement of decontamination from ruthenium is being studied for sites where ruthenium may be a major contributor and for possible transient surges of ruthenium at ORNL. Decontamination factors for Ru-106 tracer from tap water varied somewhat with the iron concentration when caustic copperas was used:

FE, ppm	DF	Fe, ppm	DF
0	9.4	10	10.8
5	9.6	20	10.8

The difference between the d.f.'s with 0 and 10 ppm of iron would probably be much greater with actual waste. However, the added cost for chemicals and for handling the additional bulk precipitate produced render the increase from 5 to 10 ppm of iron infeasible unless it is necessary for stabilization of the sludge blanket operation in the clarifier.

The ruthenium remaining in solution after caustic-copperas treatment could be further decreased by contact with an anion-exchange resin. The ruthenium distribution coefficient was 250 with a quaternary strong base (styrene) anion exchange resin, compared to 2 for the same solution with the carboxylic-phenolic cation exchange resin.

4.0 ENGINEERING, ECONOMICS, AND HAZARDS EVALUATION

R. L. Bradshaw, J. J. Perona, J. T. Roberts

A comprehensive study has been undertaken to evaluate the economics and hazards associated with alternative methods for ultimate disposal of highly radioactive liquid and solid wastes. All steps between fuel processing and ultimate storage will be considered, and the study should define an optimum combination of operations for each disposal method and indicate the most promising methods for experimental study.

The study of salt mine space required to dissipate the fission product heat in the waste from a 15,000 Mw_e (56,000 Mw_t) nuclear power economy was continued. In a previous report of this series plots of peak temperature rise, heat flux, and gross mine area against age of waste at burial were obtained from the infinite slab heat calculation assuming that all the wastes were generated at the same time (16) (all future reports, however, will use the term "net" area to indicate the actual mined room area used for storage). The actual case will more nearly approximate a continuous generation of wastes, and the slab calculations were therefore redone with the assumption of a continuous accumulation of wastes with optimum dead storage time in tanks as defined in a previous cost study (17).

4.1 Liquids in Salt

The new slab calculations affect the curves in Figs. 4.1-4.3 of ref. 16 over the region from 0.33 to 8 years age of waste at burial. At 0.33 year and from 8 to 30 years the curves are unchanged. Between 0.33 and 8 years the curves of the previous Figs. 4.1 and 4.3 are shifted upward, the maximum shift being ~ 20% at waste ages around one year. The previous Fig. 4.2 is shifted downward correspondingly over the same region. The net result is that slightly more mine area is required to store wastes aged < 8 years, e.g., 36 acres/year, gross, for 1-year old wastes rather than the 31 acres indicated in the previous Fig. 4.3.

4.2 Calcination Vessels Above Floor

Mined areas for storage of calcined solid wastes in rooms in salt deposits were calculated with temperature limits of 1650°F at the cylinder axis and 400°F at the surface of the salt room. The rooms were assumed to lie in the same horizontal plane, and the dissipation of heat into the salt was calculated with the slab code. The convection coefficient between the vessel wall and the room air was calculated from

$$h = 0.27\left(\frac{T_W - T_A}{D}\right)^{1/4} \qquad (1)$$

where h = natural convection coefficient, Btu/hr/ft/°F

T_W = temperature at wall of vessel, °F

T_A = temperature of air, °F

D = vessel diameter, ft

Heat fluxes to the floor and ceiling of the room were assumed equal, and coefficients were calculated from

$$h = 0.22\,(T_W - T_S)^{1/3} \qquad (2)$$

where T_S = ceiling or floor surface temperature, ^{o}F.

Most of the heat is transferred from the vessels to the salt surface by radiation. The assumption of a view factor of unity for all cases was subsequently found to be a good one because the amounts of floor and ceiling area per vessel are large in all cases at the minimum burial time if the vessels are uniformly spaced. An emissivity for stainless steel vessels of 0.5 was assumed.

Permissible heat generation rates subject to the limiting temperatures were calculated with parameters of waste type, vessel diameter, and mine area per vessel. Permissible heat generation rates were converted to age of wastes by the use of Fig. 4.1. The minimum storage age before burial for each type of waste for a given vessel diameter was obtained by plotting the area per cylinder vs waste age to give $T_W - T_S = 1250^{o}F$, and on the same graph the curve of $T_S = 400^{o}F$ calculated with the infinite slab code. A plot for acidic Purex waste in 6-in.-dia vessels is given in Fig. 4.2. The intersection of the curves gives the minimum permissible age of the waste at burial.

The mine area per cyclinder at the intersection is optimum in the sense that the permissible temperature rise in both the calcined waste and the salt is fully utilized. Minimum ages at burial and required mine areas per cylinder at the minimum age are given for the various waste types in Table 4.1. These minimum ages supersede those given in ref. 16. The net yearly amount of mine space required for each waste type if buried at the minimum age varies from 1.26 acres/year for acidic Thorex in 24-in.-dia vessels to 11.45 for reacidified Purex waste filled twice in 6-in.-dia vessels (Table 4.2). Figure 4.3 shows the net mine area required to store solid wastes above the floor as a function of the age of the waste at the time of storage. It is assumed for this figure that Purex and Thorex wastes are buried at the same age.

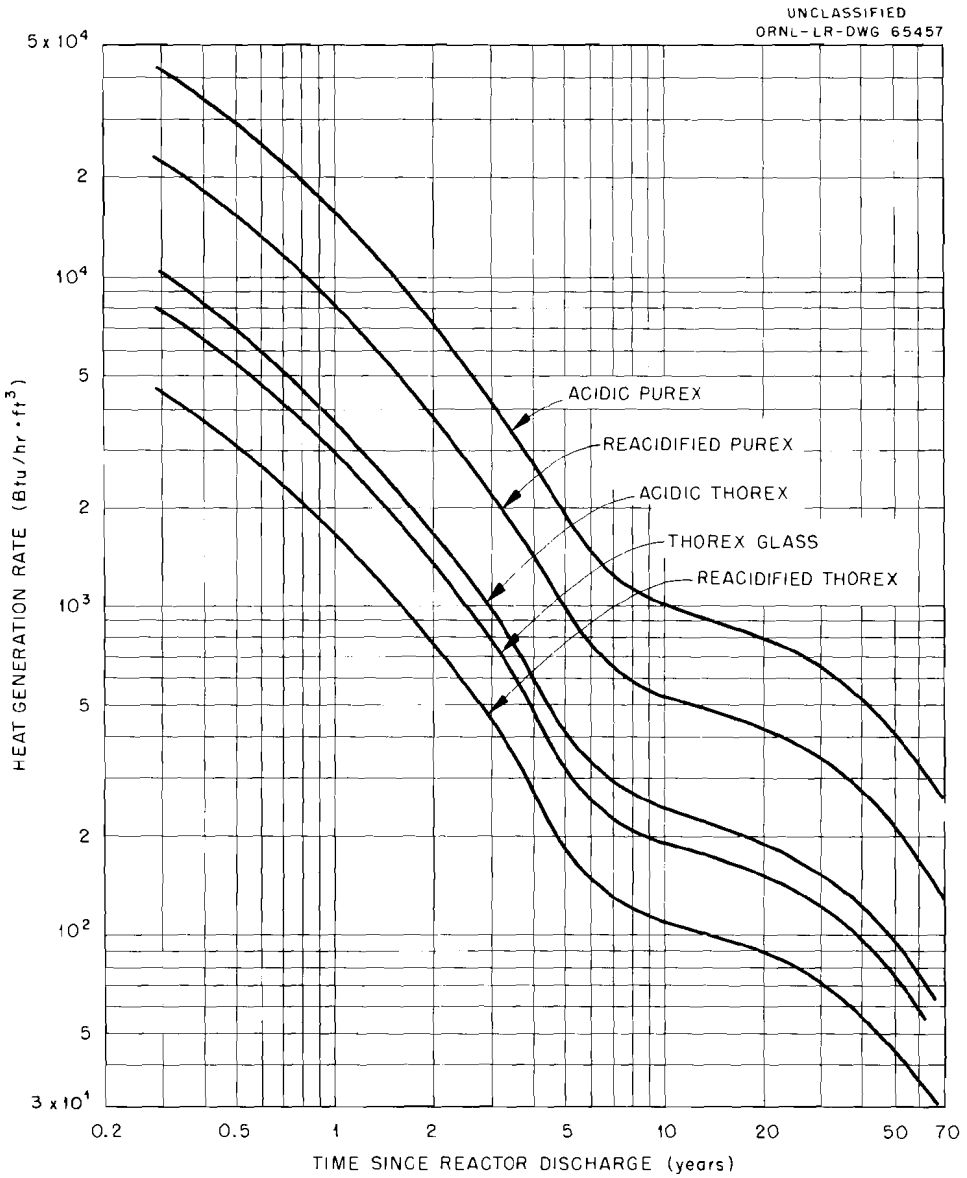

Fig. 4.1. Heat Generation Rate as a Function of Age for Calcined Solid Wastes Assuming Optimum Dead Storage Times.

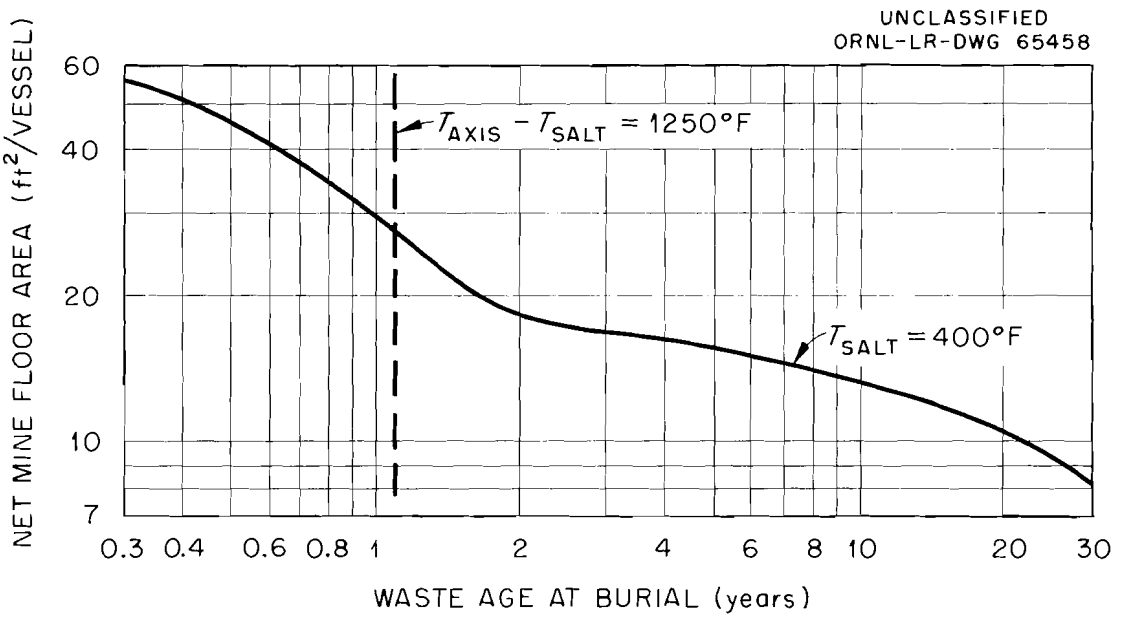

Fig. 4.2. Determination of Minimum Burial Age of Calcined Acidic Purex Waste in 6-in.-dia Vessels Stored in Salt Rooms.

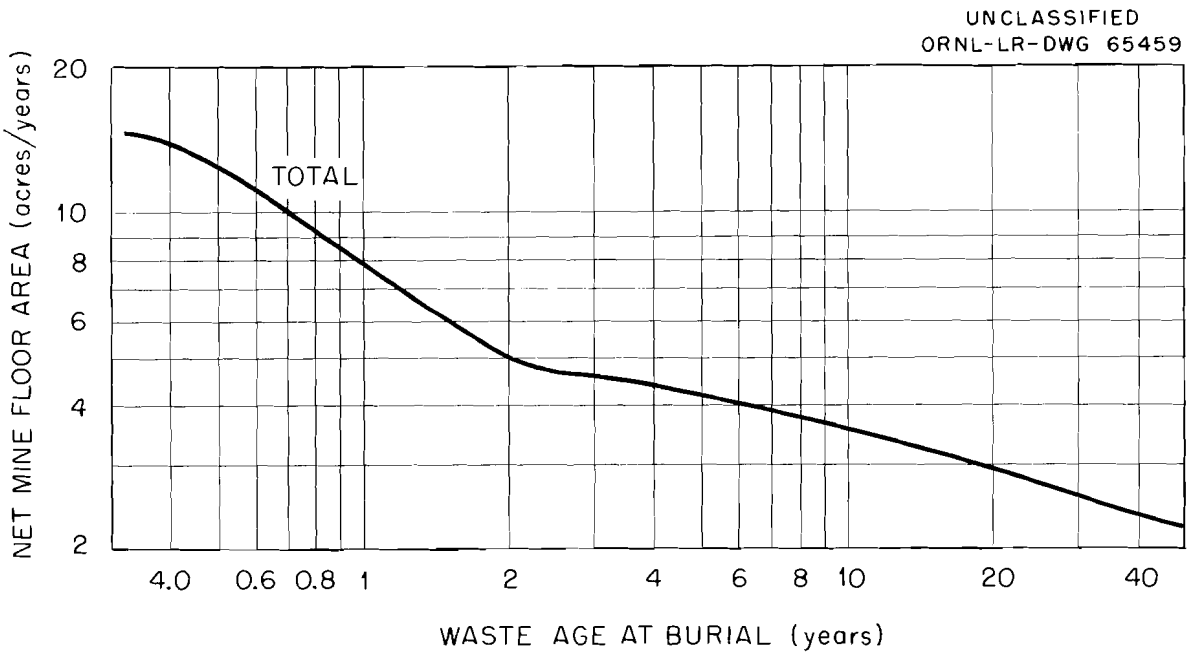

Fig. 4.3. Net Mine Area Requirements for Storage of Solids Above the Floor. Assumes 400°F thermal properties of salt, 325°F maximum salt temperature rise, 75°F ambient, and optimum dead time in tank storage. Purex waste area is 75% of total.

Table 4.1 Minimum Burial Ages* and Required Mine Area per Vessel at Minimum Age for Calcined Purex and Thorex Wastes in Salt Rooms

Waste Type	Vessel Radius = 0.25 ft		Vessel Radius = 0.50 ft		Vessel Radius = 1.0 ft	
	Min. Age (years)	Area (ft^2/vessel)	Min. Age (years)	Area (ft^2/vessel)	Min. Age (years)	Area (ft^2/vessel)
Acid Purex	1.07	280	3.05	670	8.3	2200
Reacidified Purex	0.33	142	0.84	345	2.5	720
Reacidified Purex filled twice	0.33	215	0.84	520	2.5	1080
Acid Thorex	0.33	128	1.1	255	3.2	630
Reacidified Thorex	0.33	28.5	0.33	115	0.63	340
Reacidified Thorex filled twice	0.33	43.0	0.33	175	0.63	500
Acid Thorex glass	0.33	100	--	--	--	--

*Ages at burial < 0.33 year not considered, since this is assumed as the age at which the uranium and thorium are processed.

Table 4.2 Yearly Mined Space Requirements for Calcined Wastes Stored in Salt Rooms[a]

Waste Type	Net Yearly Space Required (acres/year) Vessel Radius 0.25 ft	Vessel Radius 0.50 ft	Vessel Radius 1.0 ft
Acid Purex	5.9	3.6	2.9
Reacidified Purex	11.4	6.9	3.6
Reacidified Purex filled twice	11.4	6.9	3.6
Acid Thorex	4.1	2.0	1.3
Reacidified Thorex	4.1	4.1	3.0
Reacidified Thorex filled twice	4.1	4.1	3.0
Acidic Thorex glass	4.1	--	--

[a]At minimum permissible burial age. These area requirements are based on 100% area utilization, not 50% as was assumed in ref. 16.

To compare with the similar curve for storage of liquid wastes, Fig. 4.3 in ref. 16, the present curve must be multiplied by 2 to get the gross area, since the previous curve assumed 50% excavation, with the remainder of the salt left as pillars to support the roof. For example, 10-year-old solid wastes stored above the floor require a net of 3.55 or a gross of 7.1 acres per year, while the same waste stored in liquid form requires a gross area of 16.3 acres/year. Thus, storage in solid form reduces the area requirements by a factor of 2.3, made up of a factor of 2.6 difference in the assumed maximum permissible temperature rise combined with the poorer heat dissipation properties of the salt at the higher temperature.

4.3 Calcination Vessels in Floor

Temperature profiles for vessel spacings of 4-40 ft were calculated, using 10-ft line sources to approximate cylinders in a salt medium for times after burial from 100 hr to 36 years. These results are being used to calculate mine space requirements for burial of vertically positioned cylinders in the floors of rooms in salt media.

5.0 DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing

5.1.1 First Fracturing Experiment (W. de Laguna)

The purposes of the first fracturing experiment were to determine whether fractures that follow the bedding planes can be formed hydraulically in the Conasauga shale and to see if the testing method gives an equivocal picture of the fracture pattern. The test showed that the method was capable of developing an essentially conformable fracture in the shale under the conditions of the experiment, and that the fracture tended to follow the bedding plane into which it was injected despite a moderately complex structure of open folds, small drag folds, and minor faults. It also showed that the test method was capable of giving a clear picture of the location and extent of the fracture, limited only, for practical purposes, by the number of test wells drilled to locate the grout.

Preparations. The experiment was carried out at the "Four Acre Site," studied in 1954 and 1955 as a possible location for a high-activity waste storage tank. Five wells had been drilled: a central 6-in.-dia churn-drilled well, 300 ft deep, and four 3-in.-dia core holes, each 200 ft deep, located radially in approximately the four cardinal compass directions, 200 ft from the central well. A geologic map and cross sections of the area were prepared from the cores, from the samples from the 6-in. churn well, from surface outcrops, and from exposures made by a bulldozer. Hydrologic tests showed that the unweathered shale below a depth of about 20 ft was nearly impermeable, except that, locally, small volumes of ground water could move through fractures in the shale to a depth of 150-200 ft.

Three hundred feet of 3.5-in.-o.d. J-55 type (high strength) steel casing was cemented into the 6-in. well, and the four core holes were plugged by pouring sand into them slowly. Twenty-eight permanent bench marks were set 6 ft or more into the weathered shale, in four lines radiating out in the four cardinal compass directions from the injection well, at distances from it of 25, 50, 75, 100, 200, 350, and 500 ft. Approximately 30 days after the bench marks had been poured, their relative elevations were determined with a standard engineer's level.

A 25,000-gal tank was set up near the injection well as a source of water for the test. Specifications for the fracturing experiment required injection into the shale of 20,000 gal of water mixed with Portland cement, ground limestone, and diatomaceous earth or other fillers or additives such that it would have a minimum crushing strength of 500 psi after 21 days.

Fig. 5.1. First Fracturing Experiment: Cutting the Slot in the Casing with the "Abrasajet."

A 30-gal stainless steel drum to contain radioactive tracer solution was set up next to the injection well and connected to a small Milton-Roy high-pressure metering pump of 1.7 gal/hr capacity at a pressure of 2500 psig. The tracer, whose presence in the grout would permit identifiying the grout seam by gamma-ray logging, was taken through high-pressure autoclave tubing to a fitting welded into the casing of the injection well just above ground level. Drum, tubing, and pump cylinder were shielded with lead bricks (Fig. 5.1). Although 1 curie of Cs-137 could be detected in 25,000 gal of grout, it was not certain that there would be uniform mixing or complete retention of the tracer in the grout. Calculations showed that it would be possible to transport, transfer, and handle safely in the shielded drum 50-100 curies of Cs-137, and 35 curies of Cs-137 plus 8.7 curies of Ce-144 were used. It is doubtful that the cerium contributed to the effectiveness of the tracer. The radioactive concentrate was added to 9 gal of water in the drum, sufficient for 5-6 hr pumping.

Injection of the Mixture. The Dowell Company did the actual injection. On Oct. 12, 1959, they cemented the casing into the injection well. On Oct. 14, they cut a slot in the casing at a depth of 290 ft, using an "Abrasajet" hydraulic sand jet, through which was pumped 2000 gal of water, 1000 lb of 20-40 mesh sand, at a pressure of 3000 psi. Ten pounds of "J 79" additive was mixed with the water to increase its vicosity slightly for better carrying of the sand. During the 30 min. required for pumping, the jet was slowly rotated to cut a full circular slot completely through the casing and out into the shale (Fig. 5.1). The "Abrasajet" was then removed from the well.

Two "Appalachian" pumping units were used to pump 1400 gal of water into the well to initiate the fracture. Pressure was built up slowly by stages to 2300 psi, at which point the shale fractured and the pressure fell abruptly to 1000 psi, and in 15 min to 700 psi, while the pumping rate increased from 0 to 300 gpm. When the pumps were shut down, the pressure dropped abruptly to 300 psi, the apparent static pressure in the fracture if allowance is made for the pressure of the column of water in the well, which would add ~ 125 psi. The water was then bled back out of the well.

On Oct. 16, pumping was again started with water, and the fracture reopened at 1000 psig, this pressure falling rapidly to 400 psig at 190 gpm. A total of 750 gal of water was pumped into the fracture in this operation, and then the cement mixture was injected. This mixture consisted of 66 sacks (66 cu ft or 6200 lb) of dry Class A Portland cement powder, 22 sacks (66 cu ft or 1100 lb) of "Lite poz 2" diatomaceous earth, and 36.5 lb of fluid-loss additive M-29, dry mixed in a Ready-Mix concrete truck. Twenty-one truck loads were used for a total of: (1) cement, 1370 cu ft or 130,000 lb; (2) diatomaceous earth, 1370 cu ft or

23,000 lb; 3) fluid-loss additive, 713 lb. This, added to 20,000 gal of water, made up a total of 3469 cu ft or 27,000 gal of grout.

The tracer concentrate was transported to the site in a lead "pig," which; together with the heavy sheet-lead cover of the shield drum was handled by a crane. The first of the Transit-Mix trucks was spotted alongside one of the Appalachian pumpers (Fig. 5.2), and the grout mixture was started into the well. At the same time the Milton-Roy pump was started and the tracer mixture was injected into the top of the well casing at a rate of about 1.7 gph. This rate was later decreased slightly, and the 9 gal was all used in 6 hr. The pressure increased very slightly, to 500 psi, as the cement was added, but gradually decreased during the pumping of the grout, to 450 psig after about 3 hr, and to 400 psig after about 3.5 hr. At the time, this was believed to be due to widening of the slot in the casing by erosion. The maximum injection rate was 90 gpm, the average 78 gpm.

When the first truck load of dry cement mixture had been pumped into the well by the first pumper, this unit was stopped and the pumping taken over by the second unit, using the mixture from the second Transit-Mix truck. Six Transit-Mix trucks were used to supply the pumpers, alternately at roughly 15-min intervals.

A serious problem developed after about 1 hr of pumping, shortly after the fourth load was started down the well by the second pumper. The pressure required to inject with this pumper was somewhat higher than with the first, and it was apparent the high-pressure line from this truck to the "Y" on the injection well was plugged. Pumping was therefore stopped, and the valve was opened to permit the pressure in the line to "bleed" back into the tank on the pumper. This is standard oil-field procedure. Unfortunately, in this case, the check valve permitted some of the "tagged" grout to bleed back into the tank on the pumper before the valve in the "Y" at the injection well was closed. The bottom of the tank on the pumper was found to read about 20 mr/hr, and the higher-pressure line was also contaminated. The plugged check valve was removed and pumping resumed. Sand was added to the contaminated tank and agitated with the motor-driven mixer blades with which the tank is equipped, and the sand was then pumped down the well with the next batch of grout from this truck. Some of the contamination was removed in this way, and the rest was removed later before the pump was returned to the contractor. Virtually all the tracer stayed in the cement grout, small amounts of which set up in the crevices in the hose connections between the piping on the pumper. Replacing these short sections of hose removed all the activity. The pump itself was not contaminated, as the return flow was directly into the tank on the truck.

After 7.5 hr of elapsed time and a total of 6 hr of actual pumping, the last of the grout mixture had been injected, and this was followed up with 400 gal of water to flush the last of the

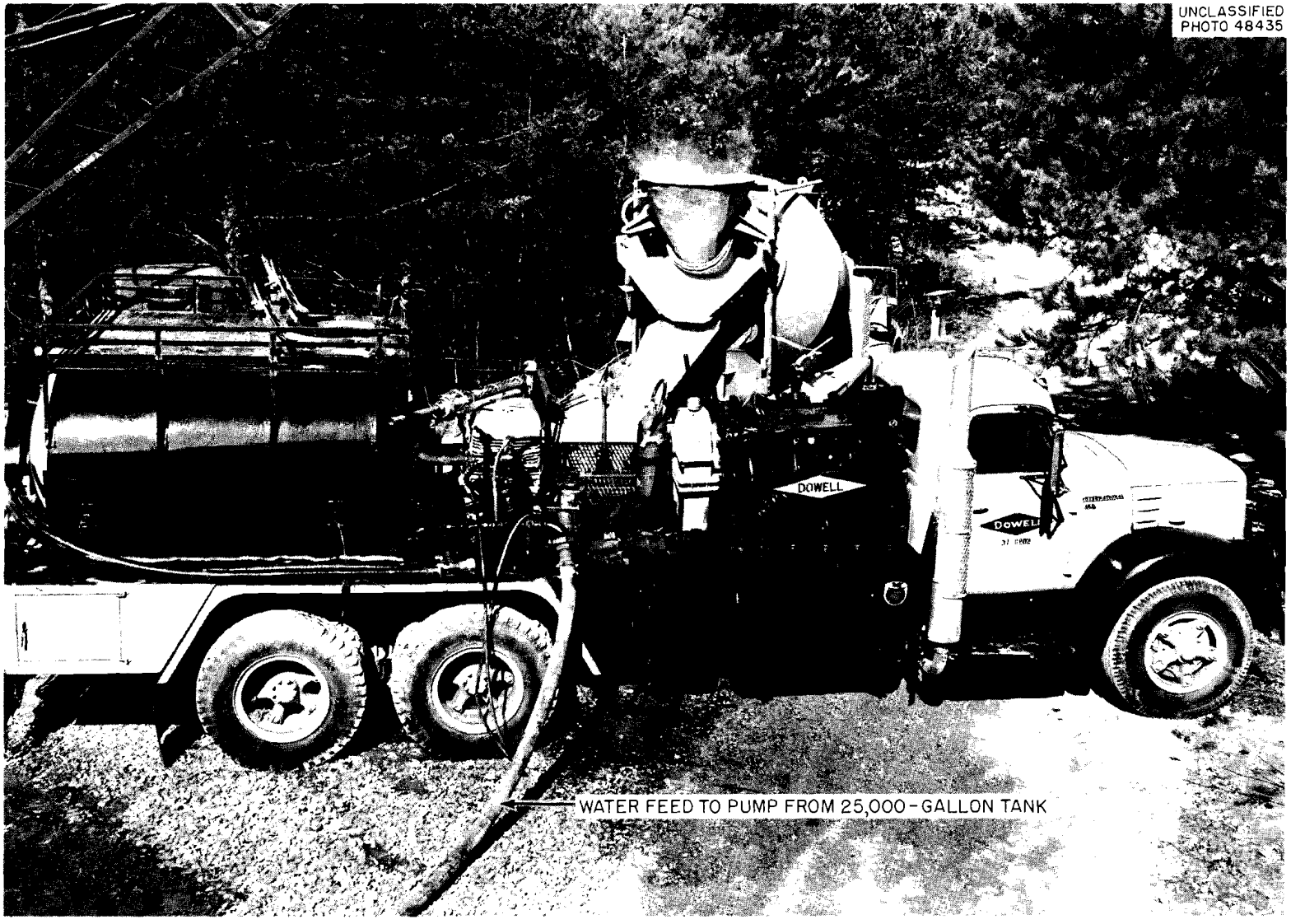

Fig. 5.2. First Fracturing Experiment: Dowell "Appalachian" Type Pumper and Transit-Mix Truck Delivering Dry Cement-Diatomaceous Earth Mixture. High-pressure steel line to well is behind pumper.

grout down the well. As the last of this water was being pumped in, grout was observed flowing very slowly out of the 3-in. core hole, 200 ft north* of the injection well. Pumping was immediately stopped and the injection well shut in. Grout continued to flow slowly out of the core hole, and it is estimated that 200 gal of grout came out in a few hours. By next morning, water was flowing very slowly from the core hole; it continued to flow at a slowly decreasing rate for about two months. The total volume of water that came out was estimated very roughly to be 2000 gal, or as much as 10% of the water pumped in.

The north well, like the other pre-existing core holes, had been plugged with clean sharp building sand of the type used for making mortar. It must have held back the grout since the fracture, which intercepted the bottom of this well (Fig. 5.3), continued 200 ft farther up-dip to the north. However, the grout did not bind the water and, apparently, relatively clean water, filtered free of cement and diatomaceous earth by the bottom layer of sand packing, flowed up the well.

The grout and the dirt around the well were dug up a few days later, after the grout had set, and buried in Burial Ground 4. No detectable activity escaped from the immediate vicinity of the core hole.

Test Drilling. Three rock units are identifiable in the test area (Fig. 5.3). The upper is a gray calcareous shale containing many thin beds and lenses of limestone. Below this, and to some extent interbedded with it, is a dark red or maroon shale, which is seldom calcareous. Locally, there are beds or lenses of red shale in the gray calcareous shale; and, locally, in the red shale, there are gray or very faintly reddish beds which appear gray in the drill cuttings, so that the color changes are not always sharp and clear, either in the records obtained from the drilling, or, in all probability, in the rock itself. There is, however, one principal transition from gray above to red below which is quite generally recognizable. In the east-west section drawn through the injection well, shown in Fig. 5.4, this contact is at an elevation of about 725 ft. Immediately above this contact, or separated from it by a few feet of gray shale, is a distinctive group of three limestone beds, each 2-3 ft thick and covering an interval of 15-20 ft. These three beds can sometimes be recognized by their hardness as drilling penetrates them, but they can be identified with assurance in the gamma-ray log of virtually every well passing through them. They, and the color change from gray to red just below, form a key horizon marker at the site. No other individual beds in the area can be identified with assurance in the field, in the cores, or in the gamma-ray logs, although in the gamma-ray logs it is, in general, possible to distinguish between the red and the gray calcareous shale. In the western part of the area, a hard

*"Plant coordinates" are used to describe directions in this report "North" in this system is up-dip and is actually north-north-west.

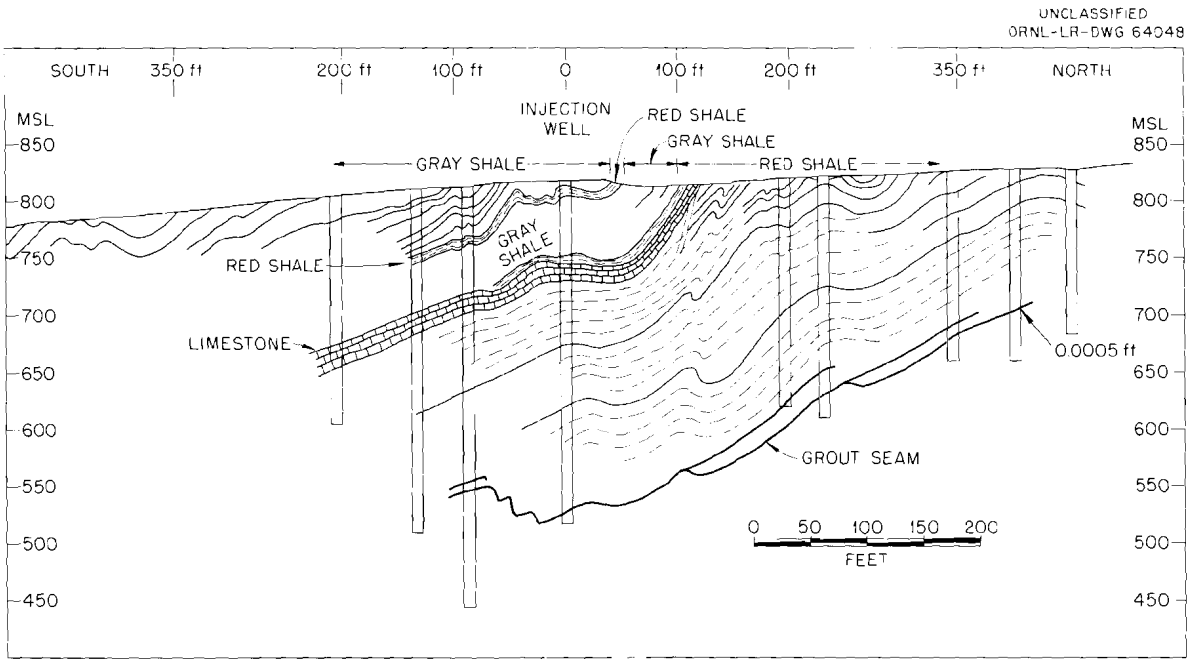

Fig. 5.3. South-North Cross-Section of "Four-Acre" Site Through Injection Well of First Fracturing Experiment, Showing Surrounding Test Wells and Grout Seam.

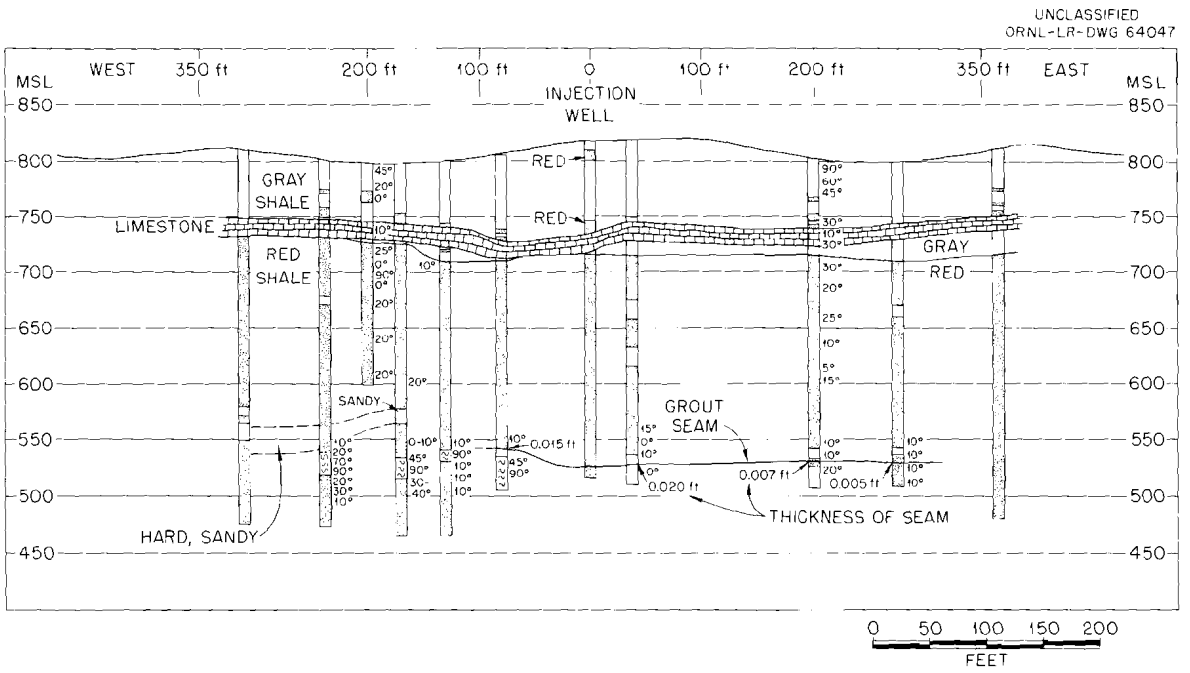

Fig. 5.4. East-West Cross-Section of "Four-Acre" Site Through Injection Well of First Fracturing Experiment, Showing Surrounding Test Wells and Grout Seam.

sandy bed was encountered in three of the wells at an elevation of about 550 ft.

Test drilling was begun in the area a month after the grout had been injected and was continued for about nine months. A total of 18 wells were drilled, and one pre-existing core hole (200 E) was deepened. Figure 5.5 shows the distribution of the grout sheet as determined by this drilling. The outer edge of the grout sheet could be drawn somewhat differently from the position shown and is less regular than indicated, but the drilling appeared to have defined the general extent of the fracture formed.

The fracture moved out on strike to the east for ~ 300 ft. Just east of the injection well it consisted of two sheets about 0.5 in. apart and each about 0.010 ft thick. Two hundred feet east it was observed as two sheets about 5 ft apart with an estimated combined thickness of 0.007 ft, and at 273 ft east as a single sheet 0.005 ft thick. The stratigraphic position and elevation of the fracture were remarkably uniform in this direction.

On strike to the west the fracture moved out a total distance of only about 100 ft. In this direction the horizon into which the grout was injected is much distorted by drag folding starting roughly 50 ft from the injection well, and apparently, the fracture was deflected upward about 11 ft by this crumpled rock.

To the north the fracture extended a little over 400 ft; at 400 ft it consisted of a paper-thin layer of grout in the shale. In forcing out in this direction the fracture had to follow and, in part, cut across moderately complex open folds, drag folds, and a few minor faults, which could be mapped in detail in artifically created exposures at the surface but only by inference underground.

The grout-filled fracture extended about 100 ft south of the injection well, but, instead of following out along the bedding-plane horizon into which it had been injected, it broke upward about 50 ft stratigraphically and was found 260-270 ft below the surface, roughly 30 ft less than the depth of injection. The fracture in moving south was deflected upward and separated into two sheets by some small irregularity in the structure, possibly the fault observed at the surface about 110 ft north of the injection well.

Surface Uplift. Releveling the bench marks after injection of the grout gave interesting but inconclusive results. Apparently, the level was not in good adjustment when the first survey was made, and the preinjection values for the relative elevation are suspect. However, on the assumption that the mark 500 ft north of the injection well had not moved, the data shown in Fig. 5.6 were calculated. To the north, east, and south, the extent of uplift very nearly coincides with the extent of grout sheet, and the amount of uplift and the thickness of grout are of the same

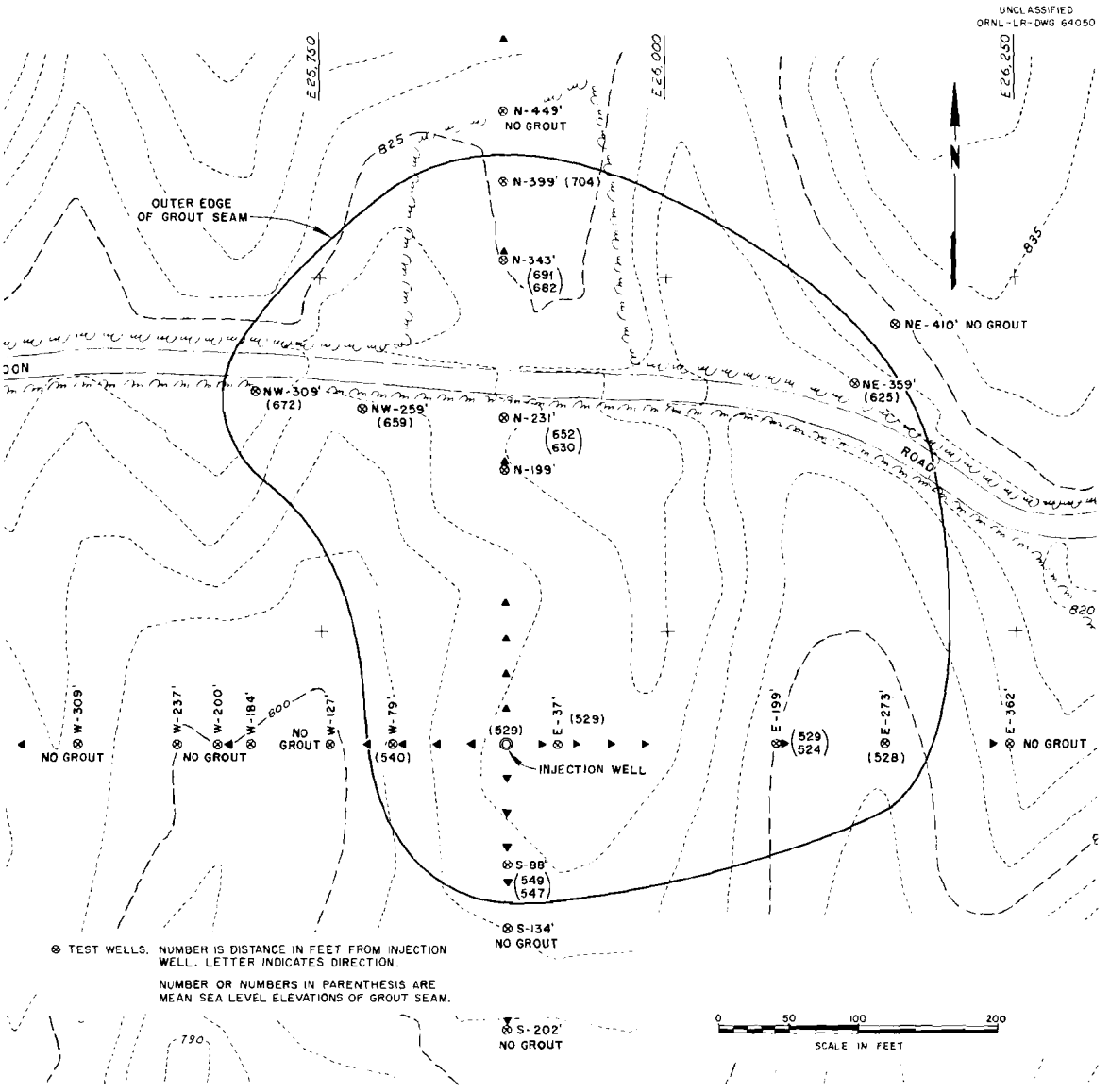

Fig. 5.5. Distribution of Grout Seam of First Fracturing Experiment as Determined by Test Drilling.

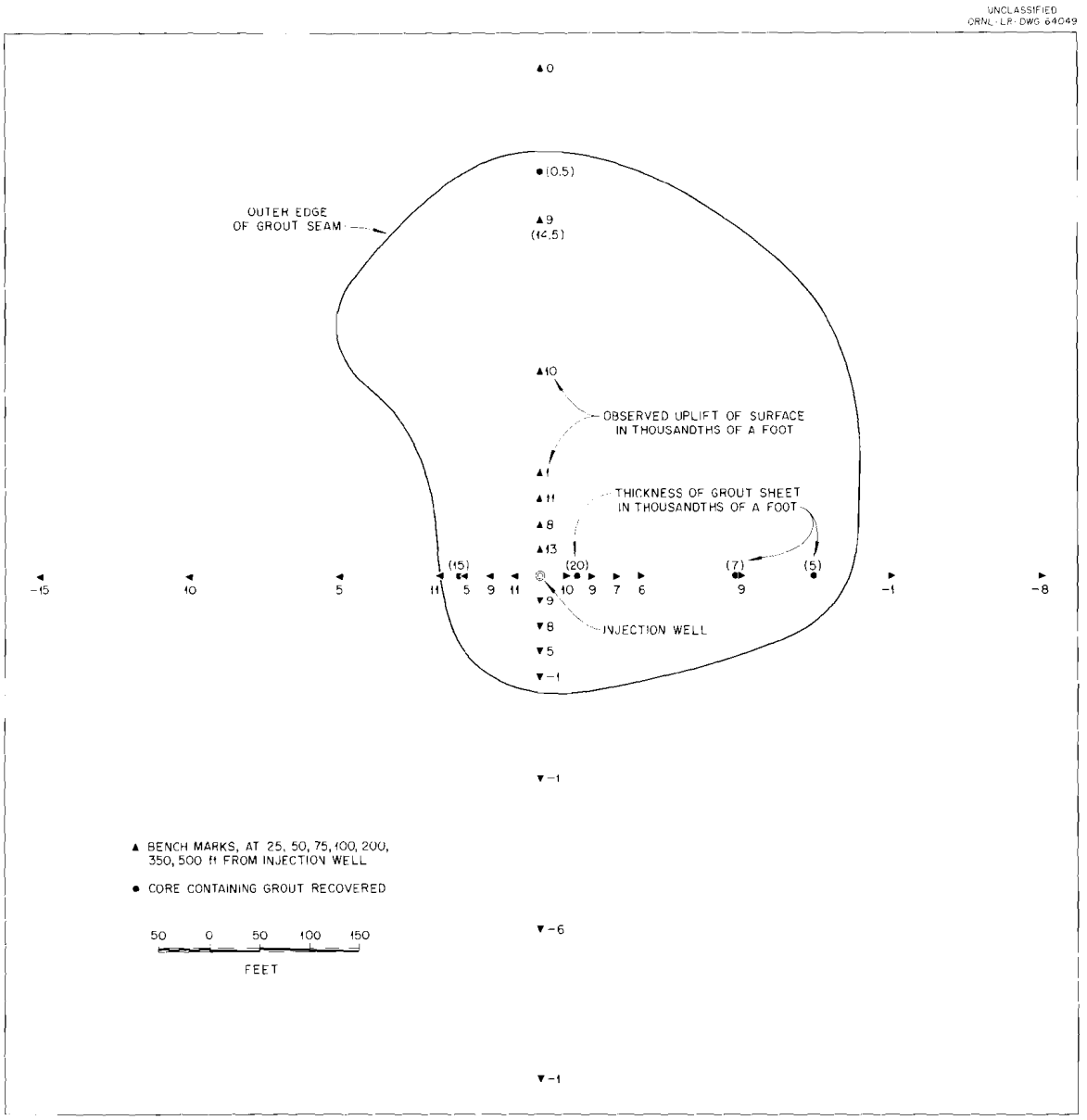

Fig. 5.6. Estimated Extent of Grout Seam of First Fracturing Experiment as Determined by Measurements of Surface Uplift.

order of magnitude. To the west the uplift apparently extends out beyond the limit of the grout sheet.

The area of the grout sheet inferred from the drilling is roughly 200,000 ft^2. If the average thickness is taken as 0.010 ft, then the volume in place after solidification would be 2000 cu ft, or about 15,000 gal. If the average thickness is taken as 0.015 ft, the volume in place would be roughly 3000 cu ft or 22,500 gal. The grout mixture used, however, was not compounded to enable it to retain the excess water after the cement had set up, and the fluid loss additive used was intended to permit maximum extension of the fracture in the face of possible fluid loss to the shale during the injection. Samples of the solidified grout had a specific gravity (after drying in air) of roughly 1.5 to 1.6, or 94-100 lb/cu ft. If the 15,000 lb of cement and diatomaceous earth used in the mix had incorporated an additional 20 wt % water which could be retained despite air drying, there should be 183,000 lb, or between 1830 and 2000 cu ft, of grout in place. Because of the water loss to the shale over the very large surface area of the grout sheet, this value for the volume of grout in place is believed more realistic than that of the total volume of mixture pumped and agrees well with the estimated volume of the grout sheet found by the test drilling.

5.1.2 Second Fracturing Experiment (W. de Laguna)

Test drilling at the site of the second fracturing experiment is now nearly completed and the lateral extent of the grout sheets appears to be sufficiently defined. However, the well now being drilled is encountering the several key horizons and the upper grout sheet at depths so much shallower than did the two immediately adjacent wells that at least one and perhaps all of these holes must depart considerably from the vertical. Until these and the other test holes are surveyed,the conclusion that the injection well was, by chance, drilled into a downfolded or downfaulted block is unwarranted. It now appears that both the structure of the rock and the shape of the two grout sheets is much more regular than at first believed.

Attempts to show a materials balance between the amounts of cement injected and the amounts found in the three grout seams were moderately satisfactory for the first experiment and for the upper seam in the second experiment, but did not give good agreement for the lower seam. Information on the thickness of this seam is poor, however, and if it is possible to photograph it in the test wells from which no core of it was recovered a better materials balance may be possible.

Examination of the cores from the 3265-ft-deep test well is not yet finished,but it is clear that there is a substantial thickness of rock apparently suitable for fracturing between depths of 1500 and 3000 feet. Some further tests will have to be made in them before they can be used for disposal by fracturing.

A study by the MIT Practice School suggests that the safe limit for disposal by hydraulic fracturing, if the waste mixture in place is not to overheat, is of the order of 2000 curies per gallon of waste six months old. The thermal problem then is not likely to place much restriction on the type of waste handled, although somewhat longer aging before disposal might be desirable.

5.1.3 Mix Development (T. Tamura)

Three separate phases of study have been initiated by Westco Research, a subsidiary of The Western Company (Fort Worth), under a subcontract.

Phase 1. Initial studies will consider the waste composition listed in Table 5.1 as a reference type for defining behavior

Table 5.1 Weighted Average Composition of Waste Stream Discharge to Seepage Pits 2, 3, and 4[a]

Chemical	Molarity	Chemical	Molarity
$NaOH$	0.22	$NaNO_3$	0.315
NH_4NO_3	0.025	Na_2SO_4	0.037
$Al(NO_3)_3$	0.022	$NaCl$	0.006

[a]Data furnished by D.G. Jacobs, ORNL.

characteristics. Different proportions of cement and waste are being mixed and the set-time and set-strengths determined, after which the composition will be changed to determine the effect of increasing or decreasing the major components and of different chemical reagents substituted for those normally used.

Phase 2. Gel chemistry in high-pH highly salted solutions containing cements and/or muds will be studied. The development of a pumpable slurry may require water or solution in excess of the amount necessary for the final set of the cement, and the excess may inhibit retention of the radionuclide in leaching or development of a mix of high final set-strength. The gels will be studied as agents for reducing the free water in the set cement, retaining radionuclides, optimizing the slurry properties of the mix, and maximizing the amount of radioactive waste that can be incorporated into a given amount of cement.

Phase 3. Cement and mud chemistry will be studied with specific emphasis on controlling and reducing soluble calcium and cesium salts. An understanding of the fate of calcium is particularly important since available evidence shows that strontium behavior is very similar to that of calcium. The major cationic component of dry cement (Table 5.2) is calcium,

Table 5.2 Products in Cement[a]

Dry Cement	Hydration Products at Atmospheric Temperatures and Pressures
1. Tricalcium silicate ($3CaO.\ SiO_2$)	Calcium silicate hydrate and calcium hydroxide ($1.5\ CaO.SiO_2.1.0\text{-}2.5\ H_2O$ + $Ca(OH)_2$)
2. Tricalcium aluminate ($3CaO.Al_2O_3$) Gypsum ($CaSO_4.2H_2O$) Alkaline sulfates (Na_2SO_4 + K_2SO_4)	Calcium sulfoaluminate, hydrated calcium aluminate, and alkali ($3CaO.Al_2O_3.3CaSO_4.31H_2O$ + $3CaO.Al_2O_3.6H_2O$ + KOH + NaOH)
3. Titracalcium alumino-ferrite ($4CaO.Al_2O_3.Fe_2O_3$) or as ($6CaO.Al_2O_3.Fe_2O_3.2CaO.Fe_2O_3$) Gypsum ($CaSO_4.2H_2O$) Calcium hydroxide ($Ca(OH)_2$)	Calcium sulfoaluminate and hydrated calcium sesquioxide ($3CaO.Al_2O_3.3CaSO_4.31H_2O$ + $3CaO.R_2O_3.6H_2O$)
4. Magnesium (MgO)	Magnesium hydroxide ($Mg(OH)_2$)
5. Free lime (CaO	Calcium hydroxide ($Ca(OH)_2$)

[a]Data from ref. 18.

the soluble compounds of which may release strontium on contact with leaching waters. The possibility of reducing the free magnesia and free lime contents is also being considered.

Cesium may be removed by addition of selected clays. The general use of bentonites as an additive in cement slurry makes it desirable to investigate the possible use of heat-treated bentonites for cesium fixation. Any additive that may be used for the formulation will be evaluated not only for its ability to decrease the soluble calcium or strontium and cesium salts but for its effect on the set-time and set-strengths of the slurry.

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

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

In the storage of high-level radioactive solids in holes in the floor of a salt cavity it may be desirable in some cases (e.g., for calcined solids assumed in the economic study of Sect. 4.0) to allow the peak salt temperature to rise above 300°C. Samples of

rock salt disintegrated violently when heated in a muffle furnace to 250-300°C, and such shattering in situ might affect heat transfer properties.

The first test will be carried out in a drilled hole 8 in. dia by 10 ft deep. The heater will have an active length of 4 ft made up of six 8-in. lengths of Cooley "clamshell" heaters with an o.d. of 5-3/4 in. The heaters will be placed in a 5-ft length of 6-in. Sch 40 type 304L stainless steel pipe. Five thermocouples will be placed on the pipe, spaced 1 ft apart vertically, and two additional thermocouples will be placed on the heater sections to monitor the heater temperature. The assembly will be centered at the bottom of the 10-ft hole, and thermal insulation will be placed above the pipe to minimize convection losses.

Thermocouple holes 1-3/16 in. dia will be drilled to a depth of 15 ft at distances of 6 in., 1, 2, 4, and 8 ft from the edge of the heater hole. These holes will be drilled as near vertical as possible and then the exact location established to make possible more precise evaluation of the temperatures observed. Several thermocouples will be installed in each hole.

Initially, power will be applied at a constant rate sufficient to achieve a salt-wall temperature of approximately 300°C in two or three days. If the surrounding salt does not shatter, the power input will be maintained until heat loss through the floor invalidates the comparison of measured salt temperature with theoretical calculations for the line source in an infinite medium. If no shattering has taken place by this time, the i.d. of the hole will be measured for comparison with preoperation measurements to obtain information on the closure due to thermal expansion and plastic flow, after which the experiment will be restarted at a higher power level and operated until shattering occurs or plastic flow freezes the heater in place. Additional tests will be run as indicated.

6.2 Cumulative Gamma Radiation Dose in Salt Mine Disposal Pot-Calcined Solid Wastes (W. J. Boegly, Jr.)

Previous studies (20) on the effect of gamma radiation on the structural properties of rock salt have shown that gamma dosages to 1×10^8 r produce negligible changes in creep rate and compressive strength, but that dosages above this value may produce significant changes (i.e., decrease in compressive strength, slight decrease in creep rate). Since the salt in rooms containing radioactive waste will continue to be exposed to radiation for long periods of time, it is possible that the 1×10^8 r dose will be exceeded at the surface of the walls.

The MIT Engineering Practice School developed a computer program for the IBM-7090 and with it estimated the gamma dose in salt and in the room for pot-calcined solids stored in the floor of a salt mine (21). The variables in the computer program are:

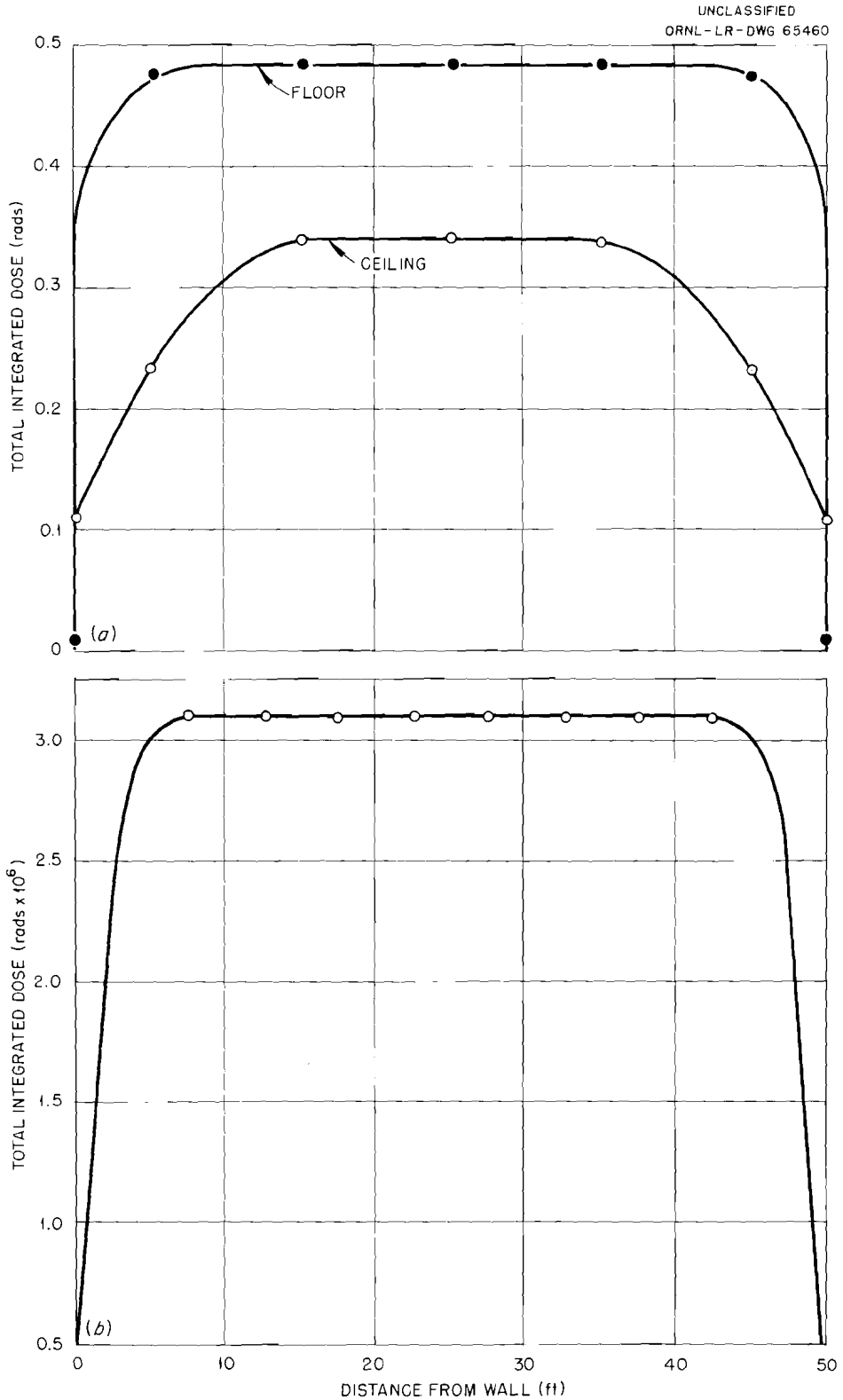

Fig. 6.1. Gamma Dose (a) to Ceiling and Floor and (b) in Floor Between Pots as a Function of Distance from Wall.

room height and width, depth of pot burial, rectangular pot spacing, pot diameter, number of energy groups considered, activity vs time for each energy group, properties of the material, and distance of the first row of pots from the wall. The output from the program gives: (1) the gamma dose in salt for each energy level per time increment and sum of increments, (2) the accumulated gamma dose in salt for each energy level at each time increment, and (3) the sum of these or the total accumulated gamma dose from time of storage to time t. For the air dose in the room above the buried pots, the dose rate in milliroentgens per hour can be obtained at any desired time.

Limitations of the computer program as written are that the pot spacing must be rectangular in plan view, that the dose cannot be calculated for gamma rays passing through more than two media, and finally that the pots are considered as line sources and the dose close to the pots cannot be computed accurately. However, for the purpose intended, the results are satisfactory.

As an example, calcined acidic Purex waste in 6-in.-dia pots buried 7 ft beneath the floor of a 15-ft-high 50-ft-wide very-long room was considered. The pot spacing was assumed to be 5 ft. Figure 6.1 shows the variation of total dose (for storage times from 2 to 10^6 years) with distance from the wall for (a) points on the ceiling and floor of the room, and (b) points between the pots. Results indicate that the gamma dose in the ceiling is less than that in the floor, and that the dose between pots is nearly constant across the room. The only sources that contribute significantly to the dose at a point are the two pots on either side of it. Figure 6.2 shows the variation of the total gamma dose

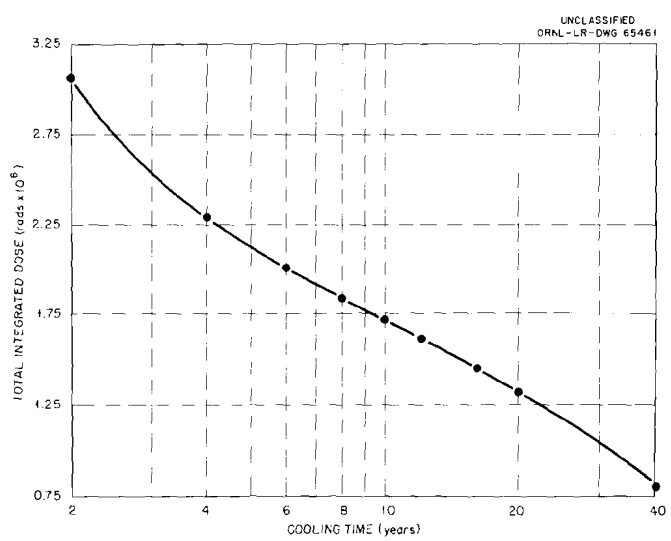

Fig. 6.2. Gamma Dose Between Pots as a Function of Cooling Time.

between pots as a function of waste cooling time. If cooling time before storage is increased from 2 to 14 years, the dose is reduced more than half.

Results of this study indicate that gamma dose at the center line between pots will not exceed 3×10^6 rad for 2-year-cooled waste and thus that the irradiation of the bulk of the salt surrounding the room will not exceed the dose at which structural damage will occur. In local areas near the pots the dose may exceed 1×10^8 r; however, the volume of salt will be small and the corresponding effect of a decrease in compressive strength will also be small. These calculations are being extended to cover spacings of cans that are not rectangular and the effect of cylindrical vs line sources. When the extent of salt having a dose greater than 1×10^8 r is known, calculations will be made on the effect of this factor on the structural integrity of the room.

7.0 CLINCH RIVER STUDY

7.1 Estimate of Activity in Bottom Sediments (P. H. Carrigan*)

Studies of the longitudinal distribution of radioactivity in Clinch River bottom sediments have indicated that the maximum activity is associated with sediments deposited midway in the study reach (CRM 4.7 to 20.8) (22). Mechanical analysis (16) showed the smallest median particle size in the sample from CR mile 11.9.

In further experiments, the pH and calcium content were found also to be maximum at the midway point (Table 7.1). However, exchange capacity determinations indicated a nearly constant exchangeable magnesium throughout the study reach. In every case the total cations exceeded the total determined capacity, a likely explanation for which is that the total cations represent contributions not only from the exchange complex of the clay minerals but from calcium carbonate in the sediment. The pH readings for all samples exceeded 7.0, which is also indicative of a calcareous sediment. Future studies will determine the calcium carbonate concentration in the sediment.

Table 7.1 Exchange Capacities and pH of Clinch River Bottom Sediments

		Exchange Capacity (meq/100 g)						
CR Mile	pH	Na	K	Ca	Mg	Total Cations	Total Determined Capacity	Excess Cations
4.7	7.50	0	0	13.4	5.6	19.0	11.0	8.0
7.6	7.60	0	0	16.0	6.2	22.2	11.9	10.3
11.9	7.85	0	0	21.1	5.6	26.7	10.7	16.0
15.3	7.28	0	0	14.4	6.9	21.3	11.7	9.6
19.2	7.78	0	0	15.0	5.8	20.8	11.2	9.6

*On Loan from Tennessee District Surface Water Branch, Water Resources Division, U. S. Geological Survey.

The results of mineralogic determinations by X-ray diffraction intensities show that the sand and silt-size particles of the bottom sediments are mostly quartz with traces of feldspars. The low mica and vermiculite contents of the clay-size fraction of sediments, as shown in Table 7.2, help explain the low exchangeable potassium,

Table 7.2 Mineral Content of Clay-Size Particles of Clinch River Bottom Sediments

CRM	Mineral Content (parts per 10)				
	Quartz	Vermiculite	Mica	Kaolinite	Randomly Interstratified Vermiculite-Mica
4.7	4	2	2	1	1
7.6	3	2	2	2	1
11.9	3	2	2	2	1
15.3	4	2	1	2	1
19.2	4	2	1	2	1

because fixation of potassium is commonly associated with these minerals. More accurate determination of the minerals would require further analyses of the sediments.

Core samples of bottom sediments used in the determinations were collected at ten equally spaced intervals along four cross-sections previously monumented by TVA, CRM 4.7, 7.6, 11.9, and 19.2, and at another cross-section, CRM 15.3, and composited. The composites were submitted to the Denver Laboratories of the Geochemistry and Petrology Branch, U. S. Geological Survey, for mineralogic and exchange capacity analyses. Exchange capacities were determined by leaching the samples with 1 M NH_4Cl. The leachates were retained for cation analyses (flame photometry for Na and K and versene titration for Ca and Mg). The samples were then washed with C_2H_5OH. The ammonia was distilled off and titrated with 0.1 N HCl for the total capacity. The pH's of the samples were determined on a 1:10 soil:water ratio.

Dilution Factors. Radioactive releases to the Clinch River from White Oak Creek are diluted proportionally to the ratio of the two flows. The minimum monthly dilution factors, Clinch flow/White Oak flow, were computed for the period 1951-60 to be < 570. The maximum monthly dilution factors were > 570 except in March and April. From the duration curve of the daily dilution factors, the median was found to be 570, with a minimum of 5.6 and a maximum of 4400. Frequency studies showed minimum daily dilution factors of 20, 12, 8.8, 7.0, and 5.6 for recurrence intervals of 2, 4, 6, 8, and 10 years, and minimum monthly dilution factors of 120, 81, 72, 70, and 68 for the same intervals.

During the base period the cumulative departure of precipitation from the average for the long-term meteorological station at Clinton, Tennessee, was zero. Flow records for the period were available for the Clinch River near Scarboro, Tennessee, but not for White Oak Creek at White Oak Dam for the entire period. Flows for the missing periods were determined from correlation curves with records for stations on White Oak Creek upstream from the dam.

7.2 Meetings of Steering Committee (R. J. Morton)

The Clinch River Study Steering Committee, established in December 1959, is composed of nine members: one representative each from Oak Ridge National Laboratory, U.S. Geological Survey, U.S. Public Health Service, Tennessee Valley Authority, Tennessee Game and Fish Commission, and Tennessee Department of Public Health, the active participating agencies; and an ex officio representative from each of the AEC offices, Division of Reactor Development, Division of Biology and Medicine, and Oak Ridge Operations.

It is responsible, generally, for decisions on the scope and direction of the program, co-ordination of work by the various participating agencies, and dissemination of information obtained in the study. Details of the Steering Committee's functions are performed by subcommittees, of which there are at present four: water sampling and analysis, bottom sediment sampling and analysis, aquatic biology, and safety evaluation. The committee holds open sessions and executive meetings about twice a year, with additional special meetings called when necessary. An open session and an executive meeting were held on Oct. 27, 1961, and a special executive meeting on Nov. 21, 1961.

The open session was conducted as an information meeting, and was attended also by members of the study staff and invited visitors. Progress and results in the programs being carried out on water sampling and analysis, studies of bottom sediments, hydrologic measurements, and ecological investigations were presented in ten oral reports by members of the staff and chairmen of subcommittees. Written summaries of these reports will be incorporated into "Status Report No. 3 on the Clinch River Study," which is in preparation.

At the executive meeting on October 27, the Steering Committee discussed with a representative of the Public Health Service's water-quality network the interrelation of network sampling and analysis with the Clinch River study. It was decided to co-operate and exchange data with the USPHS water quality network program. The committee approved release for publication of three papers: (1) "Density Gradient Separation of Plankton and Clay from River Water" by W. T. Lammers, (2) "Biogeochemistry of Strontium and Calcium in Clams" by D. J. Nelson, and (3) "Radiation Effects on Biota - Estimated Radiation Dose Received by Diptera with Life Stages in Bottom Sediment" by D. J. Nelson, all three of which were

based on data obtained in connection with the Clinch River study. The committee also authorized and appointed members to a new Subcommittee on Safety Evaluation to analyze potential hazards and evaluate the safety of waste disposal to the Clinch River as now practiced or envisioned for the future.

The November 21 meeting of the Steering Committee was attended also by members of the Subcommittee on Safety Evaluation, for the purpose of defining the responsibilities and criteria to be used by this subcommittee. The subcommittee was instructed to consider safety downstream from White Oak Creek; consider the hazards of radioactive waste in river, streams, and lakes; base its analysis of safety on summaries of data primarily from the Clinch River study but also from other sources; consider the radiation protection guides of the Federal Radiation Council as a basis for evaluating safety; and consider the safety of discharges of wastes from routine operations. As a check list of potential waste-disposal hazards, the Steering Committee adopted and slightly revised "Exposure Pathways of Released Radioactive Wastes" from a statement by H. M. Parker in Hearings on Industrial Radioactive Waste Disposal before the Special Subcommittee on Radiation of the Joint Committee on Atomic Energy, U. S. Congress, Jan.28 to Feb.3, 1959 (Vol.3, pages 2359-64).

8.0 FUNDAMENTAL STUDIES OF MINERALS

8.1 Ruthenium Sorption by Sulfide Minerals and Vermiculite (D. G. Jacobs, A. L. Mohan*)

Most of the cationic fission products in the highly basic ORNL intermediate-level waste are retained, by a combination of selective ion exchange and precipitation, in the seepage pits excavated in Conasauga shale, thus reducing their rate of travel to a small fraction of that of the ground water. However, ruthenium moves through the ground nearly as rapidly as the ground water, although at some distances from the pits its concentration in the ground water is lower than predicted by simple dilution and decay (23), indicating some removal by the shale. A study of ruthenium retention was undertaken because, in spite of the comparatively high permissible limits for Ru-106, its continued discharge to the environment constitutes a nuisance. Because of the chemical nature of ruthenium, a twofold approach was attempted: (1) replacement of ruthenium for other lattice ions at the surface of sulfide minerals, taking advantage of the insolubility of laurite (RuS_2); and (2) reduction of ruthenium to a positively charged species for subsequent sorption by natural cation exchangers.

Experimental Results. Radioactive solution obtained from a seep near Waste Pit No. 4 was used to prepare the experimental solutions. By far the most abundant radionuclide was Ru-Rh-106

*Alien Guest from Atomic Energy Establishment, Trombay, Bombay, India.

(Table 8.1), and the chief salt was $NaNO_3$ (sodium was not determined, but it is the major cation of the intermediate-level waste discharged to the seepage pits). The pH of the seep solution, 8.6, is considerably lower than that of the discharged waste, which averages 0.22 M NaOH. The seep solution was diluted to decrease the activity level and then brought to the chemical concentration of the discharged waste stream (Table 8.2). Increasing the hydroxyl ion concentration of the solution to 0.22 M OH^- resulted in precipitation of $Mg(OH)_2$, which scavenged ~ 9% of the ruthenium activity. The decanted supernatant was then used for subsequent experiments. Experiments were also conducted with a synthetic solution of the same composition as the actual waste, containing Ru-106 Cl_3 obtained from the ORNL Isotopes Division. The four sulfide minerals used as sorptive media — pyrite (FeS_2), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S)m and stibnite (Sb_2S_3) — were obtained from Wards Natural Science Establishment, Rochester, N.Y.; the vermiculite (BO-4) was from the Zonolite Company, Travelers Rest, S. C.

Table 8.1 Analysis of Solution Obtained from a Seep Near Waste Pit No. 4, April 3, 1961

Radiochemicals	Amount (d/m/ml)	Stable Chemicals	Amount (ppm)
Ru-Rh-106	9.30×10^5	NO_3^-	4,770
Co-60	5.51	SO_4	500
Cs-137	2.90	Mg^{++}	85
Sr-90	~ 1	Ca^{++}	28
TRE	1.8	Ni^+	10
		Sr^{++}	5
		Fe^{++}- Fe^{3+}	< 15
		Mn^{++}	< 5

Table 8.2 Weighted Average Composition of Waste Stream Discharged to Seepage Pits 2, 3, and 4[a]

Component	Amount (M)	Component	Amount (M)
NaOH	0.22	$NaNO_3$	0.315
NH_4NO_3	0.025	Na_2SO_4	0.037
$Al(NO_3)_3$	0.022	NaCl	0.006

[a]Data provided by K. E. Cowser.

Slurry studies of the effect of particle size of the sulfide minerals were inconclusive. Sorption of ruthenium on 0.1 g of pyrite or stibnite ore from 100 ml of diluted seep solution at pH 11.8 was negligible for all particle size ranges from 100 mesh to less than 270 mesh ore. Sorption by 0.1 g of chalcopyrite or chalcocite was measurable, but there was no regular dependence of sorption on particle size.

With varying pH (pH 3 to 0.22 M OH^-), ruthenium removal was greatest between pH 6 and 11. This is the range in which maximum concentrations of polymeric ruthenium dioxide would be expected. The systems studied contained 1 g of chalcopyrite ore per 100 ml of solution.

Ruthenium removal from diluted seep solution (pH 11.8) by < 270 mesh chalcopyrite ore was maximum with 1 g of ore per 100 ml of solution (Fig. 8.1). The amount of ore varied from 0.1 to 4.0 g/100 ml, and removal actually decreased when the amount of ore was increased from 1 to 2 g/100 ml, then increased slowly with higher amounts of sorbent. Analysis of the supernatant solutions for iron, copper, and sulfide ion and for pH showed no significant difference with varying amounts of ore. Addition of 100 ppm Cu^{++} or Fe^{3+} did not eliminate the peak sorption at 1 g ore/100 ml, but sorption was decreased slightly with all amounts of ore. The addition of 100 ppm sulfide ion not only markedly decreased ruthenium sorption but also eliminated the peak in the sorption curve. No explanation was found for the occurrence of the peak in the sorption curve or its elimination by the addition of sulfide ion. Furthermore, the sorption peak did not occur when the series was reproduced using the same solutions but with freshly ground chalcopyrite ore.

Sorption of ruthenium by formation of RuS_2 at the surface of sulfide minerals should be facilitated by reduction of the ruthenium, and the addition of increasing concentrations of sodium hydrosulfite actually did increase ruthenium sorption (Fig. 8.1). Use of the reducing agent also yielded a smooth sorption isotherm, eliminating the sorption peak at 1 g ore/100 ml. Ruthenium sorption in all four sulfide ores was much higher from synthetic waste prepared with Ru-106 Cl_3 (Fig. 8.2) than from the diluted seep solution of the same stable chemical composition. The lower sorption of ruthenium from dilute seep solution coupled with a sorption isotherm that asymptotically approaches less than 100% sorption with increasing amounts of sorbent suggests the presence of more than one species of ruthenium in the seepage solution.

In a short series of experiments in which the dilute seep solution was run through a 0.5-in.-dia column containing 100-150 mesh sulfide ores under the same conditions as the slurry studies mentioned above, leakage of ruthenium through

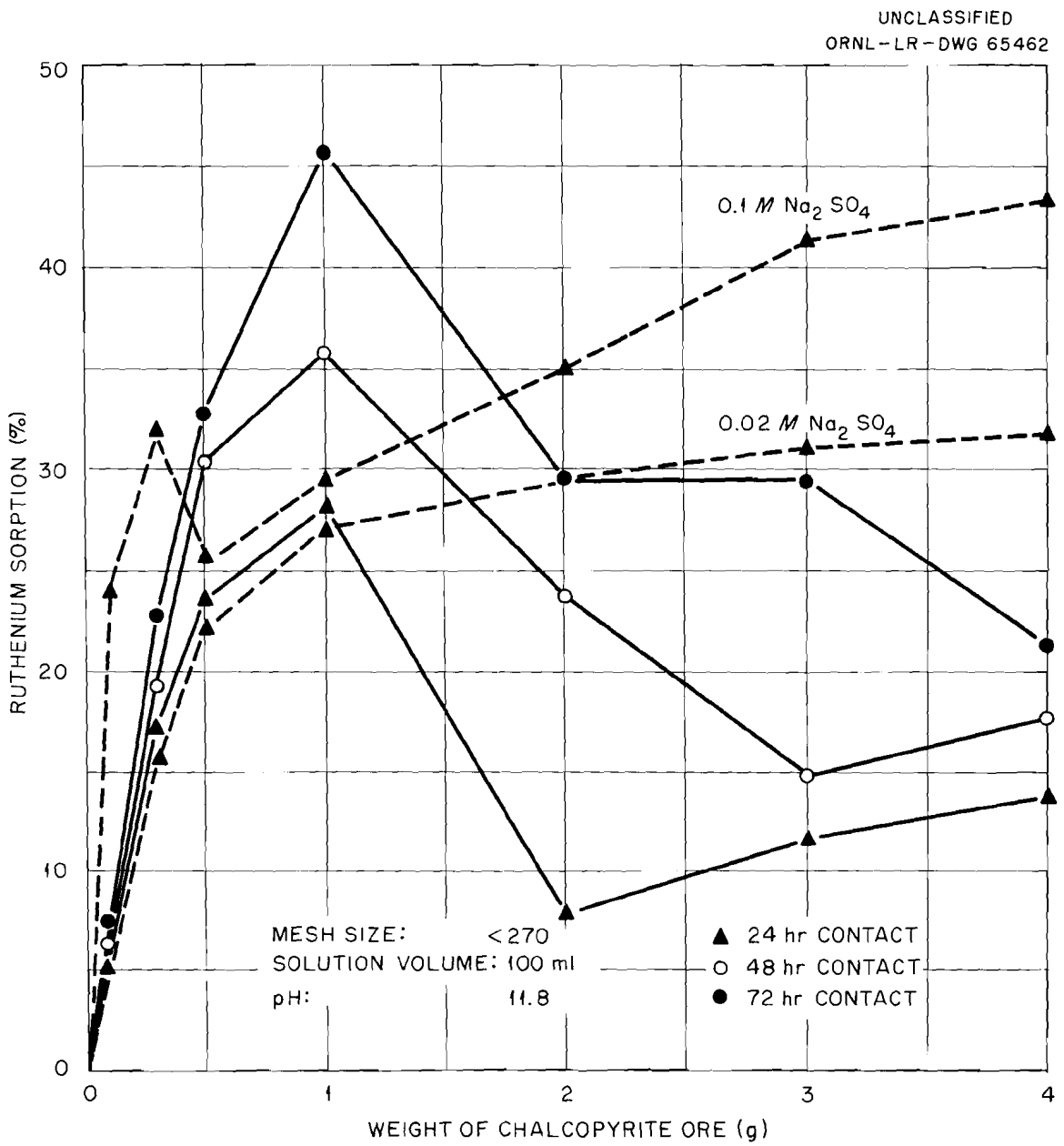

Fig. 8.1. Sorption of Ruthenium on Chalcopyrite Ore in the Presence and Absence of Sodium Sulfate.

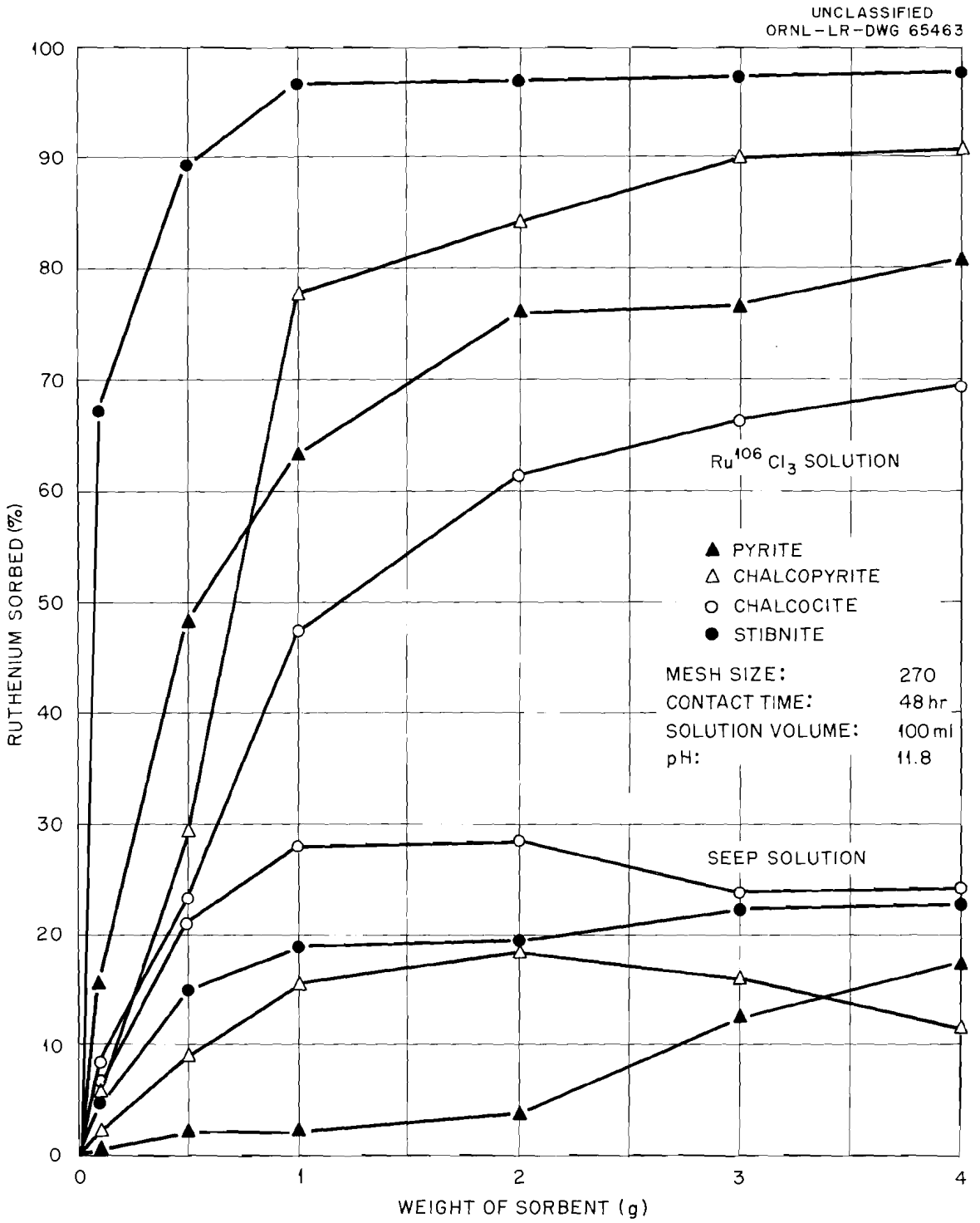

Fig. 8.2. Sorption of Ruthenium on Various Ores from Seep Solution and from Synthetic Solution.

the column was quite high. Counting of duplicate samples of chalcopyrite and stibnite from different sections of the columns showed little or no retention (Table 8.3). For pyrite and chalcocite, retention was somewhat greater. Vermiculite columns

Table 8.3 Distribution of Ruthenium Activity in Sulfide Ore and Vermiculite Columns
Sorbent particle size: 100-150 mesh

	cpm per g/cpm per ml of influent							
Section	Pyrite	Chalcopyrite	Chalcocite	Stibnite	Vermiculite	Vermiculite After Pyrite	Vermiculite After Chalcocite	Vermiculite with 0.0133 M $Na_2S_2O_4$
Top	14.4	0.71	7.6	2.4	1.14	0.44	0.34	16.0
2	14.7	0.71	12.4	2.4	1.10	0.39	0.32	3.2
3	11.7	0.89	16.2	2.4	0.99	0.50	0.40	2.4
4	8.6	1.02	15.0	2.3	0.86	0.56	0.48	2.2
5	6.2	1.05	10.8	2.6	0.73	0.55	0.59	2.7
Bottom	5.1	1.18	9.0	3.3	0.78	0.55	0.51	1.9

placed after these columns removed negligible amounts of ruthenium, indicating that these ores do not reduce the ruthenium to an exchangeable species. Sodium hydrosulfite was more effective as a reducing agent, but the quantities required were too great to suggest its use on a practical basis.

The fact that ruthenium loading was not maximum on the initial portion of the column but some distance down indicated a change in the sorbent by the continued leaching with the sodium nitrate-containing waste. A pyrite ore column that had been saturated with sodium by 3 hr continuous leaching with 3 M NaCl removed 50% less ruthenium from diluted seep solution than did an untreated column.

Summary. Ruthenium sorption from waste pit seepage solution by both sulfide minerals and vermiculite was low; however, the more easily sorbed species would have been removed as the waste percolated through the ground to the seep. Strong reducing agents in alkaline media improved sorption if sufficient quantities were used, but the sulfide minerals did not reduce ruthenium to an easily sorbed form. Sorption on sulfide minerals from synthetic waste was appreciable when the ruthenium was in a suitable chemical form. Ruthenium removal from seep solution was optimum at pH 6-11, suggesting that continued removal of ruthenium in the ground results primarily from filtration of polymeric ruthenium dioxide.

9.0 WHITE OAK CREEK BASIN STUDY*

(T. Lomenick)

Temporary water sampling stations have been installed along White Oak Creek at miles 2.6 and 3.9 and the tributary stream draining the northwest portion of the area to determine the amount and type of activity contributed to the creek from fallout and from other sources that cannot be monitored directly. In addition, these stations provide information on the chemical composition of creek water, transport of sediments, and flow in the creek. Representative samples of the effluent from the laundry and the sewage treatment plant are also taken.

The sampling instruments at the creek stations and sewage treatment plant are battery-operated scoop-type devices that take samples continuously and in proportion to the head behind the weirs or parshall flumes (Fig. 9.1). The discharge at each station is continuously recorded by water-level recorders.

Included in the drainage area of the northwest tributary stream, which comprises approximately 16% of the total area of the White Oak Creek drainage basin, are Waste Burial Ground 3 and the extreme northwest portion of the ORNL plant site. Approximately 34% of the watershed is located above the sampling station at White Oak Creek mile 2.6. Burial Ground 2 and the retention ponds of the LITR and ORR are within this area. The drainage area of the sampling station at White Oak Creek mile 3.9, which comprises about 13% of the White Oak Creek watershed, does not contain any Laboratory facilities or waste disposal areas. Thus, the activity detected at this station is the result of rainfall and surface runoff leaching and transporting soils contaminated by Laboratory and general fallout (approximately 3 curies sq mi/year). Contamination detected at the other stream sampling points includes that associated with fallout, discharges or seepage from known sources within the drainage areas, and as yet unknown or undefined sources.

The total amount of strontium detected at the stream-sampling stations from April 20 to Aug. 4, 1961, appears to vary with the discharge (Table 9.1, Fig. 9.2). This suggests that most of the strontium enters the stream due to ground and surface water leaching and not to sporadic releases or spills, etc.

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*This project, entitled "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin" (AEC Activity Number 060501000) is supported by the U.S. Atomic Energy Commission's Division of Biology and Medicine. All other projects covered in this Bimonthly Progress Report are supported by the Division of Reactor Development (AEC Activity Number 040405021).

Fig. 9.1. V-Notch Weir, Staff Gage and Stilling Well, Scoop Sampler, and Collecting Bottles at Temporary Stream Sampling Station.

The percentage of strontium sorbed on suspended solids in the creek water samples varied from 0.5 to 2.9 at the northwest tributary and from 1.1 to 17% at White Oak Creek mile 2.6 station. There is a relation between the percentage sorbed and the concentration of suspended solids in the creek (Fig. 9.3). However, the concentration of suspended solids in the water does not vary directly with discharge.

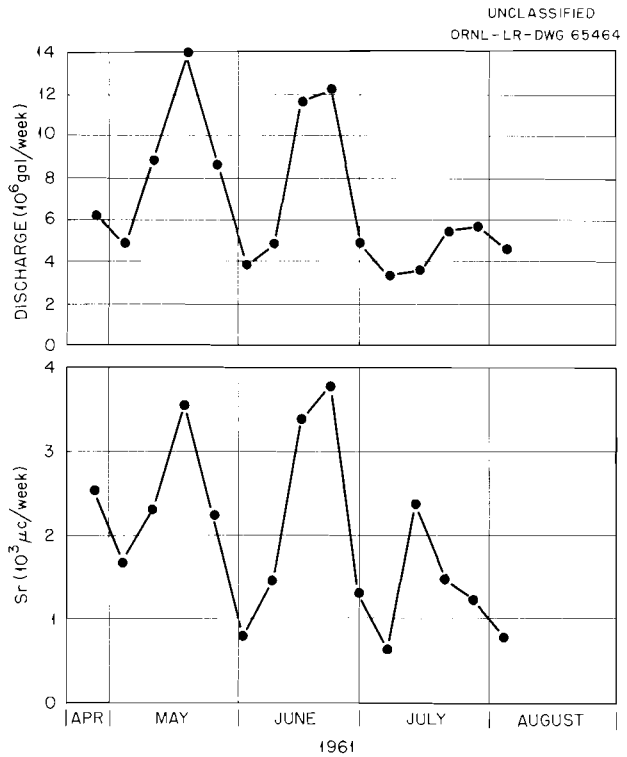

Fig. 9.2. Stream Discharge and Strontium Transport at Northwest Tributary Station.

Approximately 560 μc of strontium was detected in White Oak Creek at mile 3.9 during the period June 2-July 28, 1961. Thus, an average 1.1 μc per acre of watershed was contributed to the creek during this period. Assuming this rate to be representative of the entire drainage system, the amount of strontium associated with fallout at the White Oak Creek mile 2.6 station for the same period was 1435 μc, or 2.5% of the total detected. For the northwest tributary station,697 μc, or 4.4% of the total strontium passing the station, was due to fallout.

Table 9.1 Strontium Measured at Stream-Sampling Stations

Date	Vol Discharged (10^3 gal)	Sr-89,90 (μc)
Northwest Tributary		
4/20-27/61	6,222	2,544
4/27-5/4	4,857	1,655
5/4-11	8,757	2,254
5/11-19	13,861	3,568
5/19-26	8,649	2,226
5/26-6/2	3,755	768
6/2-9	4,776	1,464
6/9-16	11,593	3,379
6/16-23	12,243	3,754
6/23-30	772	1,301
6/30-7/7	3,314	627
7/7-14	3,517	2,396
7/14-21	5,399	1,472
7/21-28	5,551	1,240
7/28-8/4	4,527	772

Date	Vol Discharged (10^3 gal	Sr-89,90 (μc)
White Oak Creek Mile 2.6		
4/28-5/5	17,343	30,462
5/5-12	24,866	8,942
5/12-19	26,943	1,836
5/19-26	22,292	4,929
5/26-6/2	14,029	2,390
6/2-9	17,258	7,755
6/9-16	32,728	5,079
6/16-23	34,184	12,811
6/23-30	19,935	5,134
6/30-7/7	15,293	3,416
7/7-14	13,562	19,200
7/14-21	17,563	4,189
7/21-28	22,641	3,085
7/28-8/4	16,061	2,189
Mile 3.9		
5/31-6/9	2,805	48
6/9-16	7,959	136
6/16-23	9,905	169
6/23-30	4,026	69
6/30-7/7	2,101	29
7/7-14	1,830	62
7/14-21	2,526	26
7/21-28	3,135	22

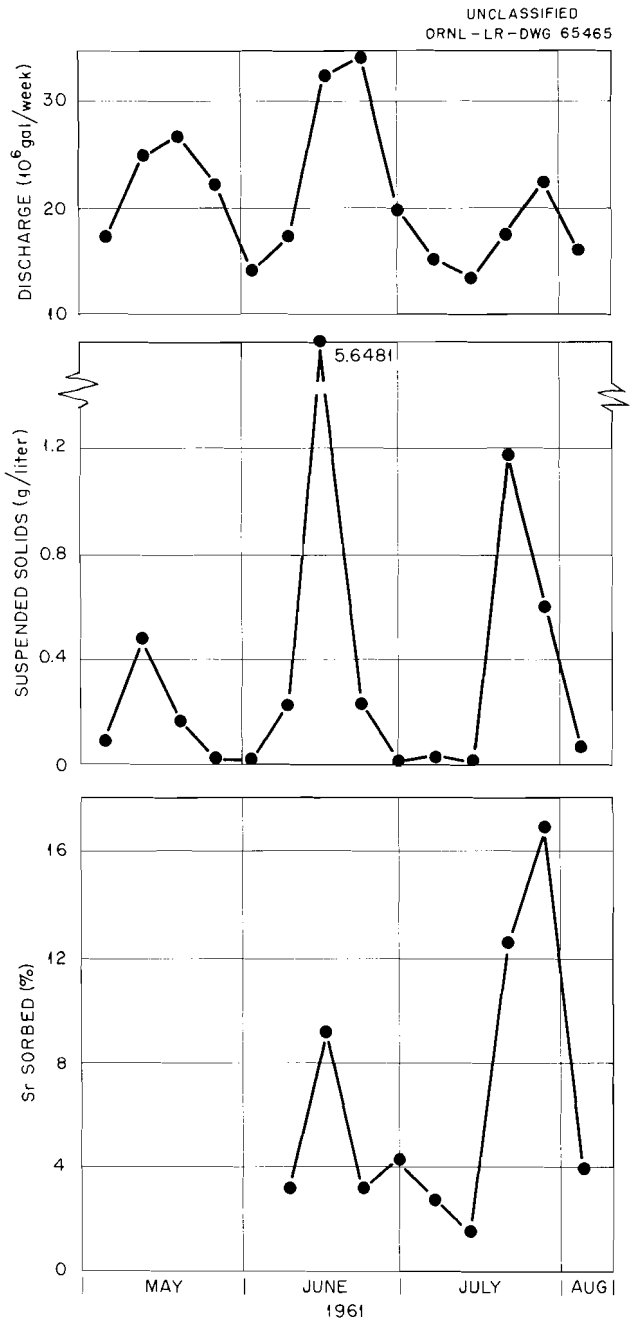

Fig. 9.3. Suspended Solids and Percentage of Strontium Sorbed at White Oak Creek Mile 2.6 Station.

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