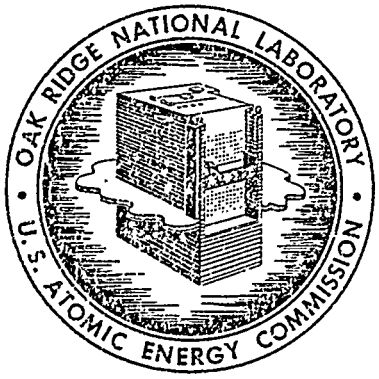
MASTER COPY



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-49

15

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR AUGUST AND SEPTEMBER 1961

ChemRisk Document No. 2005

Publicly Releasable

This document primarily for int to revision or c information is r semination with mation Control [

This document has received the necessary patent and technical information reviews and can be distributed without limitation.

d was prepared . It is subject al report. The ven public dis- egal and Infor-

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-TM-49

CHEMICAL TECHNOLOGY DIVISION

AND

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR AUGUST AND SEPTEMBER 1961

R. E. Blanco and E. G. Struxness

DATE ISSUED

NOV 29 1961

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level Waste Calcination. Nine calcination runs were completed in the engineering-scale equipment, 8-in.-dia by 90-in.-high stainless steel calcination pots. Both batch and continuous evaporators were used in processing simulated Purex and TBP-25 wastes prior to calcination. Calciner feed rates averaged 25-31 liters/hr when the pots were filled to 90% of capacity. In two runs where organic phosphates were present, average feed rates were less by a factor of 4 because of excessive foaming in the calciner.

Waste oxide from TBP-25 waste was incorporated into glassy materials at 875-1000°C by the addition of phosphate with borate and lead oxide fluxing agents. The solids had densities of 2.36 to 2.84 g/ml and represented waste volume reduction factors of 7.2-8.4. The condensates from batch evaporations of TBP-25 waste made 2 M in sodium hypophosphite contained 0.48 and 0.71% of the original ruthenium. The condensates contained less ruthenium when these feeds were made 0.25 M in PbO than when 0.25 M in $Pb(NO_3)_2$ (0.68 vs 2.18%). The principal gaseous product from the reaction between iron or aluminum nitrate (1-2 M) and phosphorous acid (1 M) appears to be nitric oxide. The best catalysts found for the reaction between nitrate and phosphite ions were silver, mercuric, and palladium ions. Vapor-liquid equilibrium conditions were investigated for simulated TBP-25, Darex, and Purex waste solutions as a function of acid and salt concentrations. Densities of the solutions were measured as a function of temperature and pressure.

A 4-in.-dia by 24-in.-high stainless steel pot calciner and related equipment for use with actual wastes in a hot cell is being designed. This equipment will be used primarily to study fission product volatility during evaporation and calcination, but will also provide solids that can be studied for radiation stability and analyzed for fission product distribution.

Preparation of chemical flowsheets for the pot calcination pilot plant at ICPP was started, with the initial objective of sizing process equipment to handle the maximum flows to be expected. The original process flowsheet was changed to delete the gas holder and recycle equipment and to provide for absorption of excess NO_2 in the acid scrubber. Design of mechanical equipment for demonstration of the pot calciner positioning, connecting, and sealing procedures is ~60% complete.

Low-Level Waste Treatment. The last demonstration run on process waste water in the semi-pilot plant facility gave effluent with <10% of the MPC for >1500 bed volumes of waste treated. Total hardness in the clarifier overflow averaged 20 ppm. The early breakthrough in an earlier run is believed to have been due to carbonate deficiency in the feed, which resulted in saturation of the resin with calcium. This will be forestalled in the pilot plant by continuous analysis of the effluent for hardness.

Installation of the 10-gpm low-activity waste pilot plant is complete, including an enclosed type 3 FLC Oliver vacuum filter substituted for an

Eimco-Burwell plate-and-frame filter to concentrate the sludge effluent from the clarifier. Approximately 300 hr of nonradioactive processing was accomplished with ORNL tap water, with the objectives of orienting personnel, optimizing operating procedures, and testing equipment. Tests by Dorr-Oliver, Inc., to classify solids in the treatment plant effluent showed that the suspended solids contained 59% of the Cs-137 and that the percentage of non-$CaCO_3$ solids increased as the particle size of the solids decreased; these results suggested the need for improving both the sorptive and the settling properties of Grundite (illite). In laboratory tests, heat-treatment of Grundite increased removal (from 83 to 96%) of Cs-137 from ORNL process waste water. Heat treatment to 600°C increased the selectivity of Grundite for cesium and decreased the percentage of small particle sizes, thus improving its settleability.

Engineering, Economic, and Hazards Evaluation. The economics of high-activity waste disposal in salt by (1) liquids in rooms with recessed floors, (2) pot calcination vessels in racks above the floor, and (3) pot calcination vessels in holes in the floor is being studied. In order to determine the amount of mine space that will be required, the infinite-slab heat calculation was used for cases 1 and 2. Gross mine area requirements for case 1 varied from 67 to 10 acres/year for decay times of 0.33 to 30 years. An equation for case 3 was programmed for the computer and the code is being "debugged."

Disposal in Deep Wells. An advisory committee to the AEC has considered several of the major problem areas encountered in the disposal of radioactive liquids to deep permeable formations and made recommendations for distributing work efforts so that the maximum utilization of the competence, facilities, and interest of the various co-operating agencies can be realized. Although ORNL will probably become involved in several phases of the program, initial efforts will be directed primarily to establishing the sorptive properties of typical permeable formations for the critical radionuclides in low- and intermediate-level waste streams.

Negotiations with Westco Research (Fort Worth) for a Laboratory subcontract to develop a waste-cement-clay mixture for use in the proposed ORNL Fracturing Disposal Pilot Plant were completed and a proposed subcontract was submitted to AEC for approval.

Disposal in Natural Salt Formations. Theoretical computations of temperature profiles around an isolated line source show reasonable agreement with measured profiles around two slender cylindrical heaters in a pillar and in the floor of the Hutchinson mine. Temperature measurements in the pillar and floor show that heat transfer is essentially the same in both locations despite the presence of shale and anhydrite in the floor. Values for thermal conductivity (3.0 Btu hr^{-1} ft^{-1} $°F^{-1}$) and diffusivity (0.10 ft^2/hr) computed from these measurements are in good agreement with measured values in single pure salt crystals (3.0 Btu hr^{-1} ft^{-1} $°F^{-1}$ and 0.11 ft^2/hr at 40°C). Preparations are underway for additional heat flow tests with multiple heat sources in geometric array in the Hutchinson mine.

Data from plastic flow gages in a recently mined room in the Hutchinson mine indicate that maximum closure of the room will amount to about 0.4% of

the opening and that 95% of this movement will take place in approximately 5.7 years.

Clinch River Studies. 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 size distribution analyses. Results of the analyses indicate that the sediments vary in texture from silty loam to loam, and that the sizes are classed as well graded clay to the upper range of sand sizes (median diameters ranging from 20 to 39 μ). The average clay content is about 14%, and the sand content varies from 30% at the lowest cross-section to 40% at the uppermost cross-section.

Results of a dispersion test, with Au-198 as a tracer, were: (1) White Oak Creek water is uniformly dispersed in width and depth of cross-section at CRM 17.1; (2) travel time from the mouth of White Oak Creek (CRM 20.8) to Centers Ferry (CRM 4.5) is 30.2 hr; and (3) the dilution factor is approximately 5000. Flow conditions under which the test was run were 7 cfs from White Oak Creek and 8000 cfs in the Clinch River, with the level of Watts Bar Reservoir held between 740 and 741 ft above mean sea level.

Fundamental Studies of Minerals. Ion exchange sites of vermiculite and montmorillonite were saturated with the cations K, Na, Li, Ca, Al, and Ba. Ba-vermiculite and K-montmorillonite sorbed the highest amounts of cesium. On slurrying 1-g equivalents of the saturated minerals with 20 ml of 1.5 M $NaNO_3$ solution containing 25 mg Cs/liter, Ba-vermiculite and K-montmorillonite sorbed 2.7 times and 1.6 times more cesium, respectively, than their natural counterparts after >150 hr contact. K-montmorillonite reached equilibrium within 1 hr after contact, while Ba-vermiculite did not reach equilibrium even after 190 hr. The c-spacings were partially collapsed in both cases; however, the exchange capacity of the saturated forms remained approximately the same as that of the original minerals.

White Oak Creek Basin Study. The rate of ground water movement in the bed of former White Oak Lake was measured by the auger hole method. Tests conducted in the upper lake bed show permeability values of 0.5 and 2.6 ft/day. In the lower portion of the lake bed the rate of ground water movement ranged from 0.2 to 2.2 ft/day.

CONTENTS

		Page
1.0	INTRODUCTION	6
2.0	HIGH-LEVEL WASTE CALCINATION	7
2.1	Evaporation-Calcination	7
2.2	Fixation in Glasses	7
2.3	Properties of Waste Solutions	15
2.4	Design of Hot Cell Evaporation-Calcination Equipment	15
2.5	Design of Calcination Pilot Plant	25
3.0	LOW-LEVEL WASTE TREATMENT	25
3.1	Scavenging-Ion Exchange Process	26
3.2	Inorganic Ion Exchange of Process Waste Water Plant Effluent	26
4.0	ENGINEERING, ECONOMIC, AND HAZARDS EVALUATION	31
4.1	Liquid in Salt	32
4.2	Calcination Vessels above Floor	32
5.0	DISPOSAL IN DEEP WELLS	36
5.1	Disposal by Hydraulic Fracturing	36
5.2	Liquid Injection into Permeable Formations	37
6.0	DISPOSAL IN NATURAL SALT FORMATIONS	40
6.1	Field Tests	40
6.2	Plastic Flow Studies	41
6.3	Thermal Studies	46
7.0	CLINCH RIVER STUDY	51
7.1	Estimate of Activity in Bottom Sediments	51
7.2	Dispersion Study	51
7.3	Error in Estimate of Sediment Activity	53
8.0	FUNDAMENTAL STUDIES OF MINERALS	53
8.1	Considerations in Cesium Selectivity	53
9.0	WHITE OAK CREEK BASIN STUDY	56
10.0	REFERENCES	57

1.0 INTRODUCTION

This report is the third of 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-level 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-level 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 this environment.

Previous reports in this series are ORNL-CF-61-7-3 and ORNL-TM-15.

2.0 HIGH-LEVEL WASTE CALCINATION

The pot calcination process for converting high-activity-level wastes to solids is being studied on both a laboratory and engineering scale to provide design information for construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes (Table 2.1) containing millicurie amounts of ruthenium but has not been demonstrated on actual high-activity-level wastes. A general flowsheet was shown previously (1).

2.1 Evaporation-Calcination (J. C. Suddath, C. W. Hancher, L. J. King)

Nine waste calcination runs (five with TBP-25 and four with Purex waste) were completed in the engineering-scale, 8 in. dia by 90 in. high, stainless steel calcination pots (Table 2.2). Six runs were made with a continuous evaporator, closely coupled to the pot, and three with feed prepared in a batch evaporator. In two of the tests with TBP-25 wastes, organic phosphates representing radiation degradation products of TBP were added.

The four Purex tests (R-43 through R-46) were routinely successful with average feed rates of 25 - 33 liters/hr. The bulk densities of the calcined solids were 1.14 - 1.55 g/cc. The quantity of water added to strip HNO_3 from the feed in the evaporator in runs R-43 and 44 was greater than necessary A more realistic value for the water-to-feed ratio would be 4 to 5.

The first TBP-25 test (R-47) was also a routine test, the pot being about 90% filled with solids. Tests R-48 and 49 were attempts to more nearly fill the pots by extending the feeding time. It was found that 10 - 20% more solids could be added to the pot by doubling the feeding time. The solids from TBP-25 feed had bulk densities ranging from 0.52 to 0.83 g/cc and appeared to have been deposited by radial deposition (Fig. 2.1).

In Runs R-50 and R-51, di- and monobutyl phosphates were each added to the feed, 1 cc per liter of waste. This is equivalent to a phosphate concentration of ~ 0.01 M. The organics caused a serious foam problem in the calciner, which resulted in reduced rates and "burp-overs" through the off-gas line.

Additional details and results of these nine runs will be presented when analysis of the data has been completed.

2.2 Fixation in Glasses (W. E. Clark, H. W. Godbee, and K. L. Servis)

Simulated TBP-25 waste was incorporated into melts at 875-1000°C. On being cooled and either quenched or annealed, the melts gave glassy solids with densities of 2.36 to 2.84 g/ml, representing volume reduction factors from 7.2 to 8.4. One of the more satisfactory mixtures, from consideration of behavior during heating, softening point, fluidity of melt, and quality of final product, gave a glass with 40.5, 25.0, 18.6, and 15.9 wt %, respectively, P_2O_5, Al_2O_3, Na_2O and PbO (Table 2.3, melt 7, and Fig. 2.2).

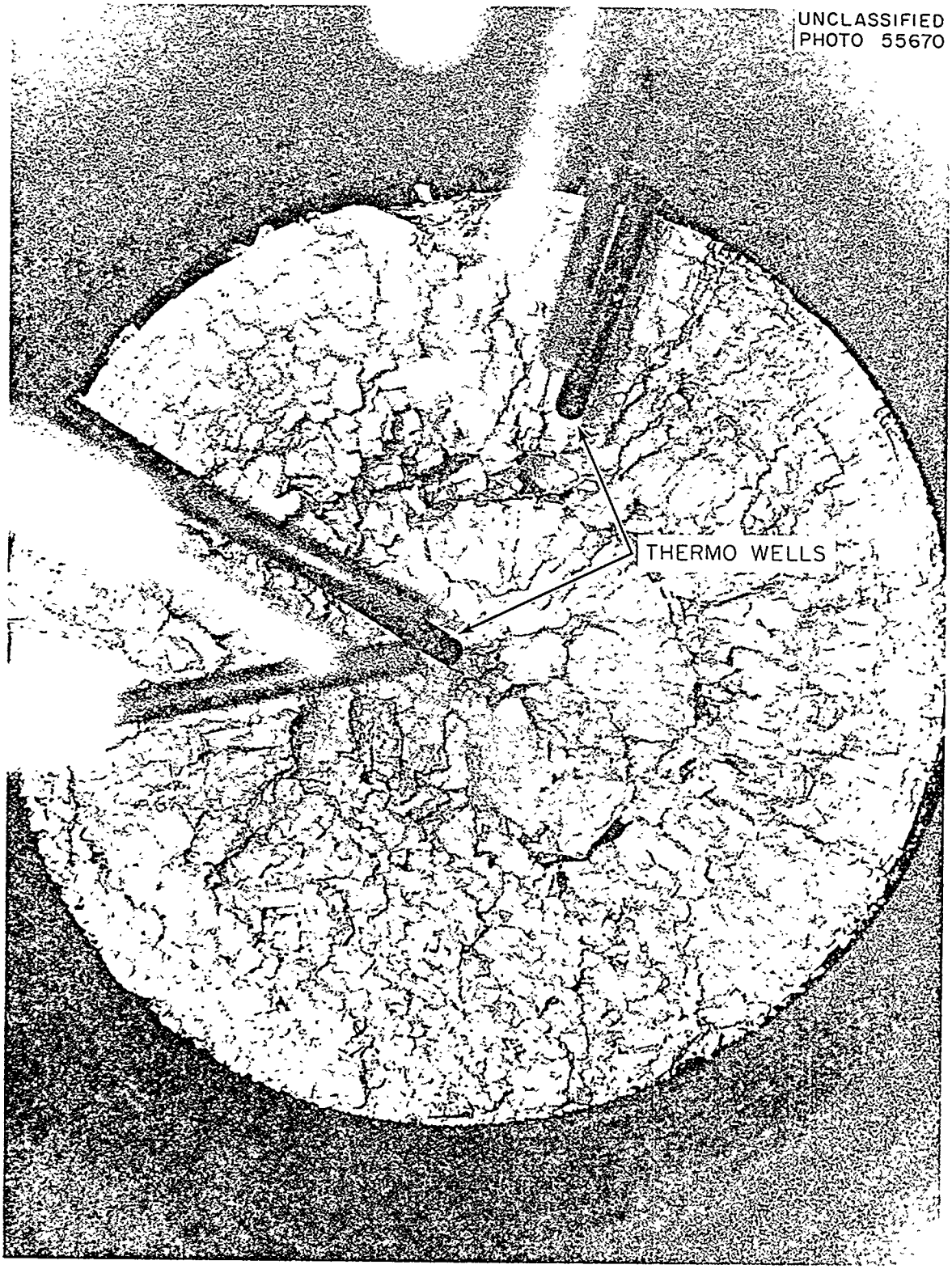


Fig. 2.1. Example of Radial Deposition of TBP-25 Calcined Solids.

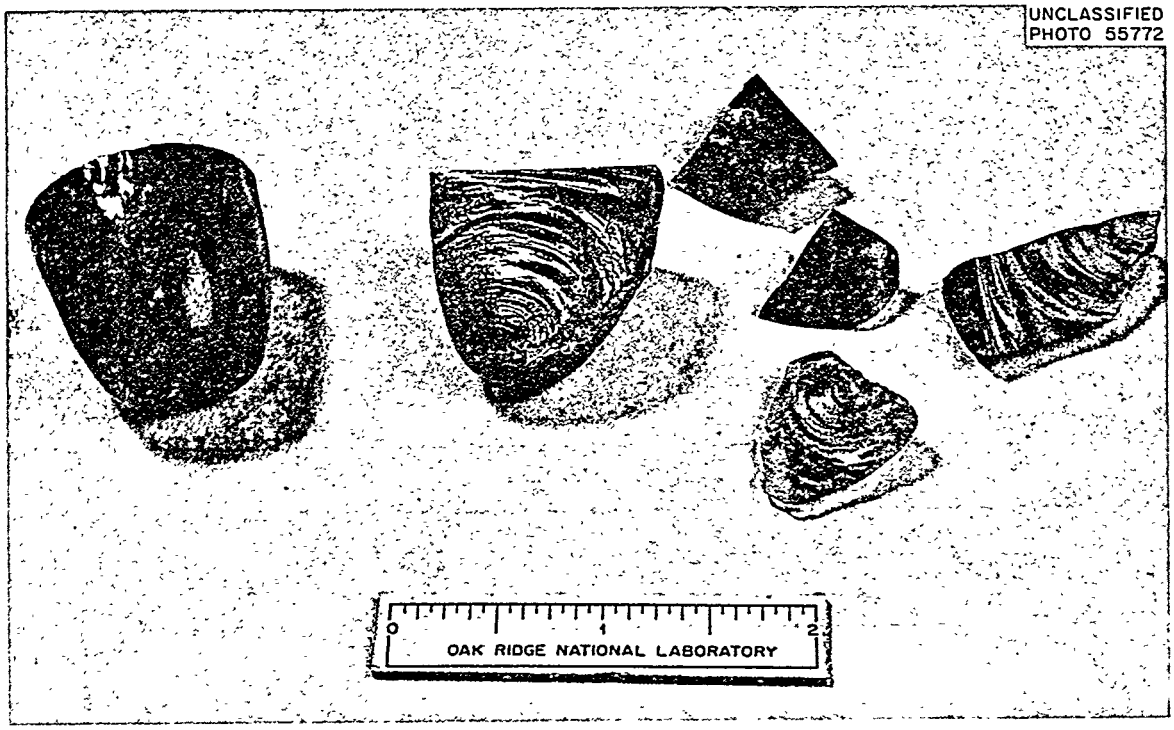


Fig. 2.2. Phosphate–Lead Glass Incorporating TBP-25 Waste Oxides. Additives per liter of waste: 2.0 moles of $NaH_2PO_2 \cdot H_2O$ and 0.25 mole of PbO.

Table 2.1. Compositions of Simulated High-Activity Wastes

Component	Amount (moles/liter)		
	Purex	TBP-25	Darex
Al^{3+}	0.1	1.72	---
Fe^{3+}	0.5	0.003	1.2
Cr^{3+}	0.01	---	0.4
Ni^{++}	0.01	---	0.2
Na^{+}	0.6	0.1	---
H^{+}	5.6	1.26	2.0
Hg^{++}	---	0.02	---
NH_4^{+}	---	0.05	---
Mn^{++}	---	---	0.04
NO_3^{-}	6.1	6.6	7.2
$SO_4^{=}$	1.0	---	---
Cl^{-}	---	---	0.001

Table 2.2. Engineering-Scale Evaporation and Pot Calcination of Wastes to 900°C

Run No.	Waste Type	Evaporator	Feed Time (hr)	Avg. Feed (liters/hr)	Calc. Time (hr)	Water/ Feed Ratio	Bulk Density[b] (g/cc)
R-43	Purex	Cont.	13	31	15	9.1	1.29
R-44	Purex	Cont.	12	33	11	7.9	1.14
R-45	Purex	Batch	13	25	11	3.8	1.17
R-46	Purex	Batch	15	28	10	3.0	1.55
R-47	TBP-25	Cont.	14	31	10	4.8	0.57
R-48	TBP-25	Cont.	38	12	10	2.8	0.77
R-49	TBP-25	Cont.	27	18	10	3.6	0.83
R-50	TBP-25	Cont.[a]	33	11	8	3.3	0.52
R-51	TBP-25	Batch[a]	43	7	7	3.1	0.59

[a] Organic phosphates added.

[b] Weight of solid after calcination divided by 60 liters, the operating liquid level.

Table 2.3 Phosphate Glasses Incorporating TBP-25 Waste Oxides

TBP-25 Waste (M): 6.60 NO_3^-, 1.72 Al^{3+}, 1.26 H^+, 0.10 Na^+, 0.05 NH_4^+, 0.003 Fe^{3+}, 0.002 Hg^{2+}, 0.003 Ru

Melt	1	2	3	4	5	6	7
Additives (moles/liter)							
$NaH_2PO_2 \cdot H_2O$	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$Na_2B_4O_7 \cdot 10\ H_2O$	0.065	0.065	---	0.032	---	---	---
NaOH	0.060	---	1.20	0.025	---	---	---
MgO	---	0.30	---	---	---	---	---
SiO_2	---	---	0.52	0.26	---	---	---
PbO	---	---	---	---	0.125	0.188	0.250
Melt composition (wt % theoretical oxides)							
Al_2O_3	28.4	28.4	26.7	27.6	27.1	26.0	25.0
Na_2O	22.7	22.4	20.4	21.4	20.2	19.4	18.6
P_2O_5	45.9	46.0	43.3	44.6	43.9	42.1	40.5
B_2O_3	2.9	2.9	---	1.4	---	---	---
SiO_2	---	---	9.5	4.9	---	---	---
PbO	---	---	---	---	8.6	12.4	15.9
MgO	---	0.2	---	---	---	---	---
Fe_2O_3	0.07	0.07	0.07	0.07	0.07	0.07	0.06
RuO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Softening point (°C)	875	900	1000	950	975	925	900
Bulk density (g/ml)	2.36	2.45	2.36	2.38	2.71	2.75	2.84
Waste oxides in glass (wt %)	29.5	29.5	27.8	28.7	28.2	27.1	26.0
Volume reduction (vol TBP-25/vol glass)	7.6	7.9	7.2	7.5	8.4	8.2	8.1
Appearance	Pale yellowish clear glass	Pale greenish white glass	Grayish green glass	Grayish green glass	Green glass, mottled with white	Green glass	Greenish white glass

Fluxing agents used to form melts were borate and lead oxide. Borate was added as tetraborate, $B_4O_7^=$, and lead oxide as PbO. Lead oxide did not lower the viscosity and softening point of melts as well as borate. However, a big advantage of lead oxide is that it does not cause foaming of the mixture prior to melting as does borate. Another advantage of lead oxide is that it yields higher density melts for the weight of additives required than do other chemicals studied. This also implies greater volume reductions. Other additives briefly investigated were magnesia and silica. Silica has the distinct disadvantage that it forms a precipitate in the original solution. Phosphate was added as NaH_2PO_2, 2 moles per liter of waste. Other studies showed that this amount of hypophosphite is needed to hold the Ru in the condensate to < 1% of the total amount in the waste.

Ruthenium Volatility. The use of hypophosphite for controlling ruthenium volatility is particularly attractive since it is oxidized to phosphate, a glass-forming agent. The addition of at least 2 moles of sodium hypophosphite per liter of TBP-25 waste held ruthenium in the condensate during evaporation-condensation to < 1% of that in the feed. The addition of lead as a fluxing agent as $Pb(NO_3)_2$ increased the nitrate in the waste and increased ruthenium in the condensate, while addition of PbO decreased the acidity and did not materially affect the ruthenium in the condensate. The calcinations were carried to about 1000°C in small all-quartz equipment described previously (1) with a 200-ml stainless steel beaker for a pot. Simulated TBP-25 waste (Table 2.1) containing 0.027 mg/ml stable ruthenium and 0.1 μc of Ru-106 tracer per milliliter was used.

In two experiments 2.0 moles of $NaH_2PO_2 \cdot H_2O$ was added per liter of waste. Ruthenium in the condensate was 0.48 and 0.71%, respectively, of the original ruthenium. In a third experiment 2.0 moles of $NaH_2PO_2 \cdot H_2O$ plus 0.25 mole of $Pb(NO_3)_2$ were added per liter of waste. Ruthenium in the condensate was 2.18% of the original. In a fourth experiment 2.0 moles $NaH_2PO_2 \cdot H_2O$ plus 0.25 mole PbO were added per liter of waste. Ruthenium in the condensate was 0.68% of the original. In none of the experiments was any detectable net off-gas produced.

Nitrate-Phosphite Reaction Products. The nature of the noncondensable gaseous products of the reaction between nitrate salts and orthophosphorous acid was not significantly different from those of the previously reported (2) HNO_3-H_3PO_3 reactions. The principal product was NO, while the second most abundant was NO_2 (Table 2.4). Small amounts of N_2 and N_2O were present. The evolution of noncondensable gases started at 120 - 130°C, compared to ~110°C in the nitric-phosphorous acid reaction. The distillate was more than 6 N HNO_3 at this point. Reaction was not complete when the experiment was terminated because of phosphorous acid decomposition. At 200°C the mixtures were still evolving gas and still contained appreciable amounts of the reducing agent. It is postulated that, at the reacting temperature, the salt nitrates hydrolyze to produce nitric acid, e.g.

$$2Fe(NO_3)_3 + 3H_2O \longrightarrow Fe_2O_3 + 6HNO_3$$

which then reacts with the phosphorous acid.

Table 2.4. Reaction of Nitrate with Phosphite

Reaction Mixture (moles/liter)					Noncondensable Off-Gas (moles/liter of mix)				Calc. H_3PO_3 for NO_3^- Reduction (moles)
HNO_3	H_3PO_3	$Al(NO_3)_3$	$Fe(NO_3)_3$	$Hg(NO_3)_2$	N_2	N_2O	NO	NO_2	
--	1.0	2.0	--	--	0.019	0.008	0.332	0.216	0.74
--	1.0	--	2.0	--	0.032	0.001	0.432	0.212	0.92
3.0	1.0	--	1.0	--	0.025	0.003	0.491	0.261	1.01
--	1.0	--	1.0	0.01	0.030	0.001	0.582	0.036	1.06

The experiments were carried out in all-glass equipment (2) with flexible polyethylene bags, connected to the system at a point between the two condensers, to collect the noncondensable off-gases. In each experiment 1 liter of reaction mixture was placed in the flask, the system was thoroughly flushed with argon, and the mixture was heated to about 200°C, the decomposition temperature of orthophosphorous acid. The off-gas passed through a nearly horizontal condenser to a downdraft condenser, and the condensate was collected in a 200-ml flask maintained at 80-90°C. The bags were calibrated to give volume as a function of gas pressure. Samples of the noncondensable gases were taken in evacuated gas sampling tubes for gas chromatographic analysis for A, N_2, N_2O, and NO; the amount of NO_2 was calculated by difference. Samples of the condensate and the residue were taken periodically for nitrate and nitrite determinations, and samples of the residue were analyzed for phosphate and phosphite.

The use of 0.01 M $Hg(NO_3)_2$ as a catalyst (Table 2.5) caused the nitrate-phosphite reaction to occur at a lower temperature and higher rate, and the noncondensable gases were almost exclusively nitric oxide, a product characteristic of mercury reduction of the nitrate ion at low hydrogen ion concentrations. Silver and palladium* ions were also good catalysts. Although exact studies were not attempted, the mechanism of the catalysis appears to be reduction of the cation by the phosphite ion followed by oxidation of the reduced form by the nitric acid present. Many of the cations which did not catalyze the reaction are either not reduced by phosphorous acid or are not oxidized by nitric acid. A hypothetical sample of such a redox catalyst mechanism is

$$H_3PO_3 + Hg^{2+} + H_2O \longrightarrow H_3PO_4 + Hg + 2\,H^+$$

$$3Hg + 2HNO_3 + 6H^+ \longrightarrow 2NO + 3\,Hg^{2+} + 4H_2O$$

$$2HNO_3 + 3H_3PO_3 \longrightarrow 2NO + 3H_3PO_4 + H_2O$$

In the exploratory experiments to investigate the catalysis, 0.0005-0.01 mole of the material under investigation was added to 100 ml of the reaction

*All radioactive wastes will contain palladium both as a fission product and from the decay of Ru-106.

Table 2.5. Catalysis of Nitrate-Phosphite Reaction

Expt. No.	Reaction Mixture (moles/liter) HNO_3	$Fe(NO_3)_3$	H_3PO_3	Additive (moles/liter)	Apparent Catalysis	Additional Observations
1	3.0	---	1.0	0.01 HgCl	No	Incomplete solution
2	3.0	---	1.0	0.01 PbO	No	Incomplete solution
3	3.0	---	1.0	0.01 CuCl	No	Bright blue solution
4	3.0	---	1.0	0.01 $Hg(NO_3)_2$	Yes	Gray ppt formed early, later dissolved
5	3.0	---	1.0	0.001 $Hg(NO_3)_2$	Yes	Same as (4) except later ppt
6	3.0	---	1.0	0.01 $AgNO_3$	Yes	Dissolved to form gray colloidal ppt which dissolved upon heating
7	3.0	---	1.0	0.01 $RuCl_x$	No	Deeply colored solution
8	3.0	---	1.0	0.01 Ru	No	Ru metal did not appear to dissolve
9	---	1.0	1.0	0.01 $Hg(NO_3)_2$	Yes	Very vigorous gas evolution
10	---	1.0	1.0	0.01 $AgNO_3$	Yes	Vigorous gas evolution
11	---	1.0	1.0	0.01 $Ce(NO_3)_3$	No	
12	---	1.0	1.0	0.01 $Mn(NO_3)_2$	No	
13	---	1.0	1.0	0.01 $FeSO_4$	?	Reaction not so vigorous as with Hg^{++} but appeared to be some catalysis
14	---	1.0	1.0	0.01 I	?	Purple fumes made observation difficult
15	---	1.0	1.0	0.01 $BiONO_3$	No	
16	---	1.0	1.0	0.01 AuCl	No	Colloidal ppt formed, on gentle heating did not dissolve
17	3.0	---	1.0	0.005 $RhCl_3$	No	
18	3.0	---	1.0	0.004 $Pd(NO_3)_2$	Yes	Metal plated out, then ppt as black spongy mass, which dissolved with vigorous gas evolution
19	3.0	---	1.0	0.005 $Pd(NO_3)_2$	Yes	Gray ppt formed, dissolved on heating; gases nearly colorless

mixture in a 150-ml Pyrex beaker. The mixture was stirred and allowed to stand ~ 15 min at room temperature and heated to boiling. Purely qualitative observations were then made as to the presence or absence of catalysis. An attempt was also made to estimate the nature of the gases being produced.

2.3 Properties of Waste Solutions (W. E. Clark, H. W. Godbee)

Vapor-liquid equilibrium, density, and boiling point data are needed in the design of the hot pilot plant to define evaporator operating conditions and to size the evaporation and rectification equipment. Vapor-liquid equilibrium for representative TBP-25, Darex, and high-sulfate Purex simulated waste solutions (Table 2.6), determined in Gillespie still distillations, and pot liquid densities are shown in Tables 2.7-2.9. The intended goal was to investigate solutions ranging in metal concentration from one-half to twice that of the so-called "standard" compositions (Table 2.1). This goal was not always attainable due to instability of the more concentrated solutions. Four different acid concentrations were investigated at each salt concentration, although here, also, solution instability sometimes prevented study of the more concentrated solutions. Each solution was equilibrated twice, once at atmospheric pressure (744-751 mm Hg) and again at 559-569 cm Hg.

2.4 Design of Hot Cell Evaporation-Calcination Equipment (J. O. Blomeke and H. O. Weeren)

Installation of equipment for evaporating and calcining actual waste solutions in a hot cell, in order to obtain information on the volatility of fission products, the buildup of pressure in the calciner pot after calcination due to radiation decomposition, and the distribution of fission products in the solids. The proposed calciner pot dimensions are 4 in. dia by 24 in. high, and the maximum size of the feed batch, as determined by the capacity of the available waste carrier, will be 5 gal. The calciner pot dimensions are the same as the dimensions of the calciner pot used in nonradioactive laboratory tests, since the results obtained there were found to be partly dependent on pot size and geometry. If a smaller-scale test appears desirable, a 2.5-in.-dia pot can be substituted without alteration to the rest of the equipment.

A series of several runs in the hot cell is currently contemplated. Besides the necessary break-in runs with nonradioactive and low-activity-level feeds, there will be several runs on feed material from Idaho and two or more runs on Hanford waste. Runs with locally produced wastes can be performed in addition to or in place of those with imported wastes, depending on the availability and suitability of the local wastes for this work.

The waste solution will be brought from Idaho or Hanford in a recently designed 5-gal liquid waste carrier. The carrier will be placed in an enclosed box on the roof of the cell and the waste solution transferred to the transfer tank by vacuum (Fig. 2.3). When transfer is complete, the waste solution will be dropped to the feed tank and the carrier will be washed and removed. The solution in the feed tank will be agitated by continuously pumping a 0.5-gpm stream out of and back into the tank. A stream of up to 100 ml/min will be pumped to the calciner pot. A separate line from outside the cell will be used to feed calcium solutions to the calciner pot when desired. A water flush will be used on both feed lines after each transfer

Table 2.6 Compositions of Simulated Waste Solutions

Solution No.	Solution Composition (M)									
	H^+	Al^{3+}	Fe^{3+}	Na^+	Hg^{++}	NO_3^-	Cr^{3+}	Ni^{++}	$SO_4^=$	Mn^{++}	Cl^-
A. TBP-25 Waste										
T-1	1.26	1.72	0.003	0.01	0.02	6.48				
-1a	0.5	1.72	0.003	0.01	0.02	5.72				
-1b	3.0	1.72	0.003	0.01	0.02	8.22				
-1c	5.0	1.72	0.003	0.01	0.02	10.22				
T-2	1.26	0.86	0.0015	0.005	0.01	3.87				
T-2a	0.5	0.86	0.0015	0.005	0.01	3.11				
2b	3.0	0.86	0.0015	0.005	0.01	5.61				
2c	5.0	0.86	0.0015	0.005	0.01	7.61				
T-3*	1.26	3.44	0.006	0.02	0.04	11.7				
3a*	0.5	3.44	0.006	0.02	0.04	10.94				
3b*	3.0	3.44	0.006	0.02	0.04	13.44				
3c*	5.0	3.44	0.006	0.02	0.04	15.44				
T-4**	1.26	2.6	0.0045	0.015	0.03	9.15				
4a*	0.5	2.6	0.0045	0.015	0.03	8.39				
4b*	3.0	2.6	0.0045	0.015	0.03	10.89				
4c*	5.0	2.6	0.0045	0.015	0.03	12.89				
B. High-sulfate Purex Waste										
PS-1	5.6	0.1	0.5	0.6		6.05	0.01	0.01	1.0	
1a	7.0	0.1	0.5	0.6		7.45	0.01	0.01	1.0	
1b	4.0	0.1	0.5	0.6		4.45	0.01	0.01	1.0	
1c	2.0	0.1	0.5	0.6		2.45	0.01	0.01	1.0	
PS-2	5.6	0.05	0.25	0.3		5.825	0.005	0.005	0.5	
2a	7.0	0.05	0.25	0.3		7.225	0.005	0.005	0.5	
2b	4.0	0.05	0.25	0.3		4.225	0.005	0.005	0.5	
2c	2.0	0.05	0.25	0.3		2.225	0.005	0.005	0.5	
PS-3	5.6	0.2	1.0	1.2		6.50	0.02	0.02	2.0	
3a	7.0	0.2	1.0	1.2		7.90	0.02	0.02	2.0	
3b	4.0	0.2	1.0	1.2		4.90	0.02	0.02	2.0	
3c	2.0	0.2	1.0	1.2		2.90	0.02	0.02	2.0	
C. Darex Waste										
D-1	2.001		1.21			7.19	0.38	0.17		0.04	0.001
1a	3.002		1.21			8.19	0.38	0.17		0.04	0.001
1b	5.003		1.21			10.19	0.38	0.17		0.04	0.001
1c	7.004		1.21			12.19	0.38	0.17		0.04	0.001
D-2	2.001		0.6			4.58	0.19	0.085		0.02	0.0005
2a	3.002		0.6			5.58	0.19	0.085		0.02	0.0005
2b	5.003		0.6			7.58	0.19	0.085		0.02	0.0005
2c	7.004		0.6			9.58	0.19	0.085		0.02	0.0005
D-3*	2.001		2.42			12.38	0.76	0.34		0.08	0.002
3a*	3.002		2.42			13.38	0.76	0.34		0.08	0.002
3b*	5.003		2.42			15.38	0.76	0.34		0.08	0.002
3c*	7.004		2.42			17.38	0.76	0.34		0.08	0.002
D-4	2.001		1.82			9.80	0.57	0.255		0.06	0.0015
4a	3.002		1.82			10.80	0.57	0.255		0.06	0.0015
4b	5.003		1.82			12.80	0.57	0.255		0.06	0.0015
4c*	7.004		1.82			14.80	0.57	0.255		0.06	0.0015

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

** This solution was not stable at room temperature.

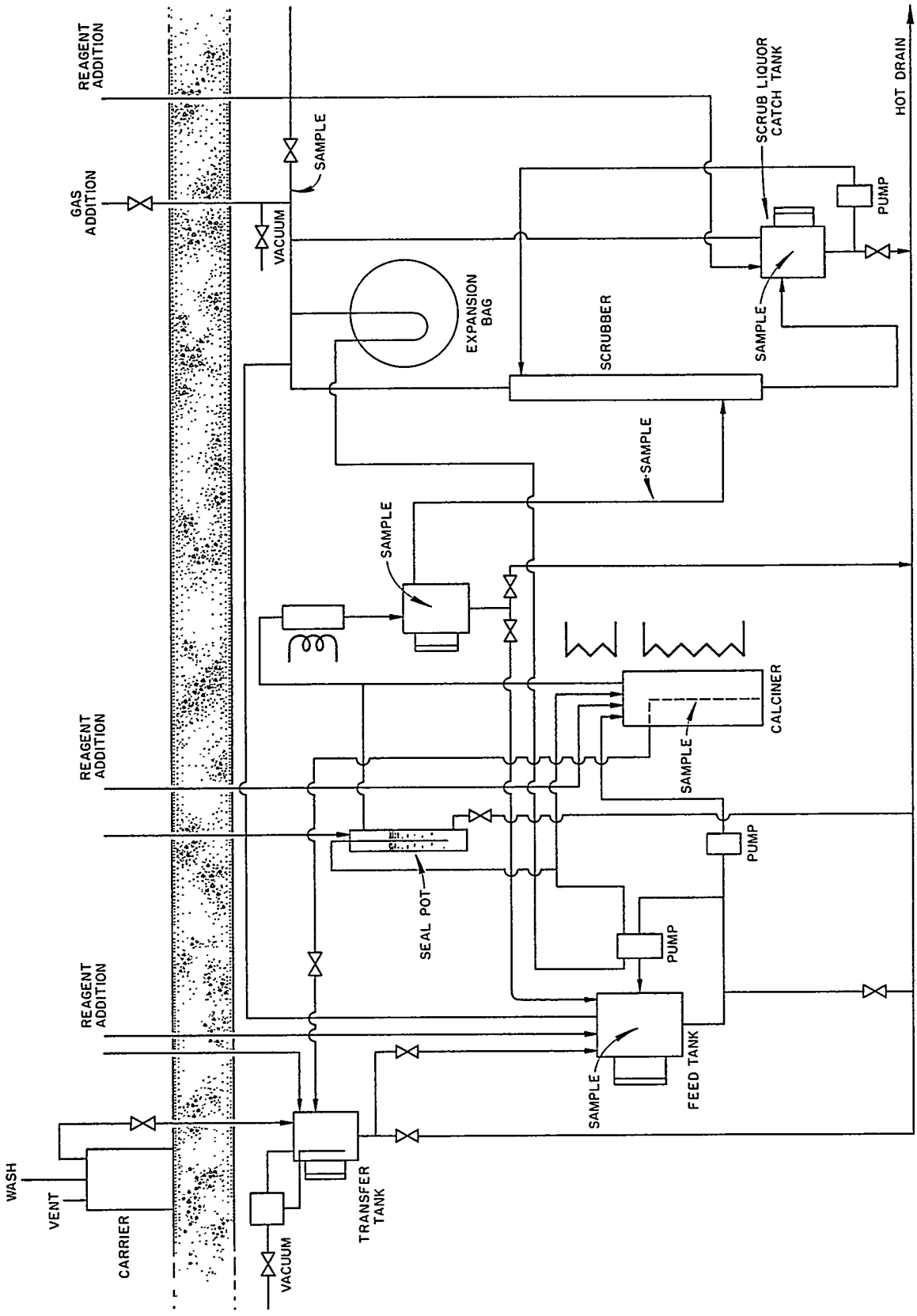

UNCLASSIFIED
ORNL-LR-DWG 63193
REAGENT ADDITION
GAS ADDITION
SAMPLE
VACUUM
EXPANSION BAG
SCRUBBER
SCRUB LIQUOR CATCH TANK
PUMP
HOT DRAIN
SAMPLE
SAMPLE
SAMPLE
CALCINER
REAGENT ADDITION
SEAL POT
PUMP
PUMP
REAGENT ADDITION
SAMPLE
FEED TANK
WASH
VENT
CARRIER
TRANSFER TANK
VACUUM

Table 2.7. Vapor-Liquid Equilibrium and Density Data for Simulated TBP-25 Waste

Solution	H^+, Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) 25°C	50°C	75°C	100°C
		Pressure 744-749 mm Hg					
T-1	1.26	109.5	748.3				
pot	1.28			1.3238	1.3072	1.2818	1.2688
distillate	0.52						
T-1 (Duplicate)	1.32	109.5	747.1				
pot	1.35			1.3194	1.3049	1.2885	1.2672
distillate	0.52						
T-1a	0.50	107.5	748.3				
pot	0.58			1.2963	1.2819	1.2580	1.2443
distillate	0.15						
T-1b	2.91	113.5	748.5				
pot	2.96			1.3725	1.3512	1.3317	1.3124
distillate	2.10						
T-1c	4.85**	117	746.3				
pot	4.86			1.4249	1.4034	1.3811	1.3574
distillate	5.45						
T-2	1.26	104	746.3				
pot	1.34			1.1922	1.1803	1.1593	1.1341
distillate	0.13						
T-2a	0.50	102.5	746.4				
pot	0.54			1.1669	1.1531	1.1361	1.1087
distillate	0.04						
T-2b	2.97	107.5	746.6				
pot	3.17			1.2478	1.2319	1.2131	1.1833
distillate	0.60						
T-2c	4.96	111.5	745.7				
pot	5.10			1.3039	1.2811	1.2609	1.2385
distillate	2.01						
T-4*		117	746.6				
pot	1.26						
distillate	1.92						
T-4-1*		119	745.7				
pot	2.22						
distillate	4.11						
T-4-2*		120.5	745.7				
pot	3.03						
distillate	6.24						
T-4-3*		121.5	744.8				
pot	3.70						
distillate	8.24						
T-4-4*		122	744.8				
pot	4.22						
distillate	9.84						
T-4-5*		122.5	744.8				
pot	4.64						
distillate	11.00						

Table 2.7 (Cont.)

Solution	H^+, Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) 25°C	50°C	75°C	100°C
		Pressure 563-568 mm Hg					
T-1s	1.26	101.5	567.5				
pot	1.32			1.3242	1.3099	1.2938	1.2710
distillate	0.51						
T-1s (Duplicate)	1.32	102	563.9				
pot	1.41			1.3279	1.3141	1.2963	1.2731
distillate	0.58						
T-1as	0.50	100	566.7				
pot	0.56			1.2961	1.2837	1.2632	1.2443
distillate	0.17						
T-1bs	2.91	105	566.7				
pot	3.02			1.3699	1.3522	1.3339	1.3102
distillate	2.03						
T-1cs**	4.85	110	---				
pot	5.12			1.4286	1.4069	1.3842	1.3589
distillate	5.95						
T-2s	1.26	96	567.5				
pot	1.41			1.1914	1.1786	1.1581	1.1320
distillate	0.58						
T-2as	0.50	94	566.7				
pot	1.34			1.1647	1.1532	1.1344	1.1087
distillate	0.092						
T-2bs	2.97	99	566.7				
pot	3.21			1.2444	1.2295	1.2110	1.1800
distillate	0.51						
T-2cs	4.96	104	---				
pot	5.25			1.3041	1.2818	1.2603	1.2356
distillate	1.88						
T-4s*		109	566.4				
pot	1.26						
distillate	1.86						
T-4-1s		111.5	566.4				
pot	2.22						
distillate	3.83						
T-4-2s		113	563.9				
pot	3.03						
distillate	5.89						
T-4-3s		113.5	563.9				
pot	3.70						
distillate	7.81						

* T-4 was not stable at room temperature. In order to obtain equilibrium data on this and the following solutions, concentrated acid was added to the pot after each distillation. Pot compositions for T-4b through T-4f are therefore calculated values.

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

Table 2.8. Vapor-Liquid Equilibrium and Density Data for Simulated Purex Waste

Solution	H^+, Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) 25°C	50°C	75°C	100°C
		Pressure 744-751 mm Hg					
PS-1	5.35	110.5	---				
pot	5.52			1.3175	1.2994	1.2773	1.2505
distillate	1.43						
PS-1a	6.75	113	747.7				
pot	6.88			1.3194**	1.2991	1.2769	1.2497
distillate	2.81			1.3175	1.2994	1.2773	1.2505
PS-1b	3.70	107.5	747.7				
pot	3.92			1.2736	1.2565	1.2377	1.2106
distillate	0.58						
PS-1c	1.88	104	750.5				
pot	1.91			1.2115	1.1974	1.1804	1.1536
distillate	0.091						
PS-2	5.50	109	747.7				
pot	5.57			1.2653	1.2470	1.2246	1.1947
distillate	1.10						
PS-2a	6.78	111	747.7				
pot	6.89			1.2944	1.2738	1.2376	1.2217
distillate	2.12						
PS-2b	3.80	106	750.5				
pot	4.08			1.2133	1.1973	1.1776	1.1487
distillate	0.44						
PS-2c	1.82	103	750.5				
pot	1.95			1.1423	1.1297	1.1129	1.0800
distillate	0.058						
PS-3*	5.25	113	750.4				
pot	5.36			1.4470	1.4272	1.4032	1.3770
distillate	2.67						
PS-3a	6.67	116	750.4				
pot***	6.81						
distillate	4.88						
PS-3b	3.67	110	744.4				
pot	3.77			1.3991	1.3810	1.3603	1.3334
distillate	1.05						
PS-3c	2.22	106.5	747.5				
pot	2.38			1.3778	1.3612	1.3426	1.3144
distillate	0.25						

Table 2.8 (Cont.)

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

* Solution precipitated on standing.

** Measurements made on duplicate samples.

*** Densities of solution not determined because of solution instability.

Table 2.9. Vapor-Liquid Equilibrium and Solution Density Data for Simulated Darex Waste

Solution	H^+, Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) 25°C	50°C	75°C	100°C
		Pressure 746-751 mm Hg					
D-1	1.83	110	746.7				
pot	1.97			1.3844	1.3665	1.3470	1.3203
distillate	0.94						
D-1a	2.75	112.5	747.1				
pot	2.99			1.4129	1.3941	1.3727	1.3469
distillate	1.86						
D-1b	4.41*	116	750.4				
pot	4.92			1.4595	1.4370	1.4126	1.3829
distillate	4.46						
D-1c	6.70	119	750.4				
pot	6.80			1.5080	1.4813	1.4485	1.4175
distillate	8.51						
D-2	1.88	105.5	747.1				
pot	2.06			1.2380	1.2200	1.2011	1.1732
distillate	0.26						
D-2a	2.80	107.5	750.4				
pot	3.11			1.2731	1.2555	1.2374	1.2149
distillate	0.59						
D-2b	4.77	111	750.4				
pot	5.16			1.3289	1.3077	1.2746	1.2602
distillate	1.81						
D-2c	6.39	114.5	749.3				
pot	7.05			1.3765	1.3513	1.3237	1.2947**
distillate	4.02			1.3764	1.3514	1.3260	1.2965
D-4***		117	749.3				
pot	1.98			1.5363	1.5167	1.4869	1.4650
distillate	3.19						
D-4a***		118.5	750.1				
pot	2.75			1.5563	1.5356	1.5100	1.4814
distillate	4.74						
D-4b***		121	750.1				
pot	4.58			1.5841	1.5598	1.5319	1.4992
distillate	8.57						

Table 2.9 (Cont.)

Solution	H^+, Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)	Density (g/ml) 25°C	50°C	75°C	100°C
		Pressure 559-569 mm					
D-1s	1.83	103	566.0				
pot	1.97			1.3874	1.3701	1.3455	1.3265
distillate	0.80						
D-1as	2.75	105	566.0				
pot	2.90			1.4168	1.3993	1.3763	1.3506
distillate	1.66						
D-1bs	4.41	108.5	562.4				
pot	4.86			1.4628	1.4396	1.4040	1.3847
distillate	4.12						
D-1cs	6.70*	111.5	559.8				
pot	6.87			1.5101	1.4831	1.4537	1.4216
distillate	8.10						
D-2s	1.88	97.5	566.0				
pot	2.00			1.2300	1.2151	1.1908	1.1707
distillate	0.20						
D-2as	2.80	99.5	566.0				
pot	3.09			1.2709	1.2539	1.2354	1.2063
distillate	0.53						
D-2bs	4.77	103	562.4				
pot	5.18			1.3257	1.3066	1.2838	1.2573
distillate	1.67						
D-2cs	6.39	106.5	559.8				
pot	7.07			1.3768	1.3529	1.3269	1.2961
distillate	3.79						
D-4***		109.5	568.1				
pot	1.94			1.5320	1.5117	1.4873	1.4587
distillate	2.91						
D-4as***		111	568.1				
pot	2.84			1.5582	1.5352	1.5104	1.4802
distillate	4.72						
D-4bs***		113.5	568.1				
pot	4.50			1.5842	1.5580	1.5293	1.4970
distillate	8.18						

* Apparent analytical error.

** Duplicate determinations.

*** Not stable at room temperature.

to prevent plugging. A third line feeding the calciner pot is a gas circulation line that serves the additional function of an emergency vent.

During the first stage of a run the waste solution will be concentrated in the calciner pot by boiling. The vapor will be discharged through a vent line to a condenser, and the noncondensables will be sent through a scrubber and then recycled to the calciner pot. The liquid level in the calciner pot will be maintained by regulating the feed rate and will be determined by thermocouple readings.

After evaporation is complete, the calciner pot will be heated to 900°C, during which mercury is expected to be driven off from TBP-25 wastes, to the piping between the top of the pot, and the disconnects will be kept at a temperature above the condensation temperature (450°C) of the mercury compounds. Off-gas flow will be the same as in the first stage of the run, i.e., through a condenser, a scrubber, and back to the calciner pot.

When calcination is complete and the pot has cooled, the furnaces will be swung aside and the calciner disconnected from the equipment. The feed and vent lines on the pot will be sealed and the pot withdrawn from the cell through a hole in the roof, into a transfer carrier, and elsewhere for observation and ultimate disposal. A new calciner pot will then be lowered into place and connected to the equipment for the next run.

For the study of ruthenium behavior during evaporation a calciner pot of slightly different design will be substituted. It will be connected to the equipment and partially filled with waste solution, and the condensate collected during the previous calcination run will then be dropped to the feed tank. The waste solution in the calciner will be brought to a boil and the condensate in the feed tank pumped in at the evaporation rate until all the condensate has been used. The ruthenium distribution between evaporator solution and condensate can then be determined by analyses.

Because one of the main purposes of the hot cell tests is to determine the volatility of fission products from actual waste solutions, it is necessary that believable mass balances be obtained. Since analysis of the calcined cake is extremely difficult even when there is no activity present and would be almost impossible for high-activity wastes, a mass balance for all volatile fission products will have to be obtained by analyzing the feed solution at the start of a run and the condensate and scrub liquor at the end of a run. Since ruthenium, in particular, tends to plate out on any surface at hand, the vent line between the calciner pot and the condenser will be decontaminated after each run and the decontaminating solution analyzed for volatile fission products.

Any pressure buildup in the calciner pots after they are removed from the cell will be noted on a pressure gage connected to one of the vent lines, and comparison of this reading with pot temperature will indicate how much of the pressure rise is due to gas generation inside the pot.

Provision will be made to run the experiment with a nitric oxide gas blanket to determine the effect of this variable, if desired.

2.5 Design of Calcination Pilot Plant (J. O. Blomeke, J. M. Holmes, E. J. Frederick)

Preparation of flowsheets for the ICPP waste calcination pilot plant is under way. A total of eight will be made, one batch and one continuous for each of the TBP-25, Darex, high-sulfate Purex, and low-sulfate Purex processes. The TBP-25 waste flowsheet is receiving prime attention since its calcination will be tested first at Idaho. However, since the equipment must be sized for maximum flow rates, feed rates for all the processes must be determined before equipment design can be started. The furnace will be designed to handle 6-, 8-, or 12-in.-dia pots with an active length of 6 ft. Over-all pot length will be 7.5 - 8 ft. The process equipment sizes will be determined by the 12-in.-dia pot size.

The off-gas equipment shown on the flowsheet in the initial proposal (3) will be simplified by omitting the gas holder and blower used to recycle gas to the acid scrubber for removal of absorbable oxides of nitrogen. Nitric oxide generated during the addition of phosphite to the process or used to purge the evaporator to minimize ruthenium volatility may necessitate the use of the acid scrubber to absorb excess off-gas after conversion of the nitric oxide to absorbable nitrogen dioxide. This provision will minimize the net volume of off-gas generated by the calcination pilot plant.

Design of mechanical equipment for demonstration of the pot calciner positioning, connecting, and sealing procedures is about 60% complete. The equipment is sized for either the Lockheed Nuclear Products cells at Dawsonville, Georgia or the ICPP Hot Pilot Plant Cell 2. A contract for the demonstration has been signed with the Lockheed Company, and work started on Oct. 1. Bid invitations for construction of the demonstration equipment are being issued, and equipment fabrication should start in November.

3.0 LOW-LEVEL WASTE TREATMENT

A scavenging-ion exchange process (4, 5) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations; ORNL low-activity-level waste is being used as a medium for study. The scavenging-ion exchange process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; the Cs/Na separation factor is 160 for phenolic groups, and 1.5 for sulfonic groups. Other cations, e.g., strontium and rare earths, are also sorbed efficiently. Inorganic ion exchange media such as vermiculite and clinoptilolite are being studied as alternatives. The waste solution must be clarified prior to ion exchange since ion exchange media do not remove colloidal materials efficiently. Water clarification techniques are being developed for both the ion exchange processes and for the ORNL lime-soda process waste water treatment plant. Work is proceeding on both development and pilot plant programs.

3.1 Scavenging-Ion Exchange Process

Demonstration Run (W. E. Clark, R. R. Holcomb). In the last run in the semi-pilot plant facility the activity in 1500 bed volumes of waste was reduced to less than 10% of the MPC. Neither Sr nor total hardness breakthrough to the 1% level was detected up to 2000 bed volumes. In this run (SPP-8), total hardness in the overflow from the sludge-blanket clarifier averaged about 20 ppm (as $CaCO_3$), compared to 60 ppm in the previous run (SPP-7) in which a premature breakthrough of activity and total hardness occurred at ~600 bed volumes (see Fig. 3.1a and b and Table 3.1). Comparison of all results supports the hypothesis that the early breakthrough was caused by a carbonate deficiency in the raw water, resulting in a higher residual hardness than normal, and the soluble calcium saturated the resin. An instrument for continuous determination of total hardness in pilot plant test effluents has been installed to detect future breakthroughs of this type. It is believed that this type of breakthrough can be prevented by addition of carbonate to the water if filtered feed hardness rises above normal.

Pilot Plant (J. O. Blomeke, J. M. Holmes, W. R. Whitson, R. E. Brooksbank, W. T. McDuffee). Installation was completed of the pilot plant for demonstration of the cleanup of ORNL process waste by scavenging and ion exchange. Details of the process flowsheet were given in reference 1, pp. 37-41. Because of the simplicity of the process and equipment the continuous operation of the pilot plant will be conducted by personnel currently engaged in a plutonium-aluminum alloy program, and the shakedown tests are under way for (1) orientation of personnel and procedures; (2) leak-testing of pipelines and equipment; (3) calibration of tanks and instrumentation; (4) determination of equipment pressure drop characteristics; and (5) determination of equipment modification needed for optimum performance. With ORNL tap water for feed, ~300 hr of nonradioactive processing was accomplished at feed flow rates ranging from 7.5 to 10 gpm. The Eimco-Burwell plate-and-frame clarifier sludge filter operated satisfactorily in tests but cannot be used when the plant processes contaminated water without extensive containment modifications. Present plans call for removal of this filter when the facility goes hot. An enclosed type 3FLC vacuum filter manufactured by the Oliver United Filter Company, now being installed, has a 1-ft-dia x 1-ft-long drum and will filter the sludge effluent from the clarifier continuously. The discharge of contaminated cake from the filter into plastic bags will comply with the containment requirements for the process.

An alarm system, which monitors critical variables in the waste treatment plant, was installed in Building 4507.

3.2 Inorganic Ion Exchange of Process Waste Water Plant Effluent (K. E. Cowser)

Heat Treatment of Grundite. Studies by Tamura have shown that heat treatment of Grundite to 600°C improves its ability to remove cesium from solutions of 1.5 M $NaNO_3$. In slurry and settling tests, Grundite heated to 600°C for various periods of time increased Cs-137 removals from 83% to 96% in synthetic waste and from 88% to 96% in spiked tap water (Table 3.2). For a particle size of less than 8-10 μ dia, heat treatment reduced the percent of fines a factor of 1.5 to 2 (Fig. 3.2). The slurry tests consisted

Table 3.1. Decontamination of Low-Level Waste in Demonstration Runs SPP-7 and 8

	Activities						
	c ml^{-1} min^{-1}		d ml^{-1} min^{-1}				
Code*	Gr β	Gr γ	Gr β	TRE	Sr	Cs	Co
			Run SPP-7				
F-100 bed vol			351.60	141.78	129.85	86.76	46.43
FF-100			229.1	47.41	85.23	19.26	1.84
Eff-100			16.67	0.344	0.01	n.d.	1.62
F-500 bed vol			460.30	146.85	151.42	111.20	76.19
FF-500			229.1	43.87	100.80	39.96	3.03
Eff-500			25.00	0.411	0.56	0.36	1.81
Eff-600 bed vol			----	----	8.59	1.08	1.46
Eff-700 bed vol			----	----	29.9	3.25	4.47
Eff-800 bed vol			----	----	59.59	5.30	10.12
Eff-900 bed vol			----	----	80.72	7.79	6.65
F-1000 bed vol			304.70	96.04	159.81	66.06	46.76
FF-1000			134.60	36.39	70.11	52.56	10.14
Eff-1000			123.20	44.73	95.24	7.61	8.01
Eff-1200 bed vol			----	48.8	69.1	13.57	5.82
F-1500 bed vol			186.70	61.75	136.40	50.04	35.78
FF-1500			90.25	15.82	62.09	27.0	3.53
Eff-1500			81.30	14.04	52.51	25.02	3.30
F-2000 bed vol			248.30	97.52	151.13	24.52	21.68
FF-2000			69.84	20.93	49.49	19.80	2.08
Eff-2000			62.36	12.1	36.40	11.66	1.91
			Run SPP-8				
F-100 bed vol	30.2	14.7		10.34	134.32	27.18	18.86
FF-1000	5.8	6.3		2.25	48.02	25.74	2.85
Eff-1000	0.3	0.92		0.015	0.0	trace	4.35
Eff-1200 bed vol	0.38	1.60		----	----	0.8	----
Eff-1300 bed vol	0.37	2.11		----	----	1.45	----
Eff-1400 bed vol	0.13	1.56		----	----	2.75	----
F-1500 bed vol	25.3	13.8		7.89	161.39	23.58	16.91
FF-1500	6.8	6.3		1.69	48.2	21.96	3.60
Eff-1500	0.43	2.3		0.024	0.05	4.82	4.64
Eff-1700 bed vol	1.3	3.01		----	----	7.48	----
F-2000 bed vol	21.1	12.4		6.92	156.20	24.84	18.60
FF-2000	5.4	5.02		1.02	41.65	22.86	3.12
Eff-2000	1.15	3.3		0.024	0.16	14.78	2.32

* F = feed; FF= precipitated-filtered feed; Eff = effluent.

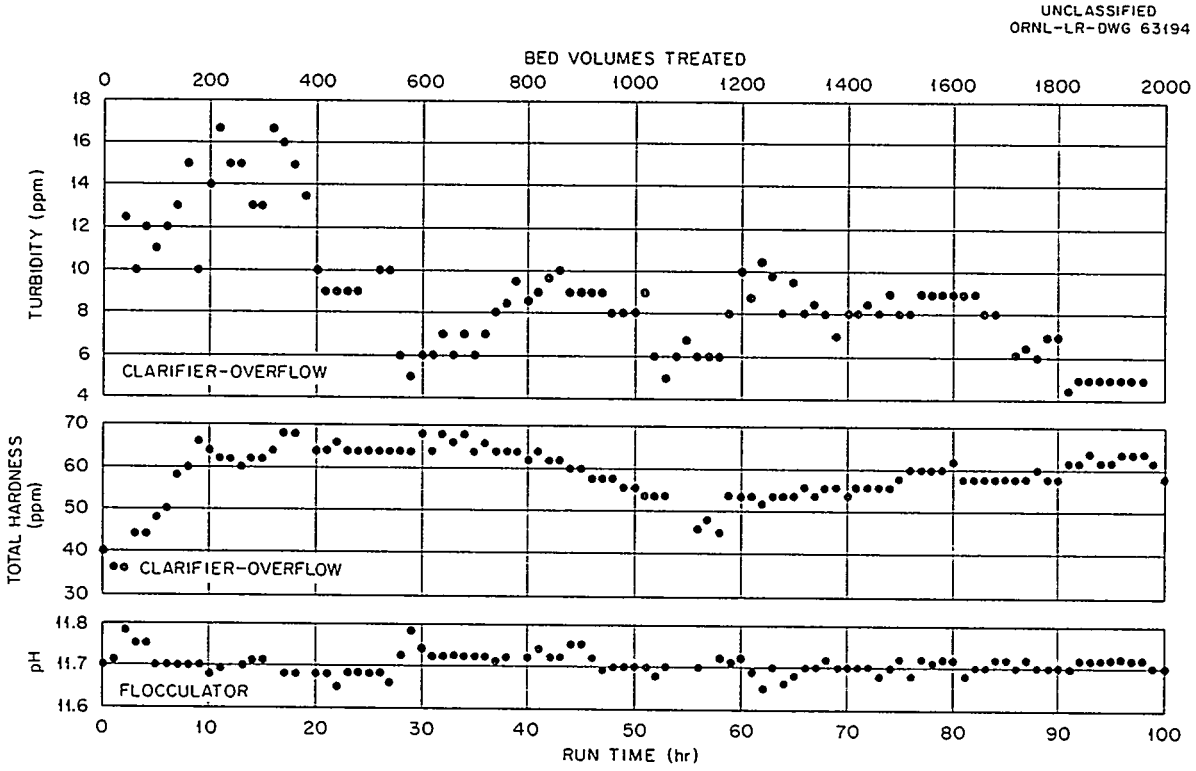


Fig. 3.1a. Data for Semi-Pilot-Plant Treatment, by Scavenging-Ion Exchange, of Process Waste Water, Run 7.

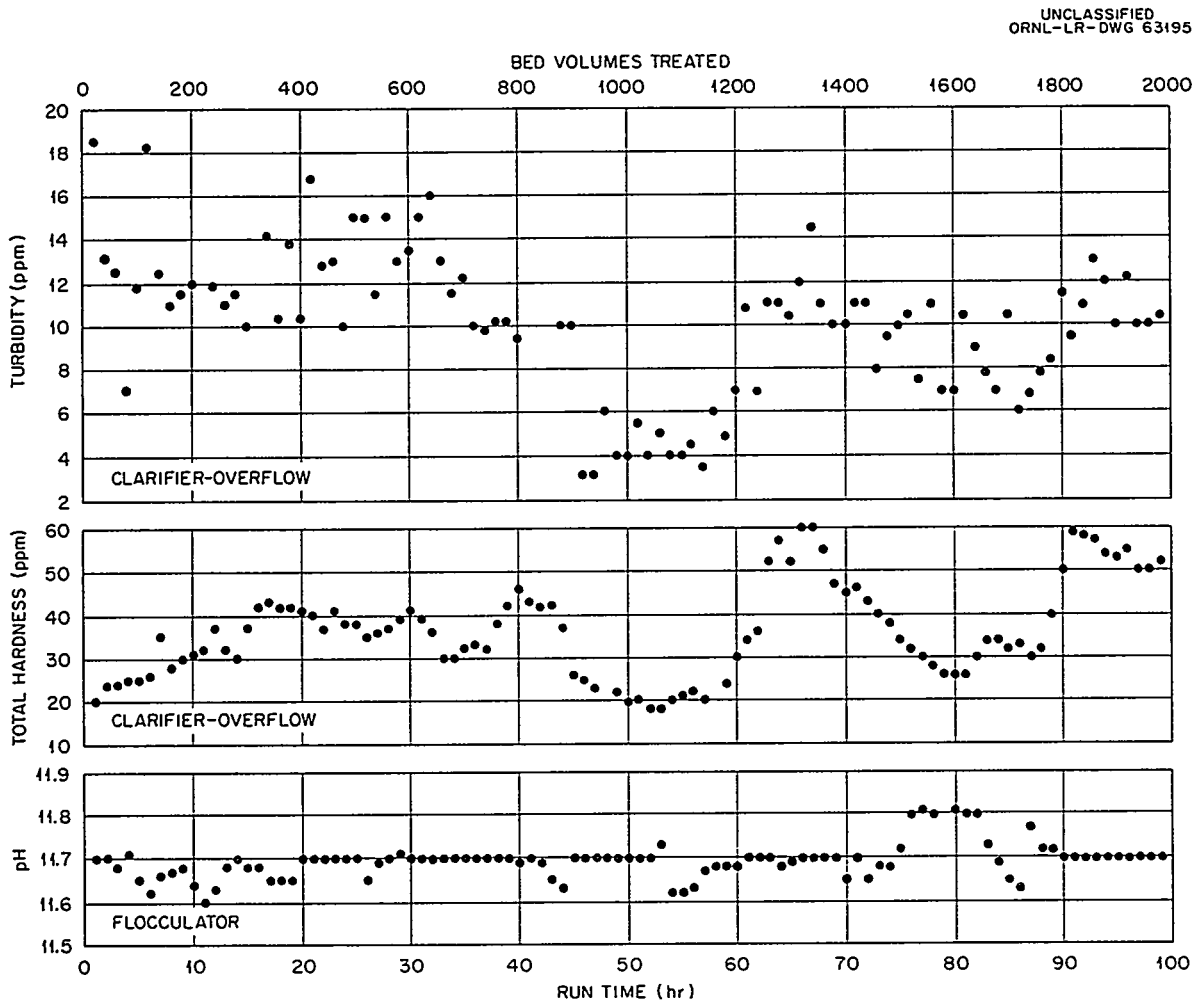


Fig. 3.1b. Data for Semi-Pilot-Plant Treatment, by Scavenging-Ion Exchange, of Process Waste Water, Run 8.

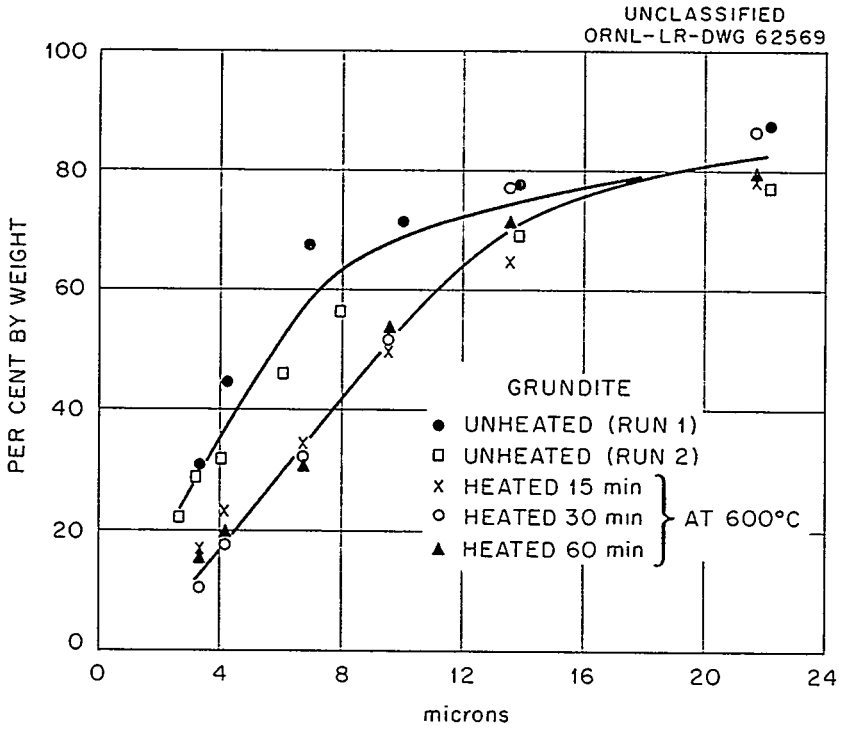


Fig. 3.2. Effect of Heat Treatment on Particle Size Distribution of Grundite.

of contacting 0.1 g of Grundite with 30 ml of tap water or 30 ml of synthetic waste for 30 and 120 min; a Cs-137 spike was used with each solution. The settling tests consisted of particle size determinations of Grundite in synthetic waste by the Andreasen pipette technique. Grundite was contacted 34 min with the waste solution, to duplicate the time of contact in the flocculators of the treatment plant, before starting the tests.

Table 3.2. Effect of Heat Treatment on Cesium Sorption by Grundite

Heating Time (min)	Cesium Removed (%)			
	Oak Ridge Tap Water		Synthetic Waste	
	30 min contact	120 min contact	30 min contact	120 min contact
0	89.0	87.8	84.8	82.0
15	96.7	96.3	94.9	95.1
30	96.2	96.0	96.0	96.0
60	96.0	95.9	96.6	96.5

In tests by Dorr-Oliver, Inc. (runs 9-13) to classify solids in the effluent of the waste treatment plant (6), a total of 64,000 gal of waste containing 30 ppm of suspended solids was passed through the hydroclones; a smaller volume of hydroclone effluent was treated with a Merco centrifuge. The suspended solids contained 48% of the gross γ activity, 59% of the Cs-137, and 34% of the Sr-90. An average of 25% of the suspended solids was collected by the hydroclone system, the median diameter of the solids collected by the smallest unit (TM) being 7.9 μ. With the Merco centrifuge (median collection diameter 6.5 μ) handling the effluent from the hydroclones (runs 12, 13), an average of 60% of the suspended solids was collected. Of the solids collected by the hydroclones, 73 wt % was $CaCO_3$ (runs 11, 12), and of those collected by the centrifuge, 47 wt % was $CaCO_3$. Approximately 40% of the suspended solids were finer than 6.5 μ and the percentage of non-$CaCO_3$ solids increased as the particle size of the solids decreased.

4.0 ENGINEERING, ECONOMIC, AND HAZARDS EVALUATION

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

The economics of disposal of high-activity waste in salt as (1) liquids in rooms with recessed floors, (2) pot calcination vessels in racks above the floor, and (3) pot calcination vessels in holes in the floor is under study. An important variable is the amount of mine space required for safe dissipation of fission product heat. For cases 1 and 2 the infinite-slab heat calculation (2) should give an adequate estimate of space requirements (see below). For case 3 the computer code for the equation presented in reference 2 was written and is undergoing "debugging."

Results of the infinite-slab calculations for Purex waste are shown in Fig. 4.1. The uranium fuel was assumed to have been irradiated for 3×10^7 sec at a flux of 3×10^{13} at an enrichment sufficient to give 10,000 Mwd/tonne. (Thorium fuel was assumed to be irradiated for the same time at the same flux but at a U-235 content to give 20,000 Mwd/tonne.) The waste was assumed to be intimately mixed with the salt in a layer 1 ft thick, and heat dissipation was by conduction alone. Thus the peak waste temperature in the center of the slab and the peak salt temperature are the same. The three curves are the temperature rises calculated from the values of thermal conductivity and diffusivity of salt at three different temperatures.

4.1 Liquids in Salt

For liquid wastes the maximum waste temperature must be kept below boiling and thus the lower curve of Fig. 4.1 (100°C thermal properties) should be used. Assuming an ambient mine temperature of 75°F, a rise of 125°F could be allowed. Figure 4.2, derived from the lower curve of Fig. 4.1, shows the maximum allowable heat generation rate, as a function of waste age at burial, for a peak waste-and-salt temperature rise of 125°F. Figure 4.2, then, makes it possible to calculate the total mine space requirements for storing the output from processing the assumed 1500 tons/year of uranium and 270 tons/year of thorium converter fuel. The gross mine area required, as a function of decay time before disposal, is shown in Fig. 4.3. For example, wastes aged 2 to 10 years would require 21 to 16 acres/year. These curves assume that only 50% of the gross mine area is used for actual waste storage but do not take any credit for lowering the peak temperature rise because of less than 100% utilization.

4.2 Calcination Vessels above Floor

If calcination vessels are stored in racks above the floor of sealed mine rooms so that it may be assumed that all heat is transferred to the floor and ceiling by convection alone, the same infinite-slab calculation should be a reasonable approximation. Since unrestrained rock salt aggregates shatter when heated above 450 to 500°F it seems desirable to limit the salt temperature to 400°F. Assuming the 75°F ambient, this allows a rise of 325°F. From the middle curve of Fig. 4.1 and the heat generation per calcination vessel (cylinder) as a function of waste age for the various waste types, curves showing the required floor area per cylinder will be calculated.

In addition to the limit on the spacing of cylinders imposed by the salt, a limit is imposed by the requirement that the axis temperature in the cylinder should not go over 1650°F. The axis temperature was calculated by assuming that the salt temperature is 400°F and adding the temperature differentials across the can, from the can to the air, and from the air to the salt. From this calculation is found the minimum waste age for each size cylinder, below which the axis temperature limit cannot be maintained no matter how great the floor area per cylinder:

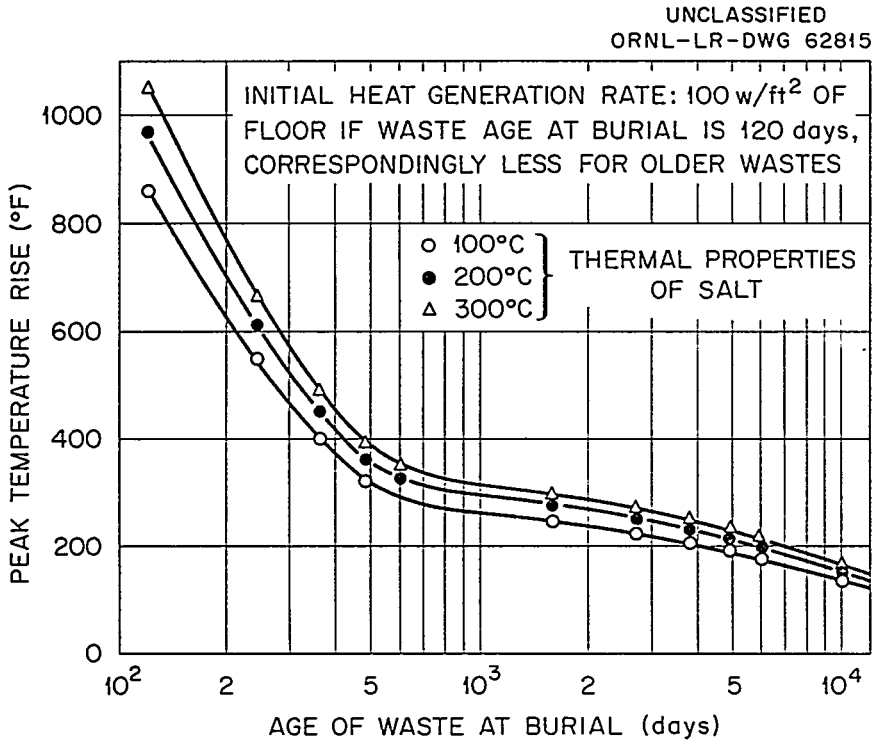


Fig. 4.1. Peak Salt Temperature Rise as a Function of Waste Age at Burial: Slab Calculation.

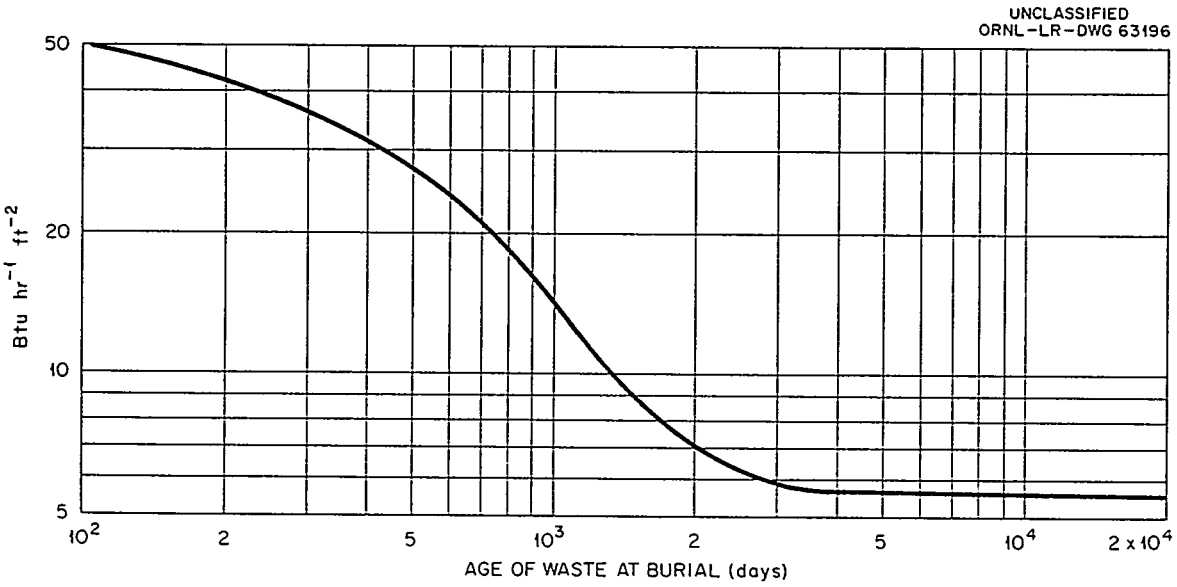


Fig. 4.2. Maximum Allowable Heat Generation Rate for 125°C Peak Salt Temperature Rise: Slab Calculation.

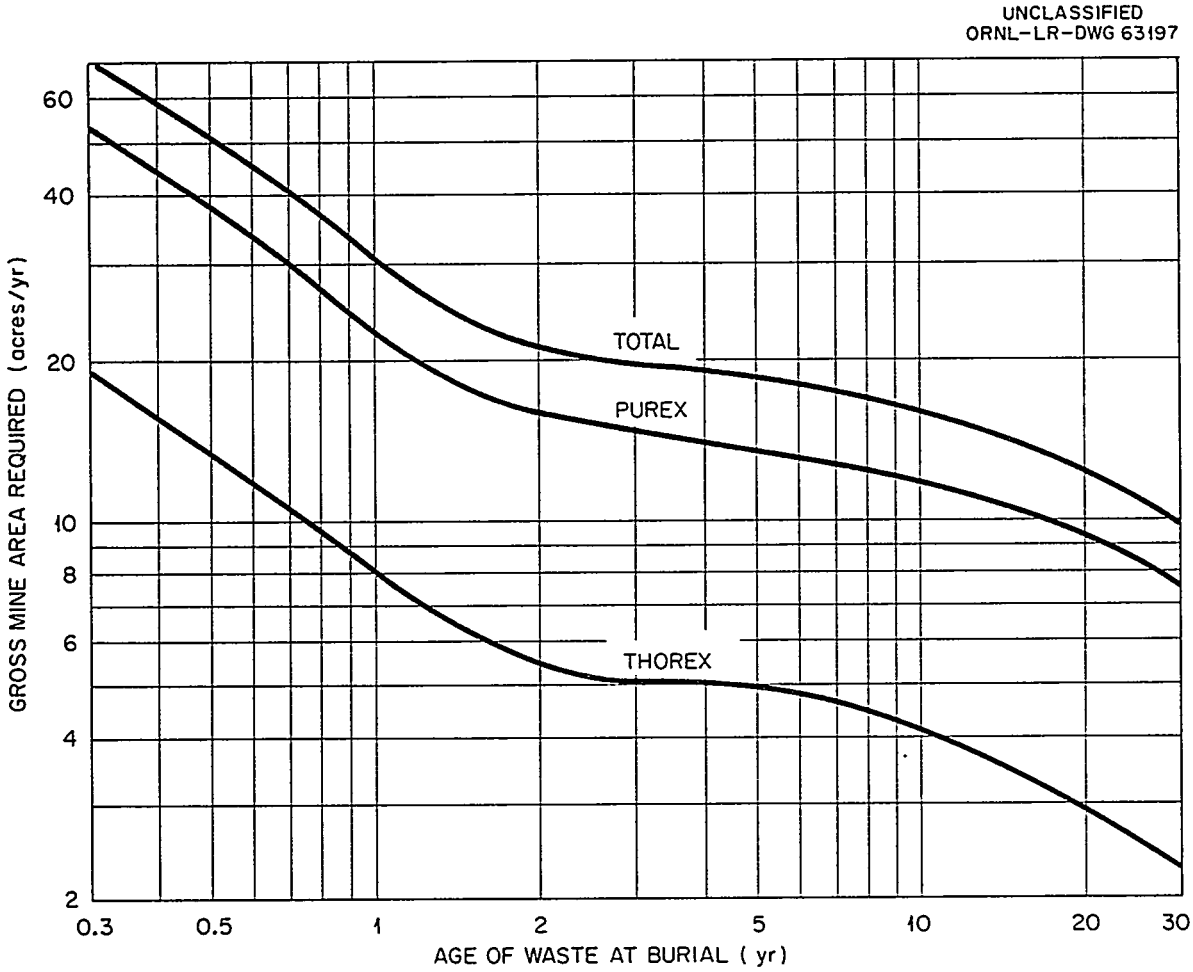


Fig. 4.3. Gross Mine Area Requirements for Liquid Waste Storage. Fifty percent utilization of gross area for waste storage is assumed.

	Minimum Decay Time (years)		
	R = 0.25 ft	R = 0.50 ft	R = 1.0 ft
Acidic Purex	1.7	4.0	19.0
Reacidified Purex	0.61	1.63	3.8
Acidic Thorex	0.45	1.5	3.8
Reacidified Thorex	0.33	0.33	1.15
Acidic Thorex Glass	0.33	-	-

5.0 DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing (W. de Laguna)

Test drilling at the experimental site has made slow progress due to interruptions in the work. A hole 100 ft south of the injection well penetrated both grout sheets at depths slightly less than that of the beds into which they were injected and also reached the quartzite at a lesser depth than anticipated. Detailed analysis of these structures will require a survey of the deviation from vertical of the test wells, and arrangements for this survey have been completed.

Mix Subcontract (E. G. Struxness). Westco Research, a subsidiary of The Western Company (Fort Worth), was successful bidder for a Laboratory subcontract to develop a waste-cement-clay mixture to be used in the proposed ORNL Fracturing Disposal Plant. Negotiations were completed and the subcontract was submitted to the Atomic Energy Commission for approval.

The scope of the work to be performed under this subcontract involves the development of a self-solidifying waste mixture to be injected into hydraulically fractured shale and subject to the following controls:

1. The ability to control viscosity during the period of injection, as a low viscosity will reduce the pumping pressures required and a higher viscosity may be needed to keep solids from settling or to control the thickness of the fractures formed.

2. The ability to control the rate of the hardening.

3. The ease of mixing and the possible use of wetting agents.

4. The possible need to use fluid-loss additives.

5. Fluid retention, whether by chemical combination, water of crystallization, or in minute pore spaces in the mix, and the permeability of the mix.

6. The possibility of gelling fluid retained in pores or raising its viscosity by suitable additives, provided the increase in viscosity can be delayed until the injection is completed.

7. Sufficient crushing strength of the solid matrix to support the load of the overburden under well conditions if fluid is to be retained in pores.

The mixture(s) will be tested in temperature and pressure environments simulating well depths of 500, 3000 and 5000 ft in interbedded shale. ORNL will co-operate with Westco in determining the effect of radiation on mixes and their ion exchange properties. The period of performance will be from the date of final subcontract approval to Dec. 31, 1962.

5.2 Liquid Injection into Permeable Formations (D. G. Jacobs)

The disposal of radioactive waste solutions to deep permeable formations provides a means for isolating large volumes of low-activity waste from the circulating regimen of ground water, surface water, and atmospheric water. Several component problem areas require further study before use of this method will be considered.

Movement of Radionuclides in the Disposal Formation. This problem will involve describing the reservoir and its limiting boundaries with regard to the continuity and uniformity of porosity, permeability, pressure gradients, chemical compatibility, and mineralogy. These factors will affect dispersion of the solution front and will impose a limit on the geometrical configuration of the disposed wastes. Dispersion of the solution front, along with chemical interactions of the waste solution, is closely related to the chromatographic distribution of radionuclides in the disposal formation.

Dissipation of Heat. Although it is unlikely that dissipation of heat will be a limiting factor in the disposal of low- and intermediate-level radioactive wastes, it becomes more important when the loading of radionuclides on the sorptive minerals is increased. Thermal conditions can be approximated if the spectra of radionuclides in the waste stream, their geometric distributions in the disposal formation, and the thermal properties of the disposal medium are known.

Protection of the Reservoir Against Plugging or Fracturing. Several factors may contribute to the decreased suitability of an injection well for radioactive waste disposal. If plugging occurs, increased pressure is required to maintain a satisfactory pumping rate, or fracturing may occur and permit rapid breakthrough of activity into pressure-relief wells without adequate contact between the waste solution and the sorptive medium. Plugging may occur because of suspended solids in the waste stream, chemical precipitation reactions between the receiving formation and the injected wastes, corrosion products from injection equipment, growth of microorganisms at the injection face of the formation, or swelling of clays in the formation when the injected waste stream is of lower salt concentration than the solution in the formation.

Corrosion. Corrosion studies may be necessary, depending on the nature of the wastes considered for disposal. Not only will corrosion limit the life of the injection system and auxiliary equipment, but products of corrosion will contribute to reducing the permeability of the receiving formation and will result in increased operating costs.

Injection Equipment Design. Design of the injection system and auxiliary equipment will depend on the type of waste to be disposed of, the activity level of the waste, the volume of waste liquid, and the injection pressures required. Although some limits for design criteria could be established now, more exact requirements will be possible only after other requirements are surveyed.

Health Physics Evaluation. The Health Physics aspects of deep well disposal are twofold. The first involves radiation protection and personnel monitoring of the operating crews. This part of the problem will deal primarily with the external radiation and required shielding for storage and injection of radioactive waste solutions as well as surface contamination problems attendant to the transfer and injection operations. A second aspect is the long-term environmental problem that will occur when the radionuclides reach the pressure-relief wells. Evaluation of this problem will require quantitative definition of the movement of the radionuclides and may require some intermediate observation wells for monitoring, in addition to the constant monitoring of the pressure-relief wells. Extrapolation of data obtained from the intermediate observation wells should be possible if the hydrodynamics and sorptive properties of the formation have been adequately surveyed.

Co-ordination of Effort. In considering any of the component problems, it is possible to overemphasize one particular phase unless a continued effort is made to co-ordinate all phases of the work. In order to co-ordinate the efforts of various co-operating agencies involved in this program, the Reactor Development Division, Washington, AEC has named Prof. W. J. Kaufman (U. of California), chairman, J. Wade Watkins (U. S. Bureau of Mines), and W. de Laguna (ORNL) to serve as an ad hoc advisory committee on programs related to the injection of radioactive liquid wastes into deep permeable formations. The committee first met in August 1961 at Berkeley, California, to discuss the general problem areas and to make recommendations on the role of the various co-operating agencies.

Although ORNL will probably become involved in several phases of the program, initial efforts will be directed primarily to a determination of the expected movement of the radionuclides in the disposal formation. Some work is planned on defining the dispersion of solution fronts, but the primary effort will be concerned with the sorptive properties of cores obtained from typical permeable formations.

Ion exchange processes play an important role in restricting the movement of cationic radionuclides through a geologic formation. However, such a simple picture is not adequate for describing the restricted movement

of many of the radionuclides of concern in low- and intermediate-level waste streams. Strontium has nearly the same exchange potential as calcium on most natural ion exchange materials, and, in systems where there is appreciable calcium, the restriction of strontium movement due to ion exchange is quite low. However, in most formations, minerals are present which form insoluble compounds with strontium and calcium in the waste stream and, when basic conditions are maintained, the waste stream is scavenged of its strontium.

The buffering capacity of a geologic formation, due to the presence of exchangeable hydrogen ions on the clay minerals, is quite high, so that the pH of the injected solution is modified as the solution moves through the receiving formation. Exchange of other stable components of the waste stream also causes considerable modification of the chemistry of the solution as it moves through the formation. These changes have some effect on the ion exchange processes involving radionuclides, but the effect on transition element behavior (e.g. Ru-106) may be much more pronounced, especially when there are changes in oxidation-reduction states. Micaceous minerals in the disposal formation incorporate cesium ions into their crystal lattices in a very slowly reversible process. The exclusion of sodium and calcium ions, the major cationic constituents of most low- and intermediate-level waste streams, is so complete that the total exchange capacity of the formation materials is secondary to the number of lattice fixation sites available when cesium removal is being considered.

Although simple models of ion exchange can be used for approximating the movement of specific radionuclides in a geologic formation, the effect of the formation on the chemistry of the percolating solution must be considered before a comprehensive picture can be developed. Outlined below is the planned method of attack:

1. Obtain representative cores wherever possible.

2. Measure the chemical, physical, and mineralogical properties of the cores.

    a. Permeability.
    b. Porosity.
    c. Acid-base stability.
    d. Particle size distribution.
    e. Clay mineralogy.
    f. Exchange capacity.
    g. Exchangeable ions.
    h. pH.
    i. General mineralogy.

3. Describe the spectrum of waste streams to be considered for disposal.

    a. Stable ion composition.
    b. Radionuclide composition.
    c. Acidity, acid deficiency, or pH.

4. Determine the solution dispersion properties of representative cores as a function of:

   a. Core length.
   b. Flow rate.
   c. Permeability.

5. Determine the sorptive properties of the core materials for various radionuclides from the various types of waste streams, evaluating such parameters as:

   a. Core length.
   b. Flow rate.
   c. Stable ion composition of the waste stream.
   d. Clay mineralogy.

6. Correlate the breakthrough curves obtained for the various radionuclides with those obtained for dispersion of the solution front.

7. Check the effect of additives to the waste stream on the sorptive properties of the sorbing minerals. (Much of this work has already been done for cesium and strontium and we can make fairly good predictions based on the clay mineralogy of the formation. However, a check is always worth the effort.)

8. Study the possible migration of radionuclides into boundary materials.

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

6.1 Field Tests (F. M. Empson)

Detailed examination of the large field cavities was completed and the cavities were filled. Instrumentation and power supply equipment was placed in standby condition for use in future experiments, and other equipment was packed for return to Oak Ridge or for disposal.

Heat Transfer Array (R. L. Bradshaw and F. M. Empson). The theoretical temperature rise around isolated cylindrical sources was checked against experimental data and found to be in reasonable agreement. Temperature rises in arrays of heat sources can be calculated theoretically by summing the contributions from individual sources; however, several factors make it desirable to have an experimental check with an array containing several heaters. An experiment is planned with a square array containing 16 heaters spaced 3 ft on centers. The heaters will be about 3 ft long and will be located 12 ft below the floor. Power input will be held constant at a rate such that the temperature in the center of the array will reach a value well over 100°C.

Figure 6.1 is a plan of the array being prepared in the mine at Hutchinson. Thermocouple holes within the array will be 15 ft deep except for the center hole which, along with those outside the heater array, will be 30 ft deep. Approximately 30 holes have been drilled.

Salt Permeability (F. M. Empson). Three horizontal holes, 3 in. dia, were drilled into the wall at the Lyons mine. One hole extends to the center of a

square column ~40 ft on each side and is located in the essentially shale-free salt 3.5 ft above the floor. Two are drilled 30 ft into a perimeter wall of the mine. One is located in a "black line" of high-shale-content salt about 5 ft above the floor, and the other is in salt relatively free of shale, just above the "black line." These holes are to be used for a test, under field conditions, of the permeability of the salt structure to gases by using a packer to seal the hole and helium or nitrogen as the test gas.

Low-Level Packaged Solids Disposal in Salt Formations (F. M. Empson). The objective of low-level solid radioactive waste disposal is to isolate the waste in such a way that contact with ground or surface water is minimized. These criteria are met by the large amount of space created in salt formations by mining operations. A disposal operation in mined space in salt would have the additional advantage that monitoring and isolation of the site would not be required after filling of the mine.

Open mine space exists in Western New York, at Detroit, Mich., in Central Kansas, in Louisiana, and in Texas. The New York and Michigan sites are more favorably located for the Northeast, where the bulk of these wastes originate, and the other sites are as convenient as the present sites at Oak Ridge and Idaho Falls. A study is in progress to evaluate transportation and long-term monitoring costs as they affect the economics of low-level waste disposal by surface burial and in mined space underground.

6.2 Plastic Flow Studies (W. J. Boegly, Jr.)

In September 1959, five Extensometers were installed in a recently mined-out area in the Hutchinson mine by representatives of the Department of Civil Engineering, University of Texas, as part of their Reactor Fuel Waste Disposal Project (7). The purpose of these gages was to obtain information on the creep of rock salt. A recently mined-out room was used since the flow rates (creep) would be high and the data could be extrapolated to estimate the flow rates just after the opening was created. Of the five gages (Fig. 6.2), four were installed to measure deformation between the floor and the ceiling, and one was installed to measure deformation between the side walls of the room.

Analysis of the measurements taken to date indicates that the rate of deformation decreases with time and, further, that an exponential equation can be derived to describe the relation between rate of floor movement (μin./in./day) and time (days) since the opening was mined, or, if desired, the time since the gages were installed. The result of statistical curve fitting for data from each gage is given in Table 6.1, and a typical plot of the data from one gage is shown in Fig. 6.3. The maximum closure predicted by integrating these equations from $t = 0$ to $t = \infty$ and the time for 95% of maximum closure are also included in Table 6.1. It is of interest to note that there does not appear to be a significant difference between the flow rates observed for any of the gages at any given time. This means, at least during the period under investigation, that there is no significant difference between the rate of movement near the center of the room and near the columns. This does not agree with measurements from the gages located in the older room (30-year opening) in which the experimental waste cavities are located (2), and may be due to the differences in age of the mined openings.

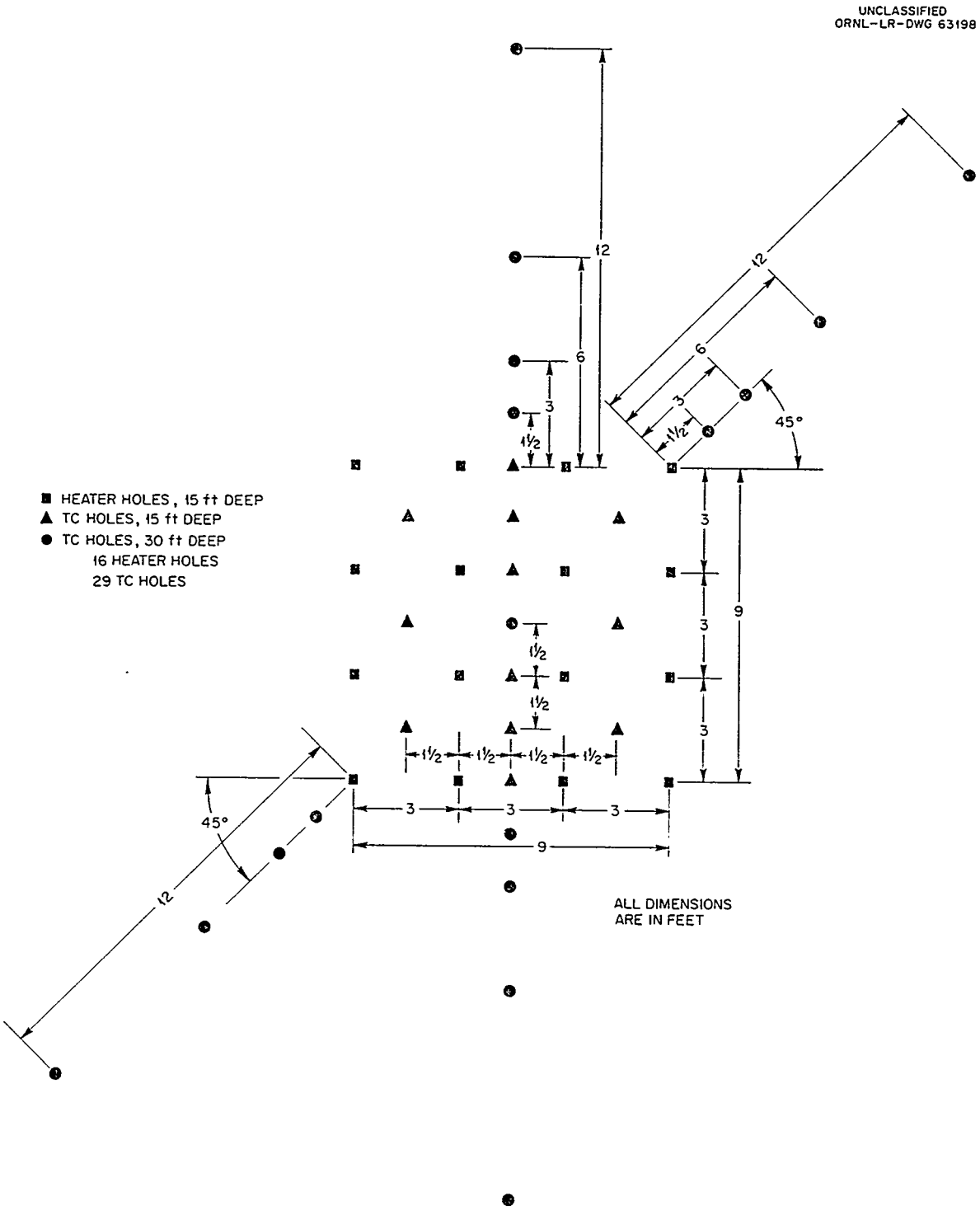


Fig. 6.1. Heat Transfer Array To Check Temperatures Resulting from Many Heat Sources.

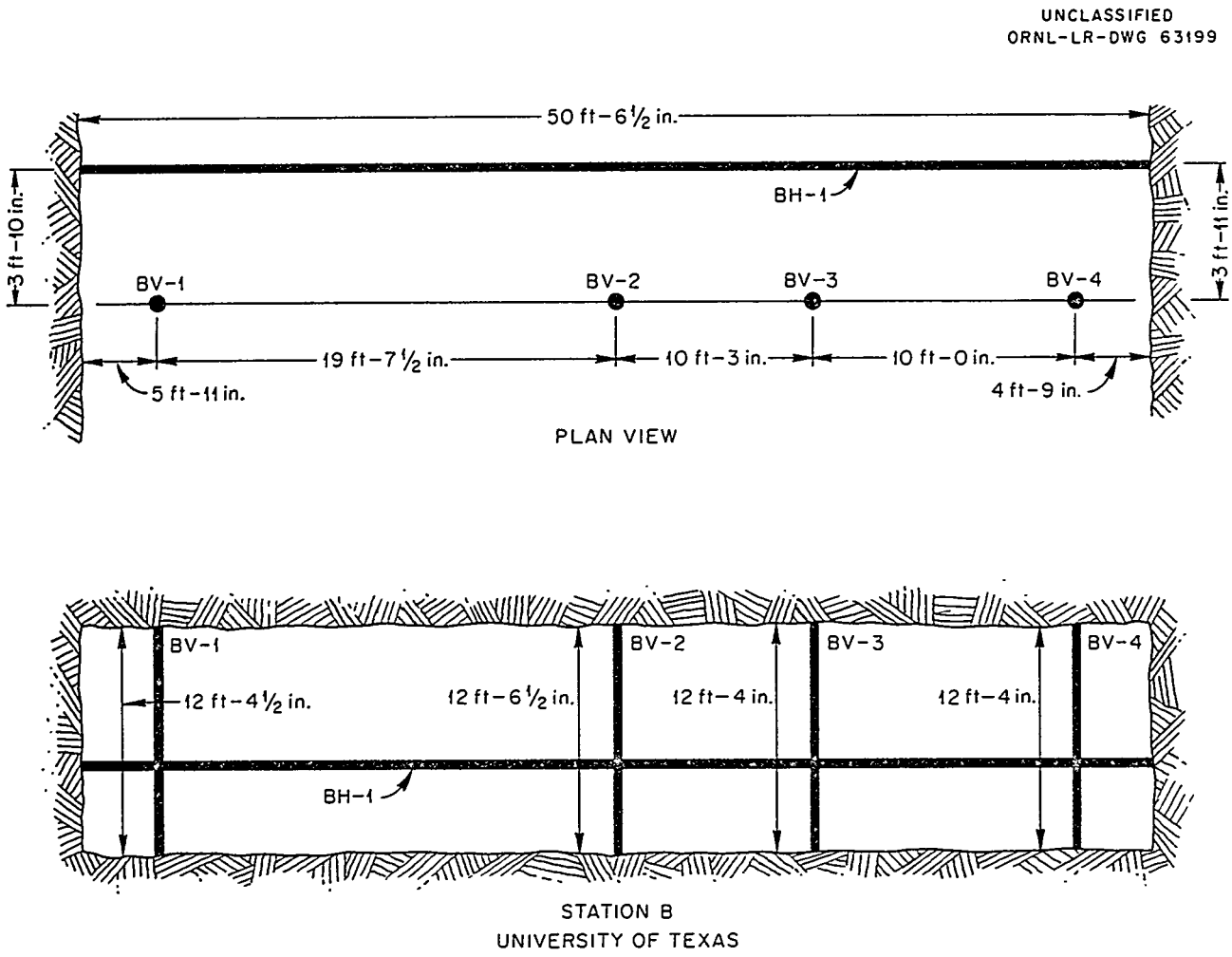


Fig. 6.2. Room Mined in January 1959.

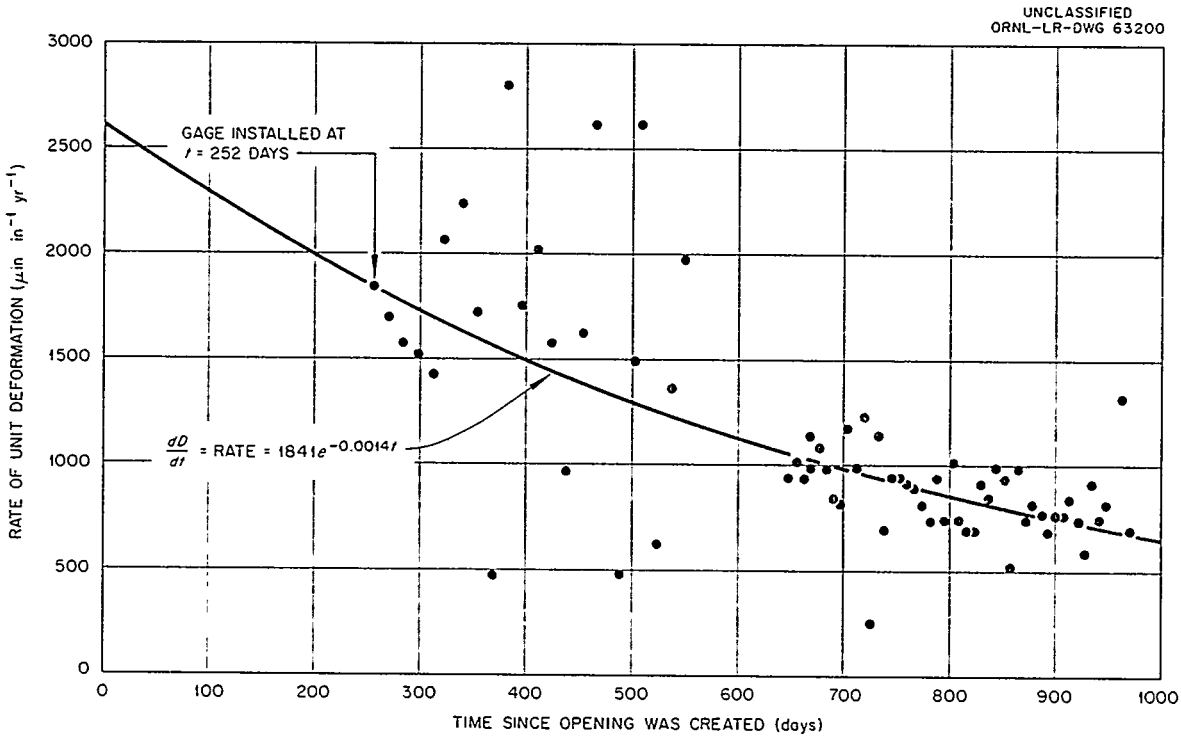


Fig. 6.3. Rate of Unit Deformation vs Time for Extensometer Gage BV-1.

Table 6.1. Flow Equations for Newly Mined Room in the Carey Mine, Hutchinson, Kansas

Gage	Rate of Unit* Deformation (μin./in./yr)	Total Movement* (μin./in.)	Max Closure (%)	Time of 95% of Total Closure (years)
BV-1	$\frac{dD}{dt} = 1841\ e^{-0.00140t}$	$D = 5.044 \int e^{-0.00140t}\ dt$	0.36	5.86
BV-2	$\frac{dD}{dt} = 2107\ e^{-0.00147t}$	$D = 5.773 \int e^{-0.00147t}\ dt$	0.39	5.58
BV-3	$\frac{dD}{dt} = 2099\ e^{-0.00150t}$	$D = 5.751 \int e^{-0.00150t}\ dt$	0.38	5.47
BV-4	$\frac{dD}{dt} = 2062\ e^{-0.00146t}$	$D = 5.649 \int e^{-0.00146t}\ dt$	0.39	5.72

*t is time in days.

Projection of the equations in Table 6.1 to a point at which t is equal to 10,000 days (~ 30 years) indicates flow rates considerably smaller than those observed in the room containing the experimental cavities. Thus, mining of the cavities upset the equilibrium of the room and initiated flow in excess of what would normally have occurred. It is not possible to verify this since the gages were not installed until the cavities had been excavated; however, it may be possible to install gages in a similar size room adjacent to the room containing the experimental cavities for measurements of flow now occurring in the salt.

Preliminary attempts to use the same type of equations for flow data around the waste cavities indicated that the nature of the flow is not the same as observed in the active area of the mine. For the period prior to heating, flow seems to occur with a constant rate, and not at a rate decreasing with time. This further substantiates the belief that excavation of the cavities had a very significant effect on salt flow in the room containing the experiments.

Three gages were installed in the Lyons, Kans., mine of the Carey Salt Company to measure flow in a mine at greater depth and with greater percentage salt extraction. One of these gages is located in the last room mined prior to termination of the mining operation, in a room which shows no visual evidence of floor "buckling" or ceiling "sag." The purpose of this gage is to obtain information on flow at greater depths and also as background information on the possible use of this area for tests with high-activity solids. The other gages are located in an older section of the mine to measure flow in the floor and ceiling of rooms of the same dimensions. The basic difference between these gage installations is that the first is attached between the salt roof and the salt floor, whereas the ends of the second gage are installed in shale located

about 1 ft above the salt ceiling and in the shale about 1 ft below the salt floor. It is hoped that data will be obtained to show that relatively thin layers of salt above the roof and below the floor are moving, or being squeezed, at a faster rate than the overlying shale. This assumption is based on observations in other areas of the mine in which the upper 1 ft of salt above the ceiling of the room has "sagged" and the relatively thin layer of the salt above the shale parting in the floor has "buckled" due to the pressure transmitted to the salt by the pillars. Not enough measurements have yet been made to predict the rate of movement or expected maximum closure of these rooms, but the few measurements made thus far indicate that the amount and rate of deformation are much less than those observed in Hutchinson; however, it is a much older mine and the flow would be expected to be very small.

6.3 Thermal Studies (R. L. Bradshaw)

Cylindrical Heat Sources. The slab calculation (2) gives a conservative estimate of space requirements for an evenly distributed heat source, but if discrete sources are used, it is necessary to correct for the temperature perturbations around the sources.

Since the cylinder is a likely storage container geometry for solid wastes it is desirable to have a solution for temperature rises about cylindrical heat sources. An equation is available for an isolated line source of constant heat-generation rate, and if a cylindrical source is long compared to its diameter, this gives a good approximation of the temperature rises in the medium surrounding the cylinder (other methods are available for obtaining the temperature profile within the cylinder itself). This equation requires numerical integration and produces only the results for a steady heat-generation rate; however, the varying-heat-source solution could be programmed in a manner similar to that used for the infinite slab. R. E. Glover of Denver, Colorado, a consultant, using the isolated line source equation, manually calculated the time-temperature profile on a line perpendicular to the center of the constant heat source at distances from the center of 1/24, 0.5, 1.0, 1.5, 2.0, and 3.0 times the length of the source, which are shown in Fig. 6.4 along with curves for additional values of x/L obtained from a cross-plot.

Two tests were run in the Carey mine using Calrod-type heaters to obtain data on the time-space temperature profiles near an isolated cylindrical heat source. One heater was located in the center of the floor of a corridor and the other half-way up the wall of a pillar. Each heater was placed in a sand-filled iron pipe. This assembly was then placed in a 1-3/4-in.-dia hole and the hole back-filled with sand. The heaters had an active heating length of 6 ft and were located with their centers 10 ft below the salt surface. Thermocouples were inserted in polyethylene tubing and placed in 1-3/4-in. holes backfilled with sand.

Figure 6.5 shows the temperature rises obtained at distances of 2, 4, 8, and 16 ft on lines perpendicular to the centers of the heaters with power input held constant at 2000 watts. The points shown were obtained in three

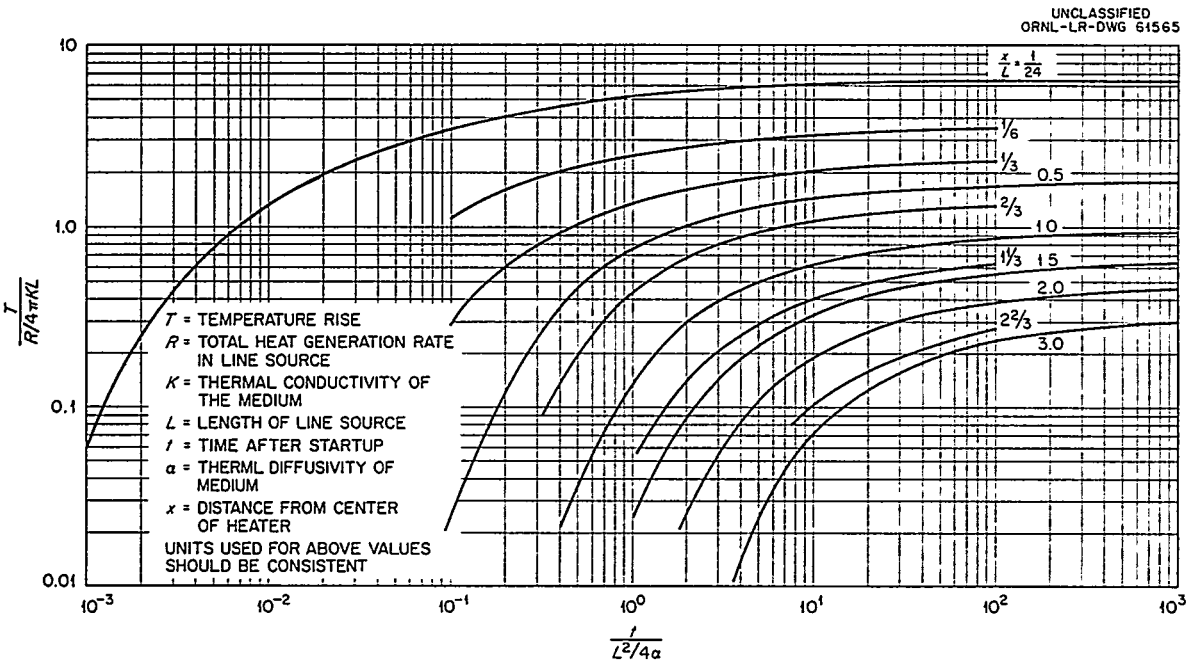


Fig. 6.4. Temperature Rise Around a Line Source with a Constant Heat Generation Rate.

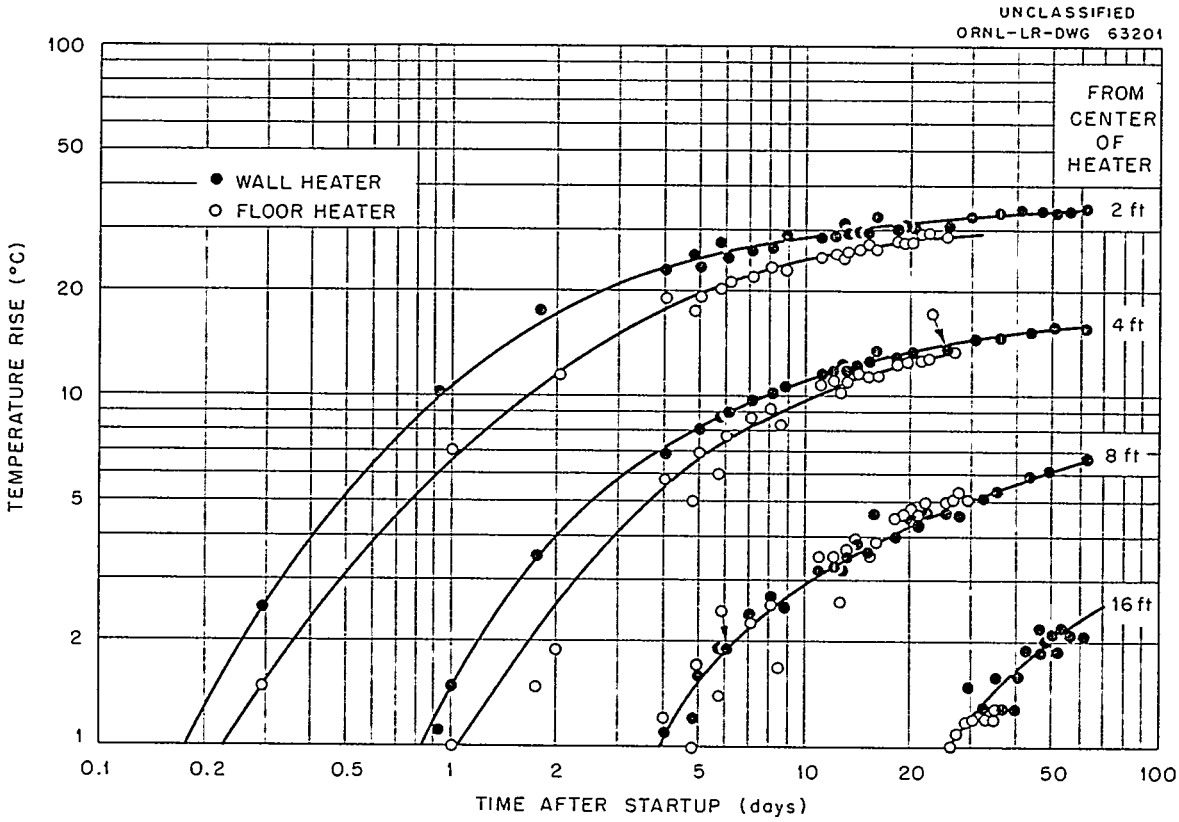


Fig. 6.5. Temperature Rise Around 6-ft Rod Heaters in Wall and Floor of Salt Mine. Heat generation rate ~2000 watts.

different runs, with the salt allowed to return to ambient temperature between runs. Although pillar and floor test results do not agree exactly, there appears to be no great difference in the heat-transfer capabilities of the two locations, even though there are considerable shale and anhydrite in the floor while the pillar is nearly pure salt. The measured temperature rises agree reasonably well with the theoretical curves of Fig. 6.4. The scatter in the experimental data does not permit accurate determination of the thermal properties of salt, but the conductivity appears to be approximately 3.0 Btu hr^{-1} ft^{-1} $^{o}F^{-1}$ and the diffusivity 0.10 ft^2/hr.

An equation for the temperature distribution about a finite-length cylinder located in an infinite array of cylinders was developed (reference 2, Sect. 4.0) in connection with the economic study of disposal in salt. The status of the computer program for computation is discussed in Sect. 4.0 of the present report.

Thermal Properties of Salt. Birch and Clark measured the temperature dependence of conductivity and diffusivity of single natural Halite ($NaCl$) crystals (8) (Fig. 6.6). Preliminary measurements made by the U. S. Geological Survey with granular salt compacted under high pressure are in substantial agreement with those of Birch and Clark for the single-crystals (9).

The conductivity and diffusivity values obtained in the field tests with cylindrical sources (preceding section) and with the 7.5-ft cubes (Sect. 6.3 of reference 2) are only 10 - 20% lower than those for the single crystal (Fig. 6.6). In addition, laboratory tests at 28°C of both irradiated and unirradiated aggregate samples indicated approximately 25% lower conductivity than that of the single crystal (10). This relatively close agreement lends confidence to theoretical calculations of temperature rise based on single-crystal values. Both the conductivity and diffusivity (Fig. 6.6) decrease rather sharply with increasing temperatures, while the theoretical equations developed to date assume constant thermal properties. To be conservative, theoretical calculations must be made with values for the thermal properties at the highest temperatures that may be reached in a particular case. It has been felt that this may impose an unduly severe restriction since only the salt in contact with the waste or waste container will ever reach this peak temperature, while salt at greater distances may be at much lower temperatures. The most recent results obtained with the infinite-slab equation (2) indicate that this need not be a concern, at least for the slab geometry, since the peak temperature rise is not a strong function of conductivity and diffusivity. For example, the peak temperature rise in the slab calculated with the 100°C salt conductivity and diffusivity was only 18% less than that calculated with the 300°C salt thermal properties, even though the conductivity was 70% greater and the diffusivity 90% greater than at 300°C.

It has been found that unrestrained rock salt aggregates shatter rather violently when heated in a muffle furnace to temperatures of 250 - 300°C. (It is speculated that this may be due to the presence of small quantities of water trapped in negative crystals or to oxidation of organic impurities.) If this shattering occurs in salt in situ it may result in poorer thermal

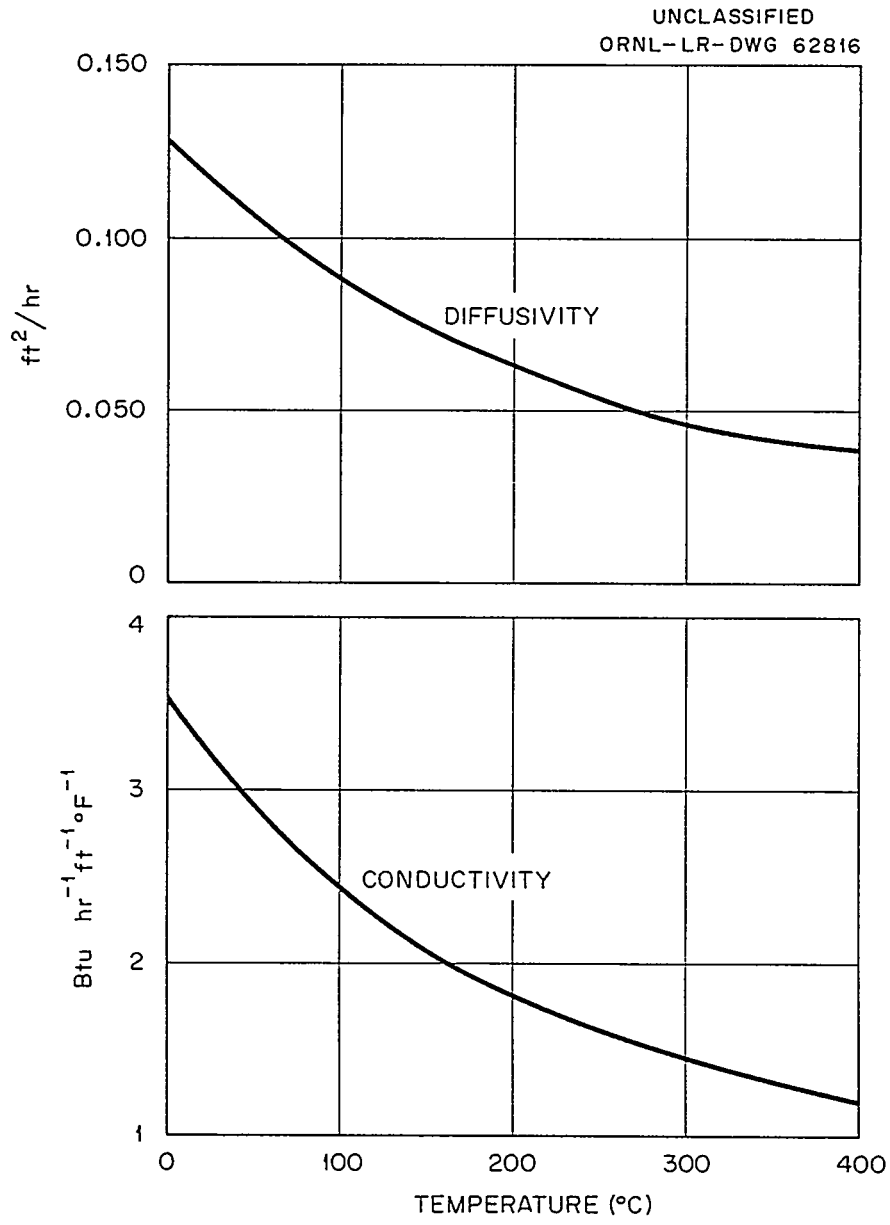


Fig. 6.6. Thermal Properties of Halite (Adapted from Birch and Clark).

conductivity and consequent increased waste temperature rise. Since this effect may place an upper limit to the allowable salt temperature rise, both laboratory and field tests are planned to investigate it.

7.0 CLINCH RIVER STUDY

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

In connection with the investigation of distribution of radioactivity in bottom sediments of the Clinch River the variation in sediment size in the Study Reach (CRM 4.1 to CRM 20.8) was studied. Studies of the longitudinal distribution of radioactivity indicated that the maximum activity is associated with sediments deposited midway in the reach.

Core samples of the bottom sediments were collected at 10 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. The cores for each cross-section were composited. The composites were submitted to the North Carolina District, Quality of Water Branch, U. S. Geological Survey, for size distribution analyses. The results (Table 7.1) indicate that the size of sediment is generally < 1 mm. The average clay content is about 14 wt %, and the sand content varies from 30% at the lowest cross-section to 40% at the uppermost cross-section. According to the U. S. Bureau of Soils classification, the sediments vary in texture from silty loam to loam. The distribution of sizes would be classed as well graded clay to the upper range of sand sizes. The average median diameter is 28 μ (0.028 mm), and the maximum median diameter (39 μ) is at the uppermost cross-section and the minimum (20 μ) at CRM 11.9. At CRM 4.7 the median size is 25 μ. Results of the study of size distribution will be correlated with other physico-chemical properties that may affect the distribution of radioactivity in the reach. The data will be applied, also, in studies of the probable magnitude of bottom sediment (bed load) movement.

7.2 Dispersion Study

On Aug. 30, 1961, 7.5 curies of Au-198 was dispersed over the full width of the mouth of White Oak Creek in 67 sec. The concentration at this point was about 9400 times the MPC_w. At the time of release of the radioactive tracer the flow from White Oak Creek was about 7 cfs, the flow in Clinch River had been steady since Aug. 28 at 8000 cfs, and the level of Watts Bar Reservoir was between 740 and 741 ft above mean sea level. Under these conditions of flow and method of injection the development of dispersion, travel time, and reduction in concentration in the study reach of the Clinch River were to be studied.

The mouth of White Oak Creek is on the right bank of Clinch River at CRM 20.8, and immediately downstream is Jones Island (CRM 20.6). The tracer released in White Oak Creek remained concentrated near the right bank of the Clinch in the vicinity of Jones Island. At CRM 19.6 the activity had spread from bank to bank, but was not uniformly dispersed. Activity had become uniformly dispersed in the width and depth of cross section at CRM 17.1, 3.7 miles downstream from the mouth of White Oak Creek.

*On loan from Tenn. District Surface Water Branch, Water Resources Division, U.S. Geological Survey.

Table 7.1. Size Analysis of Clinch River Bottom Sediments

CR Mile	Sp. Gr.	Percent Finer than Indicated Size									
		0.002 mm	0.004 mm	0.008 mm	0.016 mm	0.031 mm	0.062 mm	0.125 mm	0.250 mm	0.500 mm	1.000 mm
4.7	2.73	12	15	26	39	55	70	82	91	94	96
7.6	2.64	13	18	28	42	58	67	87	96	99	100
11.9	2.58	14	19	31	45	60	69	89	98	100	--
15.3	2.66	16	21	28	40	50	62	74	92	100	--
19.2	2.49	12	17	22	32	45	60	78	93	99	100

Because of lateral, vertical, and longitudinal dispersion the peak concentration of Au-198 in Clinch River water was decreased by a factor of 500 from CRM 20.8 to CRM 17.1. Downstream from CRM 17.1 dispersion was largely longitudinal, and therefore there was a much smaller reduction factor in peak concentration. From CRM 17.1 to CRM 4.5 (Centers Ferry) Au-198 concentration was decreased by a factor of < 10.

Travel time from the mouth of White Oak Creek to Gallaher Bridge, CRM 14.5, at the intake to the water plant of ORGDP, was 7.9 hr. The concentration of Au-198 at this cross-section was 8% MPC_w. From the point of release to Centers Ferry, CRM 4.5, the travel time was 30.2 hr and the concentration was 3% MPC_w.

7.3 Error in Estimate of Sediment Activity

The rate of change of activity with distance (curies/mile) and total activity (curies) reported previously (1) were computed incorrectly. Specific activity, listed in μc/kg, was determined for dry weight of solids in the bottom sediments. The mass of bottom sediments, in g/mile, was computed for wet weight of sample. The correction factors are not constant because of the variability of water content of the composite samples and of specific gravity. The total activity was recomputed on the basis of dry weight of solids for the reach CRM 4.7 to 21.6, as 13.2, 43.2, 4.71, 0.700, and 14.7 curies, respectively, for Ru-106, Cs-137, Co-60, Sr-90, and total rare earths.

8.0 FUNDAMENTAL STUDIES OF MINERALS

8.1 Considerations in Cesium Selectivity (T. Tamura)

Selectivity of clays for cesium was shown to be related to the collapsed-lattice minerals such as the potassium-bearing illite and micas. Since sodium-fluorophlogopite (a synthetic mica) was more selective for cesium than the potassium-fluorophlogopite, it was reasoned that the beneficial role of potassium in minerals was to maintain the collapsed lattice.

To demonstrate the effect of the collapsed lattice, vermiculite was treated with potassium chloride solutions and the lattice (c-spacing) collapsed from 14 to 10 A. The resultant K-vermiculite was more selective for cesium in spite of a decrease in exchange capacity from 65 to 17 meq/100 g. Later studies of biotite micas showed improved cesium removal if the exchange capacity of mica was increased. These studies emphasize the importance of two variables: exchange capacity and structure. The most desirable combination in a mineral would be a lattice partially collapsed for favorable cesium selectivity but partially open to retain the maximum exchange capacity of the mineral.

The possibility of attaining the desired conditions was suggested by some data on vermiculite saturation reported by Walker (11), viz., that barium and lithium ions decrease the spacing of vermiculite from 14 to 12 A. This spacing may be compared with 14 A reported for magnesium and calcium saturation and 10 A for potassium and ammonium saturation.

Cesium Selectivity of Vermiculite with Different Ion Saturation. Samples of vermiculite saturated with barium and lithium had 12 A spacing, but only Ba-vermiculite showed a significant increase in cesium selectivity (Table 8.1a). It is important, perhaps, to note that barium is close to cesium in ionic radius (1.35 vs 1.69 A) but the lithium ion is much smaller (0.60 A). Al-vermiculite showed the lowest selectivity, possibly because of the open lattice of the mineral when saturated with aluminum and the trivalent nature of aluminum. The K-vermiculite response was similar to earlier findings.

The samples of vermiculite were saturated with different cations by treating known weights of vermiculite with ~10 times the exchange capacity in solutions containing the approximate chloride salt of the cation. Excess salt was then washed from the mineral by distilled water until $AgNO_3$ tests of the wash were negative, and the samples were then air-dried. To calculate the weight of each form of vermiculite equal to 1 g on an oven-dried weight basis, a separate aliquot was heated to 105°C overnight and the weight loss determined. The samples were slurried in 20 ml of 1.5 M $NaNO_3$ solution containing 25 mg Cs/liter.

Cesium Selectivity of Montmorillonite with Different Ion Saturation. Although vermiculite is easily collapsed by simple chemical treatment, montmorillonite does not collapse to 10 A by such treatment but potassium saturation has been shown to decrease the c-axis spacing of montmorillonite from 14 to 12 A (compared to 10 A in vermiculite). In tests with montmorillonite, K-montmorillonite showed an increase in cesium sorption, but Ba-montmorillonite did not. X-ray diffraction diagrams showed a c-spacing of 14 A for the alkaline earth cations. As with Al-vermiculite, Al-montmorillonite showed the lowest selectivity for cesium. Apparently, with the montmorillonites equilibrium is established rapidly. The slow equilibrium reaction of vermiculite may be due to large particles and the presence of biotite impurities. The biotite structure prevents easy access to exchange sites and thus decreases the rate of the equilibrium reaction.

The montmorillonite was saturated with the different cations similarly to the vermiculite saturation described above and was slurried with 1.5 M $NaNO_3$ solution containing 25 mg Cs/liter.

Exchange Capacity. For better characterization of materials used in these experiments, the ion exchange capacities of samples saturated with different cations were measured. As expected, potassium treatment decreased the exchange capacity of vermiculite (Table 8.2), as a result of collapse of the lattice to 10 A, and the fixed K was not replaced during saturation with $CaCl_2$. The exchange capacity measurements of Ba-vermiculite and K-montmorillonite did not show the fixation reaction for these systems.

The experiments were made by saturating the material with Ca, leaching the calcium with sodium acetate, and titrating it with versene. The montmorillonite data suggest that the alkali ions are more difficult to replace with calcium than the divalent ions, the difference probably being caused by the ability of divalent ions to affect the exchange capacity measurements by complexing with versene.

Table 8.1. Percentage Removal of Cesium by Vermiculite and Montmorillonite Saturated with Various Cations

20 ml of 1.5 M $NaNO_3$ containing 25 mg Cs/liter contacted with 1 g equiv of material

Contact Time (hr)	Cs Removal (%)							
	Natural	K	Na	Li	Ca	Al	Ba	Mg
	a. Vermiculite							
1	11.0	12.0	9.59	11.4	9.09	7.66	10.7	--
4	13.4	16.2	13.3	14.7	14.9	16.4	23.6	--
24.5	15.2	19.3	15.3	14.7	15.9	17.5	32.1	--
77	14.6	18.0	15.2	13.4	17.9	14.0	38.0	--
190	16.0	20.6	16.9	15.1	20.0	12.5	43.2	--
	b. Montmorillonite							
1	32.7	50.3	25.1	25.5	26.0	20.4	23.1	23.8
4	30.9	49.9	26.4	25.2	27.4	20.9	24.6	23.6
24	31.7	49.1	25.6	25.6	26.6	21.7	25.6	23.6
76	30.8	48.6	25.6	24.9	27.3	21.3	27.5	24.6
144	30.6	48.3	25.5	25.5	26.8	20.7	26.0	24.0

Table 8.2. Ion Exchange Capacity of Vermiculite and Montmorillonite after Saturation with Different Cations

Exchange Agent	Saturating Cation	Capacity (meq/100 g)
Vermiculite	Natural	65.0
	Ba	62.5
	Ca	63.7
	Li	66.5
	K	16.7
Montmorillonite	Natural	91.4
	Ba	84.6
	Ca	85.1
	Li	72.0
	K	78.0
	Mg	86.9
	Na	75.3
	Al	82.2

9.0 WHITE OAK CREEK BASIN STUDY*

T. Lomenick

The rate of ground water movement in the bed of former White Oak Lake was measured by the auger hole method, i.e., by augering a cavity below the water table, allowing it to fill with water, pumping the water level down in the hole, and observing the rate of rise. The rate of rise can be reduced to standard permeability units by a suitable formula (12). Data from two sites in the upper part of the lake bed showed permeability values of 0.5 and 2.6 ft/day, while values from four sites in the lower bed varied from 0.2 to 2.2 ft/day. All cavities were 4 in. dia and 5-6 ft deep. The auger hole method measures essentially the horizontal permeability, but additional field tests are planned to determine the vertical permeability of the lake bed soil.

The alluvial material underlying the bed of former White Oak Lake consists of a complex mixture of sand, silt, clay, and gravel. Core and auger samples taken along transects at the upper, middle, and lower parts of the lake showed that, with the exception of the recent lacustrine deposit, there are no beds that persist vertically or horizontally. However, it appears that the amount of sand and gravel increases with depth while silt and clay decrease. The results of a detailed mechanical analysis of a core sample taken in the upper part of the lake bed is shown in Table 9.1.

Table 9.1 Distribution of Particle Sizes in Core Sample Taken in Upper Part of White Oak Lake

Depth (in.)	Percentage			
	> 2 mm	0.05-2 mm	0.2-50 μ	< 0.2 μ
0-3	0	17.0	54.1	28.9
3-6	0	29.5	51.1	19.4
6-9	0.2	25.4	55.2	19.2
9-12	0.3	28.8	53.0	18.4
12-18	0.6	14.9	59.7	24.8
18-25	0.1	23.2	56.0	20.7
25-33	0	31.6	47.0	21.4
33-39	1.4	27.3	51.0	20.3
39-49	2.5	41.3	35.6	20.6
49-50	0	62.4	18.8	18.8
50-59	31.6	44.6	12.6	11.2
59-66	1.4	49.9	23.8	24.9
66-70	17.9	45.7	22.2	14.2
70-75	18.2	51.3	16.7	13.8

*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).

10.0. REFERENCES

1. "Waste Treatment and Disposal Progress Report for April and May 1961," ORNL-CF-61-7-3.

2. Ibid. for April and May 1961, ORNL-TM-15.

3. J. M. Holmes, "Waste Calciner Pilot Plant Proposal," ORNL-CF-60-12-121 (Dec 14, 196).

4. J. T. Roberts and R. R. Holcomb, "A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes, ORNL-3036 (May 22, 1961).

5. R. R. Holcomb and J. T. Roberts, "Low-Level Waste Treatment by Ion-Exchange. II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin," ORNL-TM-5 (Sept. 25, 1961).

6. Dorr-Oliver, Inc., Stamford, Conn., "Informational Report," AEC Research and Development Contract No. AT-(40-1)2246, Jan. 5, 1961.

7. T. D. Reynolds and E. F. Gloyna, "Reactor Fuel Waste Disposal Project: Permeability of Rock Salt and Creep of Underground Salt Cavities," Univ. of Texas, AEC Contract AT-(11-1)-490, Dec. 30, 1960, p. 92.

8. F. Birch and H. Clark, "The Thermal Conductivity of Rocks and Its Dependence on Temperature and Composition," Am. J. Sci., 238: 552 (1940).

9. E. C. Robertson, USGS, Silver Springs, Md., letter of July 10, 1961.

10. F. Birch, Harvard Univ., letter to F. L. Parker, June 6, 1959.

11. G. W. Brindley, "X-ray Identification and Structure of the Clay Minerals," Mineralogical Society of Great Britain Monograph, London, 1951.

12. Transactions, Am. Geophysical Union, 32(4): 582-590 (August 1951).

INTERNAL DISTRIBUTION

1. ORNL – Y-12 Technical Library Document Reference Section
2-4. Central Research Library
5-14. Laboratory Records Department
15. Laboratory Records, ORNL R.C.
16-17. R. E. Blanco
18. J. O. Blomeke
19. W. J. Boegly, Jr.
20. R. L. Bradshaw
21. J. C. Bresee
22. F. N. Browder
23. K. B. Brown
24. P. H. Carrigan
25. W. E. Clark
26. K. E. Cowser
27. F. L. Culler
28. W. de Laguna
29. F. M. Empson
30. D. E. Ferguson
31. H. W. Godbee
32. H. E. Goeller
33. J. M. Googin
34. C. W. Hancher
35. R. F. Hibbs
36. R. R. Holcomb
37. J. M. Holmes
38. D. G. Jacobs
39. W. H. Jordan
40. H. Kubota
41. T. F. Lomenick
42. K. Z. Morgan
43. R. J. Morton
44. E. L. Nicholscn
45. F. L. Parker
46. J. J. Perona
47. R. M. Richardson
48. J. T. Roberts
49-50. E. G. Struxness
51. J. C. Suddath
52. J. A. Swartout
53. T. Tamura
54. J. W. Ullmann
55. M. E. Whatley

EXTERNAL DISTRIBUTION

56. E. L. Anderson, AEC, Washington
57. W. G. Belter, AEC, Washington
58. W. H. Regan AEC, Washington
59. J. A. Buckham, Phillips Petroleum Company
60. H. J. Carey, Jr., Carey Salt Company, Hutchinson, Kansas
61. C. W. Christianson, Las Alamos Scientific Laboratory
62. V. R. Cooper, AEC, Washington
63. E. F. Gloyna, University of Texas, Austin
64. L. P. Hatch, Brookhaven National Laboratory
65. W. B. Heroy, Sr., Geotechnical Corp., Dallas, Texas
66. H. H. Hess, Chairman, Earth Science Division, Commission on Ground Disposal of Radioactive Waste, Princeton University, Princeton, New Jersey
67. J. R. Horan, AEC, Idaho
68. J. H. Horton, Stanford Research Institute
69. J. F. Honstead, Hanford
70. E. R. Irish, Hanford
71. A. A. Jonke, Argonne National Laboratory
72. K. K. Kennedy, Phillips Petroleum Company
73. W. J. Kaufman, University of California, Berkeley
74. S. Lawroski, Argonne National Laboratory
75. B. M. Legler, Phillips Petroleum Company
76. J. A. Lieberman, AEC, Washington
77. J. A. McBride, Phillips Petroleum Company
78. J. W. Morris, Du Pont, Savannah River
79. R. L. Nace, Water Resources Division, USGS, Washington, NAS-NRC

80. C. M. Patterson, Du Pont, Savannah River
81. W. H. Reas, Hanford
82. C. S. Shoup, AEC, ORO
83. L. Silverman, Harvard Graduate School of Public Health
84. J. I. Stevens, Phillips Petroleum Company
85. C. M. Slansky, Phillips Petroleum Company
86. V. R. Thayer, Du Pont, Wilmington
87. J. Vanderryn, AEC, ORO
88. Abel Wolman, Chairman, National Academy of Sciences, Committee on Waste Disposal, Johns Hopkins

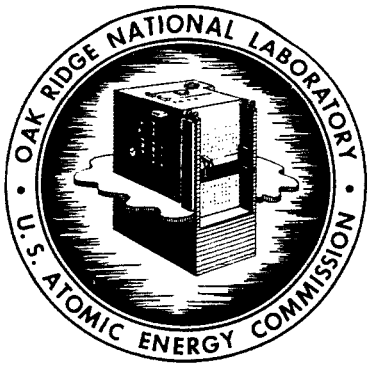
89-104. Division of Technical Information Extension

105. H. M. Roth, ORO

76

ORNL
MASTER COPY

2005



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

UNION CARBIDE

ORNL - TM - 169

15

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR DECEMBER 1961 AND JANUARY 1962

This document has been approved for release to the public by:

David R Hamrin 7/29/95
Technical Information Officer ORNL Site — Date

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM- 169

CHEMICAL TECHNOLOGY DIVISION
AND
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR DECEMBER 1961 AND JANUARY 1962

R. E. Blanco and E. G. Struxness

DATE ISSUED

JUN 15 1962

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

CONTENTS

	Page
1.0 Introduction	6
2.0 High-Level Waste Calcination	7
2.1 Evaporation-Calcination	7
2.2 Fixation in Glasses	10
2.3 Corrosion	14
3.0 Low-Level Waste Treatment	20
3.1 Pilot Plant	21
3.2 Laboratory Studies	29
4.0 Engineering, Economic and Hazards Evaluation	30
5.0 Disposal in Deep Wells	32
5.1 Disposal by Hydraulic Fracturing	32
5.2 Liquid Injection into Permeable Formations	49
6.0 Disposal in Natural Salt Formations	53
6.1 Field Tests	53
6.2 Laboratory Study of High-Temperature Effects	55
6.3 Plastic Flow Studies	56
7.0 Clinch River Study	56
7.1 Dispersion Studies	56
7.2 Analysis of Clinch River Water and Sediments	58
8.0 Fundamental Studies of Minerals	58
8.1 Dissolution of Calcium from Calcite	62
8.2 Dissolution of Calcium from Rock Phosphate	62
9.0 White Oak Creek Basin Study	64
9.1 Distribution and Transport of Radionuclides in the Bed of Former White Oak Lake	64
9.2 Geologic and Hydrologic Studies	64
10.0 References	67

ABSTRACT

High-Level Waste Calcination. Energy balance calculations for the Idaho Chemical Processing Plant Pot Calcination Demonstration, on a hypothetical Purex waste, indicate that an 8-in.-dia pot must be used for wastes decayed less than 180 days; a 12-in.-dia one may be used for older wastes. The maximum vapor rates to the fractionator for Purex wastes are approximately 20% greater than those predicted for TBP-25, but the column will operate below flooding at the higher rate.

Equipment is being designed and fabricated for a small scale demonstration of pot calcination in a hot cell at ORNL. The pot will be 4 in. dia and 24 in. high. Synthetic wastes spiked with fission products from Idaho, Hanford, and other hot operations at ORNL will be used for the pot calciner feed solutions. In nonradioactive tests, average overall evaporation-calcination rates for the full scale (90- x 8-in. dia) pot calciner decreased with increased filling (evaporation) time. This is attributed to the formation of higher bulk densities and consequently higher thermal conductivities in the final product. In 11 tests with simulated wastes, Darex, TBP-25, and TBP-25 containing organic residues, batch and continuous flowsheets were demonstrated, with satisfactory control of the continuous evaporator. Filling rates were 8.6 to 19.4 liters/hr averaged over the filling period depending on feed type, concentration, and filling time, with final solid product bulk densities ranging from 0.61 to 1.42 g/cm^3.

The product of semicontinuous evaporation and fixation of simulated TBP-25 waste to form a lead phosphate glass (additives: 2 moles of NaH_2PO_2 and 0.25 mole of PbO per liter) in a 24- x 4-in.-dia stainless steel pot had a density of 2.9 g/ml and a volume about 1/8 that of the concentrated (1.72 M Al) waste solution. Ruthenium volatility was as low as 3% during processing. The thermal conductivity of the glass varied from 1.05 Btu/hr.ft.°F at 300°F to 1.60 Btu/hr.ft.°F at 1050°F; the temperature coefficient was positive and nonlinear with temperature, indicating an amorphous solid.

Corrosion of stainless steel "pots" used for the evaporation-fixation process was maximum in every case during the period when the last acid and water were being driven off at 850-1000°C. Overall corrosion rates for evaporation-fixation of Purex and TBP-25 wastes were about 5-11 mils/mo in a 24-hr batch process, about 1.4 mil/mo of which was attributable to air oxidation. When glass-making additives were present, rates increased to 42 mils/mo for the TBP-25 lead-phosphate glass at 920°C and to 145 mils/mo for a Purex borophosphate glass at 900°C. Release of SO_3 from the Purex waste is responsible for highly aggressive intergranular attack, which can be catastrophic at temperatures above 900°C, the critical temperature depending on the melt composition. Titanium was corroded at a maximum rate of about 2 mils/mo in evaporator-calciner environments vs about 10 mils/mo for LCNA and 11.2 mils/mo for Hastelloy F.

Low-Level Waste Treatment. In four continuous runs in the waste treatment pilot plant, ORNL low-activity waste was decontaminated from Sr-90 and Cs-137 by factors of >2000 and >246, respectively. The plant effluent contained <1.5% of the current MPC_w values for these isotopes for a 168-hr week. Run times were from 71 to 100 hr of continuous operation, with the use of 1800-2100 resin bed volumes. Equipment performance was good except for the rotary-drum vacuum filter, which was replaced by a plate-and-frame pressure filter modified to meet radiation protection requirements.

In laboratory-scale studies cobalt and ruthenium removal from the pilot plant effluent was improved by addition of an anion exchange column to the system and BO-4 grade vermiculte was plugged by small amounts of solids in the stream. Nalco analytical reagents were satisfactory, 1 ppm accuracy, for pilot plant control analyses.

Engineering, Economic, and Hazards Evaluation. Space requirements to dissipate the fission product heat in the waste from a 56,000-Mw(th) nuclear power economy were calculated for cylinders of calcined waste buried vertically in the floors of rooms in salt media. Spacings between cylinders ranged from 36 ft for acidic Purex in 24-in.-dia cylinders at the minimum burial age to 1 ft for reacidified Thorex in 6-in.-dia cylinders at 30 years age. Area requirements were calculated from the cylinder production rate and spacing requirements. Net area requirements calculated for Purex wastes in acidic and reacidified forms in 6-, 12-, and 24-in.-dia vessels range from 20 acres/year after 0.65 year to about 2 acres/year at 30 years age at burial. Corresponding areas for Thorex wastes are 10 and 0.7 acres/year. Calculations were made also for an acidic Thorex glass in 6-in.-dia vessels. The primary effects of the form of the waste (acidified, reacidified, glass) and vessel diameter are to limit the minimum burial age, although area requirements may be affected by factors of 2-3 by waste form and vessel size near the minimum burial ages.

Disposal in Deep Wells. Two fracturing experiments showed that structurally conformable fractures can be formed by hydraulic fracturing in the Conasauga shale at Oak Ridge. In the second experiment, two batches of a tagged grout mixture (91,567 gal in the first batch and 132,770 gal in the second) were injected into the same well at depths of 934 and 694 ft, respectively. Average injection pressures ranged from 1650 psi at 138 gpm in the first (lower) injection to 2000 psi at 200 gpm in the second (upper) injection, substantially higher than the rule-of-thumb value of 1 psi per foot of depth. Subsequent test drilling suggests that the lower grout sheet is ~240,000 ft^2 in area, oriented north and south, and that the upper grout sheet has an area of about 245,000 ft^2 in the east-northeast direction. The average thickness of the lower grout sheet is 0.01 ft and of the upper, 0.03 ft.

Sodium-calcium-strontium exchange was studied with Richfield sand as the sorbent. Strontium is sorbed selectively over calcium by a factor of ~1.1, while the selectivity of calcium sorption over sodium, at pH 7, was ~50 g/ml. The normalized strontium breakthrough curves correspond to the anion breakthrough curves, indicating that strontium breakthrough can be predicted from the solution dispersion in the column.

Disposal in Natural Salt Formations. Laboratory experiments showed that large pieces of salt heated to 260 to 280°C are shattered with some violence, accompanied by a release of steam. To evaluate the effect of high temperature on rock salt in place, a length of 6-5/8-in.-o.d. pipe, electrically heated to simulate a container of high-activity radioactive solids, was placed in a 7-7/8-in.-dia drilled hole in the floor of the Hutchinson mine. After 3.5 days' heating, the experiment was terminated because of the presence of water and recrystallized salt in the annulus surrounding the container. Temperatures as high as 127°C (106°C rise) were measured at 9.6 in. from the center of the heater. The surface temperature of the hole, extrapolated from this value, was about 200°C.

Clinch River Studies. During a period of 20,000 cfs flow in the Clinch River, with the level of Watts Bar Reservoir at 735 ft above mean sea level, the time of travel of Au-198 tracer from the mouth of White Oak Creek to Centers Ferry was 9.3 hr, about 10% less than predicted from computation of the mean velocity.

The effect of power releases from Norris Reservoir (the flow in the Clinch River varied from 1700 to 7700 cfs in 24 hr) on the level of radioactivity at a section 15.3 miles downstream from White Oak Creek was found to be insignificant. The deviation in radionuclide concentration during the period was less than 10% of the average concentration.

In 1963, power releases from Melton Hill Reservoir may cause daily variations in the flow of the Clinch River, from 0 to 23,000 cfs. At the maximum release rate, the level of backwater from Clinch River into White Oak Creek will be 3.5 ft above present summer levels. Unless the control gate settings at White Oak Dam are changed, the backwater will flow into White Oak Lake. If the gate levels are raised to prevent inflow from the river, the inflow from the creek to White Oak Lake will raise the lake levels.

Fundamental Studies of Minerals. In studies on the role of sodium nitrate in removing strontium from calcite and rock phosphate columns, the calcium dissolved by 1 M $NaNO_3$ was 1.1 mM, almost four times the solubility of calcite in water. The dissolution of calcite was the same in three successive leaches, but the amount of calcium in solution contacted with rock phosphate decreased in each of three successive leaches. Equilibrium was reached within 15 min for calcite particles up to 0.5 mm dia; rock phosphate samples showed increasing calcium in the solution contacted with increasing contact time up to 5 hr.

White Oak Creek Basin Study. Water-level measurements, taken in observation wells in the former bed of White Oak Lake, indicate that the depth to ground water varies from <1 ft to 4 ft below the land surface. Water-contour maps show that the general direction of ground-water movement is normal to the flow of White Oak Creek in the lower lake bed, but the pattern in the upper portion is influenced by stream flow from the intermediate-level waste seepage pit area.

1.0 INTRODUCTION

This report is the fifth 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,

---

* Previous: ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, and ORNL-TM-133.

determined in this way was 2.7 Btu/hr.ft.°F (single crystal value for 70°C) and diffusivity was 0.08 ft^2/hr (130°C value).

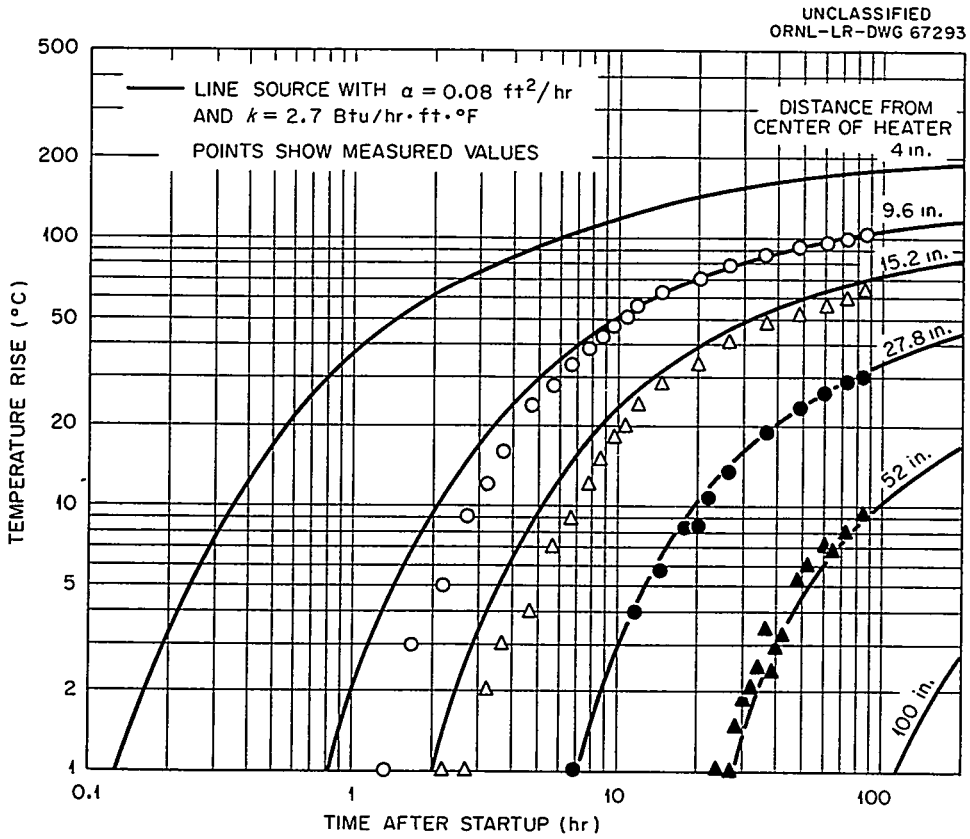


Fig. 6.2 Comparison of temperature rise in high temperature cylinder test 1 with theoretical for line source. Heater was 6 in. dia by 4 ft; power input = 3100 watts.

6.2 Laboratory Study of High-Temperature Effects (H. Kubota)

The effect of elevated temperature on salt was investigated in connection with the proposed storage of pot-calcined wastes in natural salt formations. Lumps of salt weighing 300-800 g, in the form of core drillings or pieces from mining operations in the Carey Mine at Hutchinson, were used. In each of six tests, the salt mass shattered and ruptured the metal basket used to contain the salt when the temperature reached 260 to 280°C. This effect was observed in the same temperature range regardless of the rate of heating. The shattered salt consists of crystals varying from about 10 mesh to over 1 in. in size. Three possible causes have been advanced for this phenomenon: (1) unequal strain resulting from unequal expansion along the different crystal axes, (2) oxidation of occluded organic material, or (3) pressurization of trapped water. It seems improbable that No. 1 is the cause, since the salt shattered with about the same degree of violence and at the same temperature no matter how slowly the temperature was raised.

When the heating was performed in a bomb, a cloud of steam was observed coincident with the disintegration. Analysis of the gas in the bomb showed small amounts of carbon dioxide and carbon monoxide. The amount of water released was at least an order of magnitude greater than that of the carbon oxides. At present, therefore, it is thought that the pressurization of the trapped water was also partially responsible for the fracturing.

6.3 Plastic Flow Studies (W. J. Boegly, Jr.)

Theoretical analyses of the stresses around salt mine openings, the extent of the plastic zone, and the rate and amount of flow resulting from the plastic zone were initiated by R. E. Glover of Denver, Colorado, a consultant. He is also calculating the effects of temperature on the "close-in" movement (plastic flow due to thermal stresses and thermal expansion) near cylindrical holes containing radioactive solids in the floor of a salt mine.

In order to evaluate and assist in these calculations, it will be necessary to make field measurements of the stresses around mine openings. A number of methods for stress measurement are available; however, they have been applied mainly to "hard" rocks, and their applicability to very plastic rocks must be determined. The most promising of these is the concentric borehole method, currently used by the U. S. Bureau of Mines (14), in which a small-diameter borehole is drilled into the rock and a borehole deformation gage is inserted. Next, a larger diameter hole is drilled around the borehole gage, and the deformation of the inner borehole after stress relief is measured. From these values and Young's modulus, the stress can be calculated. The values of stress obtained by this procedure check quite well with the expected stresses, provided the correct value of Young's modulus is used. Since the value obtained for Young's modulus is dependent on the test method, sample size, sample age, and various other factors, a standardized technique for determination of this plastic property is required, and studies on this are being started.

7.0 CLINCH RIVER STUDY

7.1 Dispersion Studies (P. H. Carrigan* and B. J. Frederick**)

On Feb. 1, 1962, 10 curies of Au-198, 5500 times the MPC_w, was discharged into the mouth of White Oak Creek over a period of 80 sec; the movement of gold was monitored in the Clinch River to Centers Ferry, 16.3 miles downstream.

---

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

** Research Section, Surface Water Branch, Water Resources Division, U. S. Geological Survey.

Because of turbulent diffusion, the peak concentration of Au-198 decreased as the radioactive "cloud" moved downstream. The variation in peak concentration with distance is shown in Fig. 7.1a. Downstream from Clinch River Mile 16 (CRM 16) the dispersion was largely in the longitudinal direction. Therefore, the rate of change in peak concentration with distance was much less than for upstream reaches.

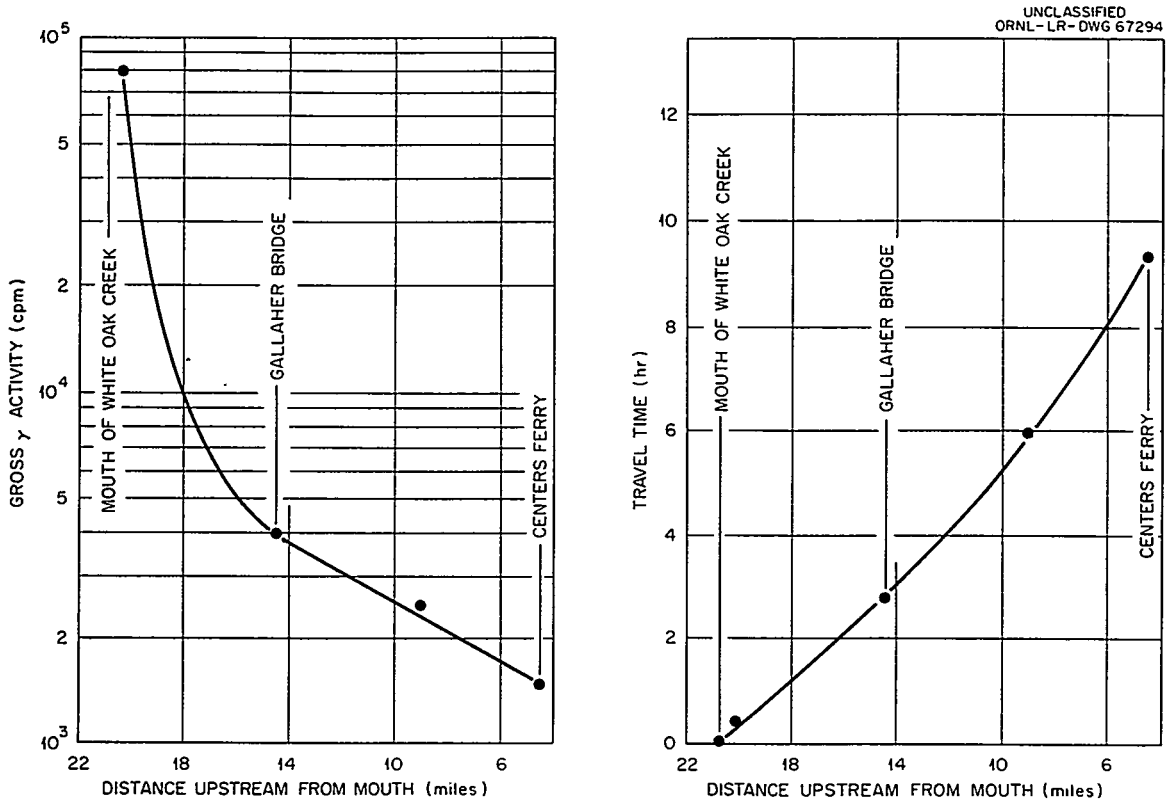


Fig. 7.1 Variation of (a) maximum concentration of Au-198 radioactivity and (b) time of travel with distance in Clinch River. Tracer study of Feb. 1, 1962.

The time of travel for the peak concentration from the mouth of White Oak Creek (CRM 20.8) to Gallaher Bridge (CRM 14.5) at the intake to the ORGDP water plant was 2.8 hr (Fig. 7.1b), and the concentration of Au-198 in this section was about 15% of the MPC_W. The time of travel for the peak concentration from White Oak Creek to Centers Ferry (CRM 4.5), 9.3 hr, is about 10% less than that predicted by TVA (15).

Frequently during summer months, power releases are made once daily from Norris Reservoir. The variation in flow of the Clinch River above Centers Ferry (CRM 4.5) produced by such a release during a 24-hr period is shown in Fig. 7.2a. The effect of these power releases on radioactivity levels in the Clinch above Centers Ferry was shown by analysis of water samples collected at 2-hr intervals. For several days prior to the test period, the variation in daily discharge at Norris

Dam was the same as for the test. The discharge of radioactivity from White Oak Creek decreased gradually during the same period (Fig. 7.2b).

Generation of electric power at Melton Hill Dam is scheduled to begin the latter half of 1963. The release of water used to generate power will cause daily variations in the water level of the Clinch River. As a result of a maximum release of 23,000 cfs immediately downstream from White Oak Dam, the backwater from the Clinch will raise the level of White Oak Creek from el. 741.0 ft to el. 744.5 ft in the summer and from el. 735.0 ft to el. 742.7 ft in the winter (16). The magnitude and deviation of these daily releases from Melton Hill Reservoir are shown in Fig. 7.3.

As a consequence of this backwater, an increase in the surface area of White Oak Lake is possible. The increase in area, without diversion of White Oak Creek around the lake, will depend on the water level of the Clinch River, the duration of backwater, the level of gate crests in White Oak Dam, and the inflow of White Oak Creek to the lake. An estimate of lake inundation for three conditions of gate operation at White Oak Dam is shown in Fig. 7.4.

7.2 Analysis of Clinch River Water and Sediments (R. M. Richardson and R. J. Pickering*)

Analyses of Clinch River water and sediments have been reviewed preliminary to tabulation and interpretation of the accumulated data. A period of high Ru-106 activity at water-sampling stations is believed to be the result of washing out of accumulated nonlocal atmospheric fallout during a period of heavy rainfall following a period during which concentrations of radioactivity in the air were slightly higher than normal. A program for submitting check samples for correlation of analyses between different laboratories is being planned.

On Jan. 31, 1962, water-sampling equipment was installed at the pump house of ORGDP by the U. S. Public Health Service. The responsibility for servicing the equipment has been assumed by personnel of the U. S. Geological Survey.

8.0 FUNDAMENTAL STUDIES OF MINERALS

(T. Tamura)

The presence of sodium nitrate in waste solution increases the removal of strontium by a calcite column (17), but decreases strontium removal by a rock phosphate column. In either system, the material beneficial for strontium removal is calcium phosphate. Based on experiments described below, a tentative hypothesis is suggested for the role of sodium nitrate: In a calcite column calcium released by the sodium reacts with soluble phosphate in the waste to form insoluble calcium

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

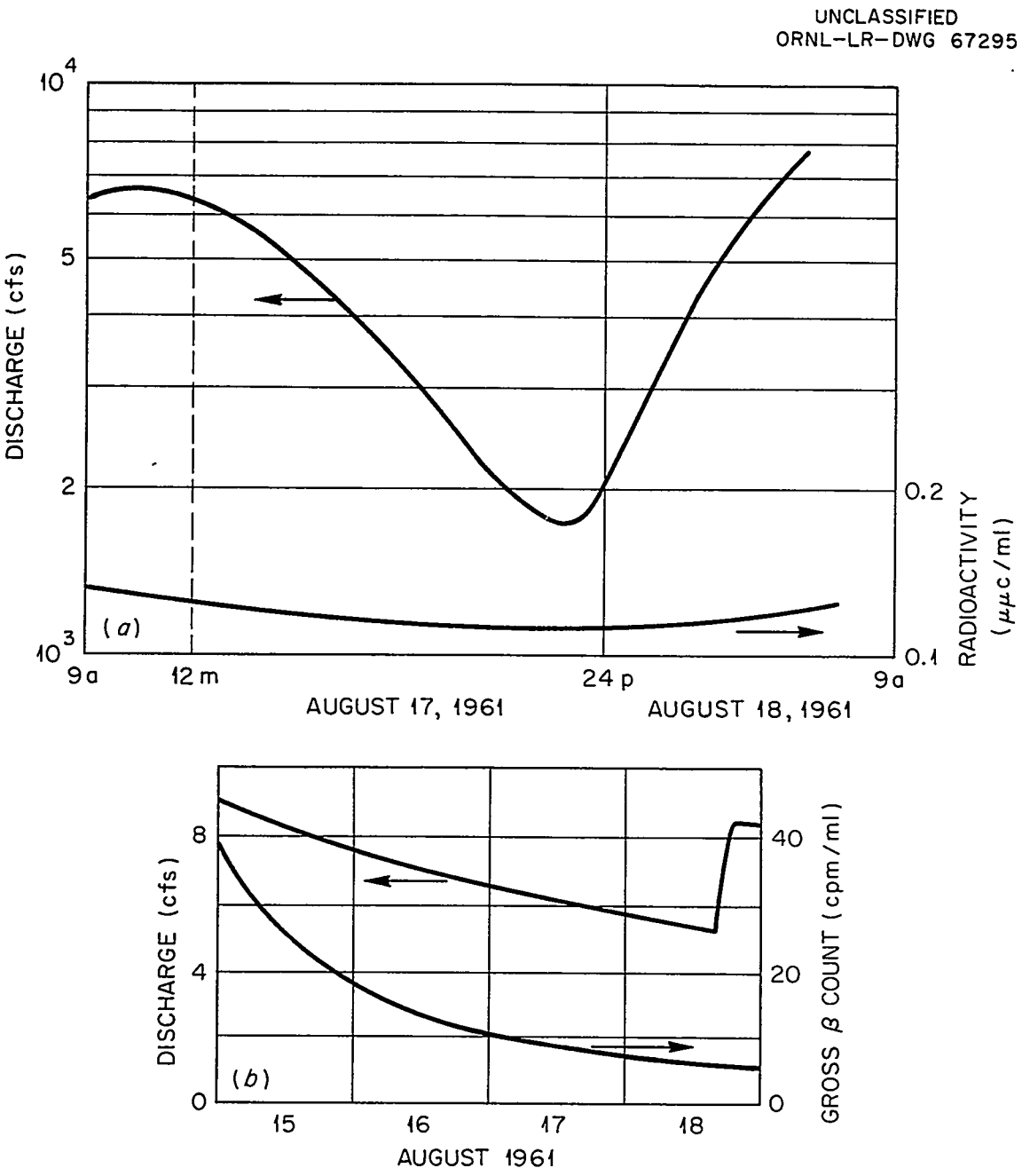


Fig. 7.2 Variation in discharge and concentration of radionuclides in (a) Clinch River during a 24-hr period and (b) in White Oak Creek during a 4-day period.

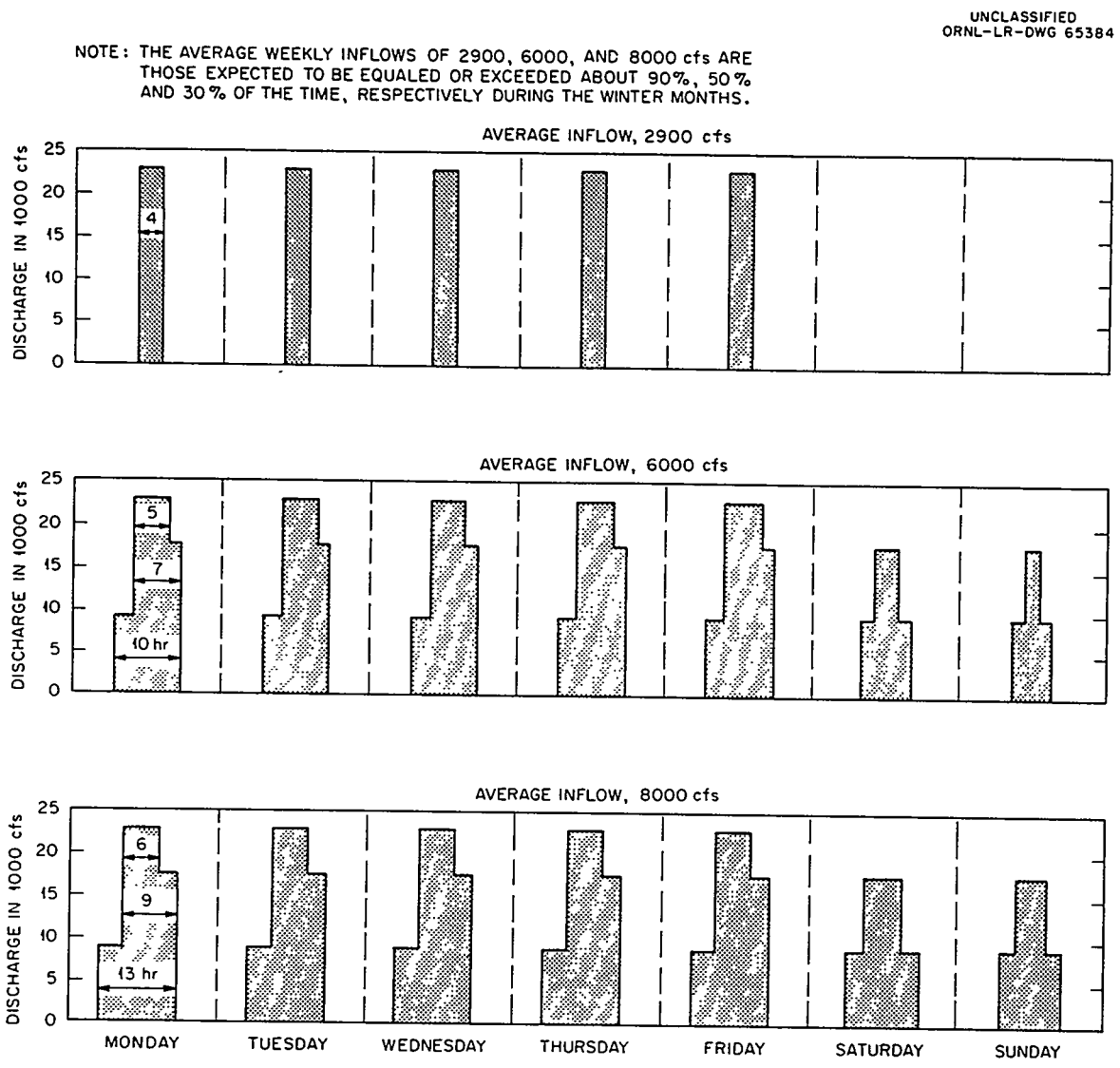


Fig. 7.3 Possible schedule of releases from Melton Hill reservoir for average weekly inflows to the reservoir.

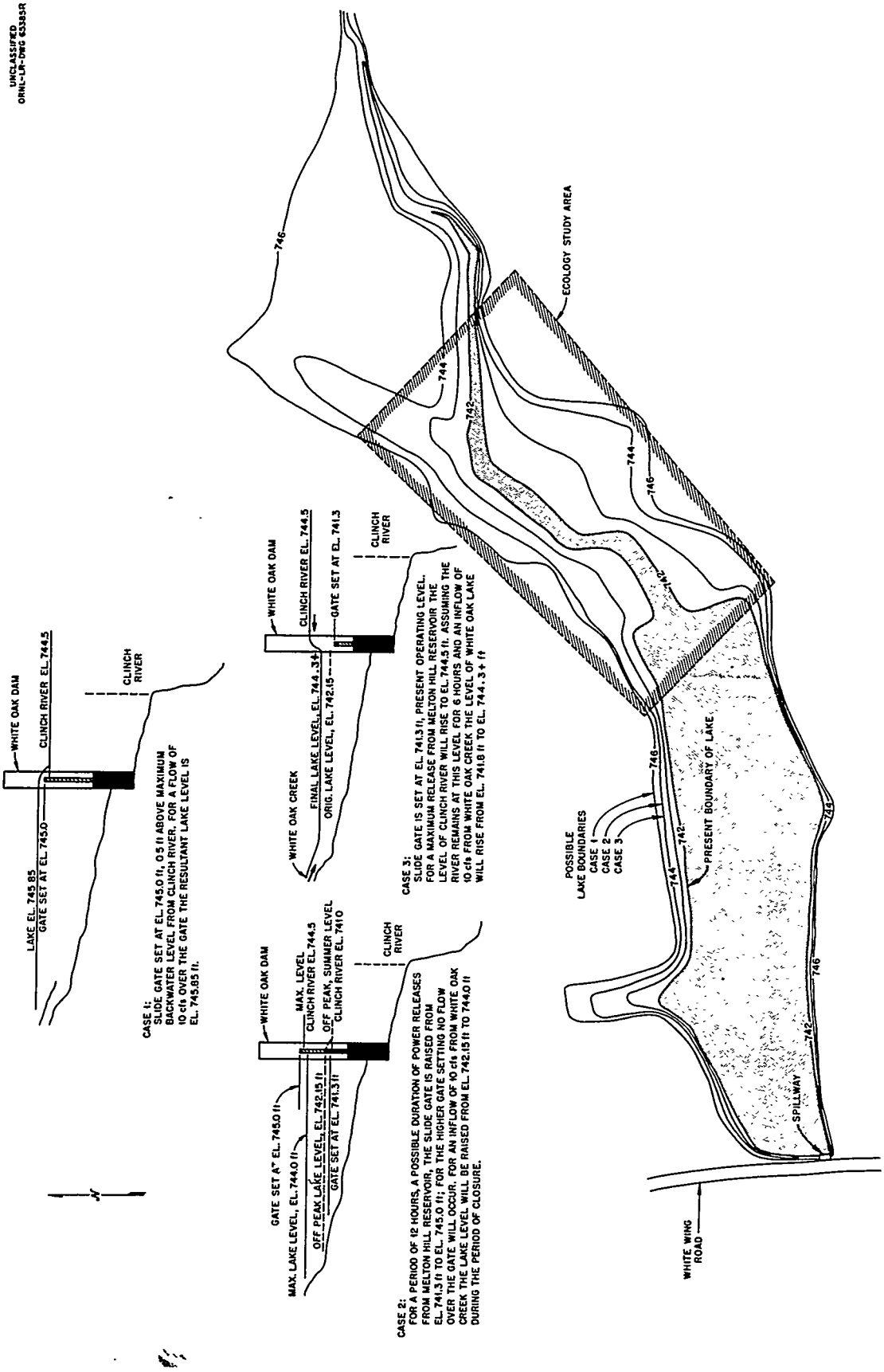


Fig. 7.4 Possible limits of inundation of White Oak Lake.

phosphate. If the phosphate concentration is in great excess, as is usually the case, the calcium would not be expected to compete with strontium for the phosphate; rather, increases in calcium concentration would favor the formation of larger amounts of calcium phosphate. In a rock phosphate column, the matrix is calcium phosphate (apatite). The released calcium does not form an insoluble reaction product with the waste solution, and the added sodium ions compete with strontium and calcium for exchange sites on the apatite.

In the experiments described below a known weight of mineral was contacted with either demineralized water or sodium nitrate solution in a stoppered vial. After being shaken for a predetermined time in a Burrell "wrist-action" shaker, the vial was centrifuged 2 min and an aliquot of the solution was titrated for calcium with Versene-eriochrome Black T, using a microburet.

8.1 Dissolution of Calcium from Calcite

More titratable calcium was released from calcite by 0.5 M $NaNO_3$ solution than by demineralized water (Table 8.1). That the difference was not due to titrating the calcium in different media was shown by the consistent calcium values obtained in analyses of calcium standards made up in demineralized water and sodium nitrate solution. The solubility of calcite is 0.0014 g/100 g of water at 25°C, or 0.28 meq of calcium per liter (18), and the amounts determined in demineralized water in these tests agreed closely. The particle size of the calcite had no effect on the results.

The results with different solvent contact times indicated that equilibrium is attained rapidly and that 15 min contact is sufficient for equilibration (Table 8.1). The difference in calcium solubility in demineralized water and sodium nitrate solution existed with all contact times tested.

Increasing the sodium nitrate concentration from 0.1 to 5.0 M increased the dissolved calcium from 0.70 to 1.13 meq/liter (Table 8.1). Calcium solubility was slightly higher in demineralized water in this series than in the earlier series, but these higher values are attributed to experimental error. That they were not totally due to dissolved CO_2 was shown with demineralized water that had been boiled, stoppered, cooled, and kept free from atmospheric CO_2 during contact with the calcite. This water dissolved ~10% less calcium, with calcium concentrations of the order of 0.28 mN. The constancy of the calcium concentrations in successive leaches suggests that the dissolution involves the entire calcite particle and not merely a surface reaction.

8.2 Dissolution of Calcium from Rock Phosphate

Tests with rock phosphate are still in progress, but preliminary results (Table 8.1) indicate differences in the response of calcite and rock phosphate. As with calcite, more calcium was dissolved in the presence of sodium nitrate, but unlike calcite, particle size and successive leachings strongly affected the results. Less calcium

Table 8.1 Dissolution of Calcium from Calcite and Rock Phosphate by Demineralized Water and Sodium Nitrate Solution

Particle Size (mm)	Contact Time (min)	Ca Dissolved by Demineralized H_2O (meq/liter)		$NaNO_3$ Soln Conc (M)	Ca Dissolved (meq/liter)		
		1st Leach	2nd Leach		1st Leach	2nd Leach	3rd Leach
Calcite							
0.5-0.25	30	0.33		0.5	1.1		
0.25-0.10		0.27			1.1		
0.10-0.05		0.27			1.1		
<0.05		0.27			1.2		
0.5-0.25	15	0.28		1	1.05		
	30	0.28			1.01		
	60	0.29			1.13		
	300	0.29			1.16		
0.5-0.25	15	0.41	0.34	0.1	0.70	0.66	0.64
				0.5	0.98	0.94	1.05
				1.0	1.18	1.12	1.07
				5.0	1.13	--	--
Rock Phosphate							
0.5-0.25	30	0.08		0.5	0.40		
0.25-0.10		0.12			0.49		
0.10-0.05		0.33			1.04		
< 0.05		--					
0.5-0.25	30			1.0	0.61	0.24	0.20
0.25-0.10					0.75	0.28	0.24
0.10-0.05					1.31	0.54	0.37
<0.05					1.97	0.79	0.50

was dissolved with successive leachings, suggesting that the high initial calcium concentration is caused by the presence of some very fine particles in each size range. The increase in calcium concentration with decrease in particle size supports this explanation. There was some indication that the sodium nitrate concentration affected the rock phosphate solubility.

9.0 WHITE OAK CREEK BASIN STUDY*

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

A series of shallow auger holes, 5-6 ft deep, was completed in the bed of former White Oak Lake to define the configuration of the water table and to determine the direction of ground-water movement. Water-level measurements in these wells, made about once each week for the period Aug. 28, 1961 to Jan. 5, 1962, indicated that the depth to ground water in the area generally varies from 3 to 5 ft below the land surface during the dry summer months and from <1 to 1.5 ft during the wet winter months when transpiration and evaporation are lower.

Water-contour maps of the area show that the general direction of ground-water movement is normal to the flow of White Oak Creek in the lower portion of the site; in the upper bed the pattern is more complex. A water table contour map for Sept. 22, 1961 (Fig. 9.1) indicates that the configuration of the water table in the upper part of the area is measurably affected by the flow of surface water onto the lake bed from two streams that drain the waste pit area. During the dry summer months, these streams recharge the ground water in the lake bed, with little or no surface water flowing directly into the creek. However, in the wet winter months, when the ground water in the lake bed is close to the land surface, some of the water from these streams flows over the surface of the bed into White Oak Creek.

These two streams transport several thousand curies of Ru-106 per year from the waste pits; however, less than half the ruthenium finds its way into White Oak Creek. It is likely that much less Ru-106 enters the creek than leaves the waste pit area during the dry seasons, as the activity must be transported by ground water through the lake bed subsoil to the creek. In wet seasons, it is assumed that the input of Ru-106 to the creek more nearly approaches the output from the waste pit area because of transport of activity by surface water over the lake-bed to White Oak Creek.

A series of core samples taken in this area are being radiochemically analyzed to determine the distribution of Ru-106 in the soil.

9.2 Geologic and Hydrologic Studies (R. M. Richardson** and W. M. McMaster**)

On December 15, William M. McMaster, geologist, was reassigned to the Oak Ridge Subdistrict Office of the Surface Water Branch of the U. S. Geological Survey to investigate in greater detail the geology and hydrology of White Oak Creek Basin.

---

*This project, entitled, "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin" (AEC Activity No. 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 No. 040405021).

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

The purpose of the investigation is to obtain a better knowledge and understanding of the way in which water moves through the basin. This is important in the management of radioactivity in the basin, as water is the principal agent that transports radioactive materials out of the basin into the uncontrolled environment.

A proof of a geologic map of the Oak Ridge Reservation was revised and transmitted to TVA for reproduction. An inventory of existing wells in the basin was made as a preliminary to establishing an ovservation well program in the basin. A reconnaissance of White Oak Creek and its tributaries to determine the location of outfalls contributing liquid wastes to the stream system was started.

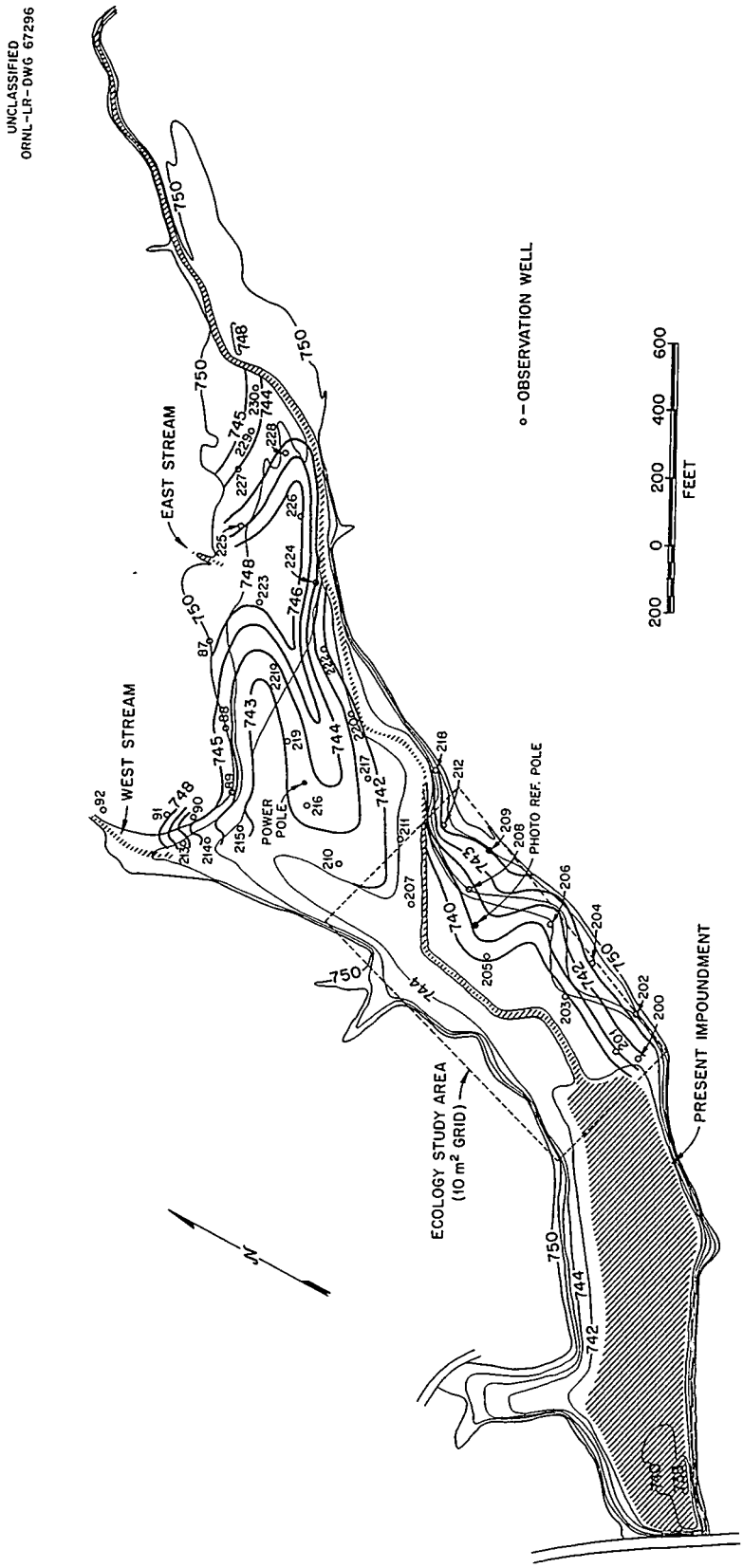


Fig. 9.1 Water table contours at White Oak Lake Bed, Sept. 22, 1961.

10.0 REFERENCES

1. "Waste Treatment and Disposal Progress Report for April and May 1961," ORNL-CF-61-7-3.

2. Ibid. for October, November 1961.

3. Ibid. for August, September 1961.

4. "Chemical Technology Division Annual Prog. Report for Aug. 31, 1960," ORNL-2993.

5. J. J. Perona and M. E. Whatley, "Calculation of Temperature Rise in Deeply Buried Radioactive Cylinders," ORNL-2812 (Feb. 3, 1960).

6. H. W. Godbee and J. T. Roberts, "Survey on the Measurement of Thermal Conductivity of Solids Produced by Evaporation and Calcination of Simulated Fuel Reprocessing Solutions," ORNL-2769 (Aug. 10, 1959).

7. W. D. Kingery and F. H. Norton, "The Measurement of Thermal Conductivity of Refractory Materials," NYO-6447 (January 1955).

8. J. T. Roberts and R. R. Holcomb, "A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes," ORNL-3036 (May 22, 1961).

9. R. R. Holcomb and J. T. Roberts, "Low-Level Waste Treatment by Ion-Exchange. II Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin," ORNL-TM-5 (Sept. 25, 1961).

10. Op. cit, June and July, 1961, ORNL-TM-15, p. 26.

11. W. H. McAdams, Heat Transmission, Third Ed., McGraw-Hill Book Company, Inc., 1954, p. 181.

12. U. S. Geological Survey, Water Resources Division, Annual Report on Current Investigations (in preparation).

13. W. J. Kaufman, University of California, private communication, Dec. 28, 1961.

14. R. H. Merrill, "Static Stress Determinations in Salt-Site Cowboy," USBM-Report APRL 38-3.1 (1960).

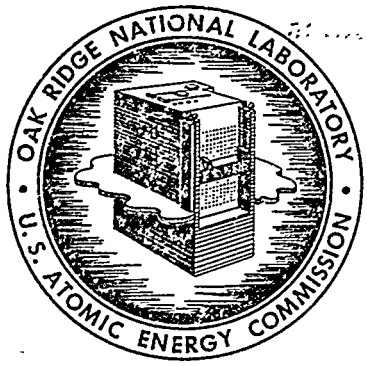
15. "Effect of Accidental Spillage of Radioactive Waste into Clinch River, Rpt. No. 1, Time of Travel, Probable Flows, and Dispersion," Hydraulic Data Branch, TVA, Knoxville, Nov. 10, 1952.

16. M. A. Churchill, Health and Safety Division, TVA, private communication, January 1962.

17. L. L. Ames, "The Removal of the Bone-Seeking Group of Radioisotopes from Solution by a Calcite-Phosphate Reaction," HW-60412 (June 1, 1959).

18. Handbook of Chemistry and Physics, 37th ed., Chemical Rubber Co., Cleveland, Ohio.

ORNL
MASTER COPY



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-252

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR FEBRUARY AND MARCH 1962

ChemRisk Document No. 2005

This documen
primarily for i
to revision or
information is
semination wi
mation Control

Publicly Releasable

This document has received the necessary patent and technical information reviews and can be distributed without limitation.

l was prepared
. It is subject
al report. The
en public dis-
egal and Infor-

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-TM- 252

CHEMICAL TECHNOLOGY DIVISION
AND
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR FEBRUARY AND MARCH 1962

R. E. Blanco and E. G. Struxness

DATE ISSUED

SEP 10 1962

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
For the
U. S. ATOMIC ENERGY COMMISSION

CONTENTS

		Page
1.0	INTRODUCTION	7
2.0	HIGH-LEVEL WASTE CALCINATION	8
2.1	Engineering-Scale Pot-Calcination Development	8
2.2	Pilot Plant Design	14
2.3	Design of Radioactive Cell Equipment	20
2.4	Laboratory-Scale Fixation	22
3.0	LOW-LEVEL WASTE TREATMENT	30
3.1	Pilot Plant	30
3.2	Process Development	33
4.0	ENGINEERING, ECONOMICS, AND HAZARD EVALUATION	39
4.1	Economics of Solids Disposal in Salt	39
4.2	Shipment of Calcined Solids	42
5.0	DISPOSAL IN DEEP WELL	45
5.1	Disposal by Hydraulic Fracturing	45
6.0	DISPOSAL IN NATURAL SALT FORMATIONS	50
6.1	High-Temperature Experiments	50
6.2	Calculation of Thermal Stresses and Plastic Deformations Around Heat-Generating Cylinders Stored in Salt	56
6.3	Trapped Moisture in Natural Salt Formations	58
6.4	Effect of Salt Extraction and Depth on Stability of Mine Openings	58
7.0	CLINCH RIVER STUDY	59
7.1	Flow Routing	59
7.2	Effect of Geology on Quality of Water of Clinch River Tributaries	63

		Page
8.0	FUNDAMENTAL STUDIES OF MINERALS	63
	8.1 Behavior of Cesium in Vermiculite Systems	63
9.0	WHITE OAK CREEK BASIN STUDY	69
	9.1 Sources of White Oak Creek Contamination	69
	9.2 Hydrology of White Oak Creek Basin	73
10.0	REFERENCES	74

ABSTRACT

High-Level Waste Calcination. Process flowsheets and an equipment layout were completed for the Idaho Chemical Processing Plant Pot Calcination Pilot Plant. A mercury trap for removal of mercury compounds from the calciner off-gas was designed and fabricated, and several welded closures for sealing pots were leak-tested at the Georgia Nuclear Laboratory; the leak rate was less than 0.2 std cc of helium per year.

A mathematical study initiated to predict the control pattern for a pot during calcination indicated that, at a certain critical cake thickness, the wall temperature of the calciner must be programmed to ensure that all portions of the cake achieve, yet not exceed, approximately 1650°F.

Decreasing the pressure from 750 to 570 mm Hg had little effect on the relative volatilities of ruthenium from 6 M HNO_3. Addition of 0.1 M H_3PO_3 to nitrate solutions of ruthenium chloride and ruthenium nitrosohydroxide with and without salts occurring in waste solutions decreased the ruthenium distillation by factors varying from 2920 for 6 M HNO_3 containing ruthenium nitrosohydroxide to 38.8 for simulated Darex waste containing ruthenium chloride.

The thermal conductivities of a lead phosphate glass were 1.05 and 1.60 Btu hr^{-1} ft^{-1} $°F^{-1}$ at 300 and 1050°F, respectively. The production of this glass on a semiengineering scale was accompanied by volatilization of 12.5% of the original ruthenium and physical entrainment of < 0.02% of the promethium as determined from counting Ru-106 and Pm-147 tracers.

Simulated Darex waste solution was incorporated into glassy and microcrystalline phosphate and borophosphate solids with softening points of 850 to 900°C and densities of 2.73 to 3.75 g/cc, and containing 13.4 to 32.3 wt % waste oxides, representing volume reductions of 2.9 to 6.6.

Low-Level Waste Treatment. The results of four demonstration runs in the Pilot Plant, with ORNL process waste water as feed, were essentially the same as previous ones: Sr-90 d.f. 2000 - 12,000; Cs-137 d.f. 77 - 3000. Plant effluent solutions contained < 3% of current MPC_w values for all isotopes at the 2000-bed volume level (56,000 gal). A resin column isotope breakthrough run (HR-6) indicated a Sr-90 release to plant effluent after 2916 bed volumes.

The pretreatment protion of the scavenging-ion exchange process was improved by the addition of calcium carbonate to the flash mixer contents, either as 25 ppm of $Ca(OH)_2$ which precipitated $CaCO_3$, or as recirculated sludge from the clarifier. The lime-caustic-copperas treatment was shown to be temperature dependent,

with minimum residual hardness at 26°C. Results of tap water treatment in a laboratory-scale sludge blanket clarifier containing an inner cone indicated that a size reduction of 10-20 is possible over present equipment.

Engineering, Economics, and Hazards Evaluation. A preliminary conceptual design and cost estimate for a solids disposal facility in salt indicated costs of from 6×10^{-3} to 30×10^{-3} mill/kwh$_e$. Sixty to 85% of the total costs were attributable to mining, indicating that the best possible estimates of this item will be required for the more detailed final study.

Heat transfer calculations of shipping containers for pot-calcined wastes of various ages showed that as many as thirty-six 6-in.-dia pots of calcined acidic Purex waste can be shipped in a single finned carrier after 2.4 years' decay without mechanical cooling enroute. Four 24-in.-dia pots of acidic Purex waste can be shipped, per carrier, after 11 years' decay.

Disposal in Deep Wells. Slurries were made with simulated ORNL intermediate-activity wastes and portland cement which met the pumping time requirements. The salts in the waste solution did not cause unexpected reactions that are undesirable for pumping operations and did not prohibitively alter the setting properties of Portland cement slurries.

Disposal in Natural Salt Formations. Four plastic-flow measurement stations have been installed in the Carey Salt Company mine at Hutchinson, Kansas. Each station consists of from seven to nine gages installed in such a way as to measure both floor and ceiling movement and movement of the columns. The stations are installed in areas of varying age, from recent to early in development of the mine. Two additional gages remain to be installed. An array of 20 holes for the study of effect of high temperatures on rock salt in situ was successfully drilled without use of a liquid drilling medium. Samples of dry shale from the holes contained 10 to 12% water.

Clinch River Study. During periods free from storm runoff in the summer months, power waves in the Clinch River study reach are classified as uniformly progressive flow. For this type of flow the storage of water in the study reach is conditioned equally by the inflow and outflow rates. By expressing the storage as a weighted function of these rates, the variations in flow due to power releases in the Clinch River above Centers Ferry, near Kingston, Tenn., may be determined from flow records obtained at the upstream gaging station on the Clinch River near Scarboro, Tenn.

Stable chemical analyses of water samples taken during base flow measurements in September 1961 show a marked difference in the quality of water between streams draining coal-bearing

clastic rocks of the Cumberland escarpment and streams draining predominantly carbonate rocks of the ridge and valley province in which Oak Ridge National Laboratory is located. Streams draining the Cumberland escarpment contain a greater proportion of sulfate, sodium, and chloride and have higher pH's than do streams draining the ridge and valley province.

Fundamental Studies of Minerals. The cesium exchange properties of vermiculite were improved by collapsing the vermiculite lattice with ammonium ions or with one of the heavy alkali metal cations. Pretreatment of the vermiculite with potassium increased the number of exchange sites at the edges of collapsed basal spacings, where cesium can be incorporated into the lattice by "edge fixation." This increased the cesium K_d in 0.5 M $NaNO_3$ by a factor of 2.7. Addition of NH_4^+, Cs^+, Rb^+, or K^+ to the influent resulted in "interlayer fixation" of cesium as a result of collapse of the lattice to physically entrap the cesium sorbed at the basal surface exchange sites. In this case the cesium K_d was increased by a factor of about 4.4.

White Oak Creek Basin Study. For the period May to October 1961, the Process Waste Water Treatment Plant accounted for about 92% of the Sr-89 and Sr-90, 91% of the rare earths (exclusive of Y-90), 72% of the Cs-137, 76% of the Co-60, and 84% of the Ru-106 discharged to White Oak Creek in Bethel Valley. Of the smaller contributors, the amount of activity detected in the sanitary sewage effluent was the most significant. The mean concentration of Sr-90 in the effluent for the sampling period was 1.7×10^{-6} μc/cc or about 40% of MPC for continuous occupational exposure, 40-hr week. Analyses of samples taken at temporary monitoring stations along White Oak Creek and its tributaries indicate a relation between the suspended solid load in the stream and cesium transport.

1.0 INTRODUCTION

This report is the sixth of 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-level 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-level 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 this environment.

*Previous reports in this series are ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, and ORNL-TM-169.

2.0 HIGH-LEVEL WASTE CALCINATION

The pot calcination process for converting high-activity-level wastes to solids is being studied on both a laboratory and engineering scale to provide design information for construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes containing millicurie amounts of ruthenium but has not been demonstrated on actual high-activity-level wastes. A general flowsheet was shown previously (1). In phase I operations, the pilot plant will demonstrate calcination with the addition of additives limited to those necessary to repress volatilization of components such as sulfate or ruthenium. In phase II, the pilot plant will demonstrate fixation where additives will transform the waste to glasses.

2.1 Engineering-Scale Pot-Calcination Development (J. C. Suddath, C. W. Hancher)

Recent data are being compiled and evaluated. A review of 21 engineering scale tests, made to develop the evaporation and calcination part of the pot-calcination flowsheet, is presented here. The tests were made with a small continuous evaporator and a large batch evaporator.

A close-coupled continuous evaporator and an 8-in.-dia by 90-in.-high calciner operated satisfactorily with simulated Purex, Darex, and TBP-25 waste (Table 2.1). The average feed rate for TBP waste was 25-30 liters/hr and for Purex, 20-25 liters/hr. The calcination time was an additional 8-10 hr, and the change-out time 8-10 hr. Purex waste from processing of 1.75-2.0 tons of uranium could be calcined in 1 day on a 2-day cycle. The average feed rate for Darex waste was 10-20 liters/hr. Average decontamination factors across the evaporator (Fig. 2.1) were about 10^3: 1200 from sulfate, 700 from iron, and 1000 from ruthenium. The evaporator was operated with little or no de-entraining medium, but, in a well-designed evaporator with adequate de-entraining space and medium, larger d.f.'s would be expected. Decontamination across the calciner is less important since its off-gas is recycled to the evaporator. Approximately 1% of the sulfate, 7% of the metal ions, and 8% of the ruthenium are expected to be returned to the evaporator (Fig. 2.1).

The system (Fig. 2.2) consists of a natural circulation evaporator equipped with a 22-ft^2 heat exchanger, which uses 100-psi steam as the heating medium. A bottom drawoff from the evaporator connects to a pump loop, which flows past the calciner pot and returns to the evaporator. To decrease changes of plugging and to maintain a constant feed to the calciner, a 10-gpm flow is maintained in this loop. The pipe for the small sidestream of liquid drawn off through a control valve into the calciner pot is kept as short as possible, 2 ft, and the control valve is placed as near the operating loop as possible. A water purge bled into the feed stream downstream of the control valve at 1 liter/hr decreases the frequency of plugging.

Table 2.1 Results of Waste[a] Calciner Tests

Run No.[b]	Type of Feed	Avg. System Feed Rate liters/hr	Feed Vol (liters)	Water Per Feed Vol Radio	Fe or Al Conc. (g/liter) In Evaporator[c]	Fe or Al Conc. (g/liter) Set Point	Off-gas[d] Feed Per Vol Radio	NO_3 in Solids (wt. %)	Solids[e] Density (g/cc)
43	Purex[f]	System leak	594		61-36	45.0		0.9 - 0.008	
44	Purex	40.9	409	7.8	106-36	63	2.02	0.14- 0.06	1.14
45-B	Purex	25.2	328	3.9	37-27	32	2.2	4.7 - 0.01	1.17
46-B	Purex	25.8	325	4.1	35-27	32	3.5	3.7 - 0.01	1.55
47	TBP-25	30.6	429	3.4	103-54	64	1.9	6.0 - 0.36	0.57
48	TBP-25	15.0	468	2.8	72-42	50	3.5	6.0 - 0.10	0.77
49	TBP-25	17.6	478	2.6	56-36	54	1.9	6.0 - 0.36	0.83
50[g]	TBP-25	11.5	346	2.4	66-35	49	2.4	4.1 - 0.08	0.52
51-B[g]	TBP-25	7.0	308	2.5	62-53	57	3.2	6.0 - 0.08	0.59
52-B[g]	TBP-25	9.8	440	2.3	65-49	55	2.4	0.18- 0.06	0.44
54	TBP-25	17.2	428	2.7	52-36	43	1.8	0.85- 0.1	0.65
55	TBP-25	19.4	469	3.5	80-35	42	1.4	0.56- 0.1	0.60
56	Darex	13.6	383	4.1	82-47	52	1.4	0.09- 0.02	0.86
57	Darex	8.9	641	3.2	99-53	73	2.2	0.53- 0.01	1.4
58	Darex	16.5	576	3.0	120-98	109	0.84		1.42
59-B[g]	TBP-25	12.4	397				1.3	1.0 - 0.07	0.61
60-B	Darex	8.6	336	5.5	128-76	110	1.8		1.29
61-B	Darex	10.6	307	3.8	112-93			2 - 0.1	1.13
62	TBP-25	16.8	446	4.5	70-36	59	1.0		0.63
63	TBP-25	16.3	421	2.3	55-39	50	0.9	2.0 - 0.2	0.61
64	TBP-25	11.6	560	2.0	54-31	47	1.19	0.2 - 0.002	0.80

[a] The Concentrations (M) are:

Waste	H^+	NO_3^-	$SO_4^=$	Cl^-	Fe^{3+}	Al^{3+}	Ni^{2+}	Cr^{2+}	Na^+
Conc.Purex	5.6	6.1	1.0		0.5	0.1	0.01	0.01	0.6
Darex	3.0	5.0		0.1	0.68	0.12		0.08	0.16
TBP-25	0.5	5.4	0.03		0.002	1.16	0.12		

[b] In "B" runs batch evaporation was used; in all others it was continuous.

[c] Concentration range during calciner feeding in Purex batch evaporations.

[d] Includes 10-20 ft^3/hr system leakage.

[e] Bulk density = weight of solid divided by 60 liters.

[f] No $Ca(NO_3)_2$ added.

[g] 1 ml each DBP & MBP added to feed before processing.

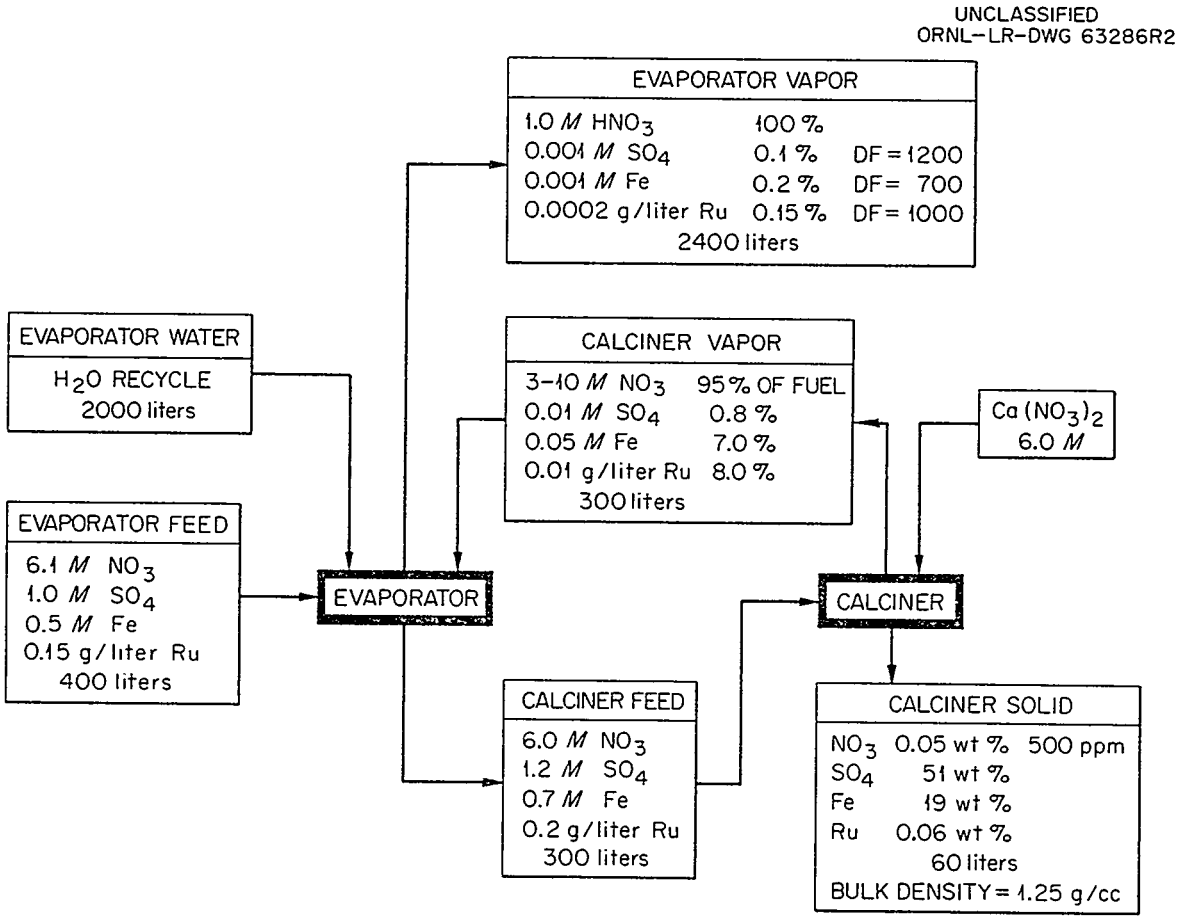


Fig. 2.1. Purex Material Distribution Flowsheet for Continuous-Evaporation System. The numbers represent best averages from a number of tests.

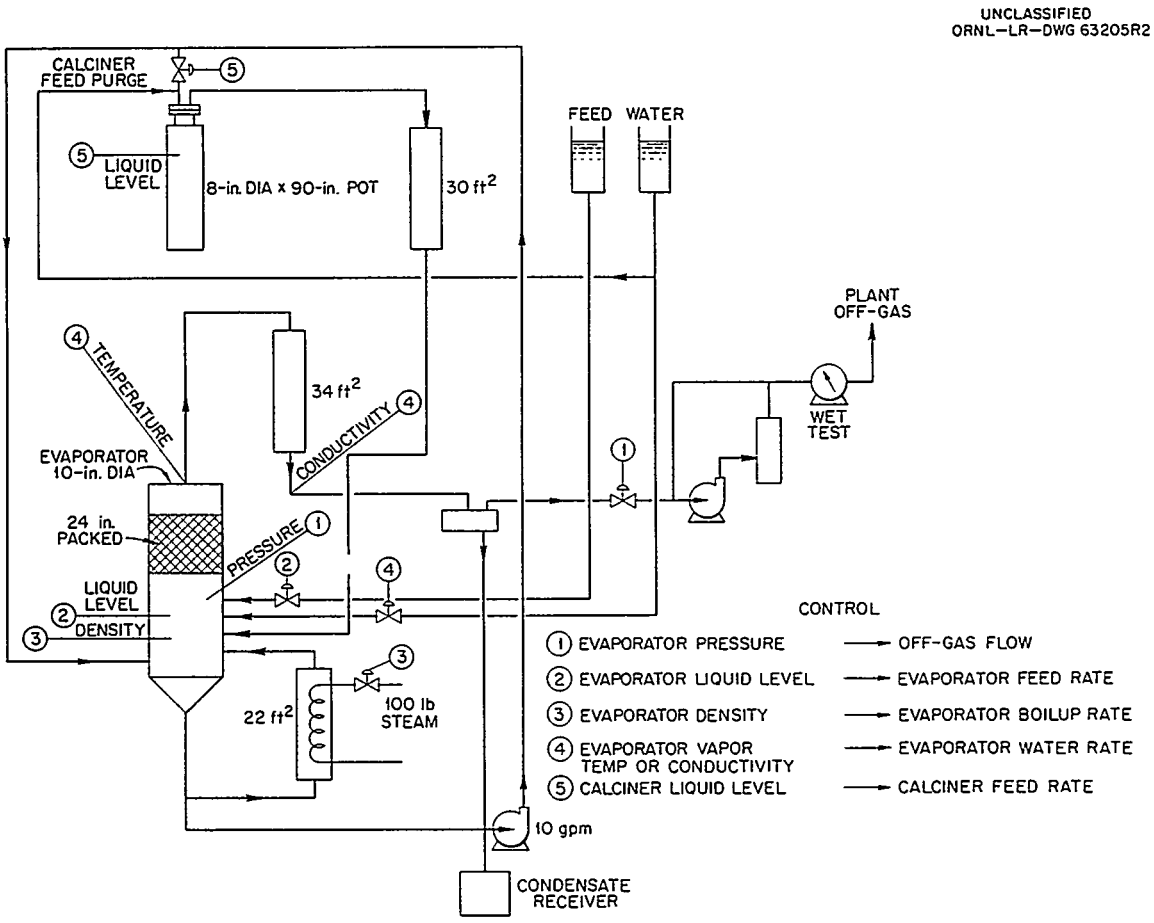


Fig. 2.2. Calciner-Continuous Evaporator Control Flowsheet.

The calciner vapor is condensed in a 30-ft^2 downdraft heat exchanger and returned directly to the evaporator. The liquid is supercooled to recover 85-95% of the nitric oxides and decrease the gas volume for better decontamination. Recycled water and feed are added to the evaporator through their individual control valves from head tanks. The evaporator vapor passes through a de-entraining section and then to a 34-ft^2 heat exchanger which operates downdraft. The condensable fraction of the vapor goes to a condensate receiver, where it is measured and discharged through a pressure seal. The noncondensable vapor goes to the off-gas system, where it is filtered and the volume is measured in a wet test meter.

The off-gas from a typical 30-hr Purex waste run was 1100 cu ft^3, or 36 ft^3/hr, of which 32 cu ft/hr was instrument purge and inleakage gas. The system operated under 1 psi vacuum. The 4 ft^3/hr of noncondensable gas averaged 3 ft^3 of oxygen per hour. Excess oxygen is always present in the off-gas from decomposition of nitrate to NO_2 and O_2 (2) and at times was as high as 34 vol %. This small amount of off-gas can be easily decontaminated and discharged to the environment.

The evaporator had a 4-6 liters/min boilup rate and operated normally with 25-30 liters holdup. The calciner pot had a nominal 1 liter/min water boilup rate at the full 54 kw heat input. As the solids are radially deposited on the walls of the vessel, the heat input to the pot is decreased. The external wall of the calciner is held at a maximum of 900°C by the furnace, which is divided into six sections, each about 13 in. high. The furnace temperature could go to 1050°C before there was danger of burnout.

The variables that must be controlled in the process are:

1. Acidity in the evaporator, which is kept below 6 M, to decrease ruthenium volatility, by recycling water or weak nitric acid from the distillation column to the evaporator. The amount recycled is controlled by the nitric acid and metal ion concentrations in the evaporator, which determine the vapor temperature (Fig. 2.3), and the preferred operating range is between 0.5 and 0.7 M iron and between 4 and 6 M H^+ for Purex waste. Increasing the rate of water addition increases the vapor volume and therefore the required capacities of the evaporator and distillation column.

2. Metal ion concentration in the evaporator, which is kept maximum, limited by solution stability, by controlling the liquid density by varying the amount of steam used to vaporize the liquid.

3. Liquid level in the evaporator, which is controlled by the amount of evaporator feed added to the system.

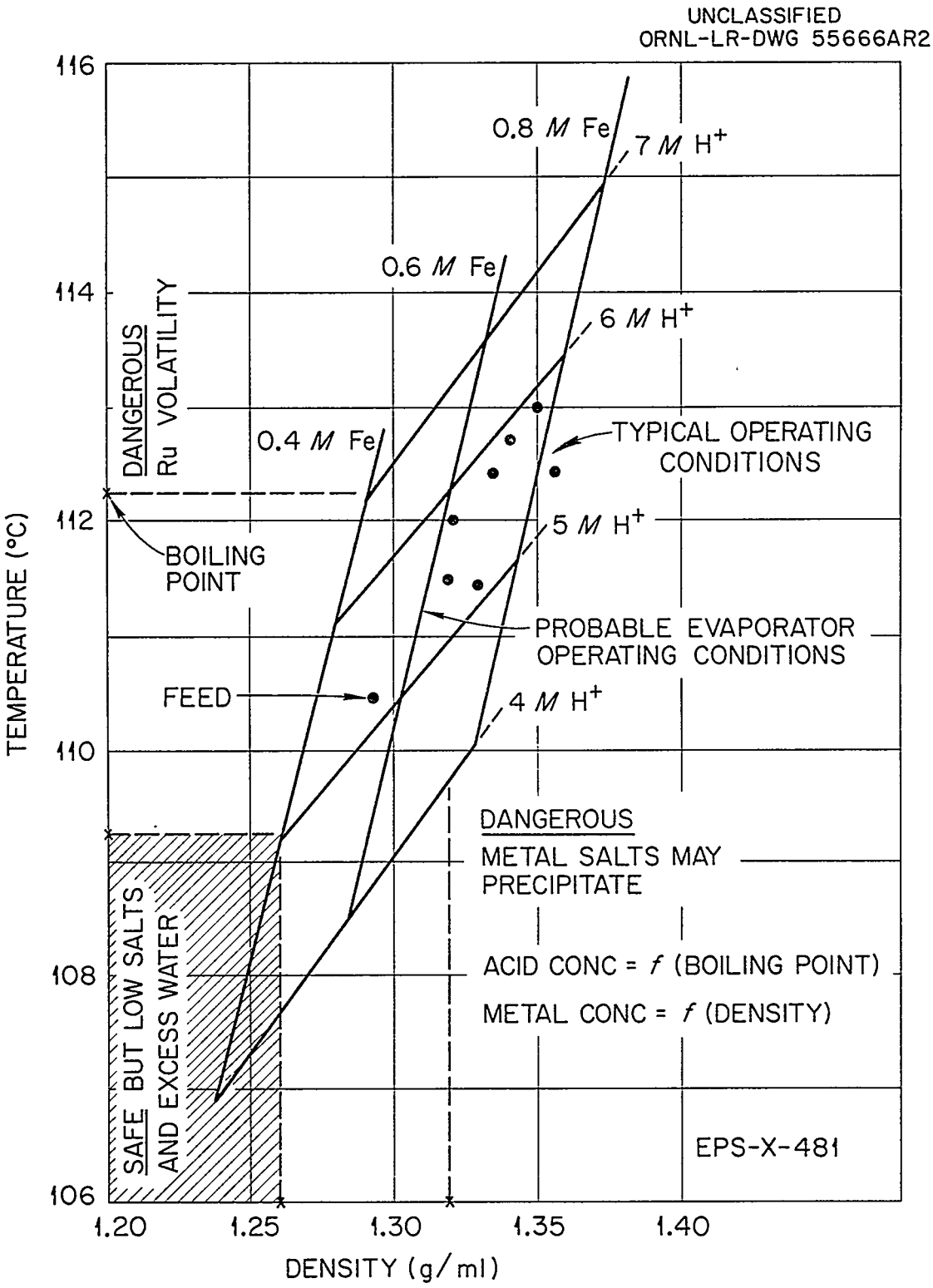


Fig. 2.3. Boiling Point at Atmospheric Pressure vs Density of Purex Waste as Function of Acid and Metal Salt.

4. Pressure in the evaporator, which is kept below atmospheric to prevent outleakage of radioactive off-gas, by regulating the off-gas vacuum pump.

5. Calciner pot liquid level, which was controlled by a differential temperature device consisting of a rod down the center of the calciner pot extending 9-12 in. below the liquid level (Fig.2.4). When the liquid level is above the lower thermocouple but has not reached the rod, the rod is heated by radiation from the walls of the pot. When liquid reaches the end of the rod, the rod begins to transfer its heat to the liquid. The temperature at the thermocouple point is a function of the height of liquid on the thermocouple rod, and, by maintaining a temperature difference of 100°C between the two thermocouples, it is possible to maintain a liquid level 4 in. lower than the thermocouple in the rod. A differential pressure bubbler satisfactorily indicated the calciner liquid level until the latter part of the test when the bubbler tubes became plugged giving a high-liquid-level signal which cut off the feed.

The control results for tests R-42 to R-64 were analyzed on the basis of the following control limits which were found suitable:

	%	
Calciner liquid level	95-20	≈ 57 to 63 liters
Evaporator density	± 5	≈ ± 0.05 g/cc
Evaporator liquid level	± 20	≈ ± 4 liters
Evaporator temperature or conductivity	± 5	≈ ± 0.05 M (HNO_3)
Evaporator pressure	± 2	≈ ± 0.1 psig

In some of the first tests the control was very poor (Tables 2.2-2.6) because of equipment failure, poor signal pickup, range control (proportional band and reset, Table 2.7, and misjudged operating variables. However, during later tests control was much improved.

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

Flowsheets. Purex waste calcination material balance flowsheets were completed for use in the design of the Pot Calcination Pilot Plant at the Idaho Chemical Processing Plant. A revised process flowsheet was issued which incorporates agreed-upon changes in the feed evaporator size, calciner, and fractionator condenser arrangement, calciner pressure relief system, calciner feed system, and the method for determining the composition of the evaporator overhead (a conductivity cell will be installed as an alternative use of the vapor temperature as a measure of its acidity). Detailed design of the equipment based on this flowsheet is proceeding at the ICPP.

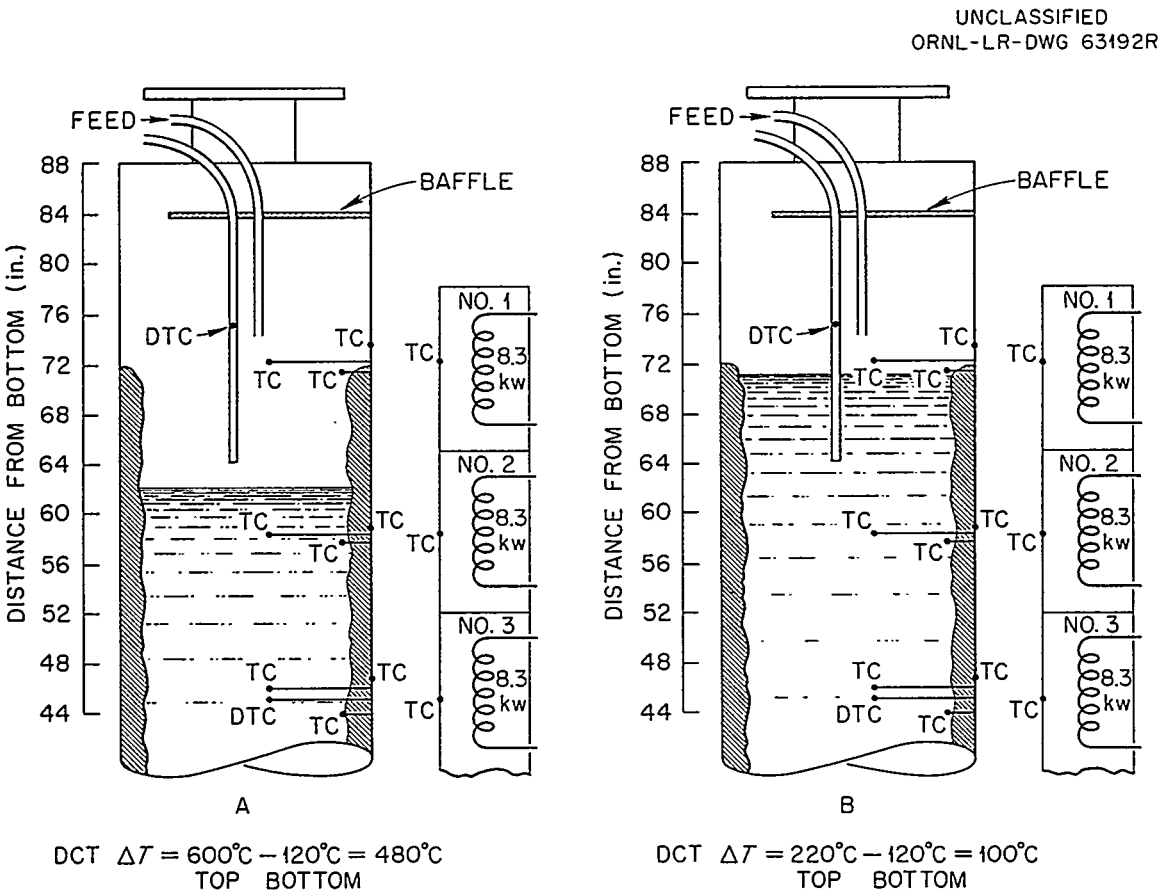


Fig. 2.4. Dual Thermocouple Temperature Control System.

Table 2.2 Calciner Liquid Level Control

Run No.	Over Limits		Under Limits		Outside Limits (% of time)	Total Control Time (hr)	Control Limits (% of range)
	% of time	No. of times	% of time	No. of times			
R-42	3.7	6	25.6	6	29		95-20
R-43	14.2	3	12.7	3	26.9	7.5	95-20
R-44	41.5	9	29.1	9	70.6	15	95-20
R-45*	5.9	6	63.5	12	69.4	11	95-20
R-46*	57.1	2	32.6	3	89.7	15	95-20
R-47	54.1	3	17.7	6	22.8	14	95-20
R-48	11.4	4	15.7	10	27.1	16	95-20
R-49	4.0	2	41.0	5	45.0	12	95-20
R-50	5.6	27	40.8	37	46.4	21	95-20
R-51*	26.7	61	53.8	70	80.5	39	95-20
R-52*	8.1	8	18.0	10	26.1	39	95-20
R-54	17.8	15	61.8	25	79.6	30	95-20
R-55	26.4	22	46.4	59	72.8	28	95-20
R-56	23.5	21	56.4	19	79.9	37	95-20
R-57	0	0	8.8	12	8.8	72	95-20
R-58	3.4	8	52.0	10	55.4	30	95-20
R-59*	0	0	57.3	6	57.3	27	95-20
R-60*	0.6	4	28.4	22	29.0	39	100-20
R-61*	2.3	2	14.1	6	16.4	22	95.20
R-62	8.6	3	10.6	7	19.2	23	95-20
R-63	0	0	16.7	4	16.7	23	95-20
R-64	13.5	1	2.8	3	16.3	32	95-20
Avg.	12.7	9.4	32.1	15.6	44.8	30.0	-

*Batch; other continuous.

Table 2.3 Evaporator Density Control

Run No.	Over Limits		Under Limits		Outside Limits (% time)	Total Control Time	Control Limits (% of set point
	% of time	No. of times	% of time	No. of times			
R-42	96.4	4	3.3	4	99.7	11	± 5
R-43	0	0	85.4	3	85.4	8	± 5
R-44	16.4	1	66.4	3	82.8	6	± 5
R-45*	40.8	5	0	0	40.8	2	± 5
R-46*	Manual						
R-47	8.7	2	63.7	6	72.4	16	± 5
R-48	51.2	7	10.5	5	61.7	16	± 5
R-49	11.1	6	27.8	8	38.9	27	± 2
R-50	21.4	7	17.9	7	39.3	23	± 5
R-51*	0.13	1	8.5	5	8.6	39	± 5
R-52*	0	0	69.7	2	69.7	7	± 5
R-54	79.2	2	17.5	2	96.7	38	± 2
R-55	18.6	3	25.0	6	43.6	25	± 2
R-56	43.0	20	12.6	9	55.6	31	± 2
R-57	0.42	3	3.0	5	3.4	72	± 5
R-58	0	0	4.2	5	4.2	30	± 5
R-59*	Manual						
R-60*	14.1	1	3.2	2	17.3	39	± 5
R-61*	Manual						
R-62	0.04	1	29.0	4	29.1	8	± 5
R-63	3.2	3	13.3	7	16.5	28	± 5
R-64	0	0	1.5	3	1.5	46	± 5
Avg.	21.3	3.5	24.3	4.5	45.6	24.8	-

*Batch; other continuous.

Table 2.4 Evaporator Liquid Level Control

Run No.	Over Limits % of time	Over Limits No. of times	Under Limits % of time	Under Limits No. of times	Outside Limit % time	Total Control Time	Control Limits + and - % of set point
R-42	4.1	4	21.9	5	26.0	22	± 20
R-43	0	0	1.2	3	1.2	15	± 20
R-44	14.7	10	7.1	8	21.8	15	± 20
R-45*	19.9	1	0	0	19.9	15	± 20
R-46*	0	0	0.11	1	0.11	15	± 20
R-47	6.2	4	0.4	1	6.6	20	± 20
R-48	11.1	3	1.8	6	12.9	16	± 20
R-49	0.4	1	1.2	3	1.6	27	± 20
R-50	18.8	14	9.5	12	28.4	24	± 20
R-51*	Manual						
R-52*	Manual						
R-54	12.2	10	2.8	4	15	38	± 20
R-55	6.8	7	2.1	2	8.9	25	± 20
R-56	32.8	17	0	0	32.8	27	± 20
R-57	9.7	6	0	0	9.7	72	± 20
R-58	3.7	3	0.2	1	3.9	39	± 20
R-59*	Manual						
R-60*	Manual						
R-61*	Manual						
R-62	8.6	3	5.6	5	14.2	16	± 20
R-63	8.1	13	0.4	1	8.5	29	± 20
R-64	5.4	5	3.6	3	9.0	38	± 20
Avg.	9.6	5.9	3.4	3.2	13	26.7	-

*Batch; other continuous.

Table 2.5 Evaporator Temperature or Conductivity

Run No.	Over Limit % of time	Over Limit No. of times	Under Limits % of time	Under Limits No. of times	Outside Limit % time	Total Control Time	Control Limits + and - % of set point
R-42	2.3	4	56.3	5	58.6	22	± 5
R-43	16.5	7	12.5	4	29	8	± 5
R-44	3.8	7	48.7	11	52.5	15	± 5
R-45*	2.4	1	32.1	3	34.5	15	± 5
R-46*	0	0	7.5	1	7.5	15	± 5
R-47	23.2	5	45.7	5	68.9	20	± 5
R-48	2.8	2	46.1	8	4.8	16	± 5
R-49	0	0	50.0	5	50.0	12	± 5
R-50	0	0	68.0	8	68.0	23	± 5
R-51*	0	0	1.3	1	1.3	18.42	± 5
R-52*	10.8	3	47.2	11	58.0	38	± 5
R-54	0.3	2	99.3	5	99.6	38	± 5
R-55	6.7	7	34.0	14	40.7	25	± 5
R-56	1.9	3	27.4	9	29.3	31	± 5
R-57	0.2	5	7.1	7	7.3	72	± 4
R-58	1.0	1	22.1	13	22.2	30	± 4
R-59*	Manual						
R-60*	3.4	1	23.7	3	27.1	39	± 4
R-61*	Manual						
R-62	3.8	6	16.2	8	20.0	25	± 5
R-63**	16.4	29	28.2	24	44.6	29	± 15
R-64**	18.0	12	16.0	8	34.0	45	± 15
Avg.	56.8	4.8	34.5	7.6	37.9	26.8	-

*Batch; other continuous.
**Conductivity

Table 2.6 Evaporator Vapor Pressure Control

Run No.	Over Limits % of time	Over Limits No. of times	Under Limits % of time	Under Limits No. of times	Outside Limit % Time	Total Control Time	Control Limits + and - % of set point
R-42	0.68	2	0.3	3	1.0	22	± 2
R-43	15.1	6	0.14	1	15.2	24	± 2
R-44	2.8	16	6.4	15	8.2	23	± 2
R-45*	14.2	6	0.06	1	14.3	27	± 2
R-46*	72.7	8	0.56	2	73.4	15	± 2
R-47	7.3	3	11.1	6	18.4	20	± 2
R-48	6.3	2	46.7	6	53.0	16	± 2
R-49	0.77	2	0.77	3	1.5	13	± 2
R-50	6.3	2	46.7	6	53.0	16	± 2
R-51*	0.3	3	0.81	3	1.1	39	± 2
R-52*	3.1	4	0.17	2	3.3	39	± 2
R-54	9.5	8	4.2	7	13.7	28	± 2
R-55	21.4	8	1.8	9	23.2	28	± 2
R-56	1.1	9	1.1	9	2.2	31	± 2
R-57	0	0	0	0	0	72	± 2
R-58	0	0	0	0	0	30	± 2
R-59*	0	0	0	0	0	31	± 2
R-60*	0	0	0	0	0	39	± 2
R-61*	0	0	0	0	0	31	± 2
R-62	0.33	1	0.	0	0.33	30	± 2
R-63	4.3	15	12.4	4	16.7	39	± 2
R-64	0.6	3	0	0	0.6	49	± 2
Avg.	7.6	4.5	6.1	3.5	13.6	3.0	-

*Batch, other continuous.

Table 2.7 Proportional Bands and Reset Times

Run No.	Cal Liquid Level (PB) (%)	Cal Liquid Level (RS) (min)	Evap Density (PB) (%)	Evap Density (RS) (min)	Evap Liquid Level (PB) (%)	Evap Liquid Level (RS) (min)	Evap Temp (PB) (%)	Evap Temp (RS) (min)	Evap Pressure (PB) (%)	Evap Pressure (RS) (min)
R-42	100	5	200	5	20	5	200	5	25	0.3
R-43	300	50	100	3	25	3	100	3	25	0.3
R-44	300	44	200	3	25	1	60	5	20	0.3
R-45*	300	24	200	3	25	4	75	5	20	0.3
R-46*	300	60	M	M	50	10	60	9	20	3
R-47	200	40	40	9	25	10	60	8	20	0.3
R-48	200	50	200	5	25	10	60	9	20	0.3
R-49	300	0	200	5	25	10	25	9	50	0.3
R-50	200	0	200	9	25	10	25	10	50	0.3
R-51*	200	0	200	9	M	M	25	10	50	0.3
R-52*	200	0	200	10	M	M	25	10	20	0.3
R-53	200	0	200	10	25	10	25	10	20	0.3
R-54	150	0	100	2	25	10	25	8	10	1
R-55	150	0	100	2	25	10	25	8	10	0.3
R-56	150	0	100	2	25	10	25	9	10	1
R-57	150	0	200	10	25	10	25	10	15	1
R-58	200	0	100	10	25	10	25	8	10	0.1
R-59*	200	0	M	M	M	M	M	M	10	0.1
R-60*	100	0	100	10	M	M	25	8	25	1
R-61*	220	0	M	M	M	M	M	M	25	1
R-62	200	240	100	10	25	10	100	10	25	1
R-63	200	240	100	10	40	10	200	8	25	1
R-64	200	240	100	10	40	10	200	10	25	1
Limits	-20%		SP ± 5%		SP ± 20%		SP ± 5%		SP ± 2%	

*Batch, other continuous.

A cell layout for the pilot plant equipment was agreed on. The calciner, evaporator, feed storage tank, feed pump, concentrated feed tank, calciner condenser, condensate hold tank, and fractioning column are to be located in cell 2 of the ICPP Hot Pilot Plant. Cell 1 will contain the fractionator condenser and condensate storage tank along with the racks of stored calciner pots under observation for temperature and pressure buildup. Shielding calculations will determine if unit shielding around the stored pots will be necessary. Substitution of a jet for feeding from the evaporator instead of the proposed air-lift eliminated the need for installing the evaporator in cell 3, which is a deep cell.

Mercury Trap. A trap for removing mercury compounds from the calciner off-gas stream was designed and fabricated for testing in the Unit Operations pilot plant. It is similar to a cyclone made of 6-in.-dia pipe 22 in. long. The 2-in.-dia inlet enters the vessel tangentially. The 2-in.-dia discharge is 6 in. below the inlet along the vessel axis. The trap will condense mercury compounds along the walls by cooling the gas stream well below its 400°C inlet temperature. The mercury compounds expected to be deposited are mercuric nitrates, mercuric oxide, and possibly some elemental mercury. A laboratory study is being made to determine the optimum temperature for operating the trap. Nozzles are provided in the trap for spraying the deposited solids with nitric acid after each run to dissolve them for simple disposal to the waste tanks. However, it may be possible to eliminate this wash by maintaining the trap temperature sufficiently low to permit incipient vapor condensation during operation. The walls of the trap may then be washed free of mercury and a disposable solution will result. A nozzle is also provided in the gas inlet to permit steam or water addition to the vapor feed in case of plugging during operation.

Mechanical Test Program. A development program for testing the mechanical operations during pot calcination is underway at the Lockheed Nuclear Products Facility at Georgia Nuclear Laboratories. Equipment design for the filling station and calcination pot was completed at ORNL and sent out for bid. The furnace dolly and mockup were delivered to Georgia Nuclear Laboratories and are currently being installed in their hot cell for testing.

Calculations (3) indicate that the probable internal pressures to cause rupture of an 8-in.-dia type 304L stainless steel pot calciner with a minimum wall thickness of 0.282 in. at a temperature of 1700°F are 100 psi for rupture in 100 hr, 235 psi for rupture in 1 hr, and 840 psi for rupture in 5 min. The design criteria for the pots during calcination was set at 10 psi for 100 hr at a calcination temperature of 1700°F. During final storage of the calcined waste, the criterion is 200 psi at 600°F wall temperature, which includes 1/8 in. corrosion allowance.

The closure test specimens (4) were welded at the Georgia Nuclear Laboratories and are now being leak tested. Environmental conditions during leak testing involve cycling the temperature between 25 and 300°C at 150 psi internal pressure to simulate pot storage conditions. To date, leak rates on three of the specimens have been less than 0.2 standard cubic centimeters of helium gas per year determined by a helium mass spectrometer leak detector. This is excellent in comparison to the specified 32 cc/yr maximum permissible leak rate.

The initial leak test on the Grayloc was unsuccessful because of a visible nick in the Grayloc seal ring, which limited the maximum obtainable vacuum to 40 μ Hg. Replacement of the seal ring permitted a vacuum of 10 μ Hg to be obtained. Leak rates will be determined under the same environmental conditions used for the welded closures.

Temperature Control During Calcination (S. H. Jury). A mathematical study was initiated to predict the control pattern for a pot during calcination. Calculations showed that during the course of radioactive-waste calcination the temperature throughout the cake that forms along the wall, leaving an internal cavity, in the calciner is less than the wall temperature until the cake reaches a certain critical thickness, dependent on the parameter QR^2/k, where Q is the radioactive heat generation rate per unit volume of cake, R is the calciner radius, and k is the cake thermal conductivity.

It was also shown that as the cake thickness continues to increase beyond critical thickness, the wall temperature of the calciner must be programmed (Fig. 2.5) to ensure that all portions of the cake are calcined at 1652°F without any portion of the cake exceeding 1652°F. The program in the figure corresponds to a parameter value that is an average for Darex and Purex wastes and a 1-ft-dia calciner. The program is based on the assumption that the calciner will be completely filled with cake.

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

Engineering flowsheets and process piping layouts for the hot cell equipment were completed and approved. Process equipment for study of fission product volatility during evaporation and calcination of actual high-activity-level wastes from ICPP and HAPO, is to be assembled on a rack in the cell mockup on the third floor of Bldg. 4505, cold tested there, and modified if necessary. When the processing cell becomes available, the equipment will be broken down into three subassemblies and reassembled in the cell.

Because of some uncertainty as to the availability of cell 1 in Bldg. 4507 for this program, alternative locations, cells B-1 and B-2 in Bldg. 3026 and the site of the intended self-sintering pilot pit experiment, are being considered. It was concluded that no modifications would be required to the process equipment to

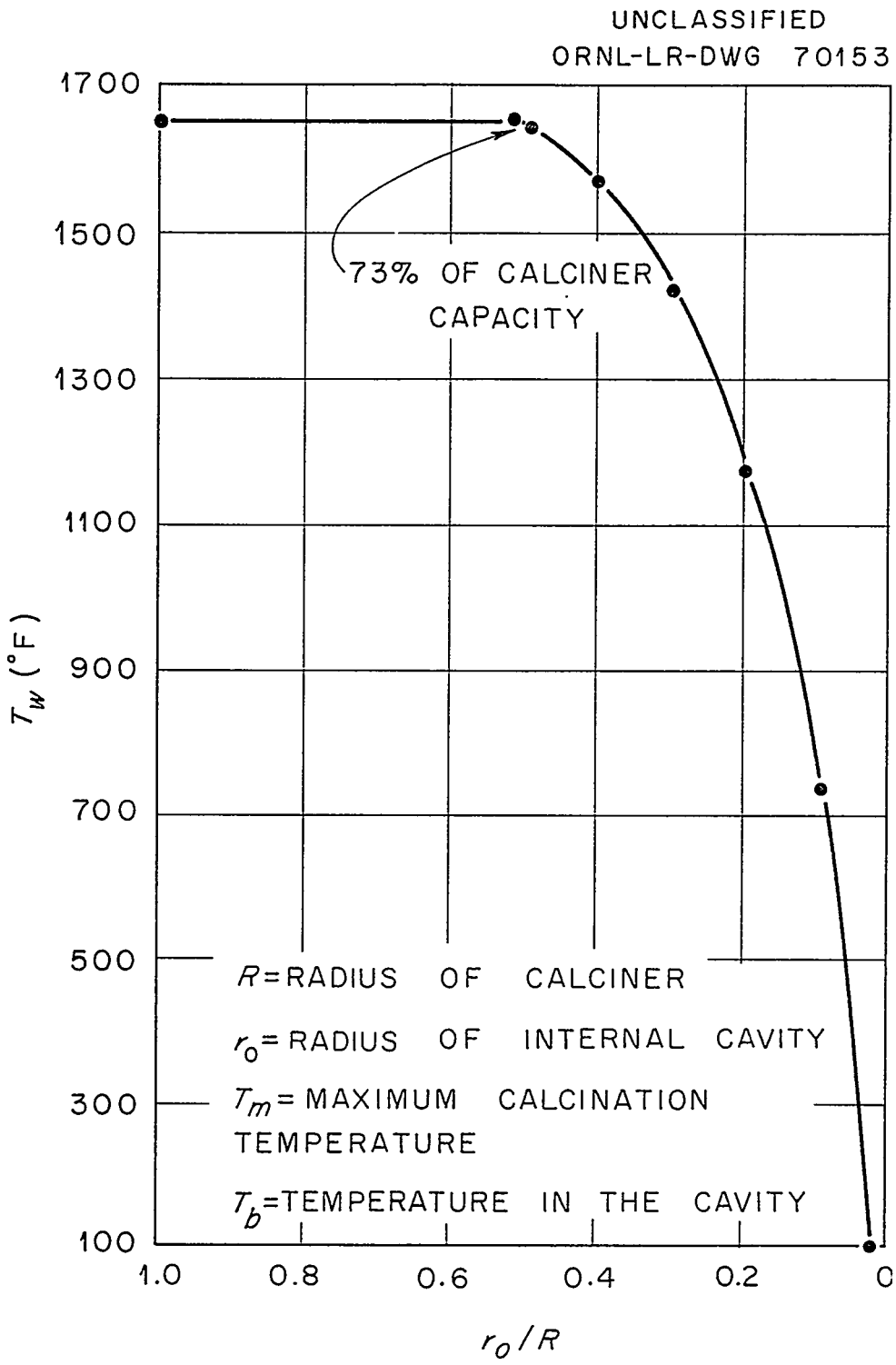


Fig. 2.5. Calciner Wall Temperature (T_w) Program That Ensures Uniform Calcination at T_m = 1652°F as the Solution-Solid Boundary Location, r_0/R, Moles Inward. T_b = 302°F (150°C); QR^2/k = 9250°F.

adapt it to operation in Bldg. 3026 but that some modifications or addition to auxiliary equipment would be required. Some modification of process equipment would be required for operation in the self-sintering pilot pit site, the details of which are still under study.

2.4 Laboratory-Scale Fixation

Ruthenium Volatility (W. E. Clark). Gillespie still studies of ruthenium volatility during evaporation of acid nitrate solutions confirmed the value of phosphite addition to TBP-25, Darex, and Purex solutions as well as to solutions of pure nitric acid (5) and reconfirmed the well known fact that ruthenium volatility varies with the species present (Table 2.8).

Lowering the distillation pressure from 750 to 570 mm Hg did not decrease the ruthenium volatility with respect to that of nitric acid in the absence of aluminum nitrate or other salts. Addition of ruthenium as the nitrosohydroxide instead of the chloride to 6 M HNO_3 increased the activity of ruthenium in the distillate from 2×10^3 to 3.76×10^5 c/min.ml and decreased the separation factor of nitric acid from ruthenium from 30 to 0.126. Addition of 0.1 M H_3PO_3 to the solution before distillation decreased the activity of volatilized ruthenium to 1.45×10^2 c/min.ml for an initial solution of comparable activity. The separation factor for nitric acid increased to 364. For the solutions studied, the addition of 0.1 M H_3PO_3 lowered the ruthenium distillation factor, Ru(vapor)/Ru(liquid), by factors which varied from 38.8 for simulated Darex waste solution to 2920 for 6 M HNO_3. The corresponding separation factors for nitric acid were increased by factors varying from 38.4 to 2866 (Table 2.9).

Of the three types of simulated waste solutions studied, aluminum-containing waste (TBP-25) showed the highest separation factors for nitric acid, 4920 with the addition of 0.1 M H_3PO_3 and 13.8 without. Corresponding values for Purex and Darex wastes were 2.21 and 117, and 1.49 and 57.4, respectively. Allowing the Darex solution to stand overnight after the addition of 0.1 M H_3PO_3 lowered the separation factor from 57.4 to 38.9 (Table 2.8). Apparently some of the phosphite was oxidized on standing.

These data and those previously reported (5) were from experiments carried out under carefully controlled conditions and probably cannot be quantitatively reproduced with real process waste solutions. Also, the total volume reduction in the present studies was only 6.9% rather than 30-50%, which may be desired prior to waste calcination. The data show that ruthenium volatility can be reproduced fairly accurately under given conditions, which should allow accurate predictions of the volatility for changes in a given system. The volatilities reported here for solutions containing no phosphite probably represent about the maximum to be expected. In a practical system an appreciable amount of

Table 2.8 Volatilization of Ruthenium from Nitric Acid Solutions

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

Feed		HNO_3, M										
Designation	Free HNO_3 (M)	In Vapor	In Liquid	HNO_3 Distillation Factor $HNO_3(V)/HNO_3(L)$	Ru-106 in Feed (10^5 counts/min.ml)	Ru-106 in Vapor (counts/min.ml)	Ru-106 in Liquid (10^5 counts/min.ml)	Ru Distillation Factor Ru(V)/Ru(L)	Separation Factor HNO_3 from Ru $\frac{HNO_3(V)}{HNO_3(L)} / \frac{Ru(V)}{Ru(L)}$	Temperature (°C) Equilibrium Stillhead	Stillpot	Pressure (mm Hg)
HNO_3 (control)[b]	6	0.79	6.39	0.124	3.88	1.67×10^3	4.04	4.14×10^{-3}	30.7	107.5	109	~748
HNO_3	6	0.79	6.39	0.124	3.52	2.08×10^3	3.78	5.50×10^{-3}	22.5	101	102	570
HNO_3	6	0.79	6.39	0.124	3.38	2.13×10^3	3.63	5.86×10^{-3}	21.2	101.5	102	~570
HNO_3	15.8	15.8	15.8	1.0	3.58	2.45×10^5	3.67	0.668	1.497	119.5	111	748.9
HNO_3 aged[c]	6	0.65	6.40	0.102	3.52	1.26×10^3	3.78	3.33×10^{-3}	30.5	100	101	559
HNO_3 + $Ru(NO)(OH)_3$	6	0.89	6.38	0.140	3.42	3.76×10^5	3.40	1.105	0.126	108	109.5	745.6
HNO_3 + $Ru(NO)(OH)_3$ + 0.1 M H_3PO_3	6	0.88	6.38	0.138	3.56	1.45×10^2	3.83	3.79×10^{-4}	364	108	109.5	745.8
TBP-25 waste[e]	1.26	0.44	1.32	0.333	3.52	9.08×10^3	3.77	2.41×10^{-2}	13.8	110	111	741.7
TBP-25 waste + 0.1 M H_3PO_3	1.26	0.68	1.29	0.527	3.48	40	3.74	1.07×10^{-4}	4920.	110	111	749.4
Darex waste[e]	2	0.84	2.09	0.402	3.32	9.64×10^4	3.58	0.269	1.49	110.5	112	747.7
Darex + 0.1 M H_3PO_3, aged[d]	2	0.83	2.09	0.397	3.47	3.80×10^3	3.73	1.02×10^{-2}	38.9	110	111.5	739.8
Darex + 0.1 M H_3PO_3	2	0.83	2.09	0.397	3.38	2.51×10^3	3.63	6.92×10^{-3}	57.4	110.5	112	752.0
Purex waste[e]	5.6	1.16	5.94	0.195	3.44	3.17×10^4	3.59	8.83×10^{-2}	2.21	110.5	112	752.2
Purex + 0.1 M H_3PO_3	5.6	1.22	5.93	0.206	3.43	6.50×10^2	3.69	1.76×10^{-3}	117	110.5	112	753.6

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

[b] Reported in TM-133.

[c] Solution aged overnight or longer after spiking with Ru-106. Normally Ru-106 was added ~1 hr before distillation.

[d] Solution aged overnight after addition of H_3PO_3; spiked with Ru ~1 hr before distillation.

[e] Waste solution compositions (M): TBP-25: H^+ 1.26, Al^{3+} 1.72, Fe 0.003, Na 0.1, Hg^{++} 0.02, NO_3^- 6.57; Darex: H^+ 2.0, Fe^{3+} 1.21, Cr^{3+} 0.38, Ni^{++} 0.17, Mn^{++} 0.04, Cl^- 0.001, NO_3^- 7.19; Purex: H^+ 5.6, Al^{3+} 0.1, Fe^{3+} 0.5, Na^+ 0.6, Cr^{3+} 0.01, Ni^{++} 0.01, $SO_4^=$ 1.0, NO_3^- 6.05.

Table 2.9 Effect of 0.1 M H_3PO_3 on Volatilization of Ruthenium During Distillation of Nitrate Solutions

Ru added as $RuCl_3$, 0.002 M, except as indicated; all solutions contained ~1 μc Ru-106 Cl_3

Solution	Reduction Factors: $\frac{Ru(V) \text{ No } H_3PO_3}{Ru(L)H_3PO_3}$	Reduction Factors: Distillation Factor $\frac{[Ru(V)/Ru(L)] \text{ No } H_3PO_3}{[(Ru(V)/Ru(L)] H_3PO_3}$	Increase in Separation Factor for HNO_3 from Ru, $\left(\frac{HNO_3(V)/HNO_3(L)}{Ru(V)/Ru(L)}\right)_{H_3PO_3} \div \left(\frac{HNO_3(V)/HNO_3(L)}{Ru(V)/Ru(L)}\right)_{No\ H_3PO_3}$
12 M HNO_3[a]	420	447	395
6 M HNO_3[b]	2593	2920	2866
1.7 M $Al(NO_3)_3$[a] + 2 M HNO_3	208	204	186
TBP-25 waste[c]	227	225	356
Purex waste[c]	48.8	50.4	53.0
Darex waste[c]	38.4	38.8	38.4

[a]Data from ORNL-TM-133, Table 2.2.

[b]Ruthenium added as the nitrosohydroxide.

[c]See footnote to Table 2.8 for solution compositions.

volatilized ruthenium will normally be deposited on the walls of the still pot above the liquid and will therefore not reach the distillate.

Thermal Conductivity (H. W. Godbee). As reported previously, the thermal conductivity of a phosphate-lead glass incorporating TBP-25 waste oxides varied from about 1.05 Btu/hr·ft·°F at 300°F to about 1.60 Btu/hr·ft·°F at 1050°F (5). Measurements beyond the softening point of the glass, about 1100°F, gave thermal conductivity values of 1.51 Btu/hr·ft·°F at 1140°F and 1.40 Btu/hr·ft·°F at 1150°F. The thermal conductivity of the glass should be somewhat lower after the glass softens since the liquid state represents a more disordered state. Since the apparatus is not designed to measure the conductivity of fluids accurately, measurements on the molten glass were not continued to higher temperatures.

Semi-continuous Glass Formation. A semi-continuous evaporation, calcination, and heating to 1000°C of a simulated TBP-25 waste solution (Table 2.10) containing about 0.1 μc/ml Ru-106 and about 2 μc/ml Pm-147 was carried out in a 24 by 4-in.-dia stainless steel pot. Additives per liter of waste were 2.0 moles NaH_2PO_2 and 0.25 mole PbO. Sodium hypophosphite was added to control ruthenium volatility and to serve as a source of phosphate for glass formation. Lead oxide was added to lower the softening point of the product formed. Promethium was added in order to differentiate between volatilized and physically entrained ruthenium.

The equipment (Fig. 2.6) consisted of a stainless steel pot in a 9-kw furnace, a downdraft condenser, packed absorber column, and off-gas jet. The objectives of the experiment were to minimize ruthenium volatility by adding hypophosphite ($H_2PO_2^-$) and to form a phosphate-lead glass with the oxides from the waste solution. As in the previous similar experiment with stable ruthenium only (5) feed was pumped to the pot at an essentially constant rate of about 50 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. This method of operation gives, after melting begins, three zones in the pot: a zone of molten glass, a zone of calcining solids, and a zone of evaporating liquid.

Solution analyses showed that 11.5, 0.016, and 52.0% of the original Ru-106, Pm-147, and mercury, respectively, were in the condensate (Table 2.10). The analyses for Pm-147 show that, of the total ruthenium volatilized, 0.02% is attributable to physical entrainment. These results with radioactive ruthenium are similar to the previous results (5) with stable ruthenium, 13.7% of original ruthenium in the condensate. The radioactive ruthenium was determined by gamma counting, while the stable ruthenium was analyzed by neutron activation.

Condensate samples taken at various periods during the evaporation-fixation varied rather widely in ruthenium content, indicating that ruthenium volatilization is largely dependent on some operational parameter. This is also indicated by the fact that ruthenium volatility was much lower in batch and small scale continuous experiments (15, 1). Attempts will be made to define these parameters in future experiments in order to obtain better ruthenium control.

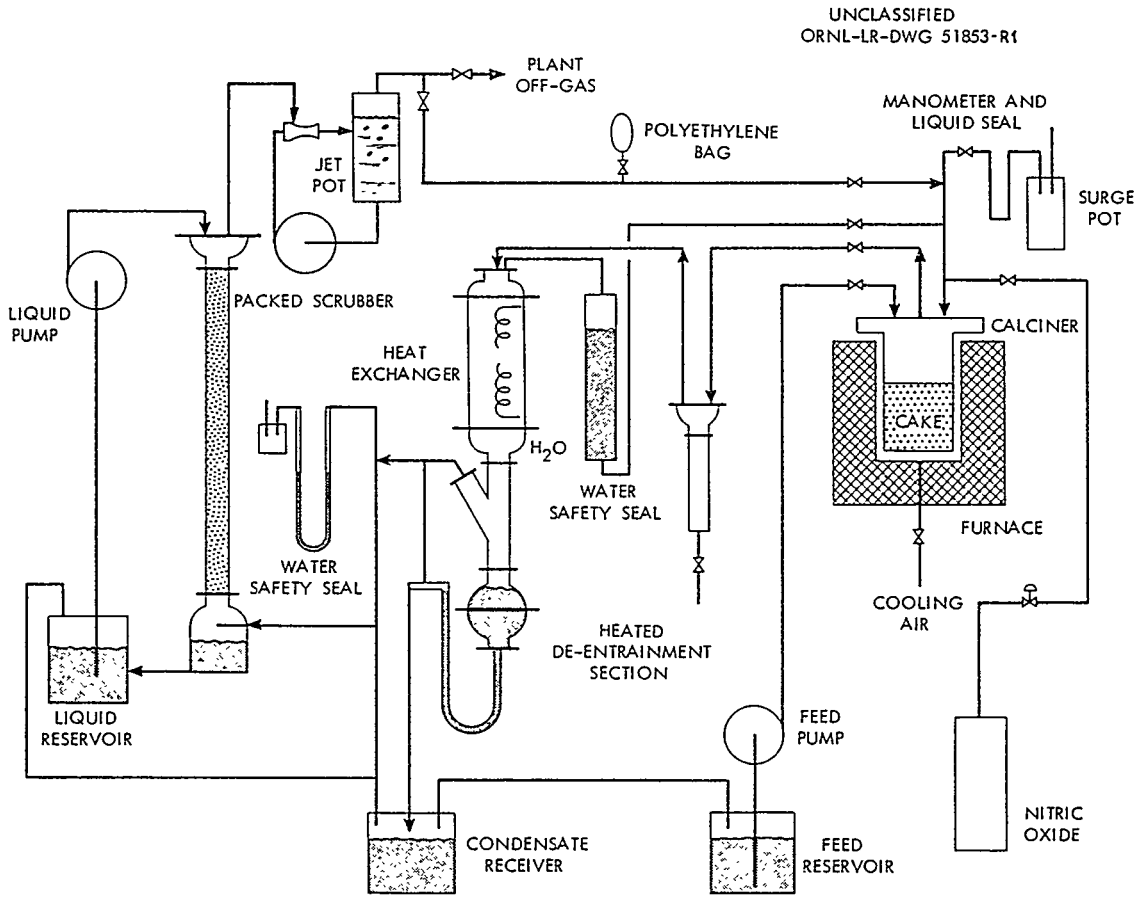


Fig. 2.6. Schematic of Apparatus for Evaporating Calcining and Melting Wastes and Scrubbing Volatile Ruthenium from Off-Gas.

Table 2.10. System Balances for Semicontinuous Glass Formation at 1000°C with TBP-25 Wastes

Waste composition: 1.72 M Al^{3+}, 0.16 mg/ml Fe^{3+}, 4.0 mg/ml Hg^{2+}, 2.4 mg/ml Na^{+}, 0.05 M NH_4^{+}, 1.26 M H^{+}, 0.2 mg/ml Ru, 160 ppm Cl^{-}, 6.6 M NO_3^{-}.

Constituent	vol, ml	dpm/ml	% of Original
		Ru-106	
Feed	21.0×10^3	2.91×10^5	
Condensate	21.2×10^3	3.32×10^4	11.5
Secondary off-gas	2.4×10^3	2.47×10^4	0.95
Jet pot liquid	5.5×10^3	12.8	0.001
Recycle liquid	24×10^3	132	0.05
			12.501
		Pm-147	
Feed	21.0×10^3	4.07×10^6	
Condensate	21.2×10^3	6.47×10^2	0.016
Secondary off-gas	2.4×10^3	2.31×10^2	0.001
Jet pot liquid	5.5×10^3	5.8	.001
Recycle liquid	24×10^3	3.7	0.001
			.019
		Hg	
Feed	21.0×10^3	4.15	
Condensate	21.2×10^3	2.14	52.0
Secondary off-gas	2.4×10^3	0.44	0.6
Jet pot liquid	5.5×10^3	0.02	0.1
Recycle liquid	24×10^3	0.05	1.4
			54.1

Fixation in Glass. Simulated Darex waste solution was incorporated into melts at 850-1050°C (Table 2.11). The products had densities from 2.2 to 3.8 g/cc and represented volume reductions varying from 2.9 to 6.6. The products (except one, melt 6) were glassy only when quenched; when cooled slowly they were crystalline.

Additives, expressed as oxides, used to form melts were Na_2O, B_2O_3, P_2O_5, Al_2O_3, and PbO. Sodium hypophosphite was used in all mixes to control ruthenium volatility. One series to investigate the use of $AlPO_4$ as an additive showed that $AlPO_4$ increased the softening point temperature without improving other properties significantly (Fig. 2.7).

Table 2.11. Phosphate Melts Incorporating Darex Waste Oxides

Waste composition (M): 6.0 NO_3^-, 0.75 H^+, 1.25 Fe^{3+}, 0.38 Cr^{3+}, 0.18 Ni^{2+}, 0.04 Mn^{2+}, 0.003 Ru.

Melt	1	2	3	4	5	6
Additives, moles/liter						
$NaH_2PO_2 \cdot H_2O$	2.0	2.0	2.0	2.0	2.0	2.0
$Na_2B_4O_7 \cdot 10\ H_2O$	---	0.5	0.5	1.0	---	---
B_2O_3	1.0	---	---	---	1.5	---
NaOH	1.0	---	---	---	1.5	3.0
PbO	1.0	---	---	---	---	---
$AlPO_4$	---	---	1.0	2.0	---	4.0
H_3PO_4	---	---	---	---	---	1.0
$NaAlO_2$	---	---	---	---	---	1.0
Melt Composition, wt % theoretical oxides						
Al_2O_3	---	---	8.9	13.9	---	23.5
Fe_2O_3	14.8	22.2	17.4	13.6	20.0	9.2
Na_2O	13.8	20.7	16.2	8.5	21.7	17.2
P_2O_5	21.1	31.5	37.2	38.7	28.4	45.9
B_2O_3	10.3	15.5	12.2	19.0	20.8	---
PbO	33.1	---	---	---	---	---
Cr_2O_3	4.3	6.4	5.0	3.9	5.8	2.7
NiO	2.0	3.0	2.4	1.8	2.7	1.2
MnO_2	0.5	0.8	0.6	0.5	0.7	0.3
RuO_2	0.01	0.01	0.01	0.004	0.01	0.003
Softening point, °C	875	850	875	900	850	900
Bulk Density, g/cc	3.75	2.97	2.88	2.73	2.86	3.17
Waste oxides in melt, wt %	21.6	32.3	25.5	19.9	29.1	13.4
Vol Reduction vol Darex/vol melt	5.6	6.6	5.0	3.7	5.7	2.9
Appearance	brown, hard, microcrystalline	greenish black, glassy if quenched	greenish black, glassy if quenched	blackish brown, flintlike product	greenish black, flintlike product	brown glass

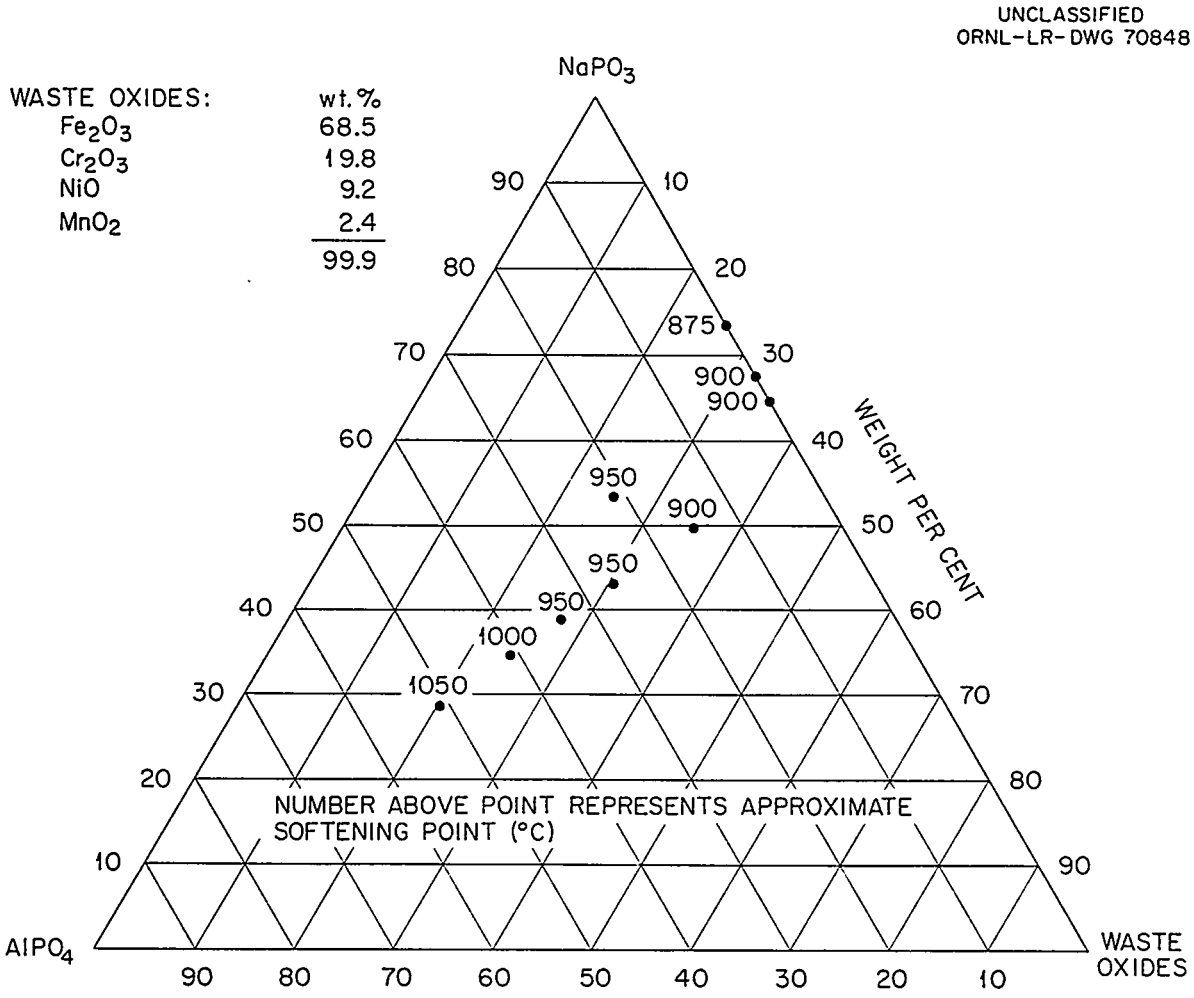


Fig. 2.7. Solid Products Incorporating Darex Waste Oxides.

3.0 LOW-LEVEL WASTE TREATMENT

A scavenging-ion exchange process (6) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations, with ORNL low-activity-level waste as a medium for study. The scavenging-ion exchange process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; the Cs/Na separation factor is 160 for phenolic groups, and 1.5 for sulfonic groups. Other cations, e.g., strontium and rare earths, are also sorbed efficiently. Inorganic ion exchange media, e.g., vermiculite and clinoptilolite, are being studied as alternatives. The waste solution must be clarified prior to ion exchange since ion exchange media do not remove colloidal materials efficiently. Water clarification techniques are being developed for both the ion exchange processes and for the ORNL lime-soda process waste water treatment plant. Work is proceeding on both development and pilot plant programs.

3.1 Pilot Plant (R. E. Brooksbank)

Four demonstration runs were completed (Table 3.1) with ORNL process waste with volumes ranging from 55,000 to 90,000 gal, representing 1980-3118 resin bed volumes. Up to 2000 resin bed volumes, the major contaminants, Sr-90 and Cs-137, were removed by factors >2000 and >70, respectively. Plant effluent contained $<3\%$ of current MPC_w values for these isotopes for a 168-hr week. Run durations varied from 90 to 146 hr of continuous operation.

Operation. In a series of four runs, the first (HR-6) was made to ascertain the resin breakthrough point. After 2000 bed volumes of solution had been transferred through the bed, the Sr-90 and Cs-137 decontamination factors (Table 3.1) agreed favorably with other runs in the series. The Cs-137 isotope was the first to break through the resin bed after 2300 bed volumes, with 50% breakthrough after 2916 bed volumes. (Fig. 3.1). At this point, the plant effluent contained 11.5 d min^{-1} ml^{-1} Sr-90, representing 520% of the MPC_w. At 2711 bed volumes, the total hardness of the resin column effluent increased from <1 to 3.5 ppm (as $CaCO_3$). It has been established that the hardness breakthrough and γ-scanning of the resin bed are reliable methods for predicting isotopic breakthrough. Figure 3.1 represents the breakthrough curve plotted from samples analyzed over the 146-hr operating period. Removal factors (Peak activity of isotope during elution ÷ activity of isotope after 10 bed vol of eluant) for Sr-90 and Cs-137 from the saturated resin bed were 3.14×10^3 and 1.75×10^3, respectively.

In addition to the standard objectives, Run HR-7 was made to observe the performance of the same resin bed used in HR-6 after complete fission product breakthrough. Essentially no ill

Table 3.1 Removal of Activity from ORNL Waste

Run No.	Bed Vol	Gross β		Gross γ		Sr-90		Cs-137		Co-60		TRE	
		DF	% Removed	DF	% Removed	DF	% Removed	DF	% Removed	DF	% Removed	DF	% Removed
HR-6	2046	--	--	--	--	2316	99.96	543	99.82	--			
HR-6[a]	3118	12	91.96	5	77.92	20	95.11	6	82.30	5	80.91	21	95.33
HR-7	2086	34	97.04	19	94.71	12,160	99.99	451	99.78	121	91.80	24	95.77
HR-8[b]	2000	4	71.43	3	65.21	4200	99.98	3444	99.90	2.7	63.33	21	95.22
HR-9	2131	26	95.4	14	93.10	>8196[c]	99.99	~ 77	98.70	12	91.20	56	98.20

[a]An extension to breakthrough.

[b]High-activity run.

[c]None of this isotope found in effluent solution by low-activity analysis methods.

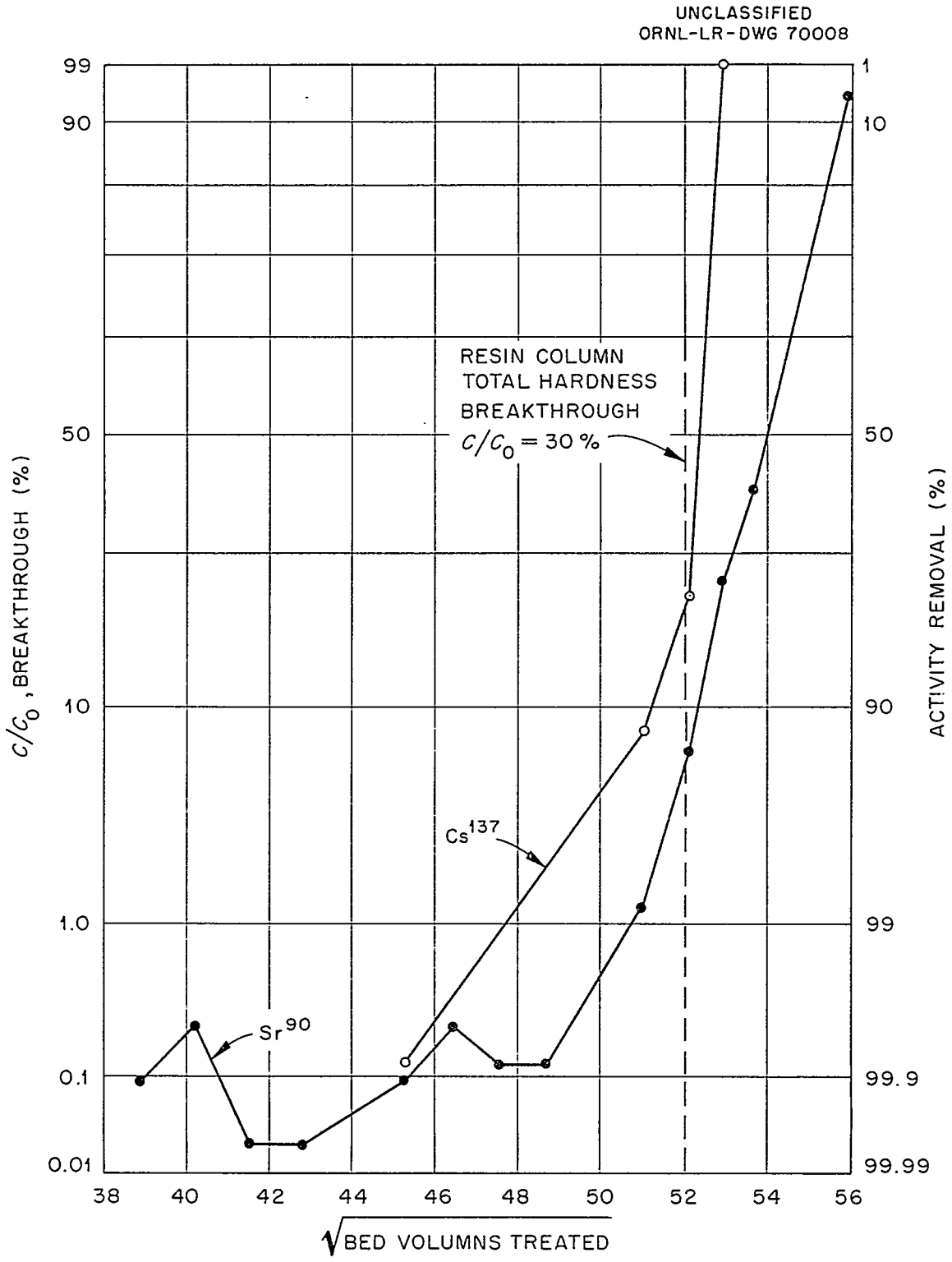


Fig. 3.1. Strontium-90 and Cesium-137 Breakthrough on Duolite Cs-100 Resin (Run HR-6).

effects were noted; decontamination factors and plant effluent fission product analysis results compared favorably with previous runs. The decontamination factor from Sr-90 in this run was the highest observed to date, 12, 160.

During Run HR-8, the plant received a surge of activity in feed solutions to such an extent that the activity of the sludge blanket increased from 20 to 200 mr/hr and that of the resin bed from 4 to 18 mr/hr. The major activity was found to be contributed by Co-60 (150% MPC_w), of which 60% was removed by the process.

Run HR-9 was made with modified sludge withdrawal piping, an inverted flow distributor in the clarifier vessel. These changes were deemed necessary to prevent clogging of the sludge withdrawal holes (3/8-in. dia) in the distribution ring and to provide a more suitable blanket.

Clarifier Hardness Reduction Studies. The major problem of concern in the pilot plant is the excessive total hardness in the clarifier effluent. The average hardness of all runs has been 60-70 ppm (as $CaCO_3$). It is hoped that decreasing this hardness will extend the present maximum on-stream life (81-98 hr) of the polishing filters.

Laboratory jar studies with slaked lime as an additive (25 ppm) to ORNL tap water indicated (Sect. 3.2) that a reduction in hardness may be possible, but in run HR-10, with 12.5 to 25 ppm slaked lime, there was no resultant decrease in clarifier effluent hardness. Later laboratory studies indicated that the temperature of the raw feed should be increased from 18 to 24°C to effect the hardness reduction. An 8-ft^2 heat exchanger has been installed and awaits testing.

At the suggestion of a representative of the Dorr Corporation, a portion of the sludge is being recycled from the clarifier to the flocculator vessel. The total hardness has not been reduced by this change, but the sludge handling characteristics (filterability, blanket distribution, etc.) have been considerably better than previously.

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

The scavenging-ion exchange flowsheet being used in the pilot plant demonstration program requires that the waste water be made 0.01 M in NaOH and 5 ppm in iron, the so-called "standard caustic-copperas" treatment. The hardness is decreased to the specified ~ 10 ppm in the polishing filters by inducing precipitation of $CaCO_3$, which decreases the life of the polishing filters. The laboratory development program has been concerned with breaking the hardness supersaturation, thus allowing removal of hardness in the sludge blanket clarifier and relieving the burden on the filters. Hopefully, an increase in strontium decontamination will accompany the increased calcium removal. A comparison of several treatment methods on ORNL

tap water in standard jar tests (Fig. 3.2) showed that the best residual hardness was obtained with 50 ppm of $Ca(OH)_2$ and 0.01 M NaOH, the standard caustic-copperas treatment being second. Subsequent tests (Fig. 3.3) showed 25 ppm $Ca(OH)_2$ as optimum with residual hardness 18 ppm or less, but from 12.5 to 50 ppm made very little difference in the resulting water quality. The same relative results were obtained when 5 ppm of iron was added to a duplicate series; however, the resulting residual hardness was 50-100% higher. This increase can be explained by a seeding out of precipitate on the $CaCO_3$ particles produced by the rapid reaction of $Ca(OH)_2$ with the bicarbonate ion present in the water. In the presence of iron, a large floc is produced which decreases the surface area of $CaCO_3$ available for seeding. The benefit obtained from the lime addition can be obtained by recirculation of sludge from the clarifier to the flash mixer, but the seeding effect is not quite so good.

Further investigation of the combination lime-caustic-copperas headend treatment showed the reaction to be temperature dependent. Residual hardness was minimum at 26°C (Fig. 3.4). A series of jar tests with the standard caustic-copperas treatment demonstrated a temperature dependence of this process, but not below 35°C.

Other standard jar tests with ORNL tap water showed that the addition of 25 ppm of $CaCO_3$ to the standard caustic-copperas treatment decreased the residual hardness after flocculation from 55 to 38 ppm, as compared to 18 ppm obtained with 25 ppm of $Ca(OH)_2$. Varying the bicarbonate alkalinity of the water from a normal 90 ppm as $CaCO_3$ to 160 ppm had no effect on the resulting water quality obtained with a lime-caustic treatment.

Variations in the flash mixing time (0.5, 5, 10, 20, and 30 min) had no noticeable effect on caustic or lime-caustic treatment either with or without iron as a flocculent. In actual ORNL waste, treatment with caustic or lime-caustic produced residual hardnesses 50-100% higher than that of equivalent tap water, very similar to results obtained when 5 ppm of iron was used as a flocculent with tap water, since the solids present in the waste formed large floc. The addition of 5 ppm of iron in the lime-caustic treatment of tap water increased the residual hardness from 19 to 36 ppm, while, conversely, the same treatment of actual waste improved the residual hardness from 88 to 55 ppm.

A laboratory-scale sludge blanket clarifier (Fig. 3.5) containing an inner cone was constructed for use in rapid evaluation of new process improvements. The unit was operated successfully in a preliminary test at a rate of ~ 250 ml/min with only 10 min holdup in the inner cone. This represents an equipment size reduction of 10 to 20 over the previous laboratory model simulating the pilot plant unit and would result in a corresponding decrease in capital cost of a full-scale plant unit. The unit operating with the standard caustic-copperas treatment and ORNL tap water has produced water with a residual hardness of 8-12 ppm as $CaCO_3$ in initial test runs.

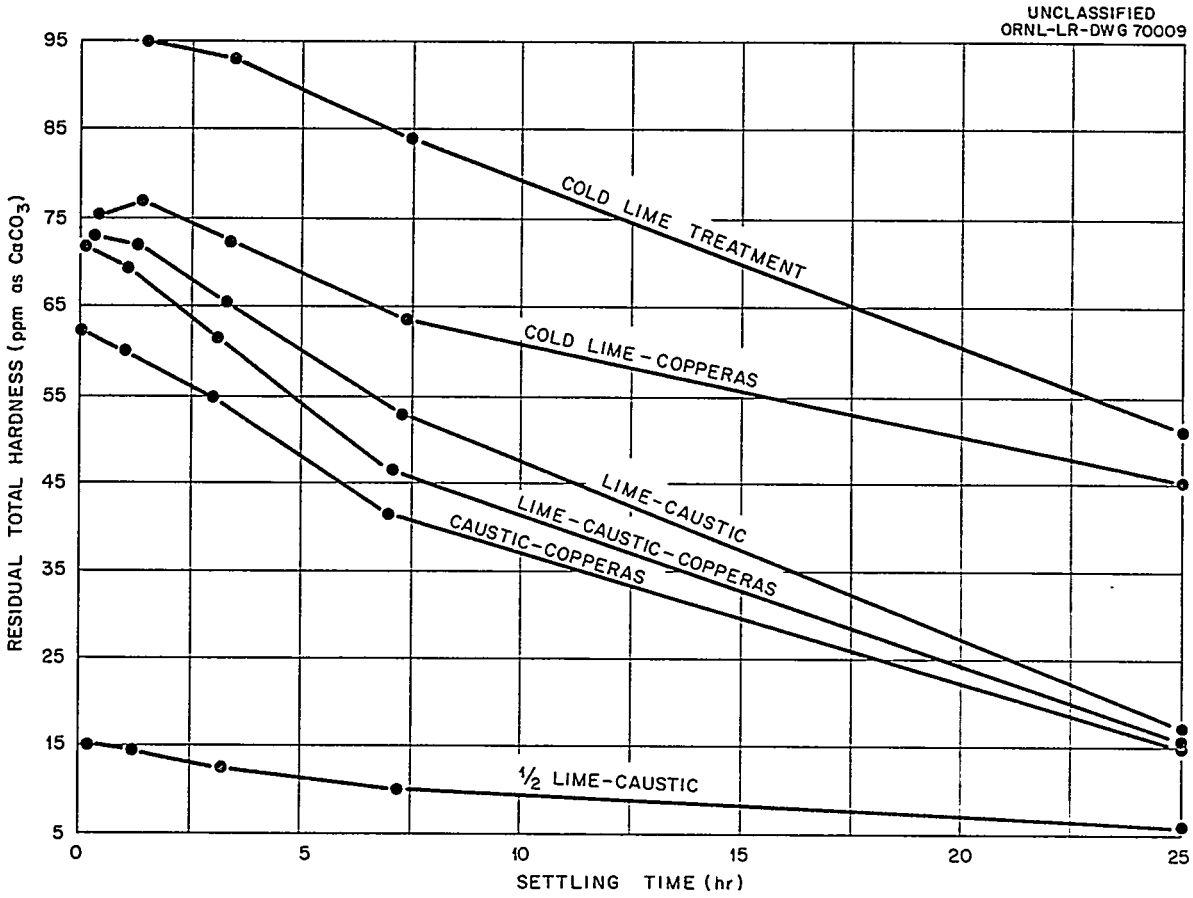


Fig. 3.2. Standard Jar Test Treatment of ORNL Tap Water by Various Methods. TREATMENT CHEMICALS: Lime — 100 ppm $Ca(OH)_2$; Caustic — 0.01 M NaOH; Copperas — 5 ppm Fe.

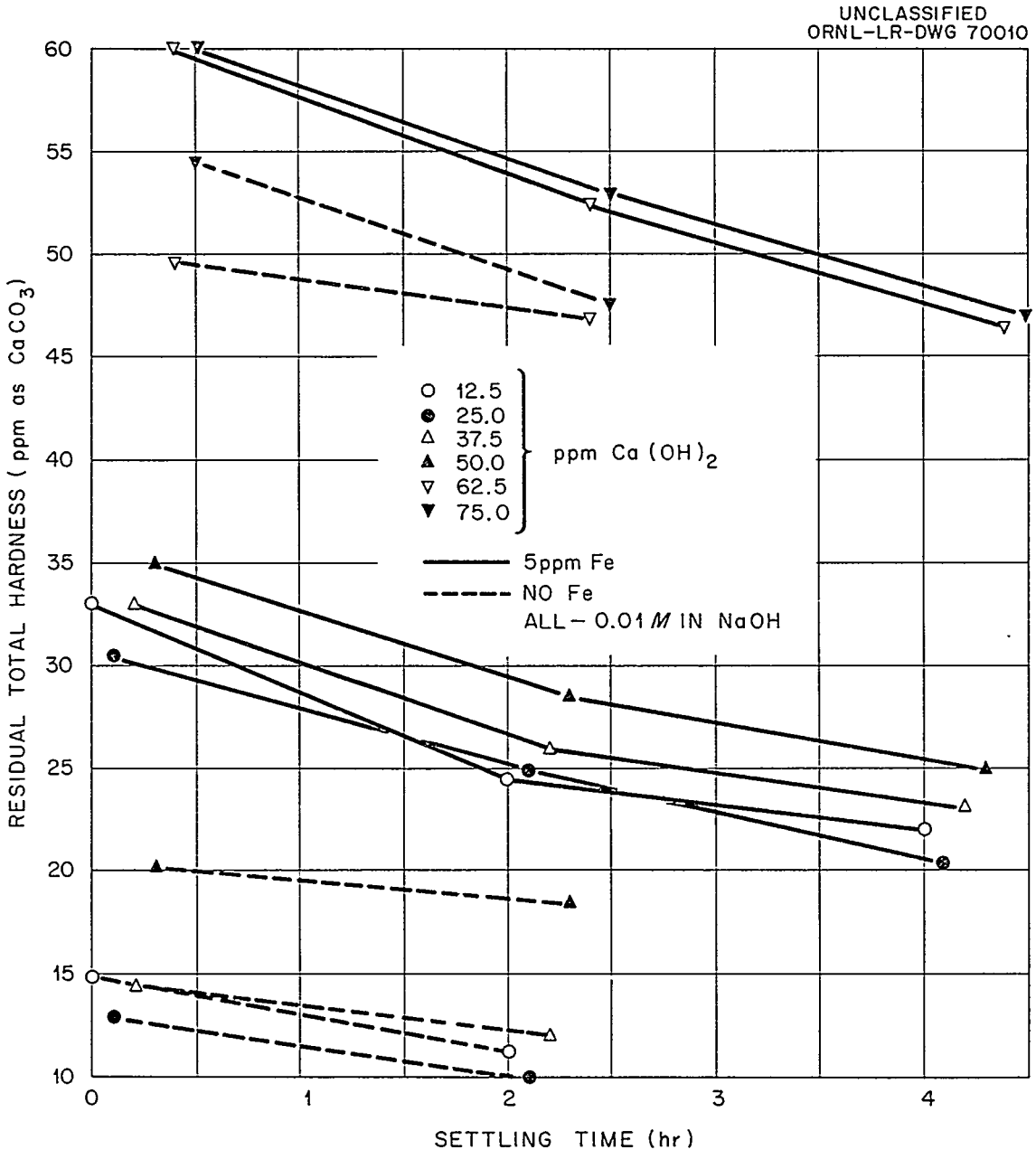


Fig. 3.3. Determination of Optimum Lime Addition to ORNL Tap Water in Standard Jar Tests.

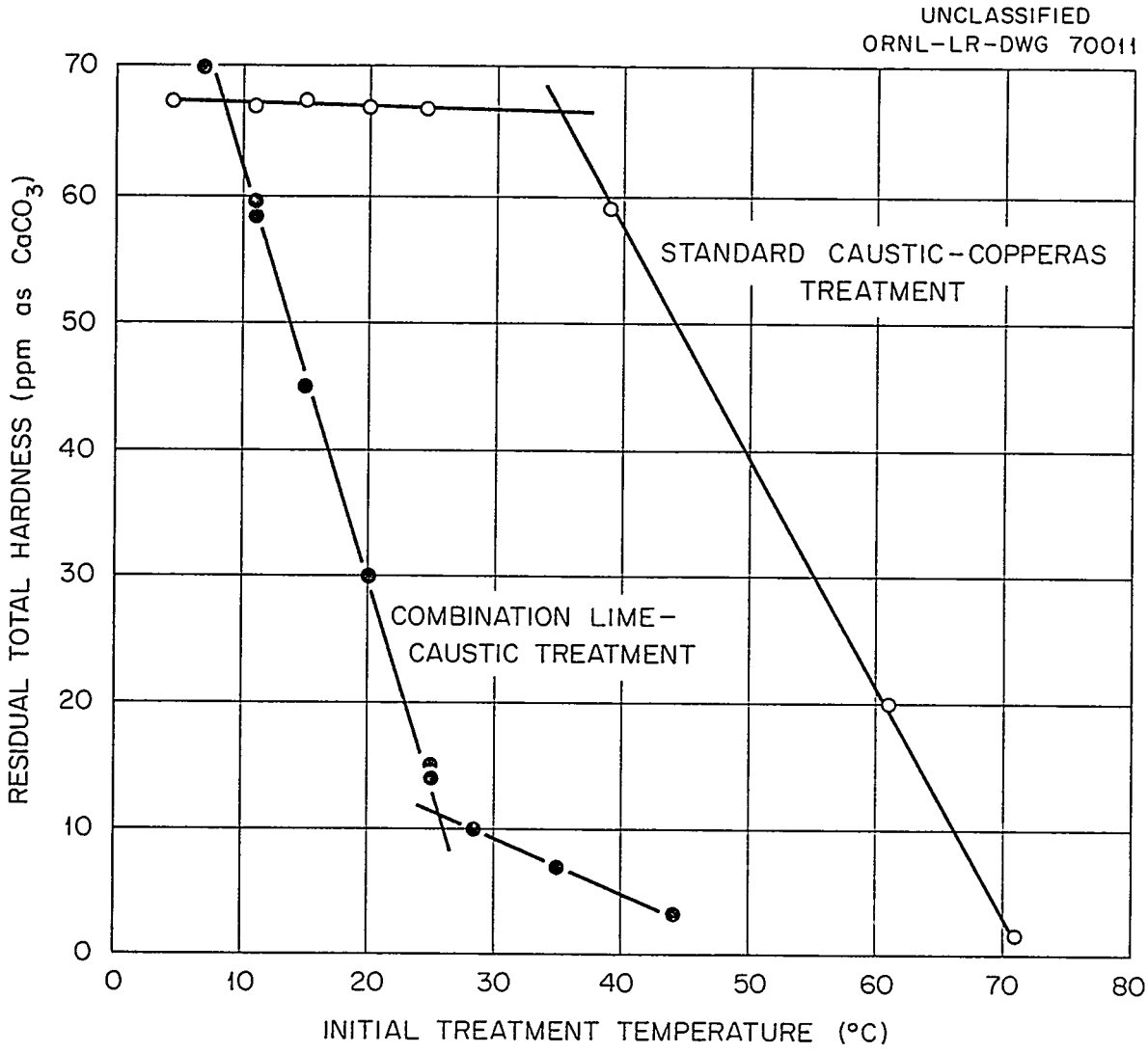


Fig. 3.4. Dependence of Effectiveness on Temperature in Treatment of ORNL Tap Water in Jar Tests.

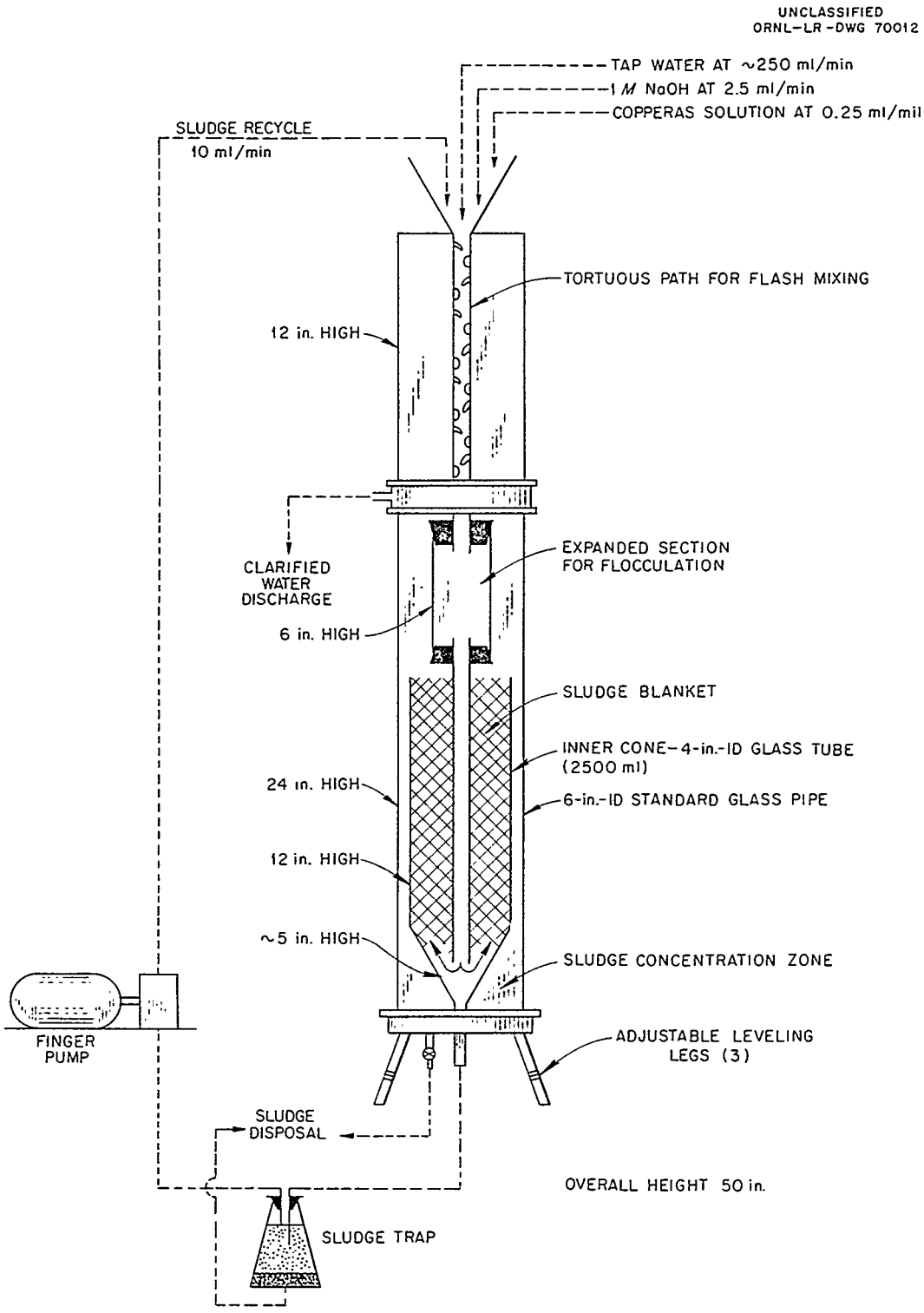


Fig. 3.5. Laboratory Sludge Clarifier.

4.0 ENGINEERING, ECONOMICS, AND HAZARD EVALUATION

R. L. Bradshaw, J. J. Perona, J. O. Blomeke

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.

Based on previously reported (4,5) calculations of salt mine space required to dissipate the heat from liquid and solid wastes a conceptual design of a disposal facility in salt for solid wastes was developed to serve for preliminary cost estimation. In addition, as the first part of a transportation study, thermal calculations were made for carriers required for shipment of pot-calcined solids.

4.1 Economics of Solids Disposal in Salt

In order to determine which variables are important contributors to the cost of storage of solids in salt mines, a conceptual design was developed and some preliminary cost figures were estimated. A more detailed design and cost estimate will be based on these considerations.

In the conceptual design, the waste container shipping cask is removed from a rail car and carried into a hot cell (Fig. 4.1) that encloses the top of the vertical mine shaft. The waste containers are then unloaded in a storage area, from which they are lowered down the shaft into a motorized carrier at the working level of the mine.

The carrier then moves out to the current disposal area (Fig. 4.2), lowers the container into a hole in the floor, and back-fills the hole with fine crushed salt. Concurrently with this operation, salt is being mined in another corridor. The 1-mile-square disposal area is assumed to be served by one set of shafts, and the operation will be conducted so that the salt mining is completely isolated from the disposal operations. Disposal operations personnel and equipment will use the mining shaft for the ingress and egress, however. The criteria of isolation and ventilation require that a double tunnel be driven completely around the quadrant and that the rooms on the outside of the peripheral tunnel be excavated before disposal operations start. Ventilating air will come down a compartment in the mining shaft, with a portion being split off into the disposal tunnel. The disposal tunnel air will travel completely around the quadrant and exist up the waste shaft. The air will be drawn from the shaft, through the hot cell and an absolute filter, and up a 200-ft stack.

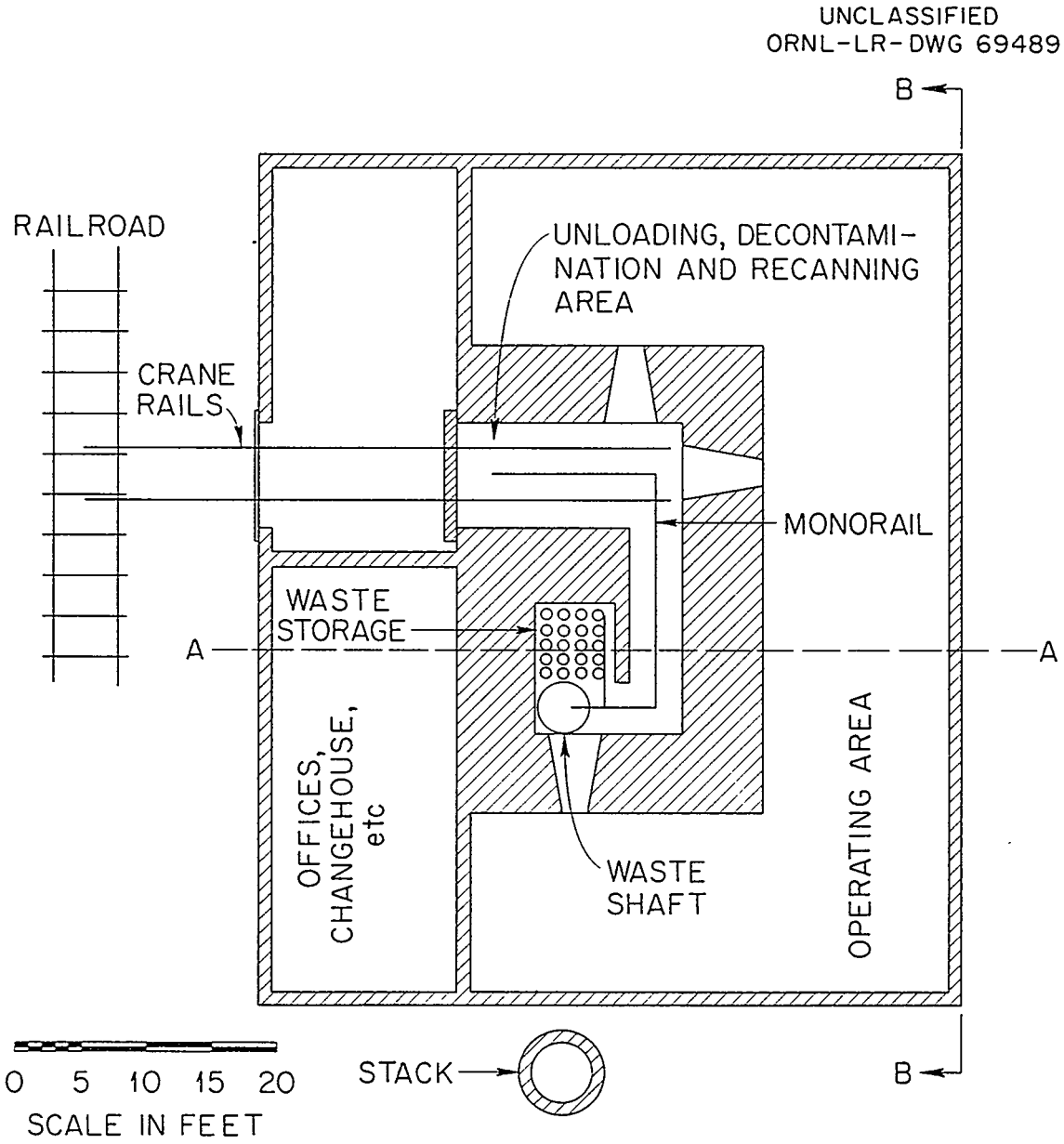


Fig. 4.1. Plan View of Waste-Shaft Surface Facility.

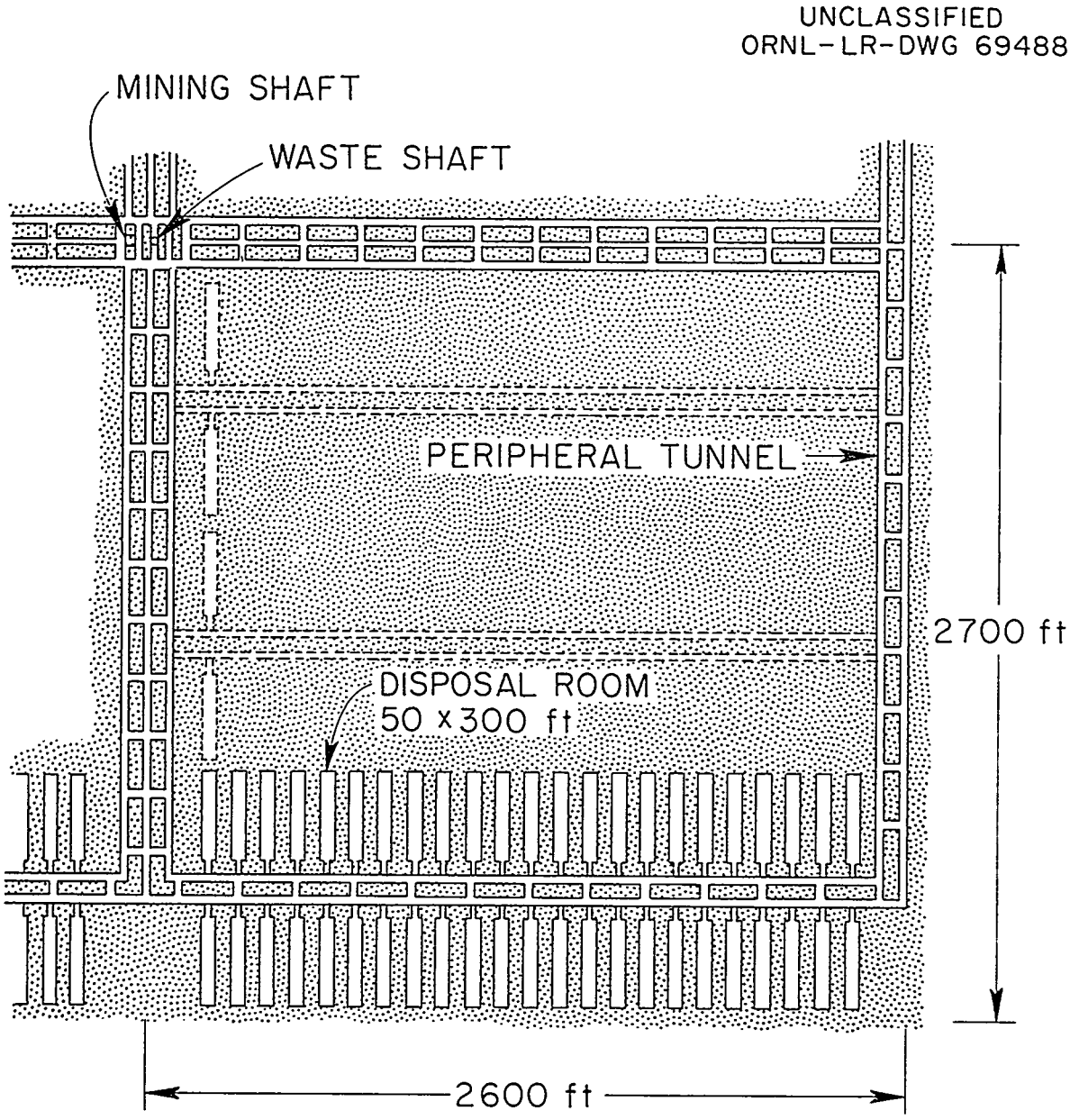


Fig. 4.2. Plan View of One Quadrant of 1-Mile Disposal Area.

In order that ventilating air shall never pass a hot storage area before it reaches the current working area, disposal operations will start at the most remote point and work back toward the shaft. One quadrant will be filled at a time.

The net yearly space requirements for storage of the various waste combinations were given previously (5). The gross requirements are dependent on the allowable salt extraction for a specified room stability condition. If no fission product heat should be involved, the extraction as a function of depth and stability criteria developed in Sect. 6.0 of this report would be adequate. With the presence of heat, the dimensional changes of the rooms due to thermal expansion and plastic flow must also be considered. The problem of predicting the thermal closure of a cavity in salt has not been completely resolved, but an approximate calculation was made for purposes of this study.

Cost figures were calculated for disposal at a depth of 1000 ft for two conditions of stability, one with very small structural flow and 2.5% dimensional closure due to thermal flow, and one with considerable structural flow and 100% thermal closure of the rooms. These figures for typical waste combinations are shown in Table 4.1 for waste ages at burial of 1, 3, 10, and 30 years. The costs of developing peripheral tunnels and storage space are based on an assumed cost of $2 per ton for salt removal. Shafts and life-of-shaft items were amortized over the time required to fill the entire square mile (8.5 years for 1 year's decay with 2.5% closure to 89 years for 30 years' decay with 100% closure). Other items were amortized over 10, 20, or 50 years.

Total costs ranged from 6×10^{-3} mill/kwh$_e$ for 100% room closure with 30-year-decayed wastes to 30×10^{-3} mill/kwh$_e$ for 1-year-decayed and 2.5% closure. Sixty to 85% of the total costs were incurred by salt removal, indicating that it is important to get more accurate figures for this item. It might be possible to sell the salt, thus decreasing these costs. Of the remaining costs, only operating appears to be appreciably more important than the others.

4.2 Shipment of Calcined Solids

Heat-transfer calculations were carried out to determine waste ages and permissible carrier sizes in the absence of refrigerating equipment or liquid coolants. Shipping carriers were assumed to be right circular cylinders, with the inner diameter of each carrier and the number of waste cylinders contained by it determined by the necessity of keeping calcined solid temperatures below the maximum calcination temperature of 1650°F. Waste cylinders were assumed held in square arrays (Fig. 4.3). A spacing structure would be required to hold the cylinders in the array as shown.

Heat transfer between cylinders in the array and between cylinders and the inner surface of the carrier was calculated as

Table 4.1 Cost of Storing Waste in Holes in Floor of Mine at Depth of 1000 ft for Representative Cases

Waste Age and Combination	Cost (1 mills/kwh$_e$ x 10^3)									
				Head Facility		Mine Facilities				
	Storage* Space	Peripheral* Tunnels	Shafts	Life of Shaft Items	10-20-and 50-yr Items	Life of Shaft Items	10-yr Items	20-yr Items	Operation	Total
1-Year										
Reacidified Purex 6-in.dia vessels										
Acidic Thorex 6-in.dia vessels										
2.5% closure	21.70	3.94	1.09	0.73	0.24	0.19	0.28	0.59	1.90	30.60
100% closure	10.70	1.41	0.48	0.33	0.24	0.08	0.28	0.59	1.90	16.00
3-Year										
Acidic Purex 6-in. dia vessels										
Acidic Thorex 12-in.dia vessels										
2.5% closure	10.60	1.94	0.63	0.43	0.24	0.11	0.28	0.15	1.05	15.40
100% closure	5.25	0.75	0.35	0.24	0.24	0.06	0.28	0.15	1.05	8.40
10-Year										
Reacidified Purex filled twice, 12-in. dia vessels										
Acidic Thorex 12-in.dia vessels										
2.5% closure	8.25	1.54	0.53	0.36	0.24	0.09	0.28	0.15	1.05	12.50
100% closure	4.06	0.61	0.33	0.24	0.24	0.06	0.28	0.15	1.05	7.00
30-Year										
Acidic Purex 12-in.dia vessels										
Acidic Thorex 24-in.dia vessels										
2.5% closure	6.29	1.20	0.44	0.31	0.24	0.08	0.28	0.15	1.05	10.00
100% closure	3.10	0.51	0.31	0.24	0.24	0.06	0.28	0.15	1.05	6.00

*Assumes cost of removing salt = ¢2.00/ton

UNCLASSIFIED
ORNL-LR-DWG 70015

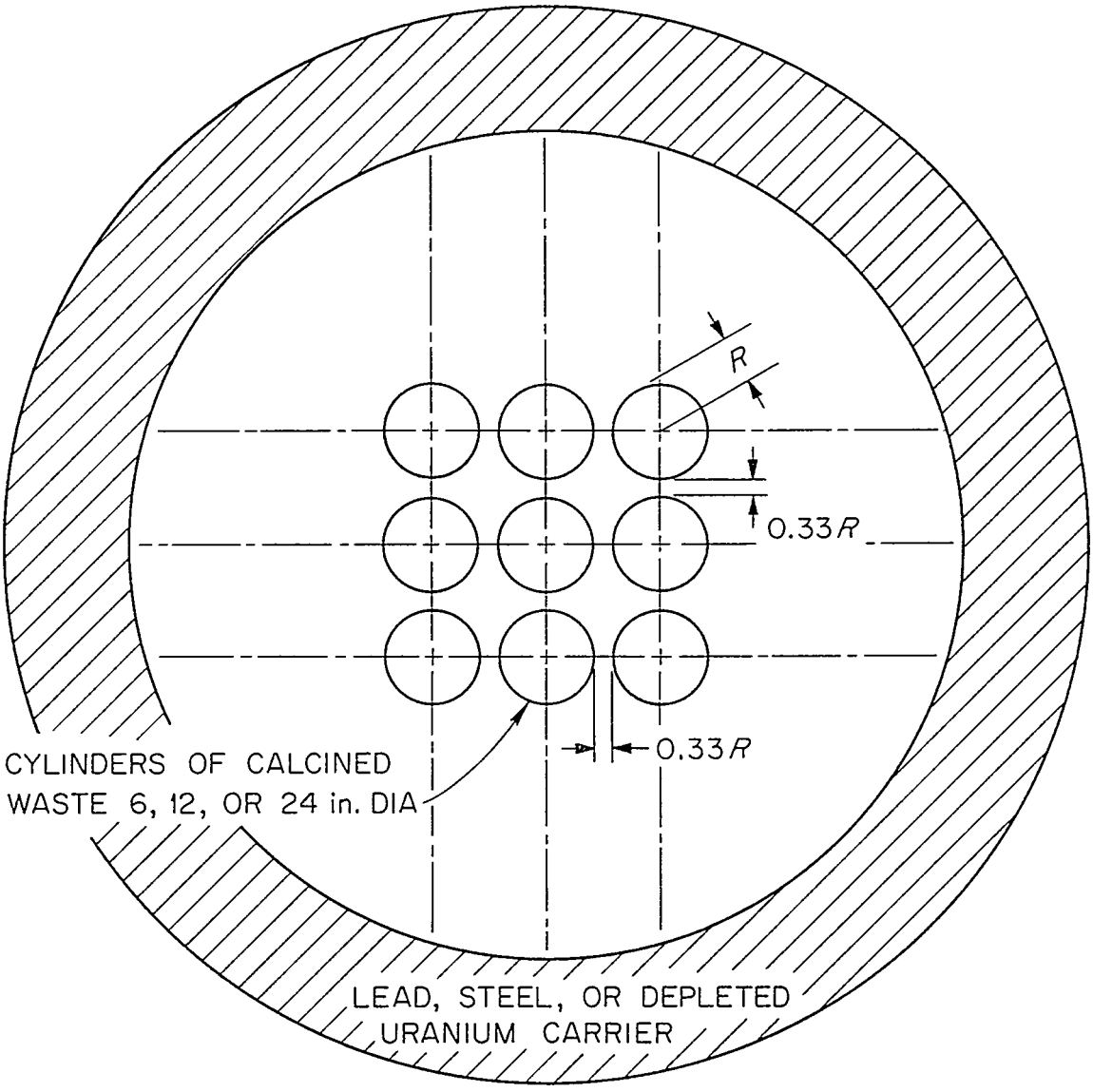


Fig. 4.3. Plan View Sketch of Carriers for Cylinders of Calcined Wastes.

if radiant heat transfer alone was contributing. Cylinders were assumed to have radially symmetric temperature distributions. The conservative procedure of neglecting convective heat transfer and conductive heat transfer through the spacing structure tends to compensate for the less than perfect thermal conductivity of the waste, which would tend to impose secondary asymmetric temperature gradients on the cylinders. Temperatures in the carriers were calculated by methods developed in a study of heat transfer in spent reactor fuel rod assemblies (7). Temperature differences across the carrier wall are small enough that the different thermal conductivities of lead, iron, and uranium do not appreciably affect the final results.

The results of the calculations for 6 and 12-in.-dia cylinders are shown in Fig. 4.4, where the maximum number of cylinders per carrier is shown as a function of age of waste for the various waste types. Acidic Purex can be shipped at less than 2 years of age if fewer than nine 6-in.-dia cylinders per carrier are shipped. A carrier for more than thirty-six 6-in.-dia cylinders or nine 12-in.-dia cylinders would weigh more than 100 tons and was assumed to be unmanageably large. The use of fins was assumed to effectively double the outer surface of the carrier. Thirty-six cylinders of acidic Purex waste can be shipped in a single carrier at 2.9 years of age or 2.4 years of age if the outer surface of the carrier is finned. The maximum numbers of 6- and 12-in.-dia cylinders of reacidified Thorex waste can be shipped at 0.33 year.

Up to four 24-in.-dia cylinders can be shipped in a carrier weighing less than 100 tons. Minimum ages for four 24-in.-dia cylinders are 13 years for acidic Purex (11 years finned), 3.5 years for acidic Thorex, 3.4 years for reacidified Purex, and 0.9 year for reacidified Thorex.

These minimum shipping ages in the absence of mechanical cooling are sufficiently close to minimum burial ages that the expense of mechanical cooling to permit earlier shipping will be justified in only a few cases.

5.0 DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing

5.1.1 Waste Mix Studies (T. Tamura)

Slurries of simulated waste, portland cement, and additives are being investigated by a Laboratory subcontractor, Westco Research, a subsidiary of The Western Company in Fort Worth. The first objective has been to gain a general understanding of the properties of these slurries and to determine the limits of pumpability. Some of the properties measured were consistency, setting time, fluid loss and compressive strength, in most cases by techniques recommended by the American Petroleum Institute (8). The slurries

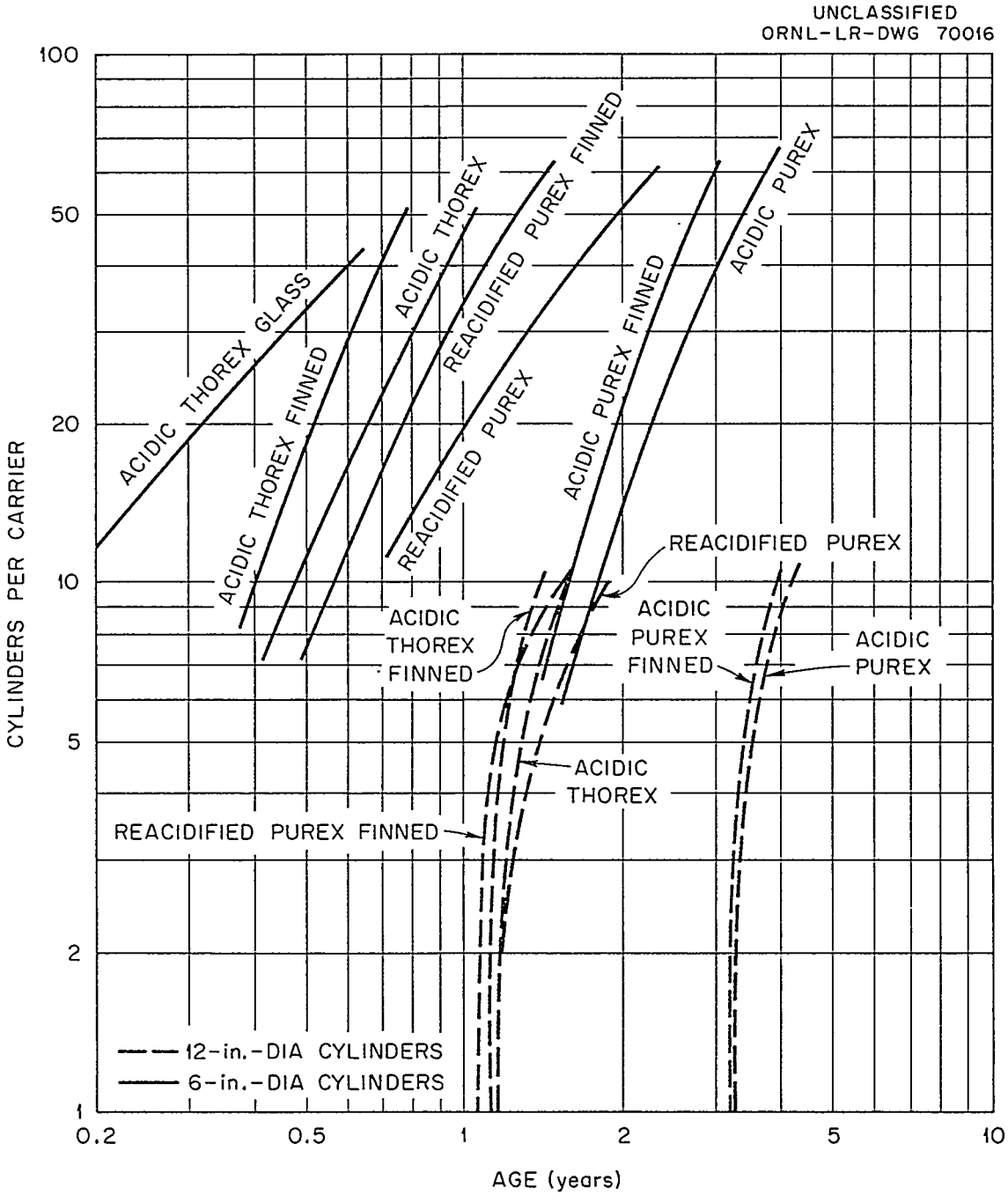


Fig. 4.4. Maximum Permissible Number of Cylinders per Carrier as a Function of Age of Waste to Keep Calcined Solids Temperature Below 1650°F.

are made up of cement from different sources and a simulated waste approximating ORNL intermediate-activity-level waste.

Waste-Cement Slurries. After being mixed in a Waring blender, the slurry is visually inspected for evidence of flash setting, initial gel strength, and viscosity. Flash setting and high initial gel strength are dependent on the chemical composition of the cement and the waste solution, and viscosity is affected by the solution-to-cement ratio and initial hardening processes. Slurries prepared with distilled water as the fluid were easily and thoroughly mixed. Slurries had a high initial gel strength when prepared from Volunteer type I cement and 208 cc of waste solution per pound of cement but not when the proportions of waste solution were larger (Table 5.1). Apparently, close attention will have to be given to the chemical composition of waste and the ratio of waste to cement in designing the ultimate mix. Further studies are underway to identify the constituent(s) in the waste responsible for this initial hardening reaction. A solution cement ratio of 208 cc/454 g is recommended by API for slurries prepared from distilled water and type I cement.

Table 5.1 Quality of Waste-Cement Slurries after Blending

Cement Source	Solution Used	Solution to Cement Ratio (cc/g)	Flash Setting	High Initial gel Strength	Pour-ability
Trinity Cement Co. Dallas, Texas	Distilled water	208/454	no	no	yes
	Distilled water	170/454	no	no	yes
	Distilled water	163/454	no	no	no
	Waste	208/454	no	no	yes
Volunteer Cement Co. Knox., Tenn.	Distilled water	208/454	no	no	yes
	Waste	208/454	no	yes	no
	Waste	220/454	no	no	yes
	Waste	245/454	no	no	yes

Pumpability Tests. Permissible pumping time is one of the most important properties of the waste-cement slurry. The Pan American thickening-time tester simulates conditions of temperature and pressure at a well depth of 2000ft at 91°F bottom-hole temperature and 1540 psi bottom-hole pressure. The value reported as pumping time is the time during which the viscosity of the slurry is less than 100 poises. Increasing the volume of waste from 208 to 245 cc, increased the pumping time from approximately 2-3/4 to 3-3/4 hr (Table 5.2). The latter value is equal to that when 208 cc of distilled water is used. Increasing the sodium nitrate concentration in the synthetic waste solution from 0.3 to 3 M, increased the pumping time to 8 hr, 20 min. These tests also suggested that the

waste composition will have a strong influence on slurry characteristics.

Table 5.2 Pumpability of Waste-Cement Slurries

Volunteer Cement (lb)	Waste Solution Vol (cc)	Pumping Time (hr:min)
2	490	3:40
2	440	3:15
2	416	2:45
2	416*	8:20
2	416**	3:43

*3 M $NaNO_3$ solution.
**Distilled water.

Although the upper limit of 100 poises is used to calculate the thickening time, this viscosity is far too high for pumping. In most cases the viscosity for pumping is held below 20-25 poises.

Compressive Strength Tests. Although the importance of compressive strength in the set grout is not yet clear, compressive strength tests are important for determining the effect of additives on the final grout. The compressive strength was much more sensitive to waste composition when the grout was cured at a higher temperature (Fig. 5.1). It remains relatively constant over a wide range of compositions when cured at 80°F. These mixes contain only waste solution and cement; no additives have been added. Additives such as bentonite, fly ash, and pozmix are often used to keep the cement suspended in the mix during setting; such additives tend to decrease the compressive strength of the set grout.

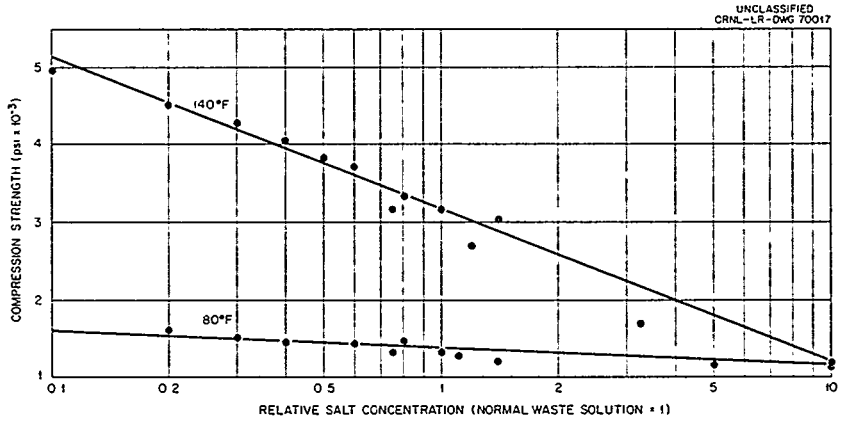


Fig. 5.1. Effect of Waste Composition on the 24-hr Compressive Strength of Grout at 80 and 140°F Curing Temperatures. Grout made from 1 lb of Volunteer Cement Type II and 208 cc of Waste Solution.

Sulfate ion concentration is detrimental to the compressive strength of set cements; in the oil-well cementing industry, special cements are used whenever sulfates are encountered in groundwater. Simulated ORNL intermediate-activity-level waste, which contains about 0.04 M sulfate ions gave a cement with a lower compressive strength than did distilled water, and excess sulfate corresponding to that in the same waste concentrated by a factor of 10 decreased the strength still more (Fig. 5.2).

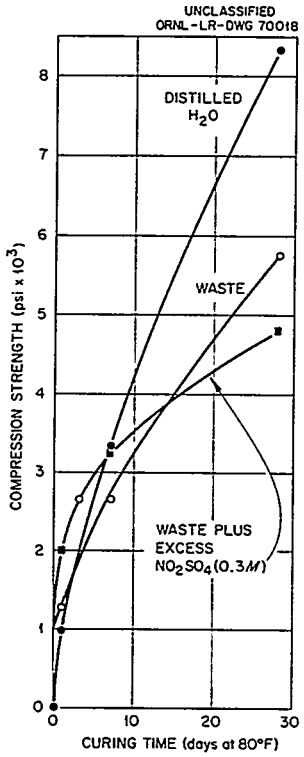


Fig. 5.2. Compressive Strength During Short-Term Curing of Cement.

Since the set grout will be subject to triaxial loading in the shale formation, methods for studying the effects of triaxial loading on properties of the set grout are being advised.

Fluid Loss Additives. The purpose of a fluid-loss additive is to decrease leakage of fluid from the slurry when it is subjected to high confining pressures in the fracture. If hairline cracks are formed during fracturing, liquid may migrate from the slurry into the pores of contiguous rock, and the liquid-deficient grout will set faster. Premature setting will limit the extent of the fracture and possibly decrease the volume of slurry that can be injected.

In the study of the effect of fluid loss, the additive of a proprietary material, CF-1, at approximately 1.3% by weight of the cement, drastically decreased the amount of fluid lost under pressure. The addition of varying amounts of Na_2SO_4 or Na_3PO_4

instead of CF-1 did not improve the slurry fluid loss characteristics. When 50 vol % of the cement was substituted with the proprietary additive pozmix, 1.3% CF-1 was even more effective in reducing fluid loss. The tests were made by applying 100 psi pressure to the slurry in a 3-in.-dia cylinder equipped with a 325 mesh screen. The liquid that flowed out of the cylinder was measured over a 15-min period. (Table 5.3).

Table 5.3 Fluid Loss Data with Volunteer Portland Cement, Type I

Additive	Fluid Loss in 15 min (ml)	
	From Waste	From Water
None	69*	120**
CF-1	18	22
CF-1 + 20% Na_3PO_4	25	35
CF-1 + 40% Na_3PO_4	--	54
CF-1 + 20% Na_2SO_4	60.5	40
CF-1 + 40% Na_2SO_4	24	--
CF-1 + pozmix	8.5	9

*Dehydrated after 30 sec.
**Dehydrated after 40 sec.

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

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

Design of the first high-temperature experiment (High Temperature Cylinder I) related to disposal of high-level radioactive solids in holes in the floor of a salt mine and operation and results of the first test were reported previously (4,5).

High Temperature Array. An array of heaters is necessary to heat a large section of the floor to a temperature above 100°C. The minimum spacing likely to be used between cylinders of calcined waste in an actual operation is about 5 ft.

Seven heaters, 4 ft long, spaced 5 ft on centers in a hexagonal array (Fig. 6.1), with a power input of 3 kw each, appear to be adequate to achieve the objectives of the test. A source of 3 kw and 4-ft length corresponds to the case of a 6-in.-dia pot of reacidified Purex, 10 ft long, filled once, and cooled about 1 year.

The central heater, which will simulate a calcined pot, is a 5-ft length of 6-in. schedule 40 stainless steel pipe, with 4 ft of Cooley clamshell heaters inside. The six peripheral heaters consist of 4 ft of furnace elements in a 2.5-inch tubing. The central heater hole will be 10 in. dia, giving a 1.5-in. annulus for observing possible shattering and/or flow of salt into the hole. Each of the

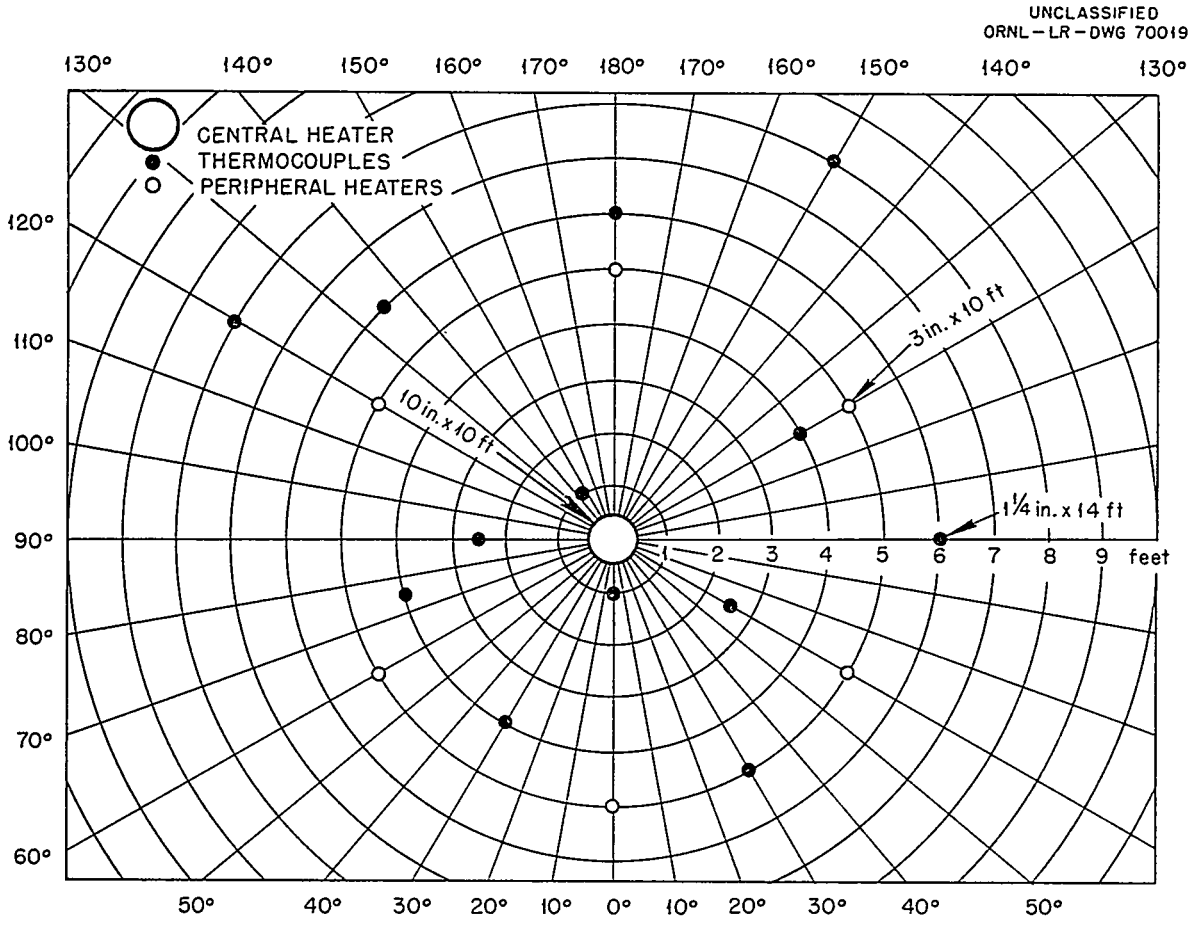


Fig. 6.1. Layout of Array — Minimum Thermocouple Requirements.

13 thermocouple holes will have five couples located at depths of 2, 5, 8, 11, and 14 ft. (The centers of the heaters will be at a depth of 8 ft.) Thermocouples will also be located on the outer side of the central heater pipe, as well as on the elements inside the pipe, and on one or two of the peripheral heater elements.

Because of the occurrence of water in the annulus of the first test hole, all holes in the array have been drilled dry with air as the drilling fluid. However, it now appears that the water may have come from the shale.

Since some water is expected to be released as vapor from the shale bands, a pipe heated to above 100°C will be inserted in the central hole annulus to a point a few inches below the top of the cylindrical heater. The upper end of this heated pipe will be connected to a condenser and be pumped at a rate of 1-5 liters/min to collect the moisture, thus preventing dissolution of salt in the upper section of the hole and recrystallization in the annulus around the heater.

The top of the center hole will be stuffed with insulation bats to prevent convective heat loss to the mine air.

In order to obtain information on thermal expansion and plastic flow, three Reid-type gages and a network of approximately 25 points for precision floor leveling will be installed. Two of the gages will measure floor and ceiling movement at points close to the center of the array and close to the well and the third, column-to-column movement. A similar array of Reid-type gages has been established about 150 ft from the center of the array for comparison. The leveling points will be scattered throughout the array and will be referenced to a point on the floor beyond the influence of the array.

Power to the heaters will be supplied from both of the Heavi-Duty power supplies used in the 7.5-ft tests. The supplies will be operated as voltage regulators with the exact power input set by means of individual variable autotransformers on each heater.

Theoretical temperature rise profiles to be expected in the plane perpendicular to the center of the heaters after 2 weeks' operation are shown in Fig. 6.2 (for comparison purposes, the profile, if only the central heaters are operated, is also shown). These were calculated from the 100°C thermal properties of salt, since the results of the previous test with one heater indicated conductivity and diffusivity values close to this. Since a circular area of about 14 ft in diameter may reach temperatures above 100°C, the effective thermal conductivity and diffusivity values in the array may be those of a higher temperature. The dashed curve was calculated from 200°C properties and shows the profile along the radial through a point midway between two peripheral heaters, the line of minimum temperature rise. It is expected that the actual

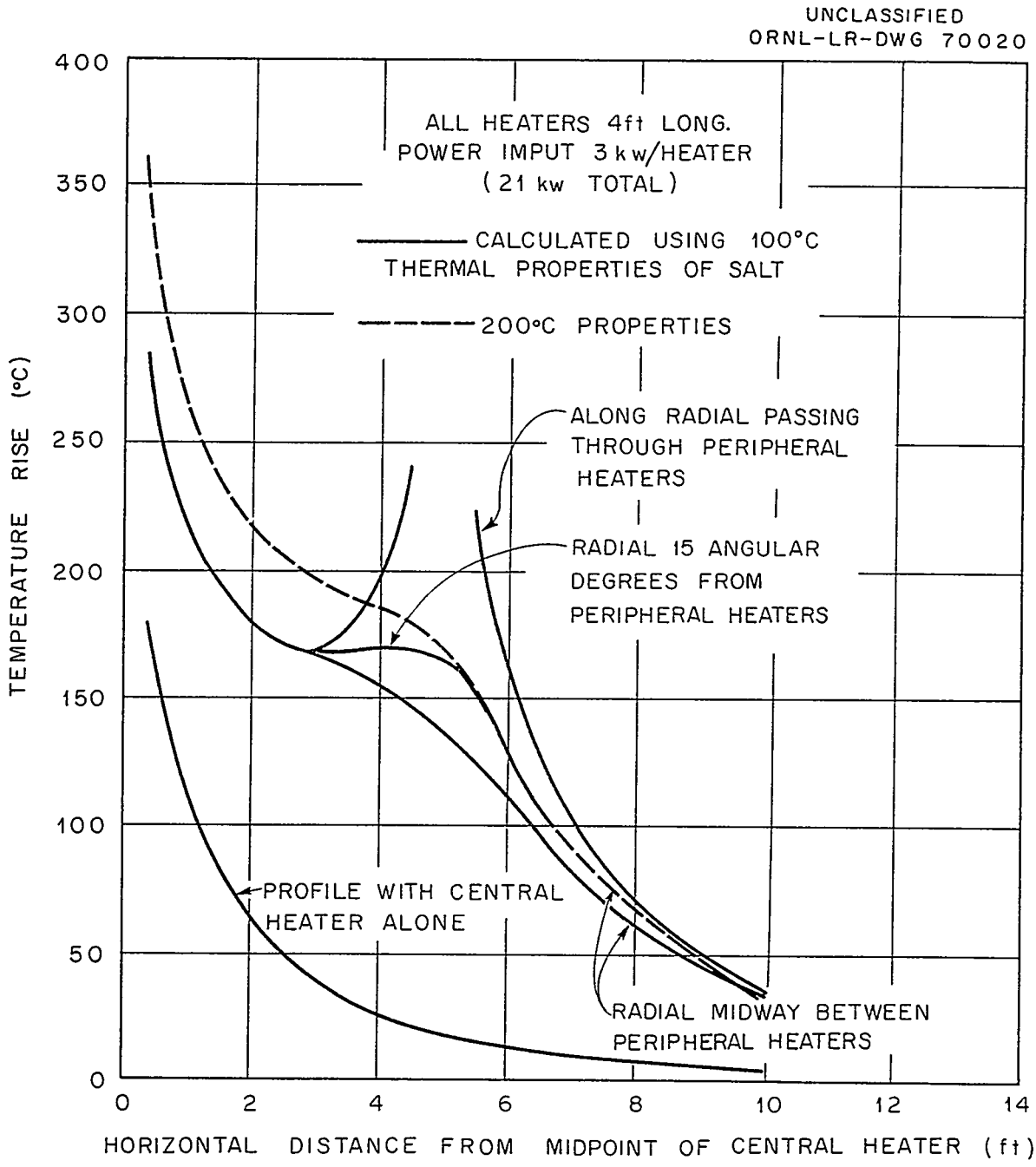


Fig. 6.2. Theoretical Temperature Rise Profiles in High-Temperature Array After Two Weeks Operation.

profile will fall between the 100 and 200°C curves.

The variation in temperature rise to be expected in the vertical direction is indicated by a comparison of curves A, D, and E in Fig. 6.3. These curves, however, are for a single heater and do not show the contributions from peripheral heaters. Curves B and C show the center-plane temperature rise profiles after 4 weeks and infinite times, respectively. After about 2 or 3 weeks, the vertical pattern indicated here will become distorted because of greater losses to the air than to the salt below the heaters. An equilibrium condition in the first 15 ft of depth should be approached in 3 to 4 months.

The central heater hole will be calipered at 1-ft intervals before the installation of the heater. After all heaters and thermocouples are installed, the Reid gages will be installed and the leveling points surveyed. Power will be turned on and adjusted to 3 kw per heater.

After about half a day of operation the temperature of the periphery of the center hole should have been above 100°C for several hours. At this time the center hole will be inspected to see that the water vapor collection system is effective. If not the sweep air will be increased.

Temperatures in the array will be logged continuously. Reid gage readings and leveling-point measurements will be taken periodically as indicated. Additional inspections of the center hole will also be made periodically, probably daily for the first few days.

The test will be terminated after about 3 or 4 months when the temperatures and effects in the vicinity of the experiment have reached equilibrium.

High-Temperature Cylinders II and III. Two tests are planned: one in the floor and one in the wall. The heated cylinders will be duplicates of the center heater in the array. However, the power input will be increased from 3.1 to 4.5 kw so that the peak temperature can be increased from about 200 to 300°C. Also, instrumentation will be provided for measuring floor rise at the floor cylinder and both column expansion and floor-to-ceiling movement about the wall installation. Holes for the high-temperature cylinders are still to be drilled.

After about half a day of operation, a peak salt temperature in excess of 100°C should have existed for several hours. At this time the hole will be inspected to ascertain if the vapor collection system is effective. If not, sweep air will be increased.

Periodic inspection, plastic flow measurements, etc., will be made as dictated by the course of the experiment. The power input

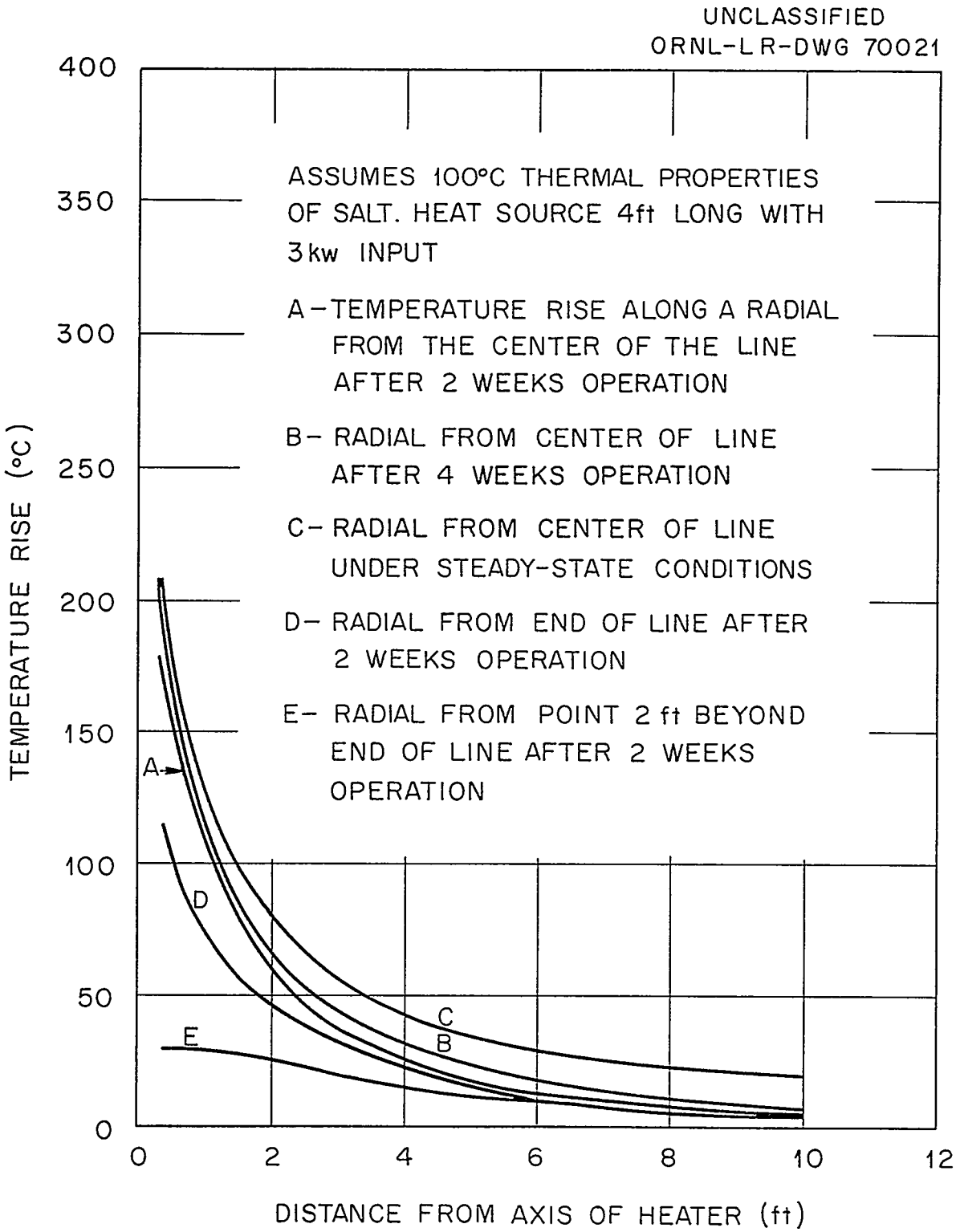


Fig. 6.3. Theoretical Temperature Rise Profiles Around a Line Heat Source.

may be adjusted upward if the desired temperatures are not being reached.

If no shattering of salt has taken place after the temperature has been at about 300°C for a day or so (probably after 1 to 3 weeks), the inner diameter of the hole will be calipered at 1-ft intervals to obtain information on thermal expansion and plastic flow. The experiment may then be restarted and run for 2 or 3 months or until the floor-to-ceiling and column-to-column movements equilibrate.

It is expected that these tests will "overlap" the array test.

6.2 Calculation of Thermal Stresses and Plastic Deformations Around Heat-Generating Cylinders Stored in Salt (W. J. Boegly, Jr., and R. E. Glover, Consultant)

The ability of salt to flow under stress will permit, when the overburden pressure is sufficiently large, the development of horizontal pressures approaching a hydrostatic state. Stress measurements in the Winnfield mine (9) at a depth of 800 ft have shown that the stresses in the horizontal directions were substantially the same as the pressure due to the overburden. These horizontally acting pressures will remain in the floor of rooms formed by the excavation of the salt. If vertical holes are drilled in the mine floor, these stresses will be relieved at the surface of the hole; and, if the salt acts elastically, the stresses in the salt surrounding the hole can be calculated from equations

$$\sigma_r = \left(1 - \frac{a^2}{r^2}\right) p_o \qquad \text{and} \qquad \sigma_\theta = \left(1 + \frac{a^2}{r^2}\right) p_o \qquad (1)$$

where σ_r = radial stress (psi)

σ_θ = tangential stress (psi)

a = radius of the hole (in.)

r = radius of the point at which the stress is desired (in.)

p_o = overburden pressure (psi)

These equations show that at the edge of the hole where $r = a$, the tangential stress is equal to $2p_o$ and the radial stress is 0. This tangential stress ($2p_o$) may be high enough to initiate plastic movement even before thermal stresses are produced. Due to the small fraction of the overburden pressure adjacent to the hole, the vertically acting stress, σ_z, will be nil and can be assumed to be 0.

In order to develop the equations for the plastic state, the criterion of Tresca (10) has been used. Tresca's yield criterion is that yielding will occur when the maximum shear stress reaches a certain value, Y, and can be expressed as

$$\sigma_1 - \sigma_3 = Y$$

where $\sigma_1 \geq \sigma_2 \geq \sigma_3$. (2)

Since the vertically acting stress, σ_z, is small and can be assumed 0 for our purposes, it will be the minimum principal stress, and the maximum principal stress will be σ_θ. Because of radial symmetry of shear stresses, $\tau_{r\theta}$ will be 0. The equation of equilibrium for an element of volume is (11)

$$r \frac{d\sigma_r}{dr} + \sigma_r - \sigma_\theta = 0 \qquad (3)$$

Since σ_z is assumed to be 0, Tresca's criterion is

$$\sigma_\theta - \sigma_z = Y \qquad (4)$$

or $$Y = \sigma_\theta \qquad (5)$$

Substituting this value in eq 3 gives

$$r \frac{d\sigma_r}{dr} + \sigma_r = Y \qquad (6)$$

A solution that meets the requirements that $\sigma_r = 0$ when $r = a$ is

$$\sigma_r = Y\left(1 - \frac{a}{r}\right) \qquad \sigma_\theta = Y \qquad \sigma_z = 0 \qquad (7)$$

It is of interest to note that this condition is completely determined by the plasticity condition, the equilibrium requirements, and the boundary condition.

The equations described above relate to a hole free of radial stress. It is also of interest to consider the effect of restraint of the inward radial displacement at $r = a$, such as would occur if the heated can were in contact with the salt walls. If the radial displacements are suppressed, σ_r and σ_θ will approach the values given by

$$\sigma_r = \frac{E\beta\theta}{(1-\mu)} \qquad \sigma_\theta = \frac{E\beta\theta}{(1-\mu)} \qquad \sigma_z = 0 \qquad (8)$$

where E = modulus of elasticity (psi)

β = coefficient of thermal expansion

θ = temperature rise (^{o}F)

μ = Poisson's ratio

When the values of σ_r and σ_θ equal the yield strength of salt, all volume expansion must find relief upward as the radial flow is restrained by the can. From eq 8, the thermal stresses in the salt surrounding the cylinder can be estimated. The upward expansion of the floor can be estimated, once the temperature rise around the cylinder and the thermal properties of salt are known, by assuming that the complete volumetric thermal expansion (three times the linear expansion) is in the vertical direction.

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

Salt from the Carey Mine in Hutchinson contains inclusions of water. When the salt is heated, this water is released as steam at a temperature of about 250 to 280°C, following a breakdown of the massive structure of the salt. Since the resultant particles vary in size from 1/8- to 1-in. cubes, it seems very likely that the heating of pockets of water randomly distributed throughout the salt is the cause of the rupture.

A study is underway to determine the total amount of water trapped in the salt in order that the extent of heated water effects can be estimated. A device has been assembled in which salt blocks weighing 50-100 g are dissolved in refluxing methanol. The extracted water is determined by a Karl Fischer titration. Other apparatus designed to determine the total water released during the fracturing is also being assembled.

It is planned to make a survey of the trapped water in salt from various mines located throughout the country.

6.4 Effect of Salt Extraction and Depth on Stability of Mine Openings

(R. L. Bradshaw and W. J. Boegly)

In order to conceptually design a disposal operation in salt, it is necessary to be able to predict the allowable percentage salt extraction as a function of depth for various conditions of structural stability. Table 6.1 is a compilation of such data as is readily available on the subject. Many of the data come from the report, "Possibilities for the Storage of Radioactive Waste in Salt Cavities in the Northeastern United States," by the Geotechnical Corporation, Dallas, Texas, February 1958. The remainder are based on personal communications and observations.

The calculated load on the pillars is based on an assumed one pound per square inch per foot of overburden.

The mines in Table 6.1 are plotted in Fig. 6.4 as a function of calculated pillar load. Boundaries of the various conditions of stability in the figure are derived from the last column in the table. From these boundaries, the desired relations between depth of the mine, percentage salt extraction, and stability conditions were calculated (Fig. 6.5). For example, if only a negligible amount of structural flow can be tolerated, then the maximum allowable pillar load is 2000 psi, and operation to the left of curve A of Fig. 6.5 must be maintained. On the other hand, if some spalling and a slight (few per cent) closure of the rooms can be tolerated, the pillar load can be increased to 3000 psi, and operation can be anywhere to the left of curve C. In the first case (negligible flow) it may be seen from Fig. 6.5 that the stability criterion cannot be met at depths greater than 2000 ft. It may also be seen that any extraction of salt at depths greater than 3500 ft will produce large structural flows.

The time factor involved in structural flow was not included in this study, and it may take several years for such things as roof falls and floor heaves to occur. In general, the greater the pillar load, the faster the flow. In Germany, some mines are operated with pillar loads much greater than in this country, and the rooms are either allowed to collapse or are backfilled soon after excavation to prevent collapse.

7.0 CLINCH RIVER STUDY

7.1 Flow Routing (P. H. Carrigan*)

No continuous records of flow in the Clinch River are obtained in the study reach downstream from the mouth of White Oak Creek. The nearest station at which continuous records are collected is 18 miles upstream from the mouth of the creek, at the gaging station on the Clinch near Scarboro, Tenn.

Flow in the study reach may increase rapidly four- or five-fold, during many days of the week due to power releases from Norris Reservoir. By storage and flood routing techniques the flow at the lower end of the study reach at the sampling station above Centers Ferry, near Kingston, Tenn., may be computed from the records collected at the station near Scarboro. In August 1961 the daily variations in the Clinch River flow due to power releases were observed simultaneously for 24 hr at the gaging station near Scarboro and the sampling station above Centers Ferry. From these observations the routing equation is to be developed.

The routing equation is based on the equation of continuity for the reach.

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

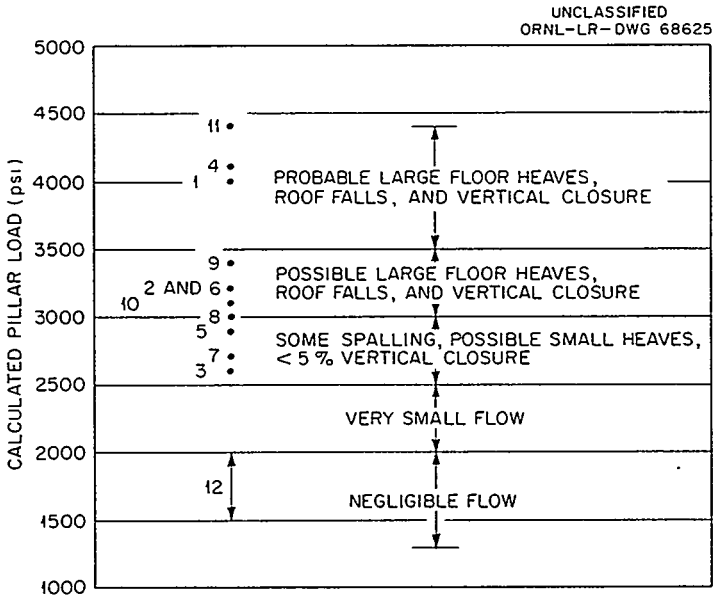


Fig. 6.4. Structural Stability in Various Salt Mines.

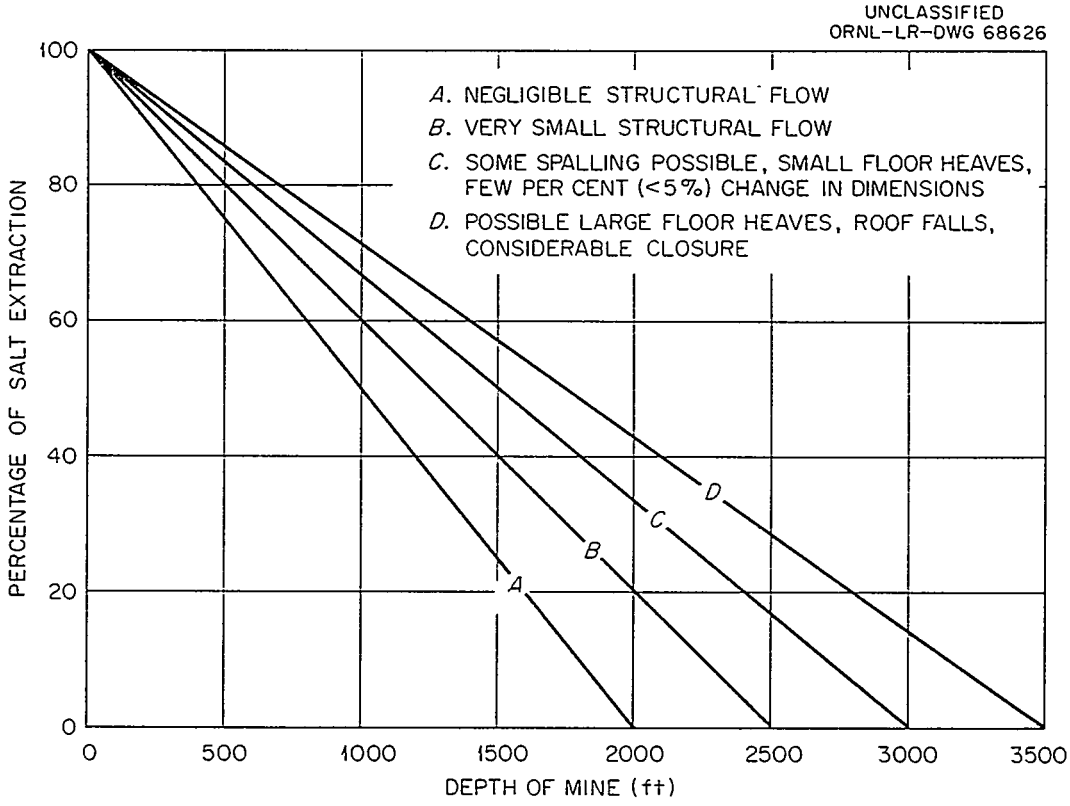


Fig. 6.5. Effect of Per Cent of Salt Extraction and Depth on Structural Stability of Mine Openings.

Table 6.1 Salt Structural Stability Conditions in Various Mines

	Mine	Location	Depth (ft)	Per Cent Extraction	Room Height (ft)	Calculated Pillar Load (psi)	Structural Conditions
1.	American	Lyons, Kan.	990	75	9	4000	Flow reported
2.	Carey	Hutchinson,Kan.	645	80	6-12	3200	Early mining; stable but some spalling
3.	Carey	Hutchinson,Kan.	645	75	12	2600	Current mining; less spalling; ~ 0.5% vertical closure
4.	Carey	Lyons, Kan.	1020	75	9-14	4100	Early mining; large floor heaves and roof falls from shale partings
5.	Carey	Lyons, Kan.	1020	65	9-14	2900	~ 1940; small floor heaves above shale parting
6.	Carey	Winfield, La.	970	70		3200	Some flow reported
7.	Carey	Winfield, La.	970	64		2700	No trouble reported
8.	Grand Saline	Grand Saline,Tex.	700	est.77		3000	Vertical closure 4%
9.	Independent	Kanopolis,Kan.	840	75	8- 9	3400	Large floor heaves and roof falls from shale parting
10.	Inter-national	Detroit, Mich.	1100	65		3100	Generally good; only one small roof fall
11.	Retsof No.1	Retsof,N.Y.	1100	75		4400	~ 1920; large floor heaves, roof falls, and heavy spalling
12.	Retsof No. 1	Retsof,N.Y.	1050	30-47		1500-2000	Current mining; no spalling or heaving

$$\frac{O_1 + O_2}{2} = \frac{I_1 + I_2}{2} - \frac{(S_2 - S_1)}{\Delta t}$$

in which the average outflow is $(O_1 + O_2)/2$, the average inflow is $(I_1 + I_2)/2$, and the change in storage is $S_2 - S_1$ during some short time interval Δt. The outflow was measured at the station above Centers Ferry by the U. S. Geological Survey. The inflow was determined from USGS discharge records collected at the station near Scarboro.

The rate of change of storage, $(S_2 - S_1)/\Delta t$, is the rate of change of the volume of water stored in the channel and may be thought of as the product of the water surface area and the rate of rise, or fall, of the water surface. This storage may be expressed as function of the weighted mean flow through the reach (12):

$$S = K \left[XI + (1 - X)\, O \right]$$

in which S, I, and O are the storage, inflow, and outflow; K is the slope of the relation; and X is a factor that weights the inflow and outflow. If this relation is substituted into the continuity equation, the resulting expression is of the type

$$O_2 = Co\, I_2 + C_1\, I_1 + C_2\, O_1$$

in which Co, C_1, and C_2 are functions of K, X, and Δt. By graphical means, outlined by Carter and Godfrey (12), the value of K was found to be 6.6 hr and the value of X, 0.5 for a routing period Δt, of 1 hr. The resultant routing equation is

$$O_2 = -0.737\, I_2 + I_1 + 0.737 O_1$$

Only slight attenuation of the power waves were observed during the period of study. Such waves are described as uniformly progressive flows (12). For this type of flow the theoretical value of X is 0.5.

The procedure of computation is a numerical step method. The flow in the Clinch River above Centers Ferry, O_2, at the end of the 1-hr routing period is determined from the outflow at the beginning of the period, O_1, and the inflows, I_1 and I_2, at the beginning and end of this same period, observed at the station on the Clinch near Scarboro. Each value of O_2 obtained is the value of O_1 used in successive computations.

The routing equation has been determined for the period in which tributary inflow to the Clinch downstream from the gaging station near Scarboro is reasonably steady and fairly low (as indicated by records of discharge for White Oak Creek at White Oak Dam, near Oak Ridge). The procedure for routing power

releases may have to be modified for periods affected by storm runoff from tributary areas and by low levels in Watts Bar Reservoir.

7.2 Effect of Geology on Quality of Water of Clinch River Tributaries

(R. J. Pickering*)

Stable-chemical analyses of water samples taken during base flow measurements in September 1961 show marked differences in the quality of water between streams draining coal-bearing clastic rocks of the Cumberland escarpment and streams draining predominantly carbonate rocks of the ridge and valley province in which Oak Ridge National Laboratory is located. Drainage areas of Popular Creek above Batley Road near Oliver Springs, Tenn., and Indian Creek above Oliver Springs are underlain by a coal-bearing sequence of sandstone and shale, while Bullrun Creek near Clinton, Tenn., and Scarboro Creek south of Oak Ridge, Tenn., drain areas underlain by dolomite, limestone, and shale.

The two streams draining clastic rocks of the Cumberland escarpment are distinguished from the streams draining predominantly carbonate rocks by their higher content of sulfate, sodium, and chloride and their somewhat lower pH. The higher sulfate content is probably the result of oxidation of iron sulfides in the coal and shale. This process and the precipitation of dissolved iron as a hydroxide in aerated water account for the lower pH of Indian and Poplar Creeks. Silica is highest in the acid water of Indian Creek. Figure 7.1 illustrates the two types of water. Poplar Creek above Batley Road receives some drainage from areas underlain by carbonate rocks and thus might be considered intermediate between Indian Creek and Bullrun and Scarboro Creeks in regard to the geology of its drainage area.

8.0 FUNDAMENTAL STUDIES OF MINERALS

8.1 Behavior of Cesium in Vermiculite Systems (D. G. Jacobs)

The behavior of cesium in vermiculite systems is of interest for two reasons: (1) vermiculite is one of the few clay minerals with a sufficiently large particle size to be of practical use in waste decontamination by columns, and (2) when it is treated with one of the heavier alkalai metal cations, the lattice spacing changes measurably, producing steric effects which alter the exchange properties of the vermiculite. Thus the study of the exchange properties of vermiculite permit a simultaneous study for improving decontamination of cesium-bearing waste streams and for depicting the possible exchange reactions of cesium in the ground.

Ion exchange by clay minerals follows the same general laws as ion exchange by synthetic resins, although a few notable differences must be considered. The exchange complex of a clay

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

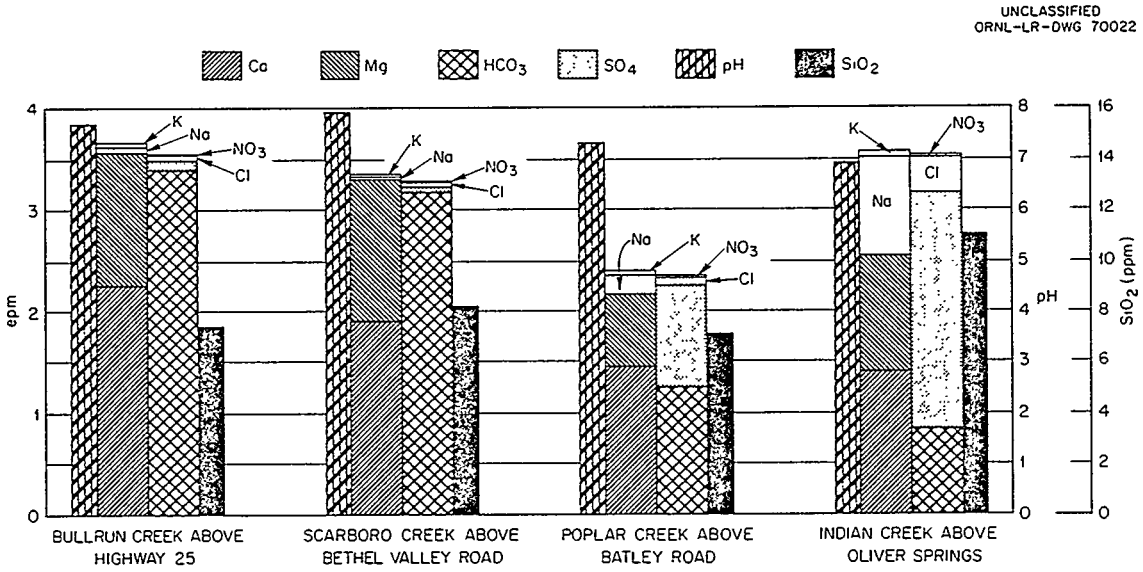


Fig. 7.1. Base Flow Analyses, September 1961.

mineral is not homogeneous, but the exchange sites differ depending on the origin of the charge deficiency. In most cases the counterions, those of opposite sign of charge from the exchanger material, cannot penetrate the clay mineral lattice to neutralize the resident charge. Thus, an electric double layer is established at the exterior of the clay mineral lattice and the atomic structure of the rigid surface of the clay mineral often limits the nearness of approach of the counterions to seats of charge residing within the crystal lattice. In many of the clay minerals, notably the 2:1 layer lattice minerals having a 10 Å c-spacing (collapsed lattice minerals), a substantial fraction of the lattice charge deficiency resides along the surface between the successive layer lattices (within the basal spacing), and migration of counterions to and from these sites is impeded because the opening between the layers is small compared to the size of the counterions. Furthermore, the basal spacing terminates in incomplete hexagonal networks of oxygen atoms, providing a void of nearly ideal dimensions for the accommodation of the heavier alkalai metal cations. When cesium, rubidium, potassium, or ammonium ions are introduced into such an exchange system they are strongly held at lattice edges by such exchange sites, migration along the basal spacing being a very slow process. Because this type of exchange site constitutes only a small fraction of the total exchange sites available, the selectivity for sorption of the heavier alkalai metal cations compared to sodium increases markedly with decreasing concentrations in a system of fixed sodium concentration. This phenomenon has been referred to as "edge fixation," to differentiate it from the less selective exchange processes occurring at exchange sites having a lower degree of steric favorability.

In the case of vermiculite, successive lattices are separated by a sufficient distance to allow rather free migration of counterions through the basal spacing. However, if vermiculite is treated with potassium the dehydrated potassium ion partially penetrates the open hexagonal network of oxygen atoms composing the basal surface, and its close approach to the seat of charge of the mineral lattice causes neutralization of the charge, reducing the repelling forces holding the lattice sheets apart and allowing them to collapse. The potassium occupying these basal exchange sites is now held strongly by "interlayer fixation" as a result of close approach of the counterion to the seat of charge coupled with steric impedance of the outward movement of the potassium ions from the basal spacing.

Pretreatment of Vermiculite with Potassium. Vermiculite (hydrobiotite obtained from the Zonolite Co., Traveler's Rest, S.C.) was pretreated with potassium to give varying degrees of collapse of the interlayered biotite-vermiculite lattices. Lattice collapse was accompanied by a drop in the exchange capacity because the exchange sites lying within the collapsed basal spacing are no longer freely accessible to the counterions (Table 8.1). Seven and a half liters of 0.5 M $NaNO_3$ containing the mass equivalent of 2 μc of Cs-137 per milliliter and tagged with Cs-137 was passed through 10-g columns of the vermiculite at an average flow rate of

1.3 ml cm^{-2} min^{-1}. After the columns were saturated with cesium, they were divided into four sections for determination of the final exchange capacity, by the calcium titration method of Jackson (13), and the cesium loading. Each solution used in determination of the exchange capacity was counted for cesium and the total cesium leached by five treatments with 100 ml of 1 M $CaCl_2$, three treatments with 100 ml of distilled water, three treatments with 100 ml of 95% ethanol, and five treatments with 100 ml of sodium acetate was computed. The K_d for cesium increased with a decrease in exchange capacity because of the increased number of edge fixation sites make available by lattice collapse. The leaching action of the sodium nitrate removed of the potassium from interlayer fixation sites, causing expansion of part of the vermiculite lattices. This was most apparent in columns 5 and 6 where the top of the column was subjected to more vigorous leaching, resulting in a higher final exchange capacity and lower cesium K_d from top to bottom in the column.

The decreased leaching of cesium from columns more nearly saturated can be accounted for by the increased number of edge fixation sites or by the cesium K_d. The sorption mechanism apparently remains the same for all columns.

Table 8.1 Effect of Potassium Treatment of Vermiculite on Cesium Sorption from 0.5 M $NaNO_3$ Containing the Mass Equivalent of 2 μc of Cs-137 per milliliter

Column No.	Initial CEC (meq/100g)	Final CEC (meq/100g)	Cesium K_d (ml/g)	Cesium Leached (%)	X-ray Diffraction (before saturation)
1	55.7	74.9	108	16.3	No change from Na vermiculite
2	48.9	73.9	112	15.1	Random interlayering with lower spacings
3	42.3	75.0	124	14.4	Equally intense maxima at 10 Å and 11 Å.
4	38.0	73.7	133	16.1	Most intense maximum at 10 Å; also peak at 11 Å
5	13.0	64.2	201	9.0	10 Å peak with random interlayering of higher spacings
6	5.9	45.9	272	7.0	Sharp 10 Å peak

Addition of Potassium to the Influent. When potassium is added to the 0.5 M $NaNO_3$ influent solution it is possible to get

simultaneous sorption of cesium and potassium. If the potassium concentration is too low to initiate lattice collapse, the potassium competes with cesium for the edge fixation sites (Table 8.2).

Table 8.2 Effect of Addition of Potassium to the Influent on the Sorption of Cesium by Vermiculite from 0.5 M $NaNO_3$ Containing the Mass Equivalent 2 μc of Cs-137 per milliliter

Potassium Conc. (M)	Cesium K_d (ml/g)	Cesium Leached (%)	Final CEC (meq/100g)	X-Ray Diffraction (after Saturation)
0.0000	154	12.6	75.4	
0.0001	147	13.0	74.9	
0.001	137	15.2	70.2	
0.01	357	7.60	60.0	
0.02	483	5.83	38.1	First signs of increased interlayering with lower spacings
0.03	695	4.90	26.2	10 Å peak with some random interlayering with higher spacings
0.04	727	4.63	17.9	
0.05	634	4.56	15.3	
0.08	373	4.10	9.1	Sharp 10 Å peak
0.10	265	3.26	8.6	

As the potassium concentration is increased, lattice collapse occurs and the cesium and potassium are entrapped by "interlayer fixation," as evidenced by a drop in the exchange capacity and a decrease in the percentage of cesium leached. Although the potassium is competitive with cesium for the interlayer fixation sites, the cesium K_d increases with increasing potassium concentration, passing through a maximum at 0.04 M KNO_3. Above this concentration the increased potassium concentration is not balanced by an increase in the number of interlayer fixation sites.

The percentage of the cesium leached is more directly related to the exchange capacity than to the cesium K_d, decreasing as the exchange capacity decreases. This is due to a shift from edge fixation to interlayer fixation as the dominant sorption mechanism. As a greater fraction of the cesium occupies interlayer fixation sites, it is less readily leached.

Addition of Other Collapse-inducing Cations to the Influent. Other heavy alkalai metal cations and ammonium ions also cause collapse of the vermiculite lattice. Since they are more strongly held than potassium, a smaller concentration is required in 0.5 M $NaNO_3$ to initiate lattice collapse and to obtain optimum cesium removals (Table 8.3). The behavior of the ammonium-treated influent

Table 8.3 Optimum Concentrations of Collapse-inducing Cations for Cesium Sorption by Vermiculite from 0.5 M $NaNO_3$ Containing the Mass Equivalent of 2 μc of Cs-137 per milliliter

Cation	Cation Conc (M)	Cesium K_d (ml/g)	Cesium Leached (%)	Final CEC (meq/100 g)
K^+	0.040	727	4.63	17.9
NH_4^+	0.010	1851	13.1	42.8
Rb^+	0.0015	556	4.22	41.0
Cs^+	0.0004	557	3.38	47.7

was somewhat different from that of the other systems; the K_d was higher but the percentage of cesium leached was also much greater than for the alkalai metal cations.

Step Increases in Influent Potassium Concentration. Because collapse of all interlayer spacings does not occur at the minimal concentration for initiating lattice collapse and because increases in the potassium concentration increase competition with cesium for fixation sites, it seemed that the optimum procedure would be to operate at the minimum $(K^+)/(Na^+)$ until the easily collapsed lattices are all in the collapsed state. This would be evident by an increase in the cesium activity of the effluent. Gradual increases of the $(K^+)/(Na^+)$ would result in additional lattice collapse and increased cesium sorption, until finally a state would be reached where all possible collapse had been accomplished. Beyond this point, increases in potassium concentration would merely interfere with cesium sorption.

Two liters of the 0.5 M $NaNO_3$ solution was passed through a 10-g vermiculite column. Complete cesium breakthrough was observed. When the influent solution was brought to 0.01 M with respect to KNO_3, the cesium activity of the effluent dropped to less than 15% of the influent activity after 200 ml solution had passed through the column. A second breakthrough wave was observed when 2 liters of this solution had passed through the column, and cesium activity in the effluent was decreased to less than 1% of the influent activity by increasing the potassium concentration of the influent to 0.02 M. A third

breakthrough wave occurred after passage of 2 liters of this solution. This was followed by 7.5 liters of 0.03 M KNO_3, 2.6 liters of 0.05 M, 1.25 liters of 0.08 M, and 0.35 liters of 0.10 M KNO_3. After this last breakthrough wave, 0.25 liter of the 0.5 M $NaNO_3$ solution was passed through the column before the final breakthrough wave was obtained. A cesium K_d of 2255 ml/g was obtained, 4.49% of which was leached off during the determination of the exchange capacity. The final exchange capacity of the vermiculite was 18.3 meq/100 g.

9.0 WHITE OAK CREEK BASIN STUDY*

9.1 Sources of White Oak Creek Contamination (T. F. Lomenick)

The PWWTP is the major source of contamination to White Oak Creek within Bethel Valley (ORNL plant site). However, significant quantities of radionuclides enter the creek from other facilities in the valley. Temporary water sampling stations were installed along White Oak Creek at miles 2.6 and 3.9 and the tributary stream draining the northwest portion of the Bethel Valley area to assess the amount and type of activity associated with fallout, burial grounds, and other sources that could not be monitored directly (see Fig. 9.1). In addition, representative samples were taken of the effluent from the laundry and the sewage treatment plant. The sampling devices used at the stations have been described previously (14). A summary of the activity detected at the laundry, sewage treatment plant, stream sampling stations, and the PWWTP for the period May-Oct. 1961 is shown in Table 9.1.

It is of interest to note that, during the 6-month sampling period, the sewage treatment plant contributed approximately 150 mc of Sr-90, 100 mc of TRE^{3+},** 32 mc of Cs-137, 7 mc of Co-60, and 7 mc of Ru-106. Although the amount detected is small in comparison to that released from the PWWTP, it is rather large for a facility that should be relatively free from contamination. The mean concentration of Sr-90 in the sewage water effluent was 1.7×10^{-6} μc/cc or about 40% of the MPC_w. The weekly contribution of Sr-90 to the creek from this facility was fairly constant, but for the remaining radionuclides the releaes were somewhat sporadic.

The amounts of activity detected in weekly samples at the stream stations vary over a wide range. (14) An apparent relation between stream discharge and strontium transport was shown, and an increase in the suspended solid load in the stream was generally followed by a corresponding increase in cesium transport (Fig. 9.2). Thus, during

*This project, entitled "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin," (AEC Activity No.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 No.0464001l).

**Exclusive of Y-90.

Table 9.1 Radionuclides Discharged to White Oak Creek from Sources in Bethel Valley May-October 1961

Station	Sr-89 & 90		TRE*		Cs-137		Co-60		Ru-106	
	(mc)	(%)	(mc)	(%)	(mc)	(%)	(mc)	(%)	(mc)	(%)
Northwest tributary stream	33	0.85	34	1.38	30	2.98	1	0.23	7	1.98
White Oak Creek Mile 2.6	123	3.17	83	3.28	153	15.21	89	20.41	43	12.15
Sanitary sewage	150	3.87	100	3.95	32	3.18	7	1.61	7	1.98
Laundry	9	0.24	11	0.44	11	1.09	6	1.37	1	0.28
Process waste water treatment plant	3560	91.87	2300	90.95	780	77.54	333	76.38	296	83.61
Totals	3875	100.00	2528	100.00	1006	100.00	436	100.00	354	100.00

*Excluding Y-90.

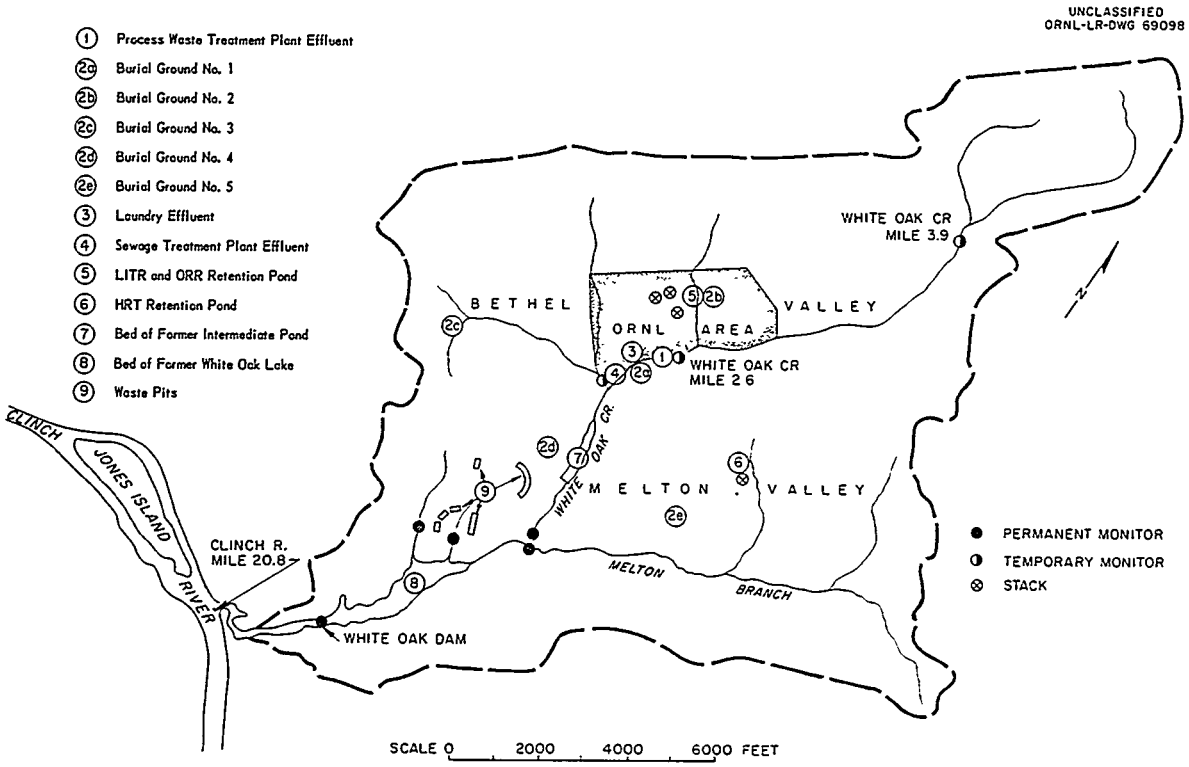


Fig. 9.1. Map of White Oak Creek Basin Showing Sources of Radioactive Contamination and Stream – Monitoring Stations.

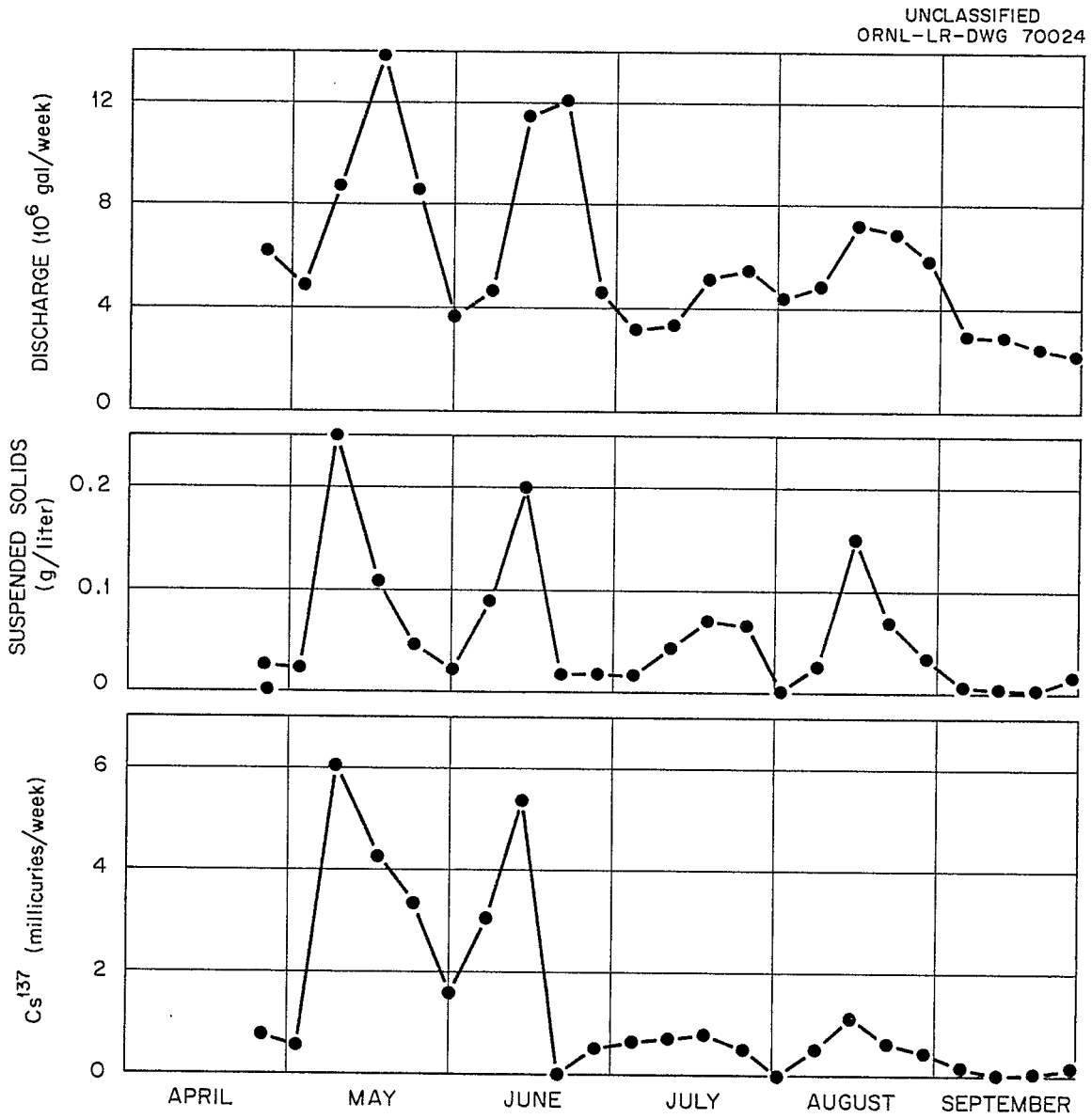


Fig. 9.2. Stream Discharge, Suspended Solids and Cs-137 Transport at Northwest Tributary Station.

periods of high stream discharge and/or a heavy suspended solid load, the transport of strontium and/or cesium is usually high. The cesium transport in weeks in which suspended-solid loads were high exceeded that in several weekly periods when the suspended solid concentration was low. This condition indicates that during most periods the transport of radionuclides past the stream sampling stations is relatively small compared to that discharged to the creek from the PWWTP, but in short times substantial amounts are transported.

9.2 Hydrology of White Oak Creek Basin (W. M. McMasters*)

Large-scale aerial photographs of the White Oak Creek basin, made in March 1959 for the Ecology Section of Health Physics Division, were obtained for use in mapping the geology of the basin. Geologic mapping began on April 2 in the northwestern part of the basin.

Invitations to bid on a 500- to 600-ft-deep churn-drill well were issued during the week of April 8. The well is to be located on Melton Hill and will begin in the Knox dolomite and finish in Conasauga shale.

A staff gage was installed on a spring-fed tributary to White Oak Creek at a point south of Bethel Valley Road and north of the cooling tower at Bldg. 3103. The gage is being rated by discharge measurements made at different stages. The tributary receives a substantial amount of plant discharge between this point and its confluence with White Oak Creek. A second gaging station is planned for installation on the tributary near its mouth as a means of approximating plant discharge to the tributary during base flow measurements.

*On loan from the Water Resources Division, Surface Water Branch, U.S. Geological Survey.

10.0 REFERENCES

1. "Waste Treatment and Disposal Progress Report for April and May 1961," ORNL-CF-61-7-3.

2. J. M. Morgan, Jr., D. K. Jamison, J. D. Stevenson, "Fixation of Radioactivity in Stable Solid Media, Report on the Second Working Meeting at Idaho Falls, Idaho," Sept. 27-29, 1960, TID-7613, Books 1 and 2.

3. R. M. Beckers, "Design Report Calciner Pot for Liquid Waste Calcination Program," ORNL-CF-62-4-20 (1962).

4. "Waste Treatment and Disposal Progress Report for October and November 1961," ORNL-TM-133, Sect. 4.0.

5. "Waste Treatment and Disposal Progress Report for December 1961 and January 1962," ORNL-TM-169, Sect. 4.0.

6. J. T. Roberts and R. R. Holcomb, "A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes," ORNL-3036 (May 22, 1961). Ibid., "Low-level Waste Treatment by Ion Exchange. II. Use of a Weak Acid Carboxylic-Phenolic Ion-Exchange Resin," ORNL-TM-5 (Sept. 25, 1961). Ibid., "The Phenolic Resin Ion Exchange Process for Decontaminating Low-Activity-Level Process Water Wastes," ORNL-CF-60-8-103, (Aug. 1960).

7. J. S. Watson, "Unit Operations Section Monthly Progress Report," ORNL-TM-34, June 1961, p. 32.

8. "API Recommended Practice for Testing Oil Well Cements and Cement Additives," API Research Paper 10B, March, 1961.

9. R. H. Merrill, "Static Stress Determinations in Salt-Site Cowboy," U. S. Bur. Mines Rept., APRL 38-3.1.(July 29, 1960).

10. R. Hill, "The Mathematical Theory of Plasticity," Oxford Univ. Press, London, 1956, p. 19.

11. S. Timoshenko and J. N. Goodier, "Theory of Elasticity," McGraw-Hill, New York, 1951, p. 406.

12. R. W. Carter and R. G. Godfrey, "Storage and Flood Routing," U. S. Geological Survey Water Supply Paper 1543-B (1960).

13. M. L. Jackson, "Soil Chemical Analysis," Prentice-Hall, Inc., Engelwood Cliffs, N. J., 1958.

14. "Waste Treatment and Disposal Progress Report for October and November 1961, ORNL-TM-133, Sect. 9.0.

15. "Waste Treatment and Disposal Progress Report for June and July 1961, ORNL-TM-15.

INTERNATIONAL DISTRIBUTION

1. ORNL - Y-12 Technical Library Document Reference Section
2-4. Central Research Library
5-14. Laboratory Records Department
15. Laboratory Records, ORNL R.C.
16-17. R. E. Blanco
18. J. O. Blomeke
19. W. J. Boegly, Jr.
20. R. L. Bradshaw
21. J. C. Bresee
22. F. N. Browder
23. K. B. Brown
24. P. H. Carrigan
25. W. E. Clark
26. K. E. Cowser
27. F. L. Culler
28. W. de Laguna
29. F. M. Empson
30. D. E. Ferguson
31. H. W. Godbee
32. H. E. Goeller
33. J. M. Googin
34. C. W. Hancher
35. C. E. Haynes
36. R. F. Hibbs
37. R. R. Holcomb
38. J. M. Holmes
39. D. G. Jacobs
40. W. H. Jordan
41. H. Kubota
42. T. F. Lomenick
43. K. Z. Morgan
44. R. J. Morton
45. E. L. Nicholson
46. F. L. Parker
47. J. J. Perona
48. R. M. Richardson
49. J. T. Roberts, IAEA, Vienna
50-51. E. G. Struxness
52. J. C. Suddath
53. J. A. Swartout
54. T. Tamura
55. J. W. Ullmann
56. M. E. Whatley

EXTERNAL DISTRIBUTION

57. E. L. Anderson, AEC, Washington
58. W. G. Belter, AEC, Washington
59. W. H. Regan, AEC, Washington
60. J. A. Buckham, Phillips Petroleum Company
61. H. J. Carey, Jr., Carey Salt Company, Hutchinson, Kansas
62. C. W. Christenson, Los Alamos Scientific Laboratory
63. E. F. Gloyna, University of Texas, Austin
64. L. P. Hatch, Brookhaven National Laboratory
65. W. B. Heroy, Sr., Geotechnical Corp., Dallas, Texas
66. H. H. Hess, Chairman, Earth Science Division, Commission on Ground Disposal of Radioactive Waste, Princeton University, Princeton, N.J.
67. O. F. Hill, Hanford
68. J. R. Horan, AEC Idaho
69. J. H. Horton, Stanford Research Institute
70. E. R. Irish, Hanford
71. A. A. Jonke, Argonne National Laboratory
72. K. K. Kennedy, AEC, Idaho
73. W. J. Kaufman, University of California, Berkeley
74. S. Lawroski, Argonne National Laboratory

MA

2005

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-376

15

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR APRIL-MAY 1962

This document has been approved for release to the public by:

David R Hamm 7/28/95

Technical Information Officer, ORNL Site — Date

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM- 376

CHEMICAL TECHNOLOGY DIVISION
AND
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR APRIL-MAY 1962

R. E. Blanco and E. G. Struxness

DATE ISSUED

NOV - 5 1962

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

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

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

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

Aluminum borophosphate glasses were prepared which incorporated up to 17 wt % Darex waste oxides, gave volume reductions of 2.5 to 3.8 and had bulk densities between 2.44 and 2.74 g/ml and initial softening points of 750 to 850°C. Incorporation of 25 wt % Darex waste oxides in similar glasses resulted in products which became devitrified to give crystalline or segregated glassy materials. A semicontinuous fixation of TBP-25 waste in phosphate-lead glass resulted in volatilization of about 16% of the ruthenium; physical entrainment of the Pm-147 present was only about 0.1%. Operation with a rising liquid level and a minimum inventory of unmelted solid appears to be advantageous for ruthenium control. A container of a similar glass held 4 weeks at 900°C developed a vacuum which eventually reached 27 in. H_2O.

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

Recirculation of 5-10% of the clarifier solids to a laboratory scale flash mixer lowered the total hardness of the clarifier effluent (caustic-copperas treatment) to 8-14 ppm (as $CaCO_3$). Addition of copperas to the flocculator instead of the flash mixer lowered the clarifier effluent hardness to 5.2 ppm. The presence of 1.7 to 2.4 ppm Turco 4324 in tests with ORNL tap water had no effect on total hardness of the effluent, but 3.2 ppm increased flash mixer and clarifier effluent hardness to 44 and 37 ppm, respectively.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

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

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

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

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

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

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

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

7.0 CLINCH RIVER STUDY

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

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

*U. S. Geological Survey

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

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

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

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

7.2 Water Sample Analyses (S. Helf*)

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

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

---

*U. S. Army, Picatiny Arsenal

8.0 FUNDAMENTAL STUDIES OF MINERALS

T. Tamura

Reagent-grade aluminum oxide powder has been shown (16,17) to selectively remove strontium from waste solutions. Hydrous aluminum oxide minerals, which occur commonly in soils, were more effective (Table 8.1) than the pure oxide after being decomposed to the oxide by heating. The experiments were made with "Arkansas bauxite," obtained from Reynolds Metal Company, Louisville, Ky., which contains 40% gibbsite ($Al(OH)_3$) and 60% kaolinite ($H_4Al_2Si_2O_9$). That the gibbsite was the active substance was indicated with samples of aluminum hydroxide, obtained from Fisher Chemical Company and identified by x-ray examination as gibbsite, and kaolinite from Georgia. The aluminum hydroxide as received removed only 2% of the strontium from a simulated waste solution, but after being heated to 450°C, removed nearly 100%. The strontium absorption capacity of the kaolinite was low, and was even lower when the kaolinite had been heated to 600°C. The kaolinite had been heated for another purpose, and the heating temperature is thus not really comparable with that of the other samples. The theoretical weight loss of pure aluminum hydroxide on heating, $2\ Al(OH)_3 \xrightarrow{heat} Al_2O_3 + 3\ H_2O$, is 34.64%, and gibbsite heated to 800°C lost 34.22% of its weight.

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

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

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

Waste solution: 0.1 M $NaNO_3$ containing 1 mg of Sr per liter
25 ml of solution contacted with mineral and system maintained at pH 10

Mineral	Wt of Mineral Used in Contact, g	Strontium Removed, %		
		1 hr Contact	4 hr Contact	24 hr Contact
Pure Al_2O_3	0.2500	79.3	86.0	9.16
Arkansas bauxite*				
Unheated	0.2500	42.4	46.4	49.6
Heated to 350°C	0.1667	96.6	98.6	99.3
$Al(OH)_3$				
Unheated	0.2500	2.44	4.40	3.44
Heated to 450°C	0.2500	99.8	99.9	99.9
Kaolinite				
Unheated	0.2500	17.3	38.2	46.4
Heated to 600°C	0.2150	15.2	18.5	23.7

* 40% $Al(OH)_3$

Table 8.2. Effect of Temperature of Heating of Aluminum Hydroxide on Surface Area*

Samples heated to weight loss equilibrium.

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

*Surface area of Al_2O_3 ignited powder (Allied Chemical Co.): 6.6 m^2/g.

Table 8.3. Strontium Removal by Heat-treated Aluminum Hydroxide

Waste solution: 25 ml of 0.1 M $NaNO_3$ containing 1 mg of Sr per liter contacted initially at pH 10 and not adjusted later
Amount of mineral used: ≃ 0.01 g of 800°C heated aluminum hydroxide

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

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

50 ml of waste used in each test

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

9.0 WHITE OAK CREEK BASIN STUDY*

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

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

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

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

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

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

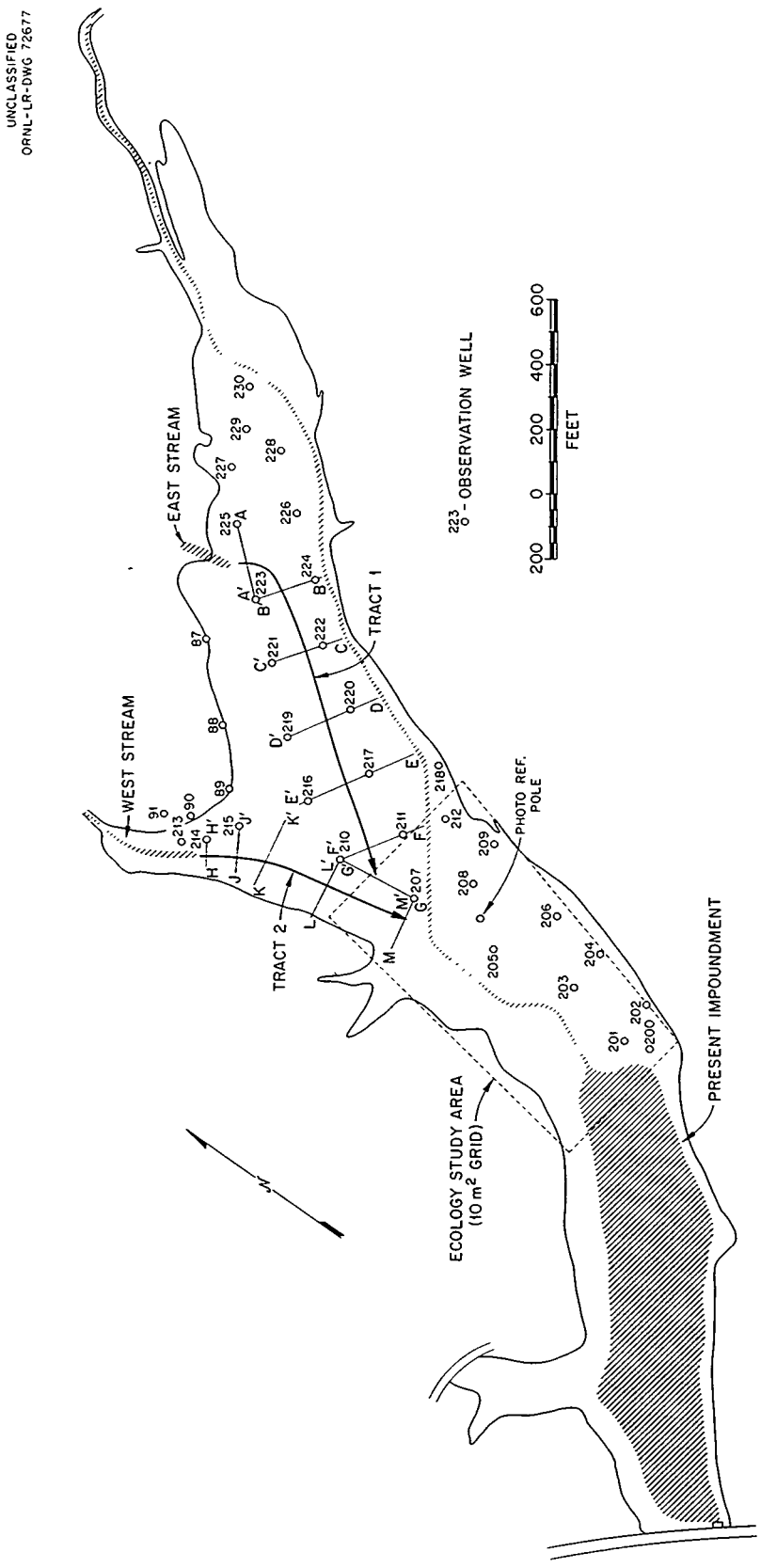


Fig. 9.1 Map of White Oak Lake bed showing transverse lines of bore holes along tracts of ruthenium seepage.

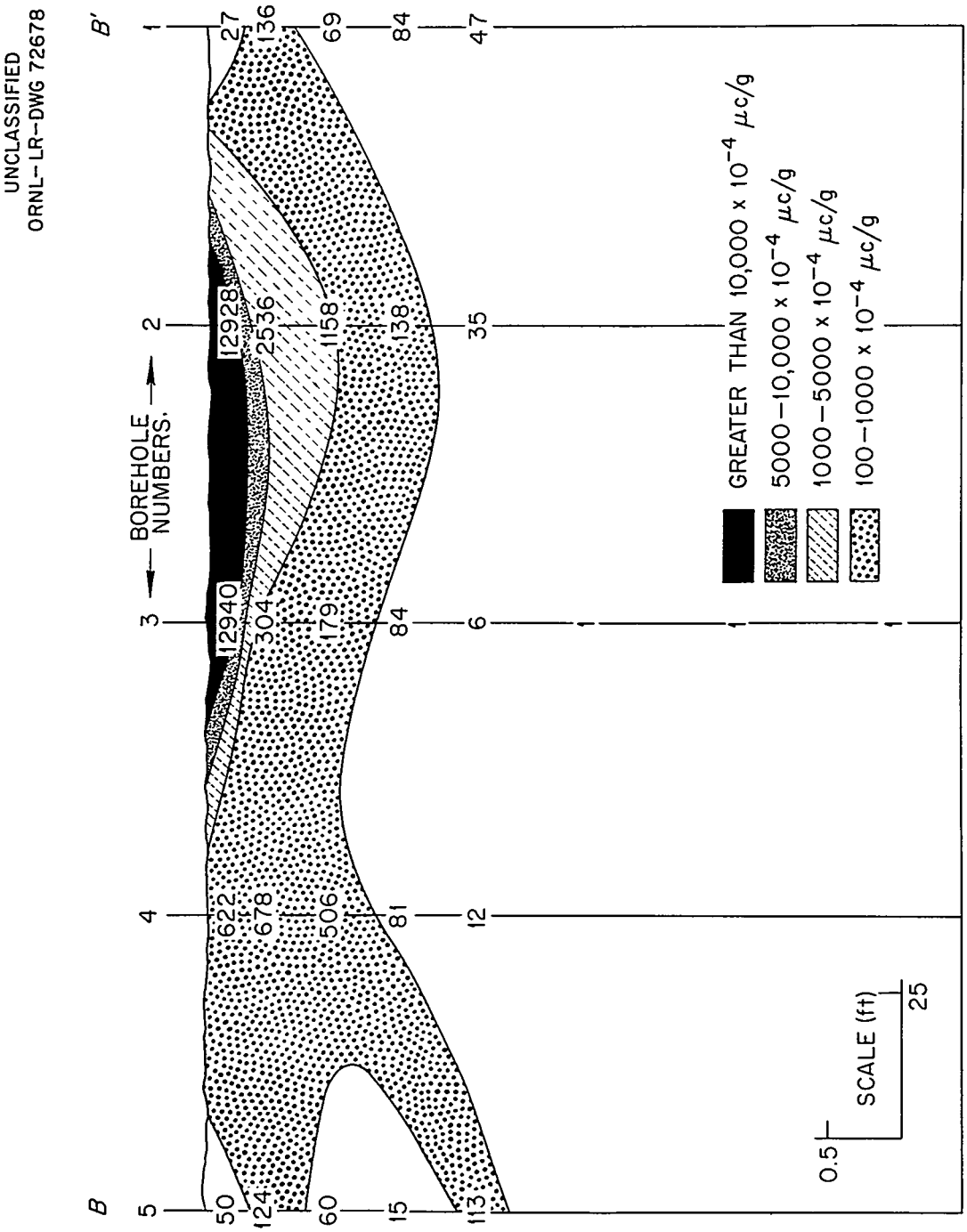


Fig. 9.2 Cross section B-B' in White Oak Lake bed showing ruthenium concentrations.

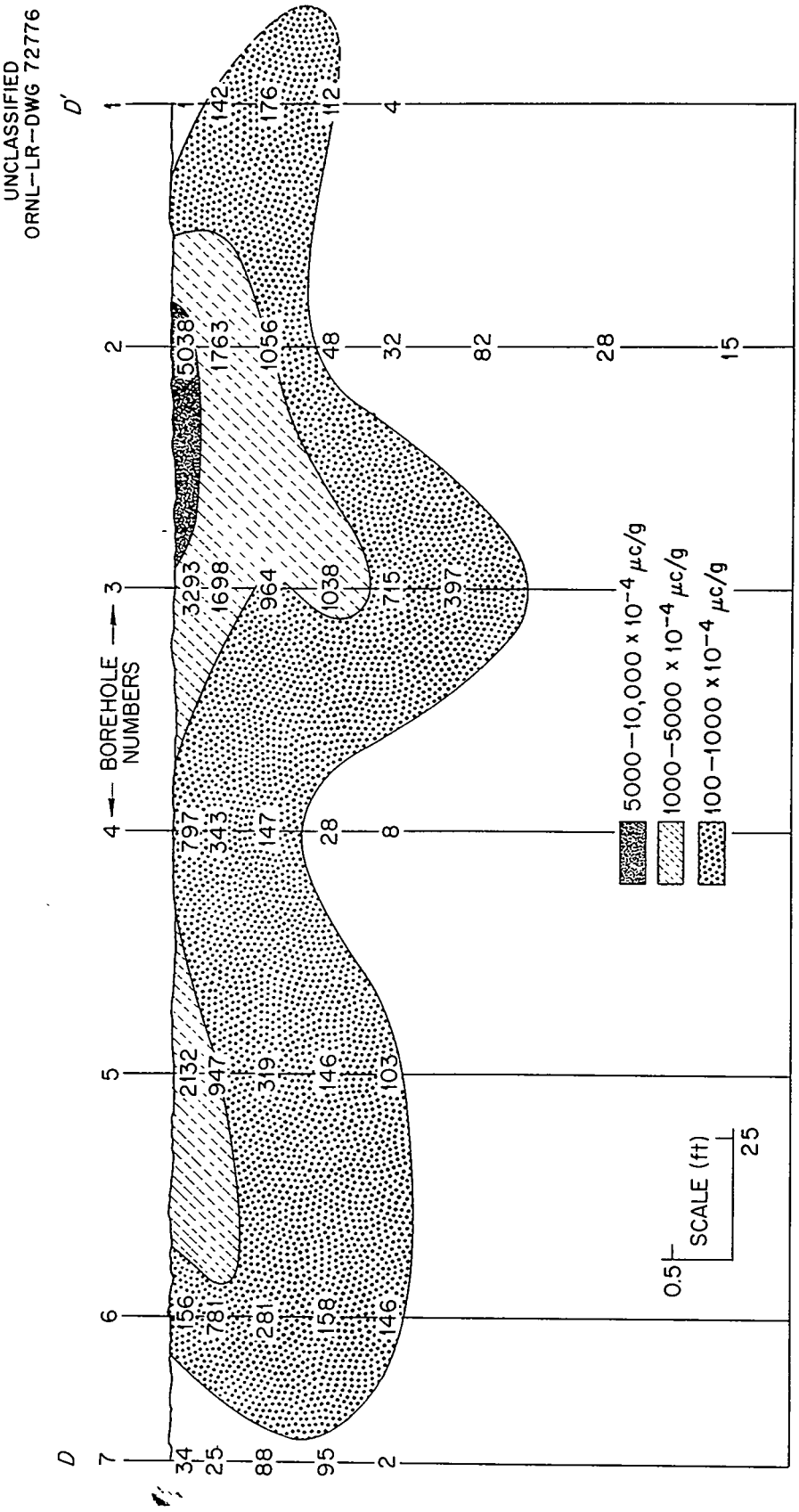


Fig. 9.3 Cross section D-D' in White Oak Lake bed showing ruthenium concentrations.

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

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

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

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

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

10.0 FOAM SEPARATION

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

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

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

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

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

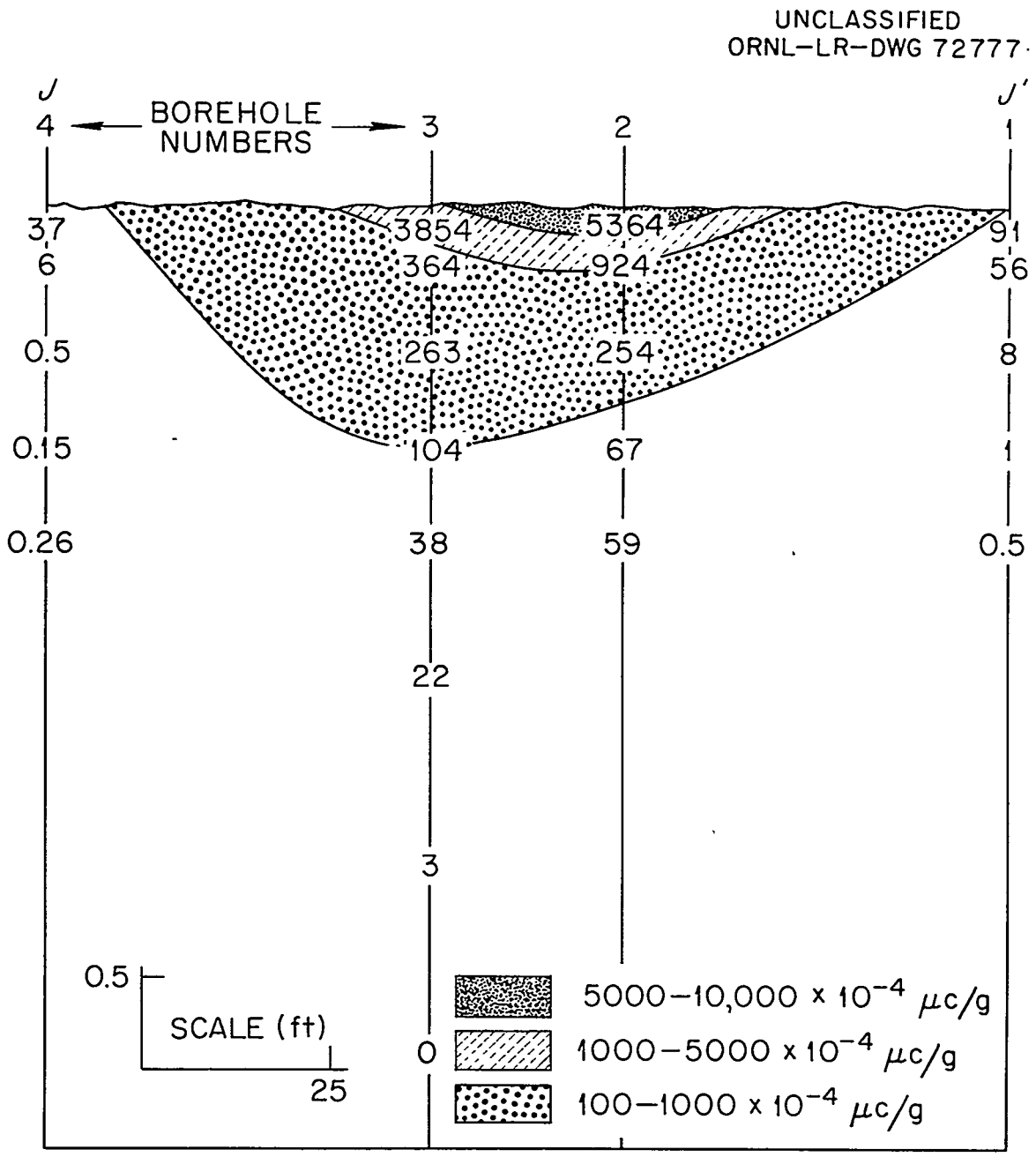


Fig. 9.4 Cross section J-J' in White Oak Lake bed showing ruthenium concentrations.

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

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

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

Water Softening Tests. Materials in low-activity waste that might interfere with precipitation of Ca and Mg by NaOH or Na_2CO_3-NaOH are Turco 4234, Fab, and components of these proprietary formulations, such as sodium dodecylbenzene sulfonate, sodium hexametaphosphate, sodium tripolyphosphate, and sodium pyrophosphate. At concentrations of 1.5 to 3 ppm in water, Turco 4234, Fab, sodium hexametaphosphate, and sodium pyrophosphate all had a more deleterious effect with NaOH softening than with Na_2CO_3-NaOH softening (Table 10.1). Sodium dodecylbenzene sulfonate and sodium tripolyphosphate had only small effects on either softening process. With three samples of ORNL low-activity waste used in the continuous softening tests described above, the effect was much greater on the NaOH softening process than on the Na_2CO_3-NaOH process. In a single test with 5×10^{-3} M NaOH, 60 ppm of orthophosphate softener, pH 11.3, the final hardness was 5.1, indicating that orthophosphate not only does not seriously interfere with water softening in this concentration range, but is the best precipitant in the presence of interferences such as Turco 4234 and Fab soap. The tests were made in beakers. The solution plus additive was agitated for 2 hr; $Fe(NO_3)_3$ was added to a level of 2 ppm Fe^{3+} and agitated for an additional 15 min; then the solution was sampled, centrifuged and finally analyzed for dissolved Ca + Mg, i.e., total hardness. With 10^{-2} M NaOH the pH was 11.7; with 5×10^{-3} M each Na_2CO_3 and NaOH, it was 11.3.

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

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

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

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

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

REFERENCES

1. "Waste Treatment and Disposal Progress Report for October and November 1961," ORNL-TM-133.

2. J. J. Perona, "The Effects of Internal Heat Generation on Pot Calcination Rates for Radioactive Wastes," ORNL-3163 (Oct. 9, 1961).

3. J. M. Holmes, "The Control of Pot Calciner Temperatures to Ensure Calcination at 900°C," ORNL-TM-259 (May 31, 1961).

4. "Waste Treatment and Disposal Progress Report for April and May 1961," ORNL-CF-61-7-3.

5. Ibid. for February and March 1962, ORNL-TM-252.

6. "Waste Treatment and Disposal Progress Report for December 1961 and January 1962, ORNL-TM-169.

7. T. E. Wilmarth, ORNL, private communication to L. Rice, March 14, 1962.

8. J. T. Roberts and R. R. Holcomb, "A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes," ORNL-3036 (May 22, 1961).

9. R. R. Holcomb and J. T. Roberts, "Low-Level Waste Treatment by Ion-Exchange. II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin," ORNL-TM-5 (Sept. 25, 1961).

10. E. G. Struxness et al., "Studies of the Use of Coagulant Aids in the Lime-Soda Treatment of Large-Volume Low-Level Radioactive Liquid Wastes," ORNL-CF-60-7-17 (Aug. 22, 1960).

11. W. Davis and E. Schonfeld, personal communication, May 1962.

12. W. J. Kaufman, R. G. Orcutt, and G. Klein, "Underground Movement of Radioactive Wastes," Sanitary Engineering Research Laboratory, University of California, Berkeley, Aug. 1, 1955.

13. F. N. Browder (ed.), "Radioactive Waste Management at Oak Ridge National Laboratory," ORNL-2601 (April 17, 1959).

14. K. E. Cowser and R. J. Morton, J. San. Eng. Div., Proc. Amer. Soc. Civ. Eng. 85 (SA3), 55 (1959).

15. K. E. Cowser et al., "Health Physics Am. Prog. Rep. July 31, 1959," ORNL-2806.

16. T. Tamura and E. G. Struxness, "Removal of Strontium from Wastes," ORNL-CF-60-10-43 (November 1960).

17. K. Z. Morgan, "Health Physics Div. Ann. Prog. Rep., July 1961," ORNL-3189, pp. 33-37.

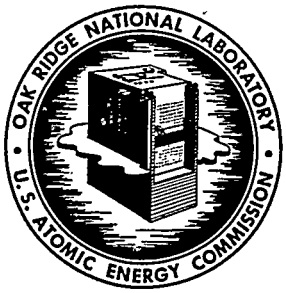
18. H. B. Weiser, "Textbook of Colloid Chemistry," 2nd Edition, John Wiley and Sons, New York, 1949, p. 313.

19. D. G. Jacobs and T. Tamura, "The Mechanism of Ion Fixation Using Radio Isotope Techniques," 7th Int. Cong. Soil Science, 2:206-214 (1960).

20. K. E. Cowser, "Movement of Ruthenium in the ORNL Waste-Pit System," TID-7628, 2nd Ground Disposal of Radioactive Wastes Conference, Chalk River, Ontario, Canada, Sept. 26-29, 1961.

21. L. C. Lasher, Operations Div., personal communication.

ORNL
MASTER
2005



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

UNION CARBIDE

ORNL- TM- 396

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR JUNE AND JULY 1962

This document has been approved for release to the public by:

David R Hamrin 7/28/95
Technical Information Officer Date
ORNL Site

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM-396

CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR JUNE AND JULY 1962

R. E. Blanco and E. G. Struxness

DATE ISSUED

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level Waste Calcination. The purpose of test R-67 was to test gravity feed to the calciner from a head tank and to try a water cooled mercury trap. Test R-67 was not completely successful. The pot overflowed and aluminum nitrate and aluminum oxide filled about half the volume of the mercury trap. The thermocouple for liquid level control didn't sense the high level soon enough. The feed valve for the gravity feed line did not open enough, therefore the pot operated at a low level for the greater part of the filling period. It took 9 hrs of filling to get up to the operating liquid level. The average feed rate was 17.0 liters/hr (391 liters in 23 hrs). The resulting bulk density was 0.50 g/cc.

The feeding period was 23 hrs and the calcining time was 24 hrs. The pot was allowed to cool for 6 hrs and then was capped and reheated to measure pressure buildup. After capping the pressure rose to 4 psig in about 1 hr and decayed slowly to atmospheric in about 4 hrs. After 96 hrs at temperature (900°C ± 25°C) an attempt was made to pressurize the pot to about 25 psig to determine if there was a leak. The pot could not be pressurized because the safety rupture disk had ruptured.

The pot top and off-gas line had a thin white film, which appeared to be aluminum oxide from foamover, but no yellow solids. The average temperature of the pot top was about 350°C and the off-gas line was about 500°C. The mercury trap was cooled with a water jacket. The temperature ranged from 30 to 160°C. The preferred temperature was 130°C to vaporize any nitric acid condensate.

Process design of the equipment for the Hanford Calcination Pilot Plant has been started. Installation will be in a cell of the new Fuels Recycle Pilot Plant which is currently under design. ORNL will continue nonradioactive engineering testing of the pot calcination process and include development of a process for making glasses in the pot calciner. Construction of the mechanical equipment at the Lockheed Nuclear Company is progressing satisfactorily.

Sulfate volatility from melts containing 39 weight % simulated Purex waste oxides was investigated as a function of Na_2O, CaO and P_2O_5 content. All compositions lost some sulfate at temperatures as high as 50 to 100°C above the softening point. In general the volatility decreased with increase of either Na_2O or CaO relative to P_2O_5, but no simple correlation was indicated. Softening temperatures were lowered by increase in Na_2O vs CaO. Ceramic solids were obtained but no true glasses. Attempts to produce glasses by addition of varying combinations of Al_2O_3, PbO, BaO, and B_2O_3 to simulated Purex waste plus phosphite were unsuccessful.

Vapor-liquid equilibrium data was obtained for simulated Darex wastes 0.6 to 1.3 M in H^+.

Low-Level Waste Treatment. The use of 0.005 M Na_2CO_3 to precipitate calcium from wastes containing up to 3 ppm of phosphate was demonstrated in four pilot plant runs and produced a decrease in the hardness of the waste leaving the clarifier. An inadvertent Sr^{90} and Cs^{137} breakthrough occurred during one run which was caused by the breakthrough of hardness from a polishing filter. Satisfactory Sr^{90} and Cs^{137} removal to less than 1% of initial concentration were obtained in two runs.

Operation of the laboratory-scale scavenging-clarification unit produced further evidence that the hardness supersaturation encountered in the pilot plant operation was due at least in part to the presence of complexing agents from decontaminants and detergents in the process waste stream. Increasing "Turco" from 2.4 to 3.2 ppm in simulated waste water raised the hardness of the clarifier effluent from less than 5 to 40 ppm as $CaCO_3$; addition of 0.005 M Na_2CO_3 reduced it again to less than 5 ppm. Increasing "Fab" from 0 to 6 ppm and then 10 ppm raised the hardness from less than 5 to 14 and 32 ppm as $CaCO_3$, respectively; the addition of Na_2CO_3 again aided hardness precipitation.

Engineering, Economics, and Hazards Evaluation. The effect of fission product removal on the cost of high-activity waste management was investigated through interim liquid storage, pot calcination, and shipment to salt mines for permanent disposal, and it does not appear that fission product removal will significantly decrease the cost of waste management. It was assumed that the costs of separation and handling of the separated fission product concentrates was borne by their sale. The costs of interim liquid storage were decreased about 30% over those of untreated wastes because of the decrease in cooling-system requirements, but pot calcination costs were unaffected except that all calcinations could be performed immediately in the least expensive 24-in. diam pots. Shipping costs for the wastes after 90% and 99% fission product removal were about 25% and 50% less, respectively, than for reacidified Purex waste because shielding can be used for the shipping casks. Minimum total costs (less costs for disposal in salt) were about 0.141 mill/kwh_e for 99% removal, and 0.147 mill/kwh_e for 90% removal, compared with 0.147 mill/kwh_e for management of acidic Purex waste from which fission products had not been removed.

Disposal in Deep Wells. Test drilling at the site of the proposed large-scale fracturing experiments with actual mixtures of waste and cement has explored all the favorable part of the geologic section from the middle Conasauga to the top of the Knox, and three particularly favorable zones were identified. These are in the lower Conasauga between depths of 692 and 1002 ft, in the upper or middle Chickamauga between 1700 and 1866 ft, and in the lower Chickamauga between 2648 and 2852 ft. While these appear to be the intervals best suited to waste disposal by hydraulic fracturing, it is probable that much of the rest of the rock can also be utilized.

Sorption of both calcium and strontium by columns of Richfield sand are reduced by the same relative amounts as the influent pH is lowered. At an influent pH of 2, dissolution of minerals from the column causes interference with the EDTA titration of calcium in the effluent and a reduction in exchange capacity from 6.21 to 2.67 meq per 100 g.

Calcium-strontium exchange from 0.005 M Ca^{2+} (calcium chloride saturated with calcium carbonate at pH 7) by mixtures of Richfield sand and calcium carbonate indicate that the calcium carbonate sorbs 1.91 meq of Ca^{2+} per 100 g, with a K_{Ca}^{Sr} of 0.31, and the Richfield sand sorbs 2.91 meq Ca^{2+} per 100 g with a K_{Ca}^{Sr} of 1.50.

Disposal in Natural Salt Formations. Both the array and isolated cylinder tests in the wall and floor of the salt mine were started in July. Operation of the cylinder tests is proceeding normally, but the six peripheral heaters in the array failed due to breakage of the heater lead wires. The cause of the failure is being investigated.

In both the wall and floor tests there has been some shattering of the salt, beginning at a salt temperature of about 280°C, but the heat transfer properties do not appear to have been significantly affected.

Clinch River Studies. Undisturbed cores of bottom sediments at 14 cross sections on the Clinch River, two cross sections on the Emory River, and two cross sections of Poplar Creek were obtained by the use of the Swedish Foil Sampler. A basket-type core retainer was required at some sampling points to obtain satisfactory core recovery. The size distribution, mineralogy, chemical composition, and radionuclide content of the river sediment will be determined when sampling is completed.

Frequency curves for minimum dilution factors of 1-, 3-, 7-, 15-, and 30-day duration have been prepared, and it is found that the minimum 30-day dilution factor is 130 for a two-year recurrence interval and is 78 for a ten-year recurrence interval. The minimum dilution factor for a two-year recurrence interval varies from 130 for a 30-day duration to about 20 for a 1-day duration.

Fundamental Studies of Minerals. The capacity of heat-treated gibbsite is approximately 4 meq per 100 g for cesium and 12 meq per 100 g for strontium. The affinity for strontium by the heat-treated material is reflected by the lessened ability of sodium ions to desorb the strontium. After the sorbent was leached with sodium equal to 23 times the concentration of cesium, 96% of the cesium was desorbed; but when strontium was sorbed, only 77% of the strontium was desorbed after leaching with sodium equal to 730 times the concentration of strontium on the sorbent.

Several other hydrous oxide minerals were heated to 500°C in order to determine whether this heat treatment could improve their

properties for sorbing strontium. Goethite ($HFeO_2$), diaspore ($HAlO_2$), and limonite ($Fe_2O_3.xH_2O$) were used; heat-treated limonite showed the best strontium-sorbing characteristics.

White Oak Creek Basin Study. A sampling train that separates suspended solids directly from creek water is being used to study the transport of suspended solids and their associated activity in White Oak Creek. Results from eight operating runs show that (1) the amount of activity transported downstream by suspended solids is small during low-creek flow rates and/or low-suspended solid loads, but during high stream flow and/or high-suspended-solid loads, significant quantities of strontium, and practically all of the cesium, is associated with sediments; (2) that suspended solids less than 9 μ in size sorb considerably more activity than larger particles; and (3) that considerable variations occur in the concentrations and total amounts of activity associated with the various particle-size groups studied greater than 9 μ in size.

Foam Separation. The total dissolved hardness in ORNL low-activity waste was reduced to less than 2 ppm by making the water 0.005 M in NaOH and 0.005 M in Na_2CO_3 and using 2 ppm of Fe^{3+} as coagulant; it was reduced to about 3 ppm by making the water 0.004 M in NaOH, 50 ppm in Na_3PO_4, and 7 ppm in Fe^{3+}. Strontium in water with such low values of dissolved hardness can readily be removed by factors of 100 to 1000 by foam decontamination. Beaker tests showed that Turco 4234, FAB, sodium hexametaphosphate, and sodium pyrophosphate in only a few parts per million interfere with the precipitation of calcium from 0.01 M NaOH solution

CONTENTS

		Page
1.	Introduction	8
2.	High-Level Waste Calcination	9
	2.1 Evaporation-Calcination	9
	2.1.1 Performance of the Mercury Trap	9
	2.1.2 Gravity-Feed Results	9
	2.1.3 Postcalcination Pressure Test	10
	2.1.4 Results and Conclusions	10
	2.2 Pilot Plant Design and Mechanical Test Program	12
	2.2.1 Welding Program	13
	2.2.2 Grayloc Seal Leak Test	13
	2.2.3 In-Cell Testing	13
	2.2.4 Calciner-Pot Irradiation Experiment	14
	2.3 Laboratory-Scale Development	14
	2.3.1 Fixation in Glass	14
	2.3.2 Vapor-Liquid Equilibrium Studies on Simulated Waste Solutions of Low Acid Content	23
3.	Low-Level Waste Treatment	23
	3.1 Pilot Plant	23
	3.1.1 Effect of Na_2CO_3 on Hardness Reduction	27
	3.1.2 Effect of Na_2CO_3 on Fission Product Removal	27
	3.2 Process Development	28
4.	Engineering, Economics, and Hazards Evaluation	30
	4.1 Effects of Fission Product Removal	30
5.	Disposal in Deep Wells	32
	5.1 Disposal by Hydraulic Fracturing	32
	5.1.1 Evaluation of the Units with Respect to Suitability for Waste Disposal by Hydraulic Fracturing	39
	5.2 Liquid Injection into Permeable Formations	40
6.	Disposal in Natural Salt Formations	43
	6.1 High-Temperature Experiments	43
	6.1.1 High-Temperature Cylinders II and III	43
	6.1.2 High-Temperature Array	46

7. CLINCH RIVER STUDIES

7.1 Dilution Factors

P. H. Carrigan[14]

The simple volumetric diluent capacity of the Clinch River has been defined as the ratio of discharges for Clinch River near Scarboro, Tennessee, to White Oak Creek at White Oak Dam for concurrent periods of record. The daily dilution factors were computed for a period of ten water years, October 1, 1950, to September 30, 1960. Frequency studies of the daily dilution factors for this period were made. Results of one study, the duration curve, was reported previously.[15] A later study of minimum dilution factors was made.

The minimum dilution factors for durations of 1, 3, 7, 15, and 30 days was determined for each water year. The factors for each duration were ranked and the recurrence interval (RI) computed:

$$RI = \frac{n + 1}{m},$$

where

RI = recurrence interval in years,
n = number of years of record,
m = rank of dilution factor; the rank for lowest factor in the period is 1, the next to the lowest is 2, etc.

The variation of the minimum dilution factor for each duration with recurrence interval is the average of time within which a dilution factor will be less than or equal to a given magnitude once.

As shown in Fig. 11 the minimum dilution factor for a 30-day period will be equal to or less than 130 every two years, on the average. In other words there is a 50% chance in any year that the dilution factor will be less than 130 for a period of 30 days. For the ten-year recurrence interval, the 30-day minimum dilution factor is 78. In this case there is a 10% chance in any year that dilution factor will be less than 78. As shown in the curves of Fig. 11 the minimum dilution factor decreases as the duration decreases for any given recurrence interval.

From the duration curve of daily dilution factors,[15] the median daily dilution factor is found to be 570. Thus, the minimum 30-day dilution factors for two-year and ten-year recurrence intervals are about four and seven times less than the median daily dilution factor.

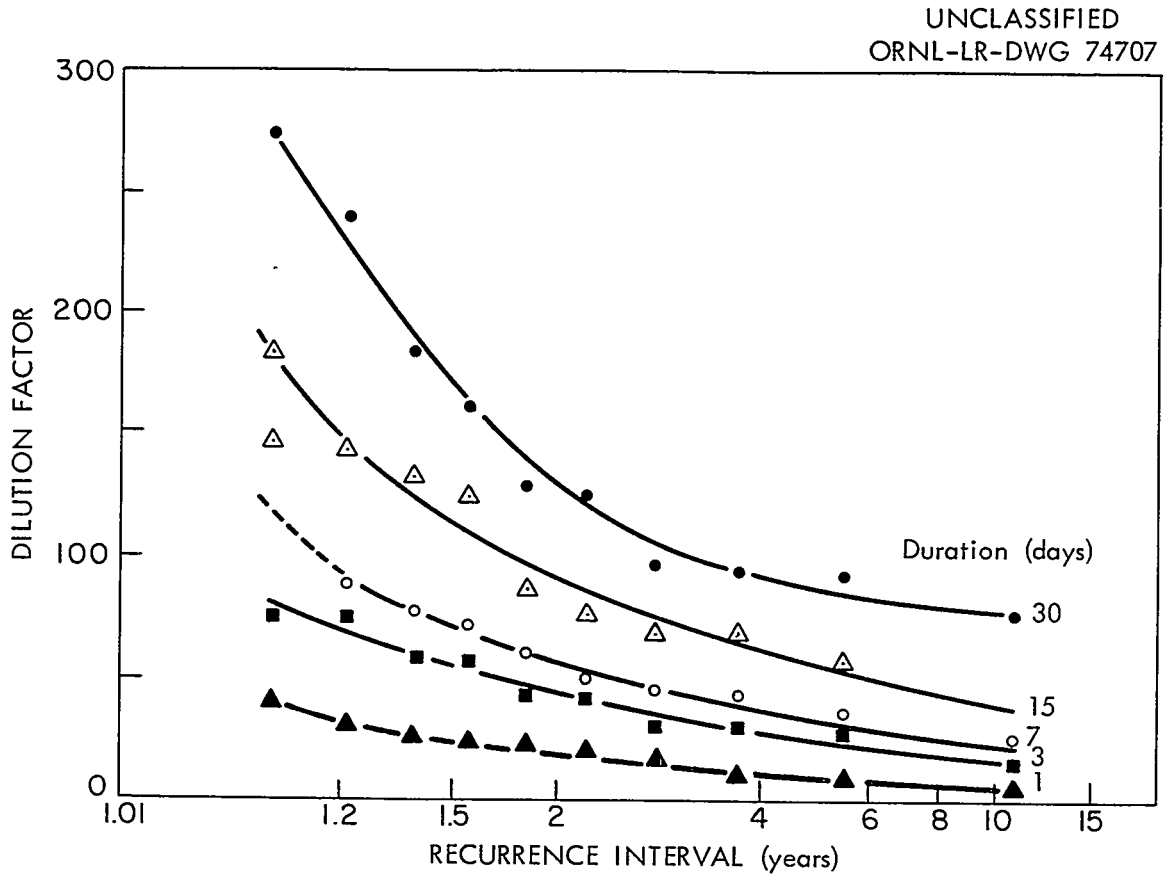


Fig. 11. Minimum Dilution Factor Frequency Curves for 1, 3, 7, 15, and 30 days, Annual Series.

7.2 Bottom-Sediment Sampling

R. J. Pickering[14]

Undisturbed cores of bottom sediments at 14 cross sections on the Clinch River, two cross sections on the Emory River, and two cross sections on Poplar Creek were obtained by the use of the Swedish Foil Sampler, operated by Sprague and Henwood, Inc., drilling contractors. The sampler utilizes a piston and thin steel strips (foils) to prevent friction between the sample tube and the sediment while coring is proceeding and to prevent loss of the core while the core tube is being raised to the surface.

Results with the sampler were excellent at points where the river sediment overlies soil, but, where soft sediment lies directly on bedrock, the lower 6 to 18 in. of sample were commonly lost. Therefore, at the request of the Radioactive Waste Disposal Section, a sampling shoe, containing a basket-type core retainer, was designed for the sampler and then produced by Sprague and Henwood, Inc. When used in conjunction with a plastic sleeve, which falls over the basket to form a nearly watertight seal, excellent recovery of soft sediment overlying hard bedrock has been obtained.

Resampling of "poor recovery" holes is in progress and will be completed during the latter part of August 1962. Core recovery at sampling points where radioactivity is believed to be present throughout the full thickness of the sediment has been between 80% and 100%. In areas where layers of sand or gravel are "sandwiched" between layers of soft sediment, poor core recovery was realized, but few such localities were encountered. Coarse gravel was sampled with dredge samplers. The size distribution, mineralogy, chemical composition, and radionuclide content of the river sediment will be determined when sampling is completed.

8. FUNDAMENTAL STUDIES OF MINERALS

T. Tamura

When gibbsite, an aluminum hydroxide, is decomposed by heating, the resultant product is a highly selective sorbent for strontium in neutral and alkaline media. Measurements of the surface area showed that the product had increased in area from about 0.3 m^2/g for the unheated gibbsite to over 200 m^2/g for the heat-treated material. For further characterization of the product, the capacity of the heated material to sorb cesium and strontium without any interfering ions was determined. The sorbed value would represent the maximum amount of the cation which the sorbent would hold at saturation.

In addition to the capacity determinations for heat-treated gibbsite, other materials were investigated to determine the effect of heating on their ability to sorb strontium. Several promising minerals have been found which show improved sorbing qualities for strontium following heating at 500°C.

8.1 Capacity of Heat-Treated Gibbsite for Cesium and Strontium

The amount of cesium and strontium sorbed by the heat-treated gibbsite is shown in Table 12. The amount of sorbed cesium remained

Table 12. Capacity of Heat-Treated Gibbsite for Cesium and Strontium

Ion	Run No.	pH	Saturation Capacity (meq/100 g)
Cesium	1	6	4.33
	2	8	4.06
	3	8	4.44
	4	10	4.83
Strontium	5	6	9.77
	6	6	11.2
	7	8	14.3
	8	8	11.8
	9	8	11.9

relatively constant over the pH range from 6 to 10. The material shows much higher affinity for strontium; approximately 2 1/2 times more strontium than cesium is sorbed by the heat-treated gibbsite.

Following saturation of the sorbent in the column by the cation, the material was leached by solutions of sodium nitrate of the same pH. When the solution became ineffective as a desorbing solution, the concentration of the sodium nitrate was increased to hasten the reaction. The results of the leaching tests are shown in Table 13. After the sorbent was leached with sodium ions at 23 times the concentration of cesium, 96% of the cesium was desorbed. The removal of cesium was accomplished quite easily. Thus, with the passage of sodium equal to 1.7 times the sorbed cesium, 57% of the cesium was desorbed; and by 3.3 times the removal was 83%.

It was more difficult to remove the strontium from the heat-treated gibbsite. After passage of sodium equal to over a hundred

The best material for strontium listed in Table 14 appears to be heat-treated limonite, and a comparison of its behavior with that of the heat-treated gibbsite is shown in Fig. 12. Like gibbsite, the heated limonite removes strontium best from alkaline pH solutions. The heat-treated gibbsite sample used here did not possess a surface area as high as some of the earlier samples. Since very few investigations have been made on these materials in order to determine the optimal conditions for preparing them, it cannot now be stated which of the hydrous oxides is best for removing strontium.

The observation that unheated limonite possesses a high affinity for strontium is significant. This mineral is a very common constituent in soils, and may be responsible along with hydrous aluminum oxides for sorbing a significant portion of the strontium present in waste streams. If the heat treatment is beneficial primarily because of the development of greater surface area, then the hydrous oxides in soils take on even greater significance, since they occur as much finer particles and would possess even greater surface area. These considerations are being investigated, and preliminary evidence suggest that the hydrous oxides play a significant role in strontium sorption in soils.

9. WHITE OAK CREEK BASIN STUDY[16]

9.1 Movement of Radionuclides in White Oak Creek

T. F. Lomenick

A sampling train that separates suspended solids directly from creek water is being used to study the transport of suspended solids and their associated activity in White Oak Creek. The unit, developed by Dorr-Oliver, Inc., specifically to classify the solids in ORNL's low-activity waste stream, consists of a Merco Bantam strainer and four separate hydroclones. The median diameters of the solids removed from the hydroclones are 29, 19, 12, and 9 μ, respectively.

To date, eight operating runs, ranging in duration from 1 to 4 hr, have been made in White Oak Creek at Mile 1.8. The flow rate of the creek for the sample periods varied from 5 cfs (half the average rate of 10 cfs) to 57 cfs, and the concentration of suspended solids in the water varied from 0.004 to 3.261 g/liter. Construction work in and around the creek, which resulted in the removal of soil cover, may account, in part, for the extremely high concentrations of suspended solids in some of the runs.

A summary of the percentages of cesium and strontiun in creek water associated with the liquid phase and with several particle-size ranges of suspended solids for the eight runs is presented in Tables 15 and 16. Note that the highest values of

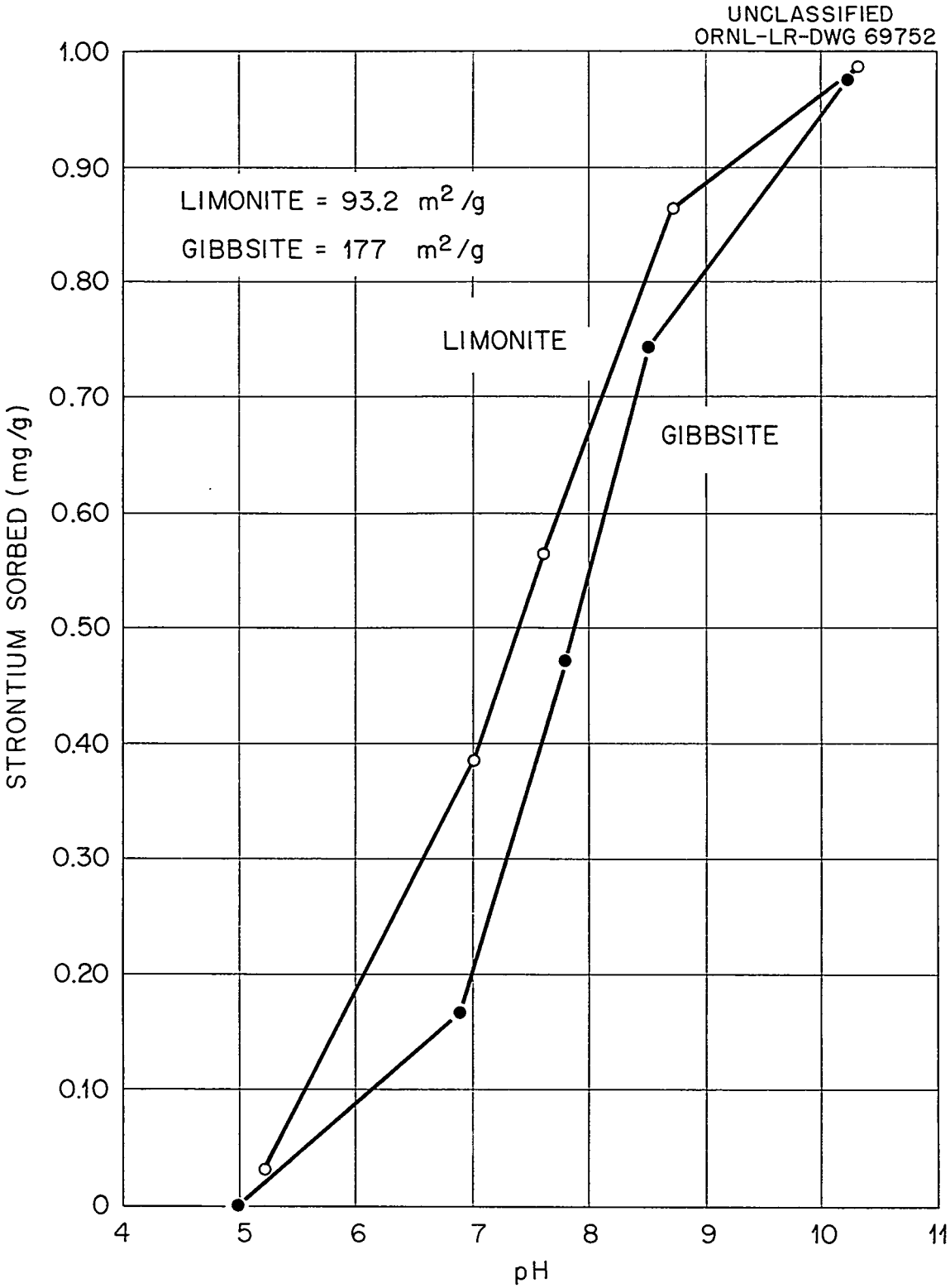


Fig. 12. Strontium Removed by Heat-Treated Minerals in 0.1 M $NaNO_3$.

Table 15. Percentage of Cs^{137} in the Liquid and the Solid Phases of White Oak Creek Water

Run Number	Creek Flow Rate (cfs)	Suspended Solid Concentrations (g/liter)	Liquid Phase	Median Diameter Particle Size (μ)					
				< 9	9	12	18	29	> 250
1	14.4	0.011	71.3	25.7	0.2	1.0	1.3	0.5	< 0.1
2	57.2	0.044	50.7	39.9	0.5	1.8	3.5	2.6	1.0
3	5.5	0.004	58.7	37.7	0.9	1.2	0.3	1.2	< 0.1
4	6.1	0.012	79.5	19.3	0.4	0.4	0.1	0.3	< 0.1
5	5.0	0.010	79.6	18.8	0.5	0.5	0.5	0.1	< 0.1
6	5.3	0.006	77.1	15.9	2.2	1.9	2.2	0.6	0.1
7	7.8	3.261	4.3	85.3	4.0	2.4	2.9	1.1	< 0.1
8	43.5	0.692	3.9	65.4	7.8	5.6	8.7	8.3	0.3

Table 16. Percentage of Sr^{90} in the Liquid and the Solid Phases of White Oak Creek Water

Run Number	Creek Flow Rate (cfs)	Suspended Solid Concentrations (g/liter)	Liquid Phase	Median Diameter Particle Size (μ)					
				< 9	9	12	19	29	> 250
1	14.4	0.011	99.26	0.61	0.03	0.03	0.04	0.03	< 0.01
2	57.2	0.044	98.09	1.01	0.08	0.17	0.47	0.17	0.01
3	5.5	0.004	99.30	0.55	0.04	0.06	0.01	0.04	< 0.01
4	6.1	0.012	99.63	0.33	0.02	0.01	< 0.01	0.01	< 0.01
5	5.0	0.010	99.43	0.52	0.02	0.02	0.01	< 0.01	< 0.01
6	5.3	0.006	99.50	0.40	0.04	0.03	0.02	0.01	< 0.01
7	7.8	3.261	75.52	18.07	3.36	1.68	1.10	0.27	< 0.01
8	43.5	0.692	92.92	3.94	0.87	0.69	1.06	0.50	0.02

sorbed cesium and strontium occur in runs 2, 7, and 8, which are the runs made during high suspended-solid loads and high stream flows. The maximum percentage of sorbed strontium was about 25% (run 7), while as much as 96% of the cesium in the creek water was associated with suspended solids in runs 7 and 8. This suggests that during low flow rates and/or low-suspended-solid loads most of the strontium and cesium in White Oak Creek is associated with the liquid phase, but for high stream flows and/or heavy suspended-solid loads practically all the cesium and a significant part of the strontium is transported downstream by suspended solids. In Tables 15 and 16 it is also seen that there is considerably more activity associated with suspended solids less than 9 μ in size than with the larger particles. For suspended solids larger than 9 μ, considerable variation was found in the amounts of activity associated with the various separated fractions within each run and between runs. It is noted that, in general, the activity is not restricted to any particular particle-size group for all the tests.

The concentrations of cesium and strontium sorbed on several sizes of suspended solids for the eight runs is presented in Table 17. These data show that there is a wide variation in the concentration of sorbed cesium and strontium for each test run and between test runs in the particle-size groups studied. For example, in run 4 the maximum concentration of cesium (21,410 dis min^{-1} g^{-1}) was associated with solids having a median diameter of 12 μ, while in run 7 the maximum concentration of cesium (2320 dis min^{-1} g^{-1}) was observed in solids having a median diameter of 29 μ. It is of interest to note too that the lower concentrations occurred when suspended solid concentrations in creek water were greatest. Thus, although more activity is transported downstream by suspended solids during periods of high stream flow and/or high sediment load, the concentration of activity sorbed on the solids during these periods is less than that sorbed when the stream flow and/or the suspended solid is low.

In summary, results to date show that (1) the amount of activity transported downstream by suspended solids is small during low creek flow rates and/or low suspended-solid loads, but during high stream flow and/or high suspended-solid loads, significant quantities of strontium, and practically all of the cesium, is associated with sediment; (2) suspended solids less than 9 μ in size sorb considerably more activity than larger particles; and (3) considerable variations occur in the concentrations and total amounts of activity associated with the various particle-size groups studied greater than 9 μ in size.

10. FOAM SEPARATION

E. Schonfeld[17] W. Davis, Jr.

Continuous runs and beaker tests on the softening of ORNL low-activity waste were continued[18] as the first step in a form separation

Table 17. Concentrations of Sorbed Activity on Various Particle Size Groups of Suspended Solids in White Oak Creek[a]

Run Number	Creek Flow Rate (cfs)	Suspended Solid Concentrations (g/liter)	Median Diameter Particle Size (μ)							
			9	12	19	29	9	12	19	29
1	14.4	0.011	16,020	15,300	12,430	14,350	5,900	1,370	1,210	2,070
2	57.2	0.044	7,820	10,060	8,460	7,980	740	900	700	340
3	5.5	0.004	18,720	17,940	13,570	15,130	3,960	4,000	974	2,140
4	6.1	0.012	17,950	21,410	16,070	15,660	2,780	2,380	1,500	1,460
5	5.0	0.010	19,620	22,090	16,000	14,200	2,860	2,850	1,600	1,670
6	5.3	0.006	19,520	19,870	16,150	14,170	3,030	2,150	1,350	2,230
7	7.8	3.261	370	480	930	2,320	120	130	140	220
8	43.5	0.692	2,220	2,290	2,120	3,500	310	340	320	260

[a]Concentrations in dis min^{-1} g^{-1}.

Table 20. Effects of Impurities, Precipitants and Flocculating Agents on Hardness Removal

Tap Water or Low-Activity Wastes, plus Additives	Final Hardness, as ppm of $CaCO_3$, after Alkalinizing to:					
	0.005 M Na_2CO_3 + 0.005 M NaOH		0.01 M NaOH		0.005 M Na_2CO_3 + 0.01 M NaOH	0.005 NaOH + 60 ppm PO_4^{3-}
	Ca + Mg	Ca	Ca + Mg	Ca	Ca + Mg	Ca + Mg
ORNL tap water	5.9	2.9	3.5	3.4		
plus 3 ppm Turco 4234	7.2	3.9	28	25		
plus 3 ppm FAB (28% P as PO_4^{3-} equivalent)	10.0	7.0	36		4.3	6.5
plus 3 ppm FAB plus 4 ppm Fe^{3+}	4.1		30		4.8	
plus 2 ppm Na dodecylbenzene sulfonate	7.7	3.2	4.5	3.8		
plus 50 ppm Na dodecylbenzene sulfonate	6.9		5.6			
plus 1.5 ppm Na hexametaphosphate	11.0	8.5	21.0	18.0	4.2	6.5
plus 1.5 ppm Na hexametaphosphate plus 4 ppm Fe^{3+}	3.7		24.0		5.3	
plus 1.5 ppm Na tripolyphosphate	7.5	3.0	8.5	7.3		
plus 1.5 ppm Na pyrophosphate	10.0	5.0	16.0	15.0		
plus 1.0 ppm PO_4^{3-} (as Na_3PO_4)	15.3		34.0		25.2	5.3
plus 1.0 ppm PO_4^{3-} plus 4 ppm Fe^{3+}	4.0		51.0		13.4	
plus 10 ppm Na EDTA.$2H_2O$	6.6[a]		4.9[a]			5.9
plus 3 ppm Am^{2} oxalate	5.4		2.4			
plus 7 ppm F^- (as NaF)	6.9		4.6			5.7
plus 0.5 ppm Cu^{2+}	6.2		4.3			
plus 1.5 ppm Na hexametaphosphate plus 0.5 ppm Cu	18.1		37.0			
Low-activity waste, 1 (total P as PO_4^{3-} eq. 2.6 ppm)	17.4		49.0			
Low-activity waste, 2 (total P as PO_4^{3-} eq. 2.8 ppm)	13.1	9.6	56.0	50.0		
Low-activity waste, 3 (total P as PO_4^{3-} eq. 3.0 ppm)	16.1	13.4	36.0	35.0		5.1
Low-activity waste, 4 (total P as PO_4^{3-} eq. 3 ppm)	29.0		54.0			
Low-activity waste, 5 (total P as PO_4^{3-} eq. 3 ppm)	19.1		49			8.7
Low-activity waste, 4 plus 6 ppm Fe^{3+}	10.9					
Low-activity waste, 3 plus 25 ppm $Ca(OH)_2$	15.6	11.2	41	37.5		
pH	1.3		~11.7		~11.8	~11.3

[a]Noncomplexed (Ca + Mg).

11. CONTENTS

1. Waste Treatment and Disposal Progress Report for April-May, 1961, ORNL-CF-61-7-3.

2. Waste Treatment and Disposal Progress Report for August and September 1961, ORNL-TM-49 (Nov. 29, 1961).

3. J. T. Roberts and R. R. Holcomb, A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes, ORNL-3036 (May 22, 1961).

4. R. R. Holcomb and J. T. Roberts, Low-Level Waste Treatment by Ion-Exchange. II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin, ORNL-TM-5 (Sept. 25, 1961).

5. T. Subbaratnam, K. E. Cowser, and E. G. Struxness, Studies of the Use of Coagulant Aids in the Lime-Soda Treatment of Large-Volume, Low-Level Radioactive Liquid Wastes, ORNL-CF-60-7-17 (Aug. 22, 1960).

6. R. R. Holcomb, Low-Level Waste Treatment, Part I: Decontamination of Low-Radioactivity-Level Process-Water Wastes by a Scavenging--Ion Exchange Process, ORNL-3322 (in preparation).

7. Waste Bimonthly for April-May 1962.

8. Summary Report for Section B, January-June 1962.

9. Letter from W. H. Reas, HAPO, to R. E. Blanco, ORNL, March 30, 1962.

10. R. L. Bradshaw et al., Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. I. Interim Liquid Storage, ORNL-3128 (Aug. 7, 1961).

11. J. J. Perona et al., Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. II. Conversion to Solid by Pot Calcination, ORNL-3192 (Sept. 27, 1961).

12. P. B. Stockdale, Geologic Conditions at the Oak Ridge National Laboratory Relevant to the Disposal of Radioactive Waste, ORO-58 (Aug. 1, 1951).

13. M. L. Jackson, Soil Chemical Analysis, p. 64, Prentice-Hall, New Jersey, 1958.

14. On loan from Tennessee District, Surface Water Branch, Water Resources Division, U.S. Geological Survey.

15. R. J. Morton, Ed., Status Report No. 3 on Clinch River Study (in press).

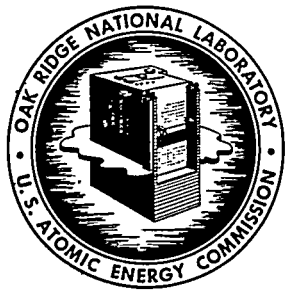
16. This project, entitled "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin," (AEC Activity 060501000) is supported by the U.S. Atomic Energy Commission's Division of Biology and Medicine. All other projects covered in this report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

17. On loan from Radiations Applications, Inc., Long Island City, New York.

18. Waste Treatment and Disposal Progress Report for April-May 1962, ORNL-TM-376.

19. Chemical Technology Division, Chem. Dev. Sect. B., Quarterly Progress Report, Oct.-Dec. 1961, ORNL-TM-177.

2005



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-516

15

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR NOVEMBER-DECEMBER 1962, AND JANUARY 1963

This document has been approved for release to the public by:

David R Hamrin 7/28/95

Technical Information Officer Date
ORNL Site

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM-516

CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR NOVEMBER-DECEMBER 1962, AND JANUARY 1963

F. L. Parker and R. E. Blanco

DATE ISSUED

JUN 12 1963

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level Waste Calcination. Two waste calcination tests were completed in the large-scale equipment: test-R-69, a TBP-25 gravity-feed calcination test, and test R-70, a formaldehyde-treated Purex-65 waste test, with continuous evaporation.

Test-R-69 was the last in a series of TBP-25 tests, and the purpose of this test was twofold: (1) rates and operating procedures were evaluated by using gravity feed as in run R-68; (2) the six-zone calcination furnace was rewired so that it would operate as a one-zone-controlled furnace. If any of the six thermocouples used for furnace control attained the set-point temperatures, all six of the furnace zones would turn off. The average feed rate was 14 liters/hr. In comparison, run R-68, a six-zone-control test, had an average feed rate of 26 liters/hr. The water-to-feed ratio for this test was 5.2. The resulting solid contained 1000 ppm of nitrate and had a bulk density of 0.64 g/cc. Control was good during this test; however, the one-zone furnace control made the over-all rate much lower.

Test R-70 was the first test of a waste composition formula that simulated 1965 formaldehyde-treated Purex waste. For this test, the furnace was split into three zones. The top and bottom zones were controlled independently, while the four middle zones were controlled as one zone. The average feed rate was 40 liters/hr, with a maximum rate of 200 liters/hr. No additional water was added to the evaporator to remove nitric acid because this waste was very dilute in total nitrate ion. The resulting solid had 200 ppm of nitrate and a bulk density of 1.25 g/cc; control was good. The calciner pot was removed and sand blasted after the test was completed, and there was seen a band of corrosion about 1 ft from the bottom, with pits as deep as 50 mils in the 100-mil-thick pot. Calcium nitrate had been added to the calcining pot to reduce the volatility of sulfate. The calcium nitrate added corresponded stoichiometrically to 10% of the sulfate plus 100% of the phosphate and fluoride in the feed.

Hard, microcrystalline solids, incorporating up to 45% Purex waste oxides, were prepared on a laboratory scale from simulated high sulfate and 1965 FTW waste solution by addition of phosphite or phosphate and sodium, calcium and/or magnesium. Simulated Darex waste was fixed on a semiengineering scale into a very hard, strong product that incorporated 25% waste oxides and represented a volume reduction of 5.17 from the waste solution. The feasibility of removing mercury from 1965 Hanford formaldehyde-treated (FTW) Purex waste by amalgamation with copper was demonstrated on a laboratory scale.

Type 304L stainless steel coupled to titanium 45A showed weight losses amounting to a maximum corrosion rate of 0.41 mil/month for 192 hr of exposure above refluxing Hanford 1965 FTW solution. Rates of solution and interface specimens were slightly lower. Titanium 45A showed slight weight gains for both coupled and uncoupled specimens.

Low-Level-Waste Treatment- The carboxylic resin, Amberlite IRC-50, effectively removed as much as 70 ppm of residual hardness from phosphate-contaminated waste prior to cesium loading on Duolite CS-100 resin. Under the worst conditions (70 ppm of hardness), the hardness broke through the IRC-50 pretreatment column after passage of about 1200 bed volumes of waste. This treatment is superior to the removal of hardness by the addition of Na_2CO_3 since the latter reduces the loading of cesium on the CS-100 resin because of competition of sodium with cesium. A residual hardness of 40 ppm, for example, caused 0.1% breakthrough of cesium on the CS-100 resin at about 570 bed volumes in the presence of the normal (0.01 M) sodium concentration vs about 900 bed volumes when the hardness was eliminated by the addition of 0.005 M Na_2CO_3 (0.02 M Na^+ total). However, removal of the residual hardness by the IRC-50 resin postponed the breakthrough to the value (about 2000 bed volumes) achieved in the absence of hardness and at the normal (0.01 M) sodium content. The IRC-50 resin, like CS-100, can be regenerated with 0.5 M HNO_3.

Design was started on the equipment and piping changes to the ORNL Low-Level Pilot Plant for demonstrating the fixed bed and continuous contractor ion exchange processes proposed by I. R. Higgins, and for the installation of a new, agitated clarifier for the scavenging precipitation-ion exchange process.

Engineering, Economics, and Safety Evaluation. In a study based on optimistic expectations of future processes for fission product separations processes, estimated costs for the management of wastes from which 90 and 99% of all fission products had been removed were from 70 to 80% of those for the management of waste from which no fission products had been removed.

This saving of 20 to 30% is not believed to be sufficient to pay for the cost of fission product removal and final disposal of the concentrates; and hence does not represent an economic route for waste management unless a substantial market for separated fission products exists to provide a substantial income.

As a basis for this study, it was assumed that after fission product removal, the waste was identical to neutralized Purex waste in volume and in the composition of the major constituents. The sequential steps in the management of waste from processing 1500 metric tons per year of uranium converter fuel irradiated to 10,000 Mwd/ton were as follows: interim storage of liquid waste, conversion to solids by pot calcination, interim storage of calcined solid waste, shipment of 1000 miles, and final disposal in a salt mine. Minimum-cost schemes were worked out involving optimum choices of interim times of liquid and solid storage, diameter of the waste-calcination cylinder, and age at time of burial in the salt.

Costs for wastes from which fission products had been removed were the smallest for calcination in 24-in.-diam vessels, were not

strongly affected by age, and fell in the range of 0.017 to 0.019 mill/kwh_e. The lowest cost for acid Purex waste without fission product removal was about 0.024 mill/kwh_e, obtained by using either 12- or 24-in.-diam calcination vessels and burying them in salt after allowing 30 years for decay of the fission products in the calcined wastes.

Man may be exposed to radiation through a number of pathways due to the discharge of radioactive fluids to the Clinch River. Contaminated bottom sediments can contribute to the total dose. Based on sediment analyses and the assumption of a uniform, infinite source, the largest bottom sediment dose rate (at contact) of 12 millirads/day of exposure would have occurred in 1959 on the Clinch River and was derived from 0.4 beta and 0.6 gamma radiation. The beta dose rate is eliminated by about 1 cm of water shielding; the gamma dose rate is reduced by an average factor of 18 after attenuation through 3 ft of water.

Calculations of the activity of the fission products and transuranic elements contained in a single 400,000-gal storage tank were completed. Initial calculations were made of the dispersion into the atmosphere of this activity, using various assumed accidental situations.

Disposal in Deep Wells. Geothermal measurements in Joy No. 1 well and well 400 S, made by the U. S. Geological Survey, were compared with the thermal conductivity of core samples and a provisional rate of heat flow from the earth's interior (0.73 ± 0.04 $\mu cal/cm^2$) was computed.

A surprising discovery of abnormally low fluid pressure in the lower Chickamauga and upper Knox, observed during the temperature survey in Joy No. 1 well after it had been cased, is discussed and its significance assessed.

Mineralogical analyses of 25 samples from the 3263-ft-deep Joy well are reported. They indicate a considerable difference in the samples from the several possible fracturing zones.

Unexplained anomalies in the pumping time of several mixes were reported by Westco, and their causes are being investigated. A program of mix evaluation was initiated by the Halliburton Company. The retention of radionuclides by the set grout was investigated, and it was shown that even under adverse conditions the bulk of the cesium and almost all the strontium will be retained.

The design of the injection well was completed, and contracts are being negotiated for drilling, logging, and cementing of the injection and observation wells. The current schedule calls for drilling and cementing the wells, completing the plant design, and installing the waste storage tanks, waste transfer line, and waste pumps this fiscal year.

Disposal in Natural Salt Formations. Additional observations were made of the condition of the heaters and of the 10-in.-diam holes used in the high-temperature heat tests. Failure of peripheral heaters in the array tests was due to localized high concentrations of nickel sulfide in grain boundaries, combined with the magnetostrictive effect. Heater sheaths made of type 304L stainless steel contained precipitated carbides at grain boundaries. Precipitated carbides were associated with intergranular corrosion. Type 304 stainless steel thermocouple sheaths also underwent heavy intergranular attack.

Removal from the structure of the wall heater hole as part of a large block made possible detailed examination and photography of the shattered zone around the heater. The maximum radius of the shattered zone from the center of the original hole was about 7 in. The limit of shattering could not be determined exactly because of the recompacting of shattered and expanded salt. Comparison of the shattered zone with temperature profiles confirms 290°C as the maximum temperature at which Hutchinson salt will shatter.

A possible explanation of the permanent increase in salt volume with increased temperature was found to be enlargement of negative crystals due to expansion of the liquid phase and creation of larger bubbles.

Clinch River Study. Gross gamma analyses of bottom-sediment cores from the Clinch River were begun. A specially designed "core scanner" is being used, and it consists of a 3- x 3-in. NaI scintillation crystal and matched phototube enclosed in a 4-in.-thick lead shield, with a 2- x 2-in. collimator slit. A hoist automatically moves the core vertically past the collimator in 2-in. increments. Results indicated that core drilling successfully samples the full depth of the radioactive sediments. Appreciable variations in radioactivity with depth have been noted in many of the cores.

Calcite deposited on a metal object suspended in the Clinch River contained concentrations of radioactive ruthenium and strontium that lie between concentrations in Clinch River bottom sediments and those in suspended sediments. Thus, if bottom sediments contain an appreciable amount of precipitated calcite, it would add materially to the radionuclide content of the sediment.

Fundamental Studies of Minerals. Strontium removals by four different sorbents were compared by using column methods. Tests were performed with a 0.5 M $NaNO_3$ solution adjusted to pH 10 and containing 10^{-5} M $Sr(NO_3)_2$; the flow rate was 3 ml $min^{-1}cm^{-2}$. Commercial-grade activated alumina was most efficient; the 50% breakthrough volume for 10 g of it was approximately 6500 cc for the first column and 27,000 for the second. The same weight of Dowex 50-X12 treated 2600 cc for the same breakthrough percentage. Both vermiculite and clinoptilolite were ineffective under these test conditions; in both cases breakthrough occurred when the throughput volume was less than 150 cc. Intermittent checks showed that the effluent pH from the

Dowex column had dropped to 9.7, whereas the pH from the alumina column showed readings generally between 8 and 9, with some readings as low as 7.5.

White Oak Creek Basin Study. A series of 250 core samples were taken in the bed of former White Oak Lake to determine the quantity, type, and distribution of radionuclides in the area. These cores show that the contaminated lacustrine sediment, which was deposited during the 1943-1955 impoundment, is as much as 20 in. thick in the lower part of the lake bed near the dam; however, there is a gradual thinning of the layer upstream and, in general, toward the shoreline.

Foam Separation. A 9-in.-diam sludge column was operated with low-activity process waste water at flow rates up to 60 gal $ft^{-2}hr^{-1}$. By making the water 0.005 M each in NaOH and Na_2CO_3 and 2 ppm in Fe^{3+}, the total dissolved hardness (as $CaCO_3$) was reduced to 2 to 5 ppm, and Sr^{90} decontamination factors of 10 to 15 were achieved. Average decontamination factors for Co^{60}, Cs^{137}, Ru^{106}, and Ce^{144} were 30, 1.1, 2.0, and 40, respectively. During these tests the average phosphate and alkylbenzene sulfonate concentrations in the process waste water were 1 to 2 and 0.75 ppm, respectively. Precipitation of calcium and magnesium by making tap water 0.004 M in NaOH and 60 ppm in PO_4^{3-} was found to be nearly complete in 3 min. The $CaCO_3$-$Mg(OH)_2$ sludge from caustic-carbonate precipitation can be incorporated in concrete.

As foam breakers, screen lined, perforated centrifuge bowls were tried. Foam was more efficiently condensed by 100- or 120-mesh-per-inch screen than by 40 or 200 mesh at low rates of dry foam than at high rates of wet foam and for lower centrifuge speeds if the capacity was not exceeded. The capacity increased as the speed increased. A 24-in.-diam column was installed for the study of scale-up problems without tracer. In a 6-in.-diam column, decontamination factors for the precipitation of calcium and magnesium (with NaOH-Na_3PO_4-$FeCl_3$), followed by foam separation using the slurry feed were 19 to 52, independent of whether "FAB" was present. Decontamination factors for this precipitation without foam separation was about 10. The strontium decontamination factors using effluent from operation of the laboratory clarifier on ORNL low-level waste (see above) was 27 for a run with flow rates selected for a strontium distribution factor of 1.7×10^{-3} cm. The strontium distribution factors of $(0.6 \text{ to } 2.4) \times 10^{-3}$ cm indicated by other column runs with clarifier effluent agree with values for about 5 ppm Ca^{2+} in laboratory studies.

CONTENTS

		Page
1.	Introduction	8
2.	High-Level Waste Calcination	9
	2.1 Evaporation-Calcination	9
	2.2 Mechanical Test Program	20
	2.3 Fixation in Glass	23
	2.4 Removal of Mercury from Waste Solutions	30
	2.5 Corrosion	32
3.	Low-Level Waste Treatment	34
	3.1 Low-Level Waste Treatment	34
	3.2 Design of Pilot Plant for Decontaminating Low-Level Waste	38
4.	Engineering, Economics, and Hazards Evaluation	42
	4.1 Engineering and Economics of Waste Management	42
	4.2 Analysis of the Safety of Routine Operating Discharges From White Oak Creek to the Clinch River	49
	4.3 Safety of Tank Storage of High-Level Liquid Wastes	55
5.	Disposal in Deep Wells	57
	5.1 Disposal by Hydraulic Fracturing	57
	5.2 Design of the Fracturing Disposal Pilot Plant	72
6.	Disposal in Natural Salt Formations	89
	6.1 High Temperature Experiments	89
	6.2 Thermal Stability of Salt	98
	6.3 Permanent Expansion of Negative-Crystal Cavities	98
7.	Clinch River Study	101
	7.1 Bottom Sediments	101
8.	Fundamental Studies of Minerals	106
	8.1 Column Study of Several Sorbents for Strontium	106
9.	White Oak Creek Basin Study	110
	9.1 Distribution and Transport of Radionuclides in the Bed of Former White Oak Lake	110
	9.2 Oak Ridge Area Hydrology	112

7. CLINCH RIVER STUDY

7.1 Bottom Sediments

R. J. Pickering* P. H. Carrigan, Jr.*

7.1.1 Gross Gamma Scanning of Bottom Sediment Cores

Calibration of the "core scanner," a device for determining the vertical variations in gamma activity in intact undisturbed cores of Clinch River bottom sediments (See previous quarterly report.), has been completed, and scanning of cores for gross-gamma activity is in progress. The vertical increment of core scanned through a 2-in.-long collimator with 2- x 2-in. and 1- x 2-in. openings has been determined by using a 3-in.-diam plane source of radioactivity. The source, which consisted of a disc of blotter paper which was impregnated with Cs^{137} and sealed between thin plastic sheets, was placed horizontally at mid-height in a plastic core tube filled with "uncontaminated" bottom sediments from Norris Reservoir. The gross gamma count rate produced by this source was determined at various distances below the center line of the collimators. The results of the determination, shown in Fig. 7.1, indicate that because the collimator will admit direct radiation from the rear edge of the source when the source is at a distance of 4-1/2 in. below the center line of the collimator slit, the core scanner "sees" a segment of core longer than 2 in.

An uncorrected gross-gamma scan of a core from Clinch River Mile (CRM) 1.3 is shown in Fig. 7.2. The results of the scan demonstrate the vertical variations in gross radioactivity within the core and indicate that the segment sampled includes the entire thickness of the zone of radioactivity.

After gross-gamma scanning of the cores has been completed, the vertical distribution of specific radionuclides in selected cores will be determined by routing the output of the core scanner through a 512-channel analyzer. The cores will then be dissected, and the radionuclide content of composites of the cores in each cross section will be determined. In addition, various physical and chemical tests will be performed on the composite samples and on selected cores or core segments in order to gain a better understanding of the processes by which the radionuclides become incorporated in the bottom sediments.

---

*On loan from Water Resources Division, U. S. Geological Survey.

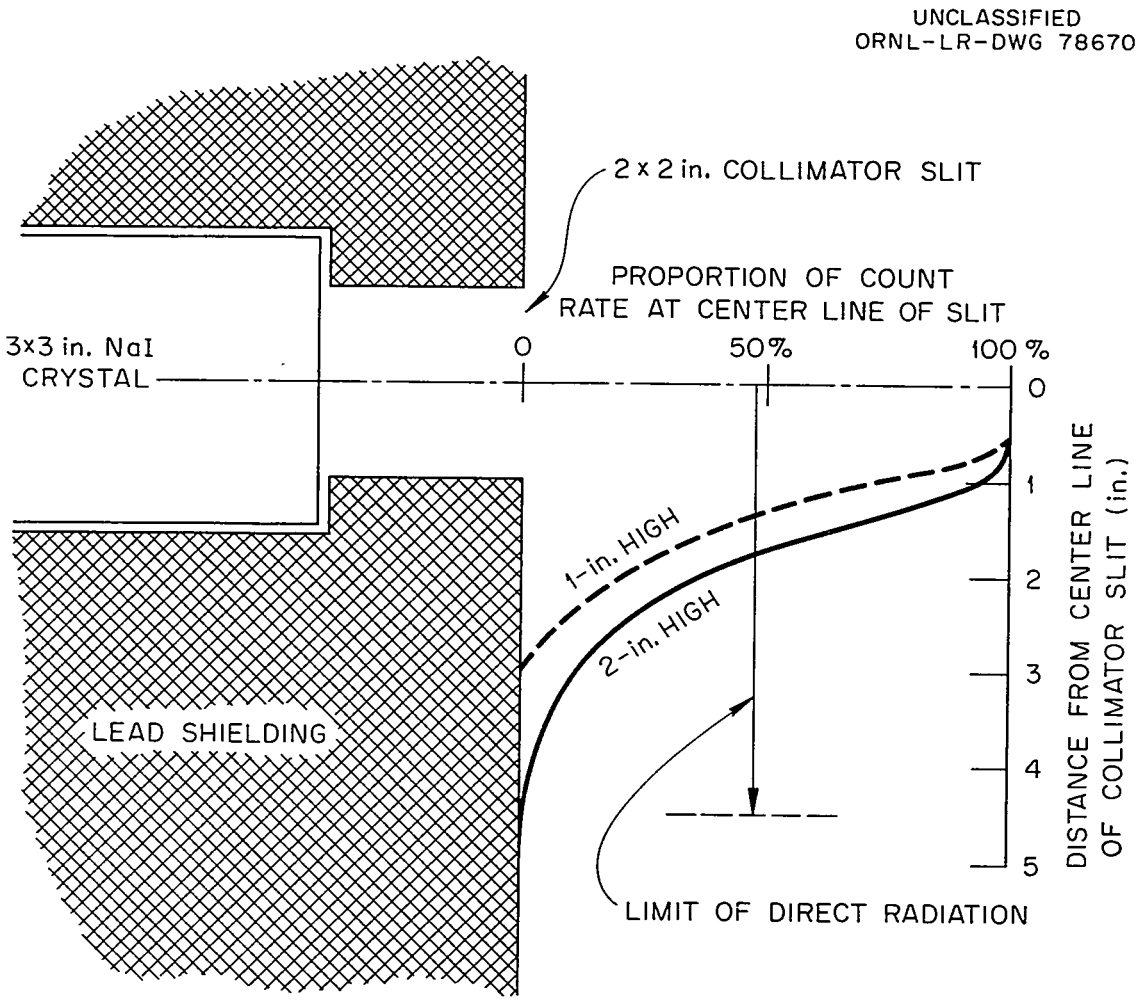


Fig. 7.1. Effective Slit Width of Collimator for 3-in.-diam Plane Source of Cs^{137} Normal to the Face of the NaI Crystal.

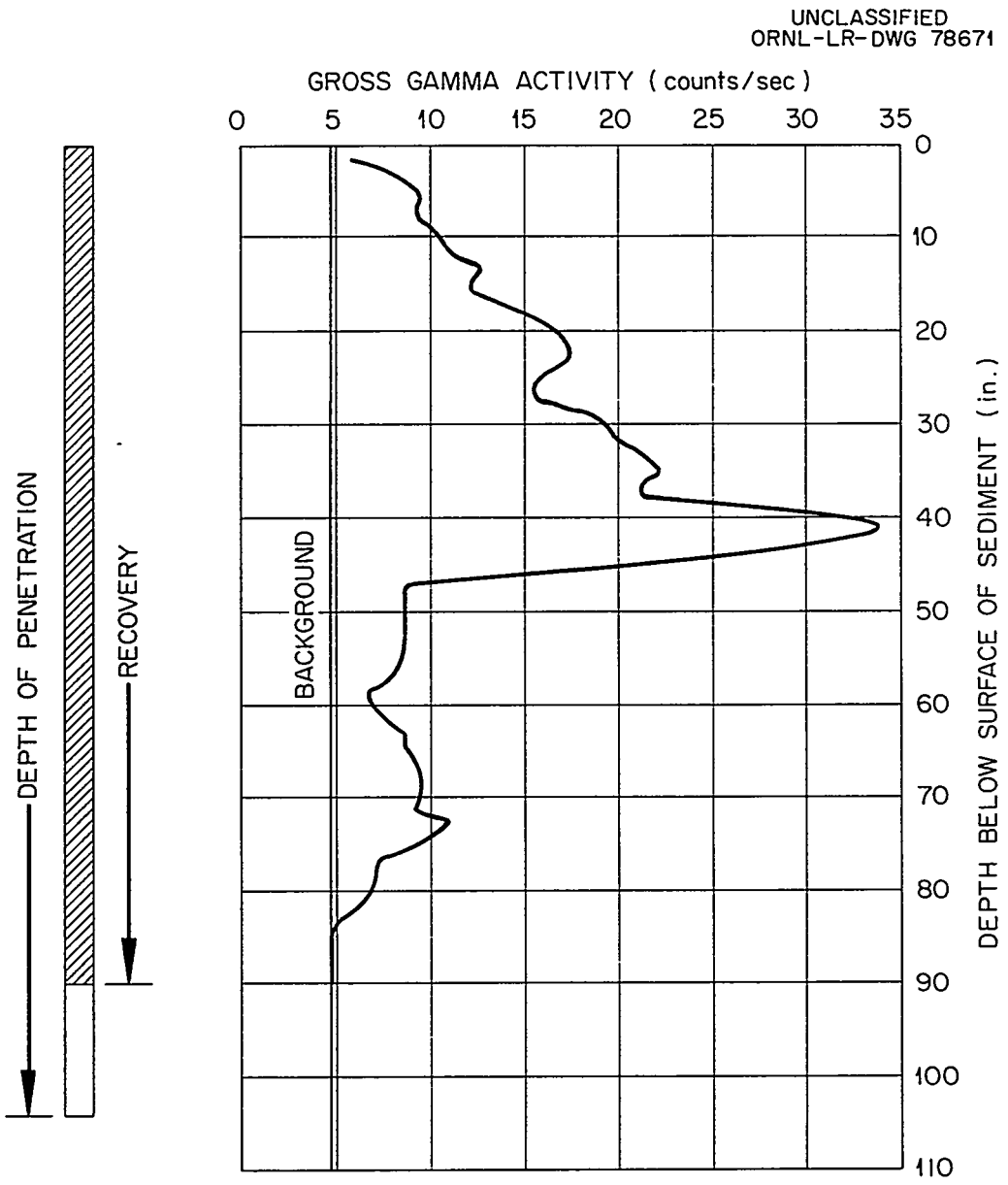


Fig. 7.2. Distribution of Radioactivity in Core 5, in Section at Clinch River Mile 1.3.

7.1.2 Variations of Radionuclide Concentrations in Bottom Sediments with Time

Determinations of the radionuclide content of samples collected annually from the upper portion of the bottom sediment in the Clinch and Tennessee rivers by the Applied Health Physics Section reveal that the content of each of the most abundant radionuclides bears a direct relationship to the total amount of that radionuclide released from White Oak Lake during the preceding 12-month period. This relationship appears to exist whether or not there has been a net gain in sediment at the particular cross section sampled. Possible explanations are: (1) that the radioactivity in the two rivers upstream from the sampling points was primarily associated with suspended solids in the water and that the sediment sampled during the annual sediment surveys, which were always conducted during the summer, had been deposited during the previous year, regardless of whether there had been a net loss or a net gain of sediment during the entire year or (2) that radionuclides in the river water more or less continuously maintain equilibrium with the bottom sediments which thus reflect the most recent radionuclide concentrations in the water. The observed relationship extends at least as far downstream in the Tennessee River as Guntersville Reservoir.

The direct relationship between radionuclide release and radioactivity in the upper portion of bottom sediments in the Clinch and Tennessee rivers might possibly be used to predict both the radionuclide content of the bottom sediments and the exposure hazard resulting from their radioactivity on the basis of information on radionuclide release alone. This possibility will be given further attention in subsequent investigations of bottom sediment radioactivity.

7.1.3 Precipitation of Calcite on Current Meter at Clinch River Mile 19.1

Recovery of a current meter that had been submerged for 14 months in the Clinch River at Mile 19.1 revealed that a dark-brown coating of calcite, 0.004 to 0.005 in. thick, had formed on all exposed surfaces of the meter. A radiochemical analysis of the coating showed that each gram (dry weight) contained 123.9 μμc of $Ru^{103-106}$ and 10.1 μμc of Sr^{89-90}. A trace of Cs^{137} was detected, and the count on total rare earths was enough above that attributable to Y^{90} to suggest the presence of other rare earths, probably primarily Ce^{144}.

As shown in Table 30, the concentrations of radioactive ruthenium and strontium in the calcite lie between concentrations of those nuclides in Clinch River bottom sediments and concentrations in suspended sediments. Thus, if bottom sediments contained an appreciable amount of precipitated calcite, the calcite would add materially to the Ru^{106} and Sr^{90} content of the sediment. Ashing of the dry calcite at 500°C resulted in a loss in weight of 5.5%.

The presence of fine-grained calcium carbonate in Clinch River bottom sediments has been inferred from the results of determinations of

Table 30. Bottom Sediment

Place Where Analyzed	Sampling Date	Clinch River Mile	Ru^{106} (μμc/g)	Sr^{90} (μμc/g)	Remarks
ORNL	1960	18.1	21.2	2.30	
ORNL	1960	19.5	27.9	1.08	
USPHS	1960	14.6	3980	5	
USPHS	1960	20.8 (-150 ft)	100	8.6	
USPHS	1960(?)	11	200.8	2.8	Evidence shown in ORNL-3202, Table 6, p. 20, that clams concentrate ruthenium and strontium
ORNL	1961	11.9	18.3	2.6	
ORNL	1961	15.3	16.7	1.0	
ORNL	1961	19.2	7.4	1.0	
		Calcite Precipitate on Current Meter			
ORNL	1962	19.1	123.9	10.1	Trace Cs^{137}, evidence of Ce^{144}
		Suspended Sediment			
ORNL	Nov. 1960 to June 1961	14.5	764 - 6696	10.8 - 851	General range of more than 30 analyses

the exchangeable cation content of five samples of bottom sediment. The amount of "exchangeable" calcium in all five samples was greater than the total cation exchange capacities of the sediment samples. These anomalous results, together with high pH values reported for the same sediment samples, appear to indicate that calcium carbonate in the sediment was dissolved during the removal of the "exchangeable" cations from the sediment and produced the unreasonably high values for "exchangeable" calcium in the sediment.

In order to determine when, or whether, calcite would precipitate from the river water onto a metal object with no electrical connections, three sets of aluminum plates have been anchored in the Clinch River at Miles 5.5, 15.0, and 19.1. Each set consists of three plates, spaced so one plate will remain near the river bottom, one will remain a short distance below the surface, and the third will remain approximately midway between the water surface and the river bottom. The plates will be observed periodically to see whether calcite has formed on their surfaces.

8. FUNDAMENTAL STUDIES OF MINERALS

T. Tamura

8.1 Column Study of Several Sorbents for Strontium

In studies with columns of sorbents for removing strontium from solution, gibbsite showed a high selectivity for strontium in alkaline $NaNO_3$ solution. This gibbsite (aluminum hydroxide) had been heated to 400°C. After investigating the properties of unheated and heat-treated gibbsite, it was concluded that the heat treatment had converted the gibbsite into a product similar to that sold as activated alumina by the Aluminum Company of America. A sample of activated alumina, labeled F-20, was obtained from Alcoa, and slurry tests showed that F-20 was also selective for strontium. This development made it highly desirable to compare several materials in column systems in order to ascertain the potential usefulness of this material for waste treatment. The four materials included in the tests were Dowex 50-X12, clinoptilolite, vermiculite, and F-20 alumina. The Dowex 50 and vermiculite were pretreated with NaCl to convert them into the sodium forms. The clinoptilolite was treated with 1 M HCl to decompose the calcite impurity in the sample. Following pretreatment, each sample was washed until tests with $AgNO_3$ for chloride were negative. No treatment was given to F-20 alumina prior to use in the first column test.

The tests were run with 1/2-in. glass tubing, containing 10 g of sorbent (weight based on the air-dry sample). The simulated waste solution was 0.5 M $NaNO_3$ adjusted to pH 10 with NaOH and containing 10^{-5} M $Sr(NO_3)_2$. The flow rate was maintained at 3 ml min^{-1} cm^{-2}.

The volume throughput and effluent activity measured in the four test runs are shown in Fig. 8.1. It appears that the flow rate was too high for both vermiculite and clinoptilolite to be efficient. The first 50-cc volume showed activity breaking through in both of these columns; the clinoptilolite did show improvement with time. The latter behavior may be due to the change-over of clinoptilolite from the hydrogen to the sodium form. The effluent from Dowex 50 showed very little activity in the first 2 liters, and, with F-20 alumina, very little activity was measured in the effluent up to 5800 cc. Unfortunately, effluent samples from the alumina column were lost in the collection procedure, and the next reliable sample showed 54% activity. The behavior of the alumina is unusual in that the continued flow of solution presumably after the alumina is saturated resulted in an effluent that contained more strontium than the influent solution. This behavior suggests that the surface-layer alumina may be dissolving or "flaking off" with continued flow (The high pH of the influent solution would facilitate this dissolution of the alumina.). After the end of the run the column was monitored along the outside wall with a G-M survey meter, and the activity distribution showed that the influent zone had a lower concentration of strontium than the effluent zone. It is also significant to note that the F-20 alumina does show sorption capacity for strontium to an extent that is competitive with other sorbents.

Since it was thought that the high effluent activity of the F-20 alumina column was caused by the high pH of the influent waste solution, another column was run to test this idea. Prior to passing the simulated waste through the column, it was decided to run 0.5 M $NaNO_3$ adjusted to pH 10 (without strontium) through until the effluent pH equaled the influent pH of 10. After this treatment the pH of system would be favorable for dissolution or "flaking," and strontium breakthrough was expected to occur after a few column volumes of waste had passed through. However after passage of 1700 cc of solution, the pH was 7.65; and this value had been reached after the first 20-cc increment had a pH of 9.4, and subsequent samples showed gradual reduction in pH. It was, therefore, decided to start the simulated waste through the column with close attention to the pH in addition to the activity of the effluent.

The results of the second F-20 alumina run are plotted in Fig. 8.2. The results of the earlier alumina run are also plotted. The pretreated alumina showed less than 1% breakthrough up to 13,000 cc, compared with 5800 cc for the first run. The effluent activity showed a gradual increase, and, after 35,000 cc, the activity was about 85% of that of the influent. The pH of the effluent, which was measured periodically, showed that it did not reach the influent pH of 10 during the entire test run. The maximum observed pH of the effluent was 9.0 in the 50-cc increment collected after passage of 23,700 cc. The minimum pH was 7.50 in the 50-cc increment collected after 15,500 cc. The pH varied continuously over the reported range during the entire run. Although the results of this column run showed improved performance over the first test run, it should be pointed out that the cause of the improvement is not known.

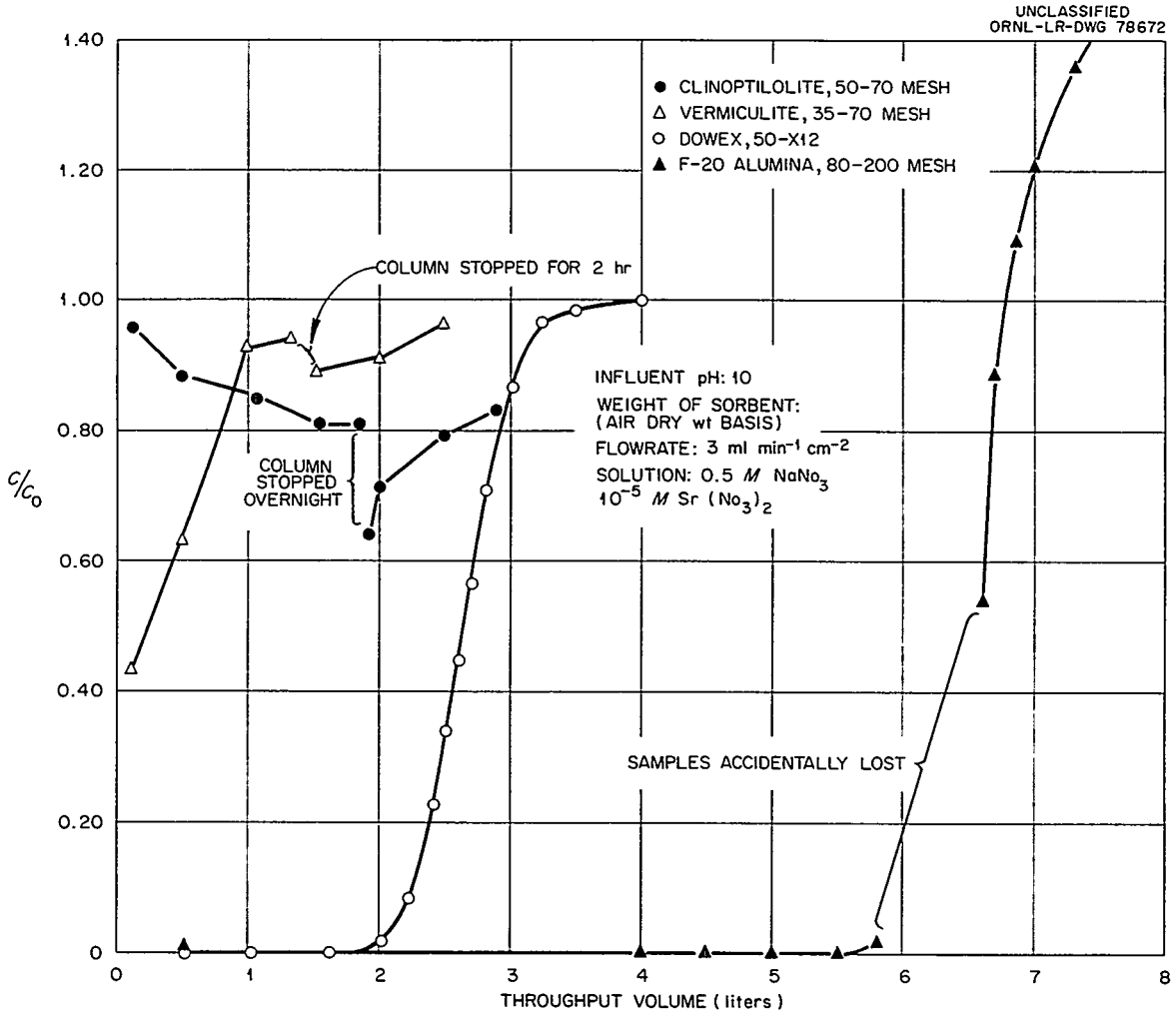


Fig. 8.1. Strontium Removal by Several Sorbents: Effluent Activity of Simulated Waste.

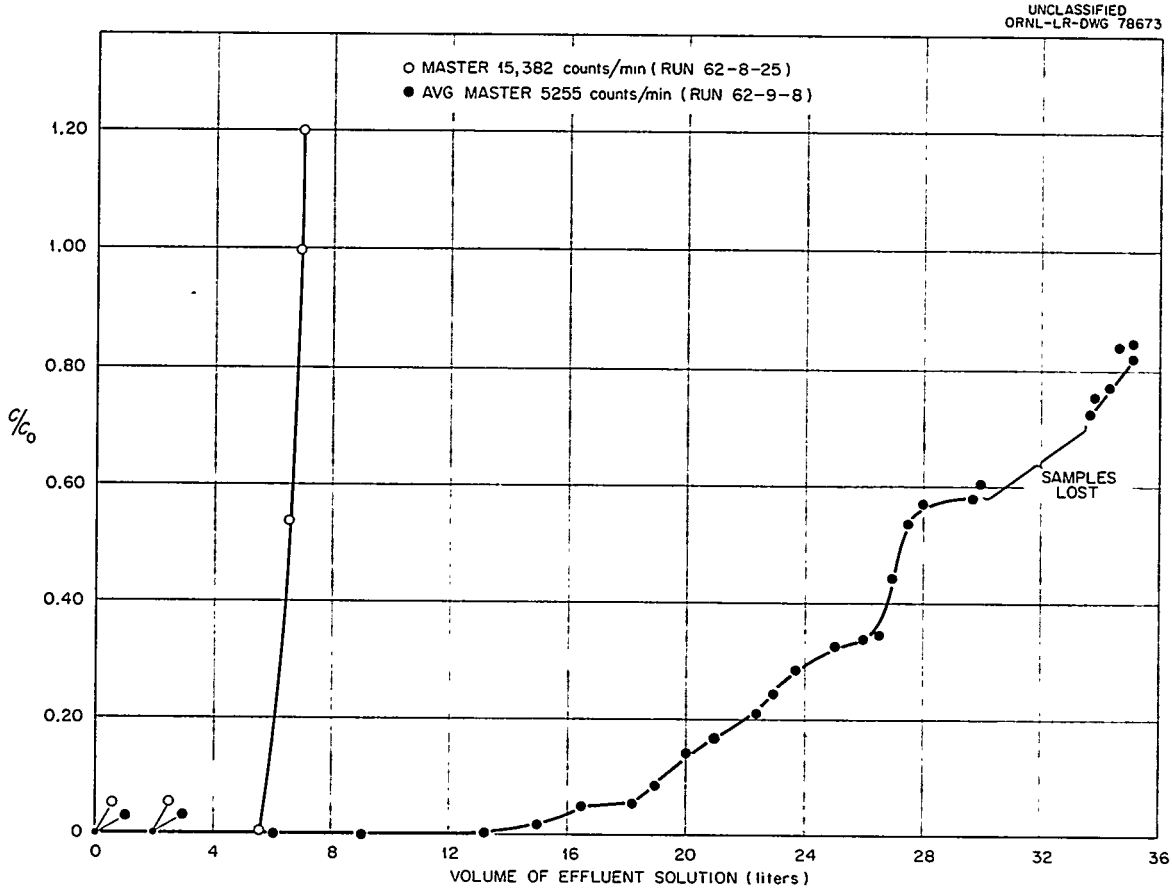


Fig. 8.2. Strontium Removal by F-20 Alumina: Effluent Activity of Simulated Waste.

These tests were run in 0.5 M $NaNO_3$ solutions; in different Na/Sr ratios or at different pH's the other sorbents could be more effective. Under acid conditions alumina is ineffective, whereas Dowex 50 would still function. With lower Na/Sr ratios the loading on the ion exchangers would favor strontium, whereas the loading on the alumina may be unaffected. The latter possibility appears plausible, since the removal of strontium occurs in a system that expends hydroxide ions, which suggests that ion exchange may not be the mechanism for removing strontium. Work is in progress to elucidate the nature of the alumina reaction, with particular attention being given to comparisons of reactions with known ion exchangers, such as Dowex 50.

9. WHITE OAK CREEK BASIN STUDY*

9.1 Distribution and Transport of Radionuclides in the Bed of Former White Oak Lake

T. F. Lomenick

During the period 1943-1955, White Oak Lake served as a final settling basin for low-level radioactive wastes discharged from the Laboratory. The temporary holdup provided by the impoundment afforded some dilution and a period for the decay of short-lived radionuclides before release to the Clinch River. It also allowed the deposition and accumulation of contaminated sediments. In 1955 the lake was drained, leaving behind about 1,000,000 ft^3 of contaminated lacustrine deposits.[29]

In order to determine the quantity, type, and distribution of radionuclides present in the lake bed and to aid in defining the migration of these products, a series of 250 core samples were taken in the area. A map of White Oak Lake bed showing the sample locations is presented in Fig. 9.1. The lake bed was laid out in a 50-ft-square grid, with sample locations being chosen by use of a table of random numbers. Note the increase in sample points per unit area for zones of progressively higher activity concentrations. The method of allocation of these points is optimum with respect to the area of sections of similar radioactivity (as determined by data collected previously) and with respect to the variability of the previously collected data. Due to the high cost of strontium and total rare earths, compared with gamma identification, only a limited number of the cores and their segmented sections are being analyzed for these nuclides.

---

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

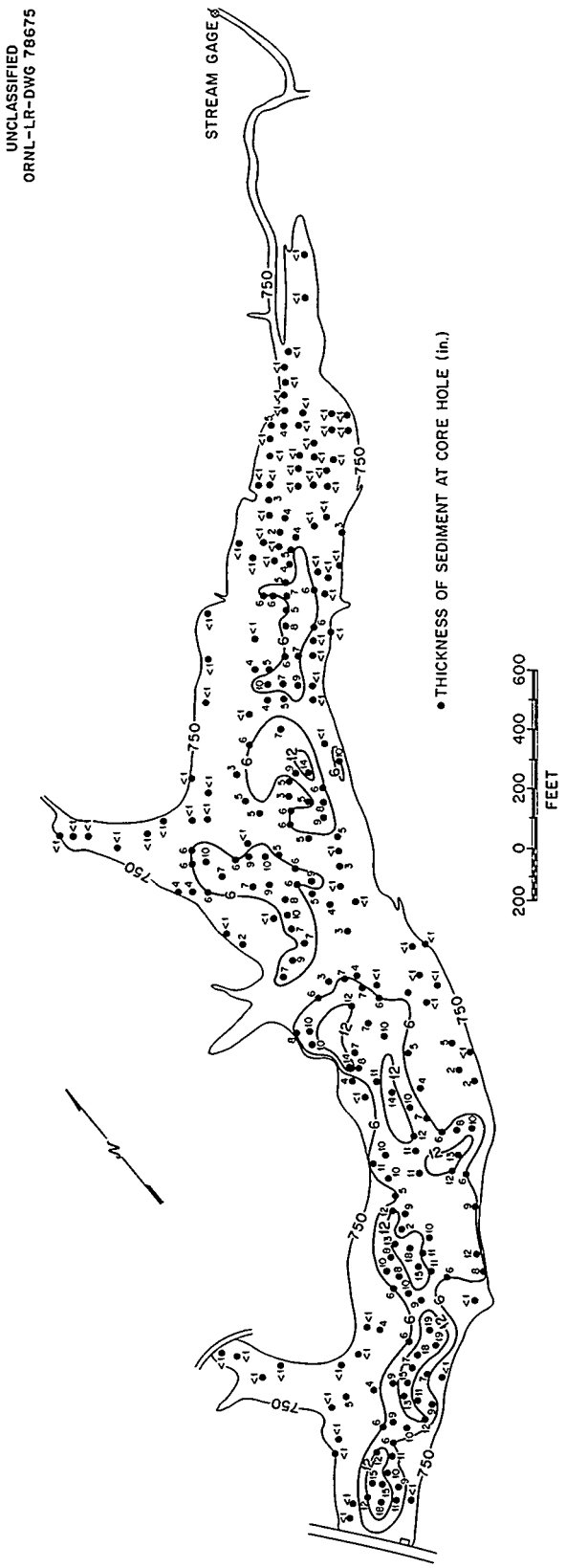


Fig. 9.1. Locations at Which 2-ft Core Samples Were Taken from the Bed of Former White Oak Lake.

A 2-in.-diam thin-wall tube, known as the Shelby Tube Sampler, was used to obtain core samples in the lake bed. The instrument was driven into the earth and recovered manually. As previous work indicated that practically all the contamination was associated with the upper few feet of soil,[30] all cores were taken to a depth of 2 ft. The samples were sliced and segmented into increments of 0 to 6 in., 6 to 12 in., 12 to 18 in., and 18 to 24 in. About 10 g from each increment was oven-dried, weighed, and scanned, using a Packard automatic gamma counting system, which consists of a spectrometer with well-type scintillation detector, automatic sample changer and control unit, digital printer, and tape punch. Concentrations of Ru^{106}, Cs^{137}, and Co^{60} are being determined by use of an IBM 7090 computer program for stripping the gamma spectrum. Standard radiochemical procedures are being used for strontium and total rare earth analyses.

By visual inspection of the recovered cores, a generalized depth of lacustrine sediment in the bed was determined (See Fig. 9.2.). It is seen that the sediment is as much as 19 in. thick in the lower part of the lake bed near the dam; however, there is a gradual thinning of the layer upstream and, in general, toward the shore line of the lake.

9.2 Oak Ridge Area Hydrology

R. J. Pickering* W. M. McMaster* R. M. Richardson*

On November 1 and 2, 1962, a 26-hr continuous sampling program was undertaken at selected stations on Bear Creek. The primary purpose of the program was to determine the significance of the effect of biologic activity on the concentration of nitrogen compounds in the water and variations in the effect with time and place.

The bulk of nitrogen occurring in Bear Creek originates in the acid waste pits west of the Y-12 Plant. Most of this material enters Bear Creek as nitrate by way of a small spring located more than 1 mile southwest of the pits; a second spring at the Roane-Anderson County line, about 2 miles southwest of the pits, discharges smaller quantities of nitrate into Bear Creek.

Sampling stations were set up at the upper spring, the spring at the county line, Bear Creek at the county line, Bear Creek at Highway 95, and Bear Creek at the U.S.G.S. gaging station near the Oak Ridge Gaseous Diffusion Plant. Flow at the gaging station remained constant through the period at 1.3 ft^3/sec.

A diurnal fluctuation was expected in the content of the various nitrogen compounds of the stream water because of biologic activity, whereas a fairly steady concentration was expected in the spring water.

---

*On loan from Water Resources Division, U. S. Geological Survey.

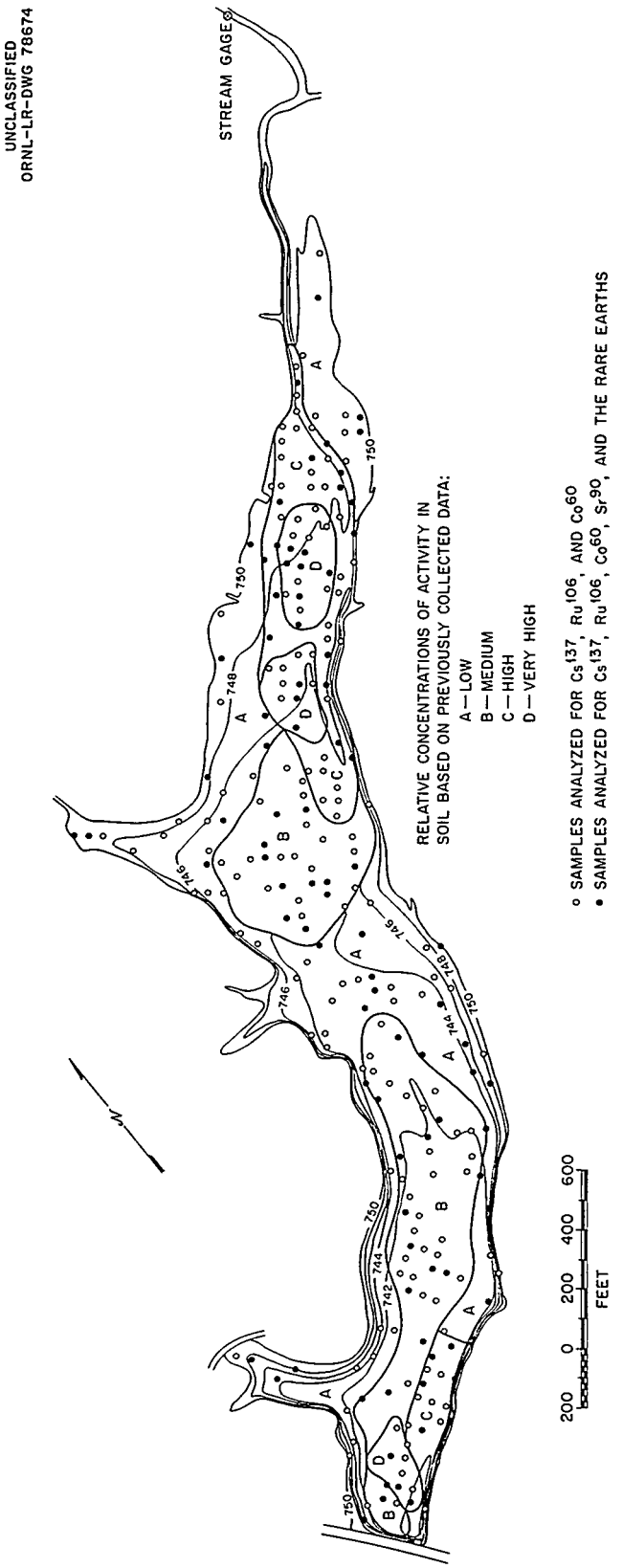


Fig. 9.2. Map of Former White Oak Lake Bed, Showing Thickness of Contaminated Sediment.

Seventy-one samples collected at the stations were analyzed for nitrate, nitrite, organic nitrogen, ammonia, calcium, magnesium, chloride, and fluoride, and measurements were made for dissolved and suspended solids and for specific conductance. From previous samples at various points on Bear Creek, it was known that nitrate concentration decreases markedly with distance from the upper spring. Dilution of the concentration with distance and additional inflow accounts for a large part of the decrease, and it is believed that biologic uptake might also account for much of the decrease. Contrary to expectations, however, the variations with time at each station were apparently random rather than diurnal, and the samples taken from the springs showed greater variation in nitrogen-compound content than the samples from Bear Creek, even though flow conditions were stable.

The most highly contaminated water was obtained at the upper spring, where the nitrate content ranged from 355 to 475 ppm. Downstream stations showed decreasing contamination with distance, and at the U.S.G.S. gaging station the nitrate content was nearly constant at 55 ppm through the sampling period. Organic nitrogen, ammonia, and nitrite concentrations varied somewhat at each station, generally remaining below 0.2 ppm, although the ammonia content at the upper spring reached 0.4 ppm at times. No diurnal cycle was apparent in any of the results.

10. FOAM SEPARATION

Foam separation is being studied as a new method for treating low-level wastes. Development work has proceeded over the past few years both at ORNL and at Radiation Applications, Incorporated, under a contract from ORNL. In one method of operation a sludge column is operated prior to the foam column in order to remove calcium and other hardness ions and thus prevent saturation of the foam-complexing agent with hardness ions. In a second method, the hardness would be precipitated in a small flash mixer, and both the precipitate and the ionic contaminants would be removed in the foam column. Both methods are scheduled to be tested in the ORNL 10-gal/min pilot plant for decontaminating low-level waste.

10.1 Laboratory Development

W. Davis, Jr. E. Schonfeld* A. H. Kibbey

Pretreatment of ORNL Low-Activity Process Waste Water.-- Since removal of strontium from water by foam separation is much more efficient if the calcium concentration is in the 5 ppm range (calculated as calcium

*On subcontract 2024 with Radiation Applications, Incorporated.

Table 36. Determination of (Γ/c) for Strontium by Continuous Countercurrent Runs with Pinching at the Feed Point

Quantity	Symbol	Units	Run Numbers					
			45A	45B	45C	46	53A	53B
Feed solution (before reagent additions)	--	--	LLW Clarifier Effluent (as collected in Bldg. 2528)					
Sr concentration	--	10^{-6} M	tracer	tracer	tracer	tracer	tracer	tracer
NaOH concentration added	--	M	.001	.001	.001	none	none	none
Effluent Trepolate F-95 concentration	--	ppm	260	260	260	260	380	220
Gas sparger used	--	--	A Spin.	A Spin.	A Spin.	EC glass	EC glass	EC glass
Countercurrent column length	z	cm	85	85	85	85	85	85
Estimated number of transfer units[a]	N_x	dimensionless	20	20	20	8	8	8
Liquid feed rate	$L + E_p$	cc/min	900	900	1200	600	600	600
Condensed foam rate	E_p	cc/min	7	3	10	19	16	8
Net liquid rate	L	cc/min	890	900	1190	580	585	590
Gas rate	V/a	cc/min	4700	2900	5700	4000	4000	4000
Surface area rate	V	10^5 sq. cm/min	2.5	2.0	2.8	4.8	4.8	4.8
Gross β in liquid feed	x_2	cpm/cc	9400	9400	9400	11500	11500	11500
Gross β in effluent liquid	x_B	cpm/cc	5400	5950	5600	2800	3350	5100
Gross β in condensed foam	$y_2V + x_2{}^*E_p$	10^3 cpm/min	5200	3450	6500	5300	3600	3300
Gross β material balance	--	%	118	104	117	100	81	87
Γ/c for Sr from x_2 and x_B	(Γ/c) Sr	10^{-3} cm	1.5	1.7	1.7	0.9	0.9	0.7
Γ/c for Sr from x_2 and $Vy_2+x_2{}^*E_p$	(Γ/c) Sr	10^{-3} cm	2.2	1.8	2.4	0.9	0.6	0.6
Decontamination factor	$DF = x_2/x_B$	dimensionless	1.7	1.6	1.7	4.1	3.5	2.3

[a]Number of transfer units for similar conditions with demineralized water.

Analyses of calcium, magnesium, and total hardness at these concentrations in the presence of 0.01 N Na^+ and variable low-level-waste impurity concentrations is difficult. Except for the effluent used for run 49, the clarifier effluents were partly collected during periods of unattended operation, and short periods of poor operation could have occurred without detection.

The strontium distribution coefficients of (1.4 to 1.7) x 10^{-3} cm determined by batch tests with clarifier effluent (Fig. 10.4, Table 35) agreed with that from continuous countercurrent runs (Table 36). Batch charges were foamed, and the distribution coefficient calculated from the slope of the concentration vs time curve by assuming one theoretical stage. These values agreed with those reported for about 5 ppm Ca^{2+} in laboratory studies.

These results indicate strontium distribution coefficients of (1.4 to 2) x 10^{-3} cm for the effluent of the clarifier as usually operated on low-level waste. This coefficient did not vary as the strontium was removed during two batch foamings. The decontamination of strontium was much less for a continuous countercurrent run than would be expected for the $(f/c)_{Sr}$ and the conditions used. This result could be explained by the existence of a strontium complex of low surface activity, which is slowly converted to the dodecylbenzene sulfonate complex of strontium or by a high saturation of the surface and a slow exchange due to the high sodium concentrations in solution. Either of these causes would explain the lower strontium distribution coefficients for clarifier effluent, compared with that expected from the effluent calcium concentrations.

11. REFERENCES

1. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

2. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for April-May 1962, ORNL-TM-376 (Nov. 5, 1962).

3. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for October and November 1961, ORNL-TM-133 (Mar. 13, 1962).

4. J. T. Roberts and R. R. Holcomb, A Phenolic Resin Ion Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes (Mar. 17, 1961).

5. R. R. Holcomb and J. T. Roberts, Low-Level Waste Treatment by Ion-Exchange, II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin, ORNL-TM-5 (Sept. 25, 1961).

6. R. R. Holcomb, Low-Level Waste Treatment. Part I. Decontamination of Low-Radioactivity-Level Process Water Wastes by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3322.

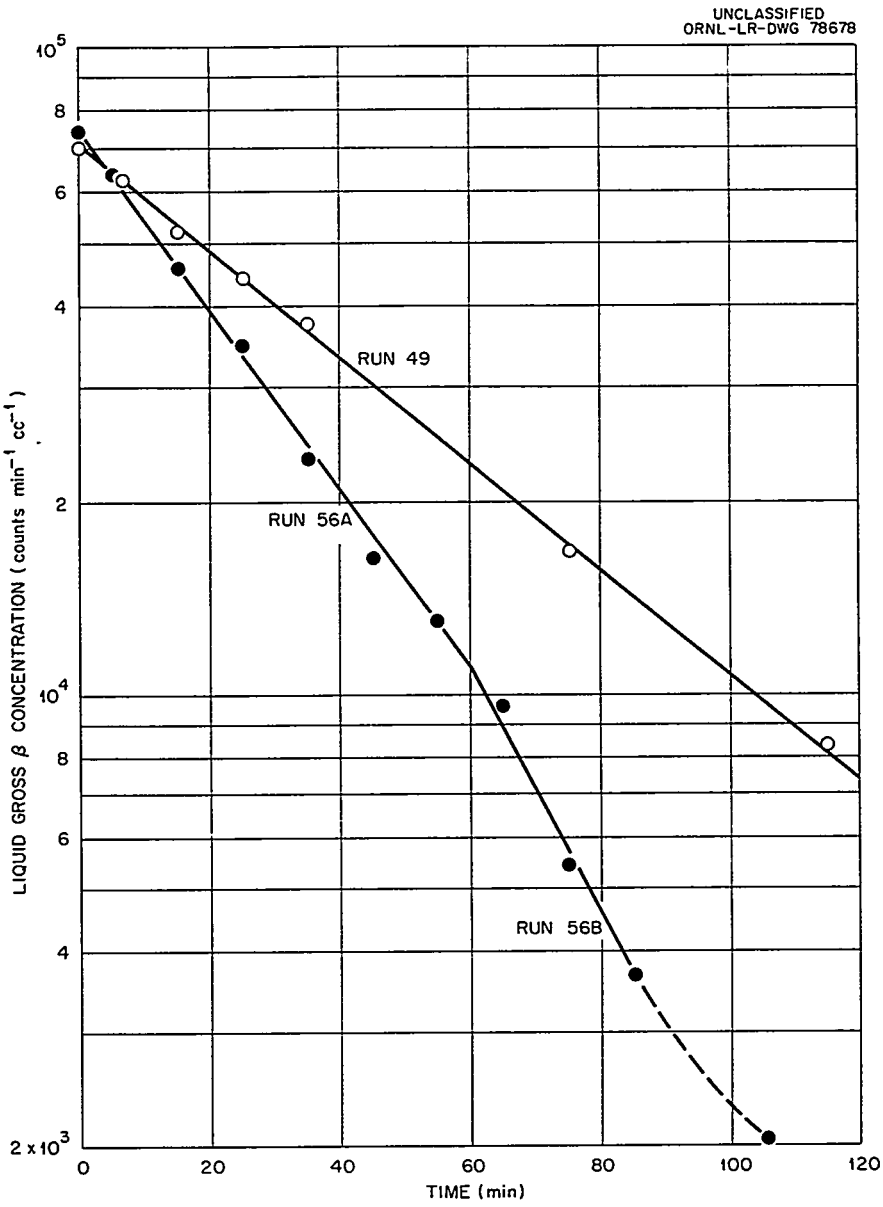


Fig. 10.4. Results of Batch Determinations of Strontium Distribution Coefficients for Effluent from the Clarifier for Low-Level Waste.

7. R. E. Brooksbank et al., Low-Radioactivity-Level Waste Treatment. Part II. Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Waste by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349.

8. P. Hamer, J. Jackson, and E. F. Thurston, Industrial Water Treatment Practice, pp 22-37, Butterworths-Imperial Chemical Industries Limited, London, 1961.

9. W. Davis and E. Schonfeld, personal communication, May 1962.

10. Calgon in Inudstry, Hagan Chemical and Control, Incorporated, Pittsburgh, Pennsylvania.

11. R. E. Blanco, Chemical Technology Division, Chem. Dev. Sec. B., Quarterly Progress Report, July-September 1962, ORNL-TM-403:

12. Letter, I. R. Higgins to R. E. Blanco, January 1963.

13. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1962, ORNL-TM-396 (Dec. 19, 1962).

14. J. O. Blomeke et al., Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. Part III, ORNL 3355 (in press).

15. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

16. W. D. Cottrell, Radioactivity in Silt of the Clinch and Tennessee Rivers, ORNL-2847 (Nov. 18, 1959).

17. R. J. Morton (ed.), Status Report No. 1 on Clinch River Study, ORNL-3119 (July 27, 1961), pp 28-42.

18. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

19. K. Z. Morgan et al., Health Physics Division Annual Progress Report for Period Ending July 31, 1959, ORNL-2806 (Oct. 23, 1959).

20. R. L. Bradshaw et al., Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes. Part 1. Interim Liquid Storage, ORNL-3128 (Aug. 7, 1961).

21. A Meteorological Survey of the Oak Ridge Area, ORO-99.

22. F. A. Gifford, Nuclear Safety 2, 56-59 (1960).

23. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for December 1961 and January 1962, ORNL-TM-169 (June 15, 1962).

24. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1962, ORNL-TM-396 (Dec. 19, 1962).

25. T. M. Kegley, Jr., Fracture of Nickel Lead Wire, Metallography Report No. 438 (Sept. 14, 1962).

26. American Institute of Physics Handbook, sec 5, p 225, McGraw Hill, 1957.

27. R. S. Crouse, Metallographic Examination of Heaters and Thermocouples from Carey Salt Mine Experiments, Metallography Report No. 449 (Jan. 7, 1963).

28. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1962, ORNL-TM-396 (Dec. 19, 1962).

29. A. S. Fry, ORNL, memorandum to M. A. Churchill, Sediment Investigations, White Oak Lake (June 30, 1953).

30. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1961, ORNL-TM-15 (Oct. 24, 1961).

31. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1962).

32. E. Schonfeld and W. Davis, Jr., Head-End Treatment of Low-Level Waste Prior to Foam Separation, ORNL-TM-260 (May 1962)

33. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1962, ORNL-TM-396 (Dec. 19, 1962).

34. Standard Methods for the Examination of Water and Waste Water, 11th ed., 1st printing, September 1960, pp 245-248, American Public Health Association, Incorporated, 1790 Broadway, New York 19, New York.

35. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

MASTER COPY

2005

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ORNL - TM - 603

15

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT

FEBRUARY-APRIL 1963

This document has been approved for release to the public by:

David R Hamrin 7/29/95
Technical Information Officer Date
ORNL Site

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM-603

CHEMICAL TECHNOLOGY DIVISION
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT FEBRUARY-APRIL 1963

R. E. Blanco F. L. Parker

DATE ISSUED

DEC 16 1963

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level Waste Pot Calcination. Three continuous evaporator-pot calcination tests using simulated FTW-65 Purex waste were completed. The average feed rates varied from 31 liters/hr to 49 liters/hr, and the maximum hourly rates from 125 to 190 liters/hr. The average feed rate is a function of the amount of concentration in the evaporator and the degree of filling of the calciner pot. The calcined solids had densities of 1.23 to 1.30. The residual nitrate composition for the calcined solids varied from 100 to 400 ppm and decreased with time that the calcined solid was above 600°C. The sulfate retention in the calciner was high, only 0.3% to 2% of the sulfate was lost. This loss is attributed to entrainment since similar values were obtained for nonvolatile ions such as iron and sodium. A catch tank, tested as a method of isolating mercury, collected only 27% of the mercury. The amount of mercury caught was proportional to the amount in the last fraction of the calciner condensate. A ruthenium decontamination factor of 3×10^3 (using non-radioactive ruthenium) was obtained in test R-72 across the continuous evaporator using an impingement plate de-entrainer.

Fixation of High Level Waste in Glass. Simulated Hanford formaldehyde-treated 1965 waste solution (FTW-65 waste) was evaporated to 1/4 of original volume without precipitation of solids. Experimental phosphate glassy melts were made by addition of phosphate, sodium and calcium to FTW-65. Generally, these melts were too soluble in water or lost SO_3 readily, but a few appeared to be insoluble and were relatively stable at high temperatures. Two semicontinuous, semiengineering scale experiments were successful although excessive solids entrainment caused an operating problem. The product contained 45% waste oxides and represented a volume reduction factor of 30. Sulfate loss was less than 2% and 24% of the ruthenium volatilized. An electrical resistance probe for sensing levels of solution, calcine and melt in the pot performed satisfactorily.

Imposition of a small cathodic current decreased the time necessary for removal of >99% of the mercury in a copper column from FTW-65 waste solution from about 25 to 12 minutes or less. More current was required than the minimum to remove the mercury to prevent dissolution of excess copper.

Exposure of 304L specimens at 300°C in bedded salt (NaCl) containing natural occurring impurities showed corrosion rates of about 0.03 mil/mo. Type 304 stainless steel and titanium 45A, both coupled and uncoupled to each other, showed low rates for exposure in refluxing FTW-65 waste solution and vapors; the maximum rate was on the coupled 304L and amounted to 0.3 mil/mo with no local attack.

The thermal conductivity characteristics of powdered MgO, Al_2O_3, and ZrO_2 were investigated as a function of void space and temperature. Over the temperature range studied (200 to 1500°F), the thermal conductivity increased quadratically with the temperature.

Low-Level Waste Treatment: Scavenging-Precipitation--Ion Exchange. The phosphate concentration of ORNL low level waste was successfully reduced from >3 ppm phosphate to 0.2-0.5 ppm during treatment of greater than 8,666 volumes of waste with one bed volume of alumina. This treatment permitted more quantitative precipitation of calcium carbonate in the scavenging-precipitation clarifier, i.e. reduction in hardness of clarified product from 70 ppm to < 10 ppm. A significant but unknown fraction of the ruthenium was also adsorbed on the alumina.

Low Level Waste Treatment: Foam Separation. Initial tests of a two-step process for decontamination of low-level waste, consisting of sludge column precipitation of calcium carbonate and magnesium hydroxide followed by a countercurrent foam column for strontium removal, were performed with Sr^{85}-spiked ORNL tap water and ORNL low-level process waste water in laboratory-scale equipment. With tap water as feed, strontium decontamination factors in the foam column and in the overall process were 2 to greater than 400 and 320 to greater than 15,000, respectively, depending on operating conditions. With process waste water, foam column and overall strontium decontamination factors were 11 to 16 and about 250, respectively, which are close to those obtained with tap water under the same operating conditions. Also tested with simulated and actual ORNL low level process waste was a one-step process which involves precipitation of calcium as orthophosphate in a small mixer and then feeding solution and solids to a foam column where flotation and foam separation occur. Strontium decontamination factors with simulated and actual ORNL waste water were, respectively, in excess of 1000 and 200 to 300.

Studies were performed of the biological degradation in ORNL process waste water of the alkylbenzenesulfonate already present in the waste water (primarily from Fab), of the alkylbenzenesulfonate in Fab, and of the branched chain sodium dodecylbenzenesulfonate of Trepolate F-95. After 2 to 3 weeks the respective amounts of degradation from existing bacteria were 20, 25 to 30, and 60 to 65%.

A 24-in.-diam foam column was operated with liquid feed introduced through tubes on a 5-in. triangular spacing; channeling was observed for 10 to 30 inches below the feed tubes. Twenty-mesh screens across the column cross sections were not effective liquid distributors since they accumulated liquid which dumped through periodically. Good drainage of foam was obtained in a horizontal drainage section. The experimentally measured foam densities agreed well with a foam drainage model. Air operated sonic whistles condensed 0.05 to 0.10 ft^3 of foam per standard cubic foot of operating air. The experimentally observed concentrations for a three-stage surfactant recovery system agreed well with concentrations calculated by using a distribution coefficient of 7×10^{-4} $(moles/cm^2)/(moles/cc)$ for the dodecylbenzenesulfonate.

Engineering, Economics, and Safety Evaluation. Atmospheric contamination from an assumed continuous accidental release of fission products at a rate of 1 curie/sec from a hypothetical storage-tank site at ORNL results in a downwind concentration of 2.5×10^{-6} and 7.5×10^{-7} μc/cc at ground level at 5 and 10 miles for typical daytime meteorological conditions. For an instantaneous release of 1 curie for daytime and

nighttime meteorological conditions, the concentrations at 10 miles downstream are 3×10^{-9} and 5×10^{-7} μc/cc.

Disposal in Deep Wells. With reference to the mix, the effect on the pumping characteristics of several contaminants and variations in the waste composition was evaluated by the Halliburton Company. It was confirmed that the proposed mix will be usable over the range of these expected variations and in the presence of these contaminants.

An analysis of the fluid lost from the proposed mix prior to setting showed that cesium and strontium were preferentially retained; the concentration of these elements in the fluid was less than 10% of their concentration in the original waste solution. In a 17-day leach test made on a five-day-cured specimen, only 7% of the cesium was leached; neither strontium or ruthenium was detected.

Detail design of the mixing and injecting equipment is in progress. The installation of the waste tanks and pumps is 80% completed.

Drilling has started on the injection and observation wells. The surface casing of the injection well was cemented; the well is at a depth of 668 ft. The observation well was drilled to a depth of 518 ft.

Disposal in Natural Salt Formations. Fuel elements of the ETR have been selected as the heat and radiation sources for the demonstration of the disposal of solid, high-level waste. The purposes of the demonstration are to perfect the equipment and method, and to investigate the combined effects of heat, radiation, and pressure on plastic flow, salt stability, and chlorine production. The demonstration will consist of a 7-can array of fuel elements, an electrical-heat-equivalent array, and two sets of electrical heaters to heat a pillar between the two arrays.

The Carey mine at Lyons, Kansas, will have its hoist and shaft renovated to handle the 7-ton loads required for the demonstration.

The heated-room model at the Hutchinson mine showed that the hole is closing at a unit rate 100 times faster at 160°C than at ambient temperature (about 10^{-4} in. in.$^{-1}$ day^{-1} vs 10^{-6} in. in.$^{-1}$ day^{-1}).

Experimental work on KCl has been used to calculate total production of chlorine in irradiated NaCl. After 200 days, 1.8 moles of oxidizing agent per can could be produced. Irradiation of NaCl indicates that these values are conservative and that for short-term storage of high-level wastes in salt, little or no production of free chlorine can be expected.

Clinch River Study. A regression analysis of bottom-sediment samples from the Clinch and Tennessee Rivers showed a strong correlation of Ru^{106}, total rare earths, and Co^{60} with Cs^{137}, indicating that similar mechanisms control the longitudinal

distribution of these nuclides. The correlation for Zr^{95}-Nb^{95} and Sr^{90} with Cs^{137} is not as good, indicating that different mechanisms may be controlling their distribution.

Pontacyl Pink was injected into White Oak Lake along the face of the dam to determine whether there was any large-scale seepage through the dam. Though small amounts of seepage were indicated, no dye passed through the dam. Other potential sources of contamination proved to be negligible.

A code was developed for calculating critical-organ burdens and dose received, taking into account individuals of different age groups in comparison to standard man, for those consuming Clinch and Tennessee river water for various periods of time.

Bottom sediments from the Clinch River were selectively leached. Salts between pH of 6 and 8 removed less than 10% of Co^{60}, Ru^{106}, and Cs^{137}. At lower pH's, ruthenium is not removed though cobalt is. At higher pH ruthenium is leached, though only moderate amounts of cobalt are released.

Mineral Exchange Studies. Sorption of trace quantities of cesium by vermiculite can be improved by pretreatment with potassium to increase the number of collapsed lattices available for edge fixation. Continued leaching of the treated vermiculite with 0.5 M $NaNO_3$, containing traces of cesium (1.7×10^{-7} M), releases the interlayer potassium and negates the pretreatment. Addition of potassium in the influent was found effective in maintaining potassium-treated vermiculite in a collapsed state. A concentration of 0.0005 M KNO_3 in 0.5 M $NaNO_3$ gave optimum cesium sorption (K_d = 366 ml/g) and a final exchange capacity of 46.8 meq/100 g compared to the initial exchange capacity of the potassium-saturated vermiculite of 5.9 meq/100 g. Higher concentrations of potassium were more effective in maintaining lattice collapse, but reduced cesium sorption due to increased ion competition.

Interlayer fixation of trace quantities of strontium was not observed when the vermiculite lattice was collapsed by addition of 0.01 to 0.04 M KNO_3 to 0.5 M $NaNO_3$ influent. The sorption of strontium was reduced by increases in the potassium concentration of the influent, and about 80% of the strontium was removed during the determination of the exchange capacity following column saturation.

White Oak Creek Basin Study. The average concentration of Cs^{137} in the upper 6 in. of soil in the bed of White Oak Lake is approximately 100 times that of Sr^{90}. In general, the highest concentrations of Cs^{137} are restricted to areas where lacustrine sediment is thickest, while the highest concentration of Sr^{90} occurs in the inundated area immediately behind White Oak Dam.

Table 21. Cavity Closure During Heating

Gage Number	Cumulative Deformation In Inches at: 30 days	40 days	Rate of Movement During 30th to 40th Days (in./day)	(in. in^{-1} day^{-1})
2	1.31	1.36	5×10^{-3}	2.1×10^{-4}
5	1.38	1.43	5	2.1
6	1.35	1.40	5	2.1
8	1.19	1.24	5	2.1
9	1.04	1.08	4	1.7
3	>0.94	---	---	---
7	> 0.35	---	---	---

6.3 Chlorine Release from Gamma Irradiated Salt

H. Kubota

Epstein[16] gives quantitative data on the amount of oxidizable substances formed in KCl upon exposure to gamma and beta radiation. The values were obtained by dissolving the salt in water and determining the oxidizing power of the solution either iodometrically or spectrophotometrically. There is considerable uncertainty in the amount of oxidizing substance released to the gas phase, on which he places a maximum of 0.5% of the amount present in the solid escaping to the gas phase. G values are given for this process in the salt, presumably the production of chlorine, and these values are 1.47×10^{-2} at 2×10^{7} rads and 5.1×10^{-4} at 3.27×10^{9} rads. Assuming that the variation in G values obeys a linear relation with respect to dose, and further assuming that the values apply to NaCl as well, the production of chlorine that could be possible from the salt around one disposal hole was calculated, and the values are given in Table 22. The dose was calculated on the basis of a 2-year-old calcined waste contained in a 6-in.-diam can. These values correspond to the total produced in the salt during the lifetime of the activity of the waste. The actural amount that is released to the atmosphere is still problematical, but is expected to be less than 0.5% of the amount produced. The time rate of production is given in Table 23.

The irradiation of NaCl in a Co^{60} source was performed using chemically pure NaCl. The irradiations performed at 35 to 50°C released no free chlorine to the vapor phase which could be detected by the gas chromatograph or chemically by the potassium iodide or o-tolidine reactions. A sample receiving a dose of 3×10^{8} rads released about 2×10^{-6} mole/g of oxidizing substance, corresponding to a G value of about 3×10^{-4}. When salt irradiated at 35 to 50°C is heated to 250°C, a fraction of the oxidizing substance, equivalent to 3×10^{-8} mole/g, is released to the gas phase. The remaining salt, which had been turned black by the irradiation, was annealed back to its original white color, and it contained a residual oxidizing power equivalent to less than 10^{-9} mole/g.

Table 22. Probable Rate of Formation of Chlorine in Solid NaCl

Time After Burial	Dose (rads)	Chlorine Produced (%)
20 days	8.6×10^6	8.5
40 days	1.7×10^7	11.0
80 days	3.4×10^7	14.0
160 days	6.9×10^7	17.0
320 days	1.4×10^8	21.0
1.75 years	3.8×10^8	30.0
3.5 years	7.5×10^8	38.0
7 years	1.5×10^9	49.0
14 years	3×10^9	63.0
28 years	6×10^9	80.0

Irradiations were also performed at 250°C, which approximates the maximum temperatures expected near the periphery of the cans containing the hot wastes. No net change in the color of the salt was observed. Gas chromatography and iodometry revealed no chlorine nor oxidizing material in the gas phase. The oxidizing power released on dissolution to an aqueous medium was 10^{-7} mole/g at a dose of 3×10^8 rads.

The work thus far indicates that under the conditions of a short-term storage of hot wastes in salt, little or no production of free chlorine can be expected. The only question that remains is whether long-term irradiation will result in a slow release of chlorine to the atmosphere, possibly by a slow, diffusion-controlled process.

7.0 CLINCH RIVER STUDY

7.1 Bottom Sediments

P. H. Carrigan, Jr.*

In a study of the distribution of radioactivity in bottom sediments in the Clinch and Tennessee Rivers, the longitudinal distribution patterns for several radionuclides were found to be similar. The longitudinal distributions of seven radionuclides were compared

*On loan from Water Resources Division, U.S. Geological Survey.

Table 23. Yield of Oxidizing Agent with Dose

Dose (rads)	G	Moles of Oxidizing Substance Per Gram of Salt	Mass of Salt Radiated (g)	Total Moles of Oxidizing Agent Produced
10^6	0.1	10^{-7}	1.38×10^7	1.4
10^7	2.3×10^{-2}	2.3×10^{-7}	6.8×10^6	1.6
10^8	5.0×10^{-3}	5.0×10^{-7}	3.6×10^6	1.8
10^9	1.1×10^{-3}	1.1×10^{-6}	1.5×10^6	1.6
1.2×10^{10}	2.3×10^{-4}	2.6×10^{-6}	2.9×10^5	0.8

by using techniques of regression analysis. The results of these comparisons are shown in Fig. 31.

The regression analysis is based on the results of the 1961 annual survey of radioactivity in bottom sediments, made by personnel of the Applied Health Physics Section, ORNL. This survey extended from White Oak Creek on the Clinch River to Kentucky Dam on the Tennessee River. Results of radiochemical analysis of composite samples from the 32 sections of the survey were available for this study.

As shown in Fig. 31, the slope of the curves for the logarithmic correlation of Cs^{137} to Ru^{106}, the trivalent rare earths (excluding Ce^{144} and including Y^{90}), and Co^{60} are nearly the same. Also, the indices of correlations for these curves are extremely good. Thus, the results shown in the figure suggest that similar mechanisms control the longitudinal distribution of these particular radionuclides.

As shown in Fig. 32, the concentration of Cs^{137} in bottom sediments decreases in the downstream direction. The concentrations for the other radionuclides decrease in the downstream direction also. The rate of decrease in concentration in the downstream direction for cobalt, ruthenium, and the rare earths is not as rapid as for cesium, however. The equation for the slope of the curves in Fig. 31 is

$$dy/dx = abx^{b-1},$$

in which

dy/dx = slope,

y = concentration of the dependent variable,

x = concentration of the independent variable,

a = value of y at $x = 1$,

b = slope of straight line on logarithmic plot.

The coefficients are shown in Table 24.

The observed rates of decrease in the concentration of cesium, ruthenium, cobalt, and the rare earths with distance downstream from White Oak Creek are much greater than rates calculated on the basis of flow dilution alone. This lack of relationship between concentration and flow dilution, and the similar longitudinal distribution pattern of the radionuclides, seem to indicate that the mechanism controlling their longitudinal distribution pattern is a sedimentation process, rather than a chemical process, such as equilibration between concentrations in the sediments and radionuclide concentrations in the water.

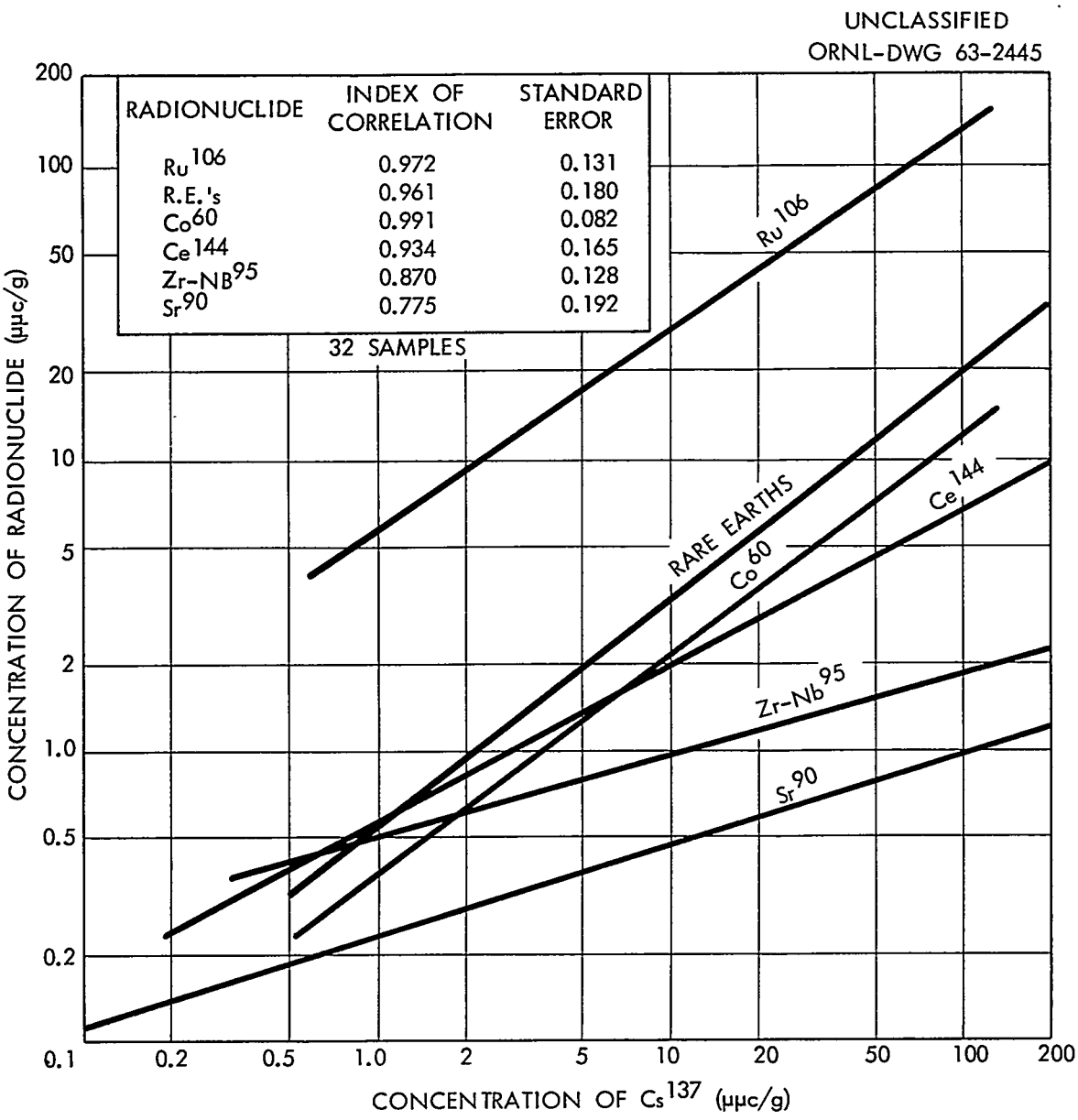


Fig. 31. Correlations Showing Similarity in the Longitudinal Distribution of Radionuclides in the Bottom Sediments of Clinch and Tennessee Rivers.

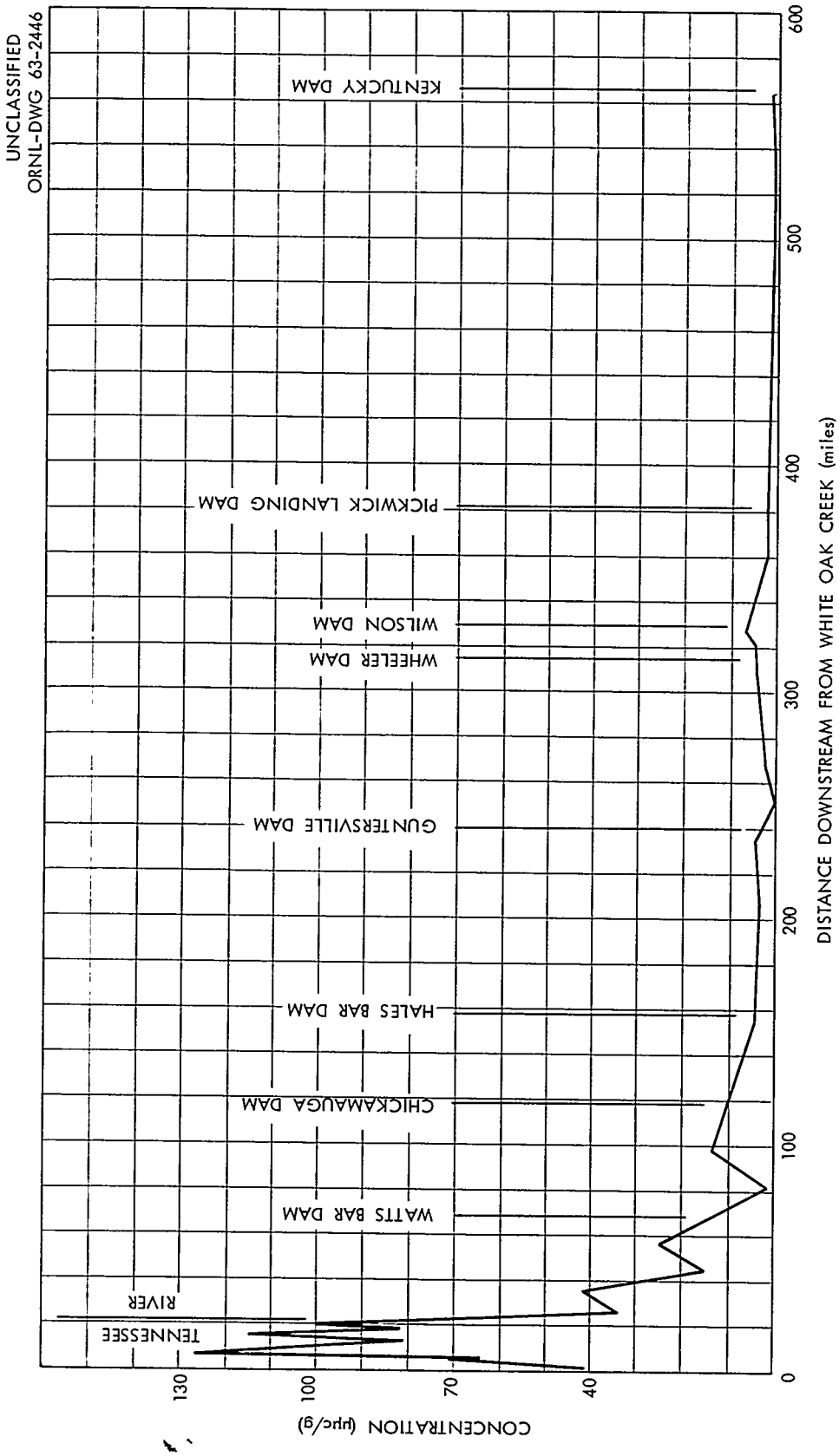


Fig. 32. Longitudinal Distribution of Cesium-137 in Bottom Sediments of Clinch and Tennessee Rivers in 1961.

Table 24. Regression Coefficients for Curves Shown in Figure 31

Correlated Radionuclides	a (μμc/g)	b
Cs^{137} - Ru^{106}	5.50	0.679
Cs^{137} - R.E.'s	0.551	0.778
Cs^{137} - Co^{60}	0.369	0.757
Cs^{137} - Ce^{144}	0.555	0.539
Cs^{137} - Zr-Nb^{95}	0.513	0.282
Cs^{137} - Sr^{90}	0.239	0.295

The slope of the curves for Zr-Nb^{95} and for Sr^{90} in Fig. 31 is less than that for cobalt, ruthenium, or the rare earths. The lesser slope indicates that somewhat different mechanisms may be controlling the longitudinal distribution of zirconium-niobium and strontium in the bottom sediments. The indices of correlation of zirconium-niobium and strontium indicate also that mechanisms affecting the distribution of cesium seem to have a lesser effect on the distribution of these radionuclides.

The index of correlation relating zirconium-niobium to strontium is 0.730, indicating that the mechanisms controlling their distribution are not exactly the same.

Relations demonstrated in Fig. 31 indicate that the longitudinal distribution in the bottom sediments of the concentrations of several radionuclides may be determined on the basis of the distribution of one or two of those radionuclides.

7.2 Calcite Precipitation

R. J. Pickering*

Recent examinations of aluminum plates that have remained submerged in the Clinch River at Miles 19.1, 15.0, and 5.4 for 3 to 4 months[4] have indicated that calcite had not precipitated on the plates during that period. However, calcite had precipitated on the steel bolts and nuts holding the plates to the supporting rope. The rough metal of the bolts and nuts may have provided a surface to which the precipitated calcite could adhere more readily than it could to the polished aluminum surfaces. A coating of calcite has been noted on several metal objects recovered from the river. Additional tests for calcite precipitation in the Clinch River are planned.

* On loan from Water Resources Division, U.S. Geological Survey.

7.3 Sources of Release to Clinch River

R. J. Pickering* B. J. Frederick*

The portion of the Clinch River Study involving the calculation of radionuclide loads in the river is based on the assumption that the only point at which low-level radioactive liquids are released to the Clinch River is the monitored release point at the White Oak Dam gate structure. It is desirable to occasionally provide assurance that no other release points exist. A three-phase investigation for this purpose was conducted during the past quarter.

The gates in White Oak Dam were closed, and fluorescent dye was mixed with White Oak Lake water along the upstream face of the dam. After 24 hr, water samples were collected for fluorescence analysis from very small seeps and small puddles on the creek bank immediately downstream from the dam. No dye was detected in the samples, but flow in the small seeps appeared to have increased slightly, and the creek bank had become more wetted as a result of the higher lake level, thus suggesting a minor amount of seepage through the earth-fill dam structure.

A visit was made to the Tower Shielding Facility, the only facility lying outside White Oak Creek Drainage Basin from which radionuclides might enter the Clinch River. The visit revealed that the reactor cooling water at the facility normally circulates in a closed system and that, when radioactive liquids must be released from the reactor, they are piped into a large closed tank and later transferred to a tank truck for transport to the Oak Ridge National Laboratory area for release. This arrangement appears to rule out contamination of the river from the Tower Shielding Facility.

Several water samples were collected from the drainage areas of small streams adjacent to White Oak Creek Drainage Basin and from streams that drain the Y-12 area. Gross-gamma counting of the samples showed no radioactivity above background.

The data collected in the surveys described above indicate little possibility of introduction of radioactive contamination, other than fallout, through surface drainage into the Clinch River at any point in the Oak Ridge Reservation except White Oak Dam and the area of the Oak Ridge Gaseous Diffusion Plant (ORGDP). Drainage from ORGDP is either within the security fence or is affected by Clinch River waters, and thus could not be readily surveyed. However, it is known that gross quantities of fission products are not handled at the plant.

7.4 Hazards Analyses

K. E. Cowser

Man may be exposed to internal and external sources of ionizing radiation due to the discharge of radioactive fluids to the Clinch River. Based on prior measurements and calculations, it is apparent that the more important exposure pathways are those

*On loan from Water Resources Division, U.S. Geological Survey.

contributing to internal sources. The maximum dose rate by immersion in contaminated water and exposure to contaminated bottom sediments in the Clinch River was calculated to be 0.027 and 12 millirad/day, respectively; from drinking Clinch River water the calculated exposure to the bone ranged from 0.06 to 0.51 of the maximum permissible concentration for water (MPC_w).[4, 17]

The fraction of MPC_w attained for the case of internal dose was calculated according to recommendations of the ICRP.[18] For a mixture of invariant composition and based on a particular organ, x, the fraction of MPC_w that is attained is given by:

$$\sum_i \frac{P_{wi}}{(MPC)^x_{wi}} , \qquad (1)$$

where

P_{wi} = the concentration of the particular radionuclide in water,

$(MPC)^x_{wi}$ = the maximum permissible concentration of the particular radionuclide in water for the organ and individual of interest and for continuous exposure.

The values of P_{wi} are average values, the period of averaging being 1 year, according to the recommendations of ICRP, NCRP, and FRC. All MPC_w values used for data relating to the Clinch River are taken as one-tenth of the occupational MPC_w values for continuous exposure. To obtain MPC_w values relating to the Tennessee River, the MPC_w for continuous occupational exposure has been reduced by a factor of one-hundredth for whole body as critical organ and by one-thirtieth with thyroid, bone, and GI tract as the critical organs.

If the fraction of MPC_w calculated from Eq. (1) is multiplied by the appropriate annual dose rate permitted in the particular organ of interest, an annual dose rate is obtained. A careful interpretation of such values is necessary, since the calculated dose only applies to a long-term and stable situation. The MPC_w values are set by the requirement that the dose rate (rems/week) after 50 years of exposure shall not exceed a recommended limit. During a 50-year exposure period, equilibrium is reached by most of the radionuclides, because their effective half life is short compared to 50 years. However, in the case of Sr^{90}, the allowable annual dose rate is reached only after 50 years of continuous exposure to the MPC_w. For this reason, the calculation of the actual dose received by the ingestion of known concentrations of radionuclides is desirable. As a second interpretation, the calculated dose rate may be considered as the dose that will be received during the next 50 years due to the exposure with P_{wi} for that period. Actually, the dose delivered after various times following the intake period depend upon the effective half-life of the isotope involved.

Because the MPC's which enter into the calculations have been estimated on the basis of so-called "standard man," the dose really represents only that which would be received by a person of physical characteristics and habits resembling standard man. Thus, the doses estimated should be considered as average values for typical adults. Very little is known at present concerning differences in metabolic rates or processes of children and adults as they relate to important radionuclides. However, dose-correction factors that take into account differences due to intake and organ size can be estimated.[19,20,21]

During ingestion of water, the activity present in a critical organ of the body at time, t (after the start of ingestion), can be expressed as:[18,22]

$$Q = f_w R X \int_0^t e^{-\lambda_e t'} dt' , \qquad (2)$$

where

Q = μc present in critical organ,

f_w = fraction of ingested radionuclide that is retained in the critical organ,[18]

R = rate of intake of water,

X = concentration of radionuclide in water during exposure,

λ_e = effective half life of radionuclide (year), and

t' = a time variable.

By assuming the concentration of a radionuclide in water is the average annual concentration and the rate of water intake is 2.2 liters/day (standard man), Eq. (2) is integrated over a time period of 1 year giving:

$$Q(I)_t = \frac{f_w R \bar{X}_t}{\lambda_e} \left[1 - e^{-\lambda_e}\right] , \qquad (3)$$

where

$Q(I)_t$ = μc present in the critical organ due to the intake of water during a particular year, t, and,

$\bar{X}_t$ = average annual concentration of a radionuclide in water during a particular year, t.

After the exposure period t, the quantity of radionuclide remaining in the critical organ is given by:

$$Q(A)_{t\tau} = Q(I)_t \, e^{-\lambda_e \tau} , \tag{4}$$

where

τ = the years after a particular intake period, t, and $1 \leq \tau \leq n$. Since the quantity of water consumed by an individual is a function of the individual's age, the critical-organ burden is also a function of the individual's age. Thus, an intake correction factor, j_γ (where γ is the individual's age during a particular intake period), must be applied to Eqs. (2) and (4). For example, assume that an individual of age $\gamma = 10$ began to consume contaminated water at the beginning of year, $t = 1$, the critical-organ burden of a particular radionuclide each year for a period of 3 years would be determined as follows:

Period	Body Burden (μc)
$t = 1$	$j_{10}Q(I)_1$
$t = 2$	$j_{11}Q(I)_2 + j_{10}Q(A)_{11}$
$t = 3$	$j_{12}Q(I)_3 + j_{10}Q(A)_{12} + j_{11}Q(A)_{21}$

(5)

The dose received by the critical organ during the period of intake, t, is

$$D(I) = \frac{MPD}{qf_2} \int_0^t Q\,dt' , \tag{6}$$

where

MPD = the maximum permissible dose rate to a particular organ,

$qf_2 = \dfrac{MPC_w \, R \, f_w}{\lambda_e} \left[1 - e^{-\lambda_e 50}\right]$, the fraction of radionuclide in the critical organ after 50 years of continuous exposure.

By substituting Eq. (2) in Eq. (6) and integrating over an exposure period of 1 year, the dose received by the critical organ during a particular exposure year, t, is

$$D(I)_t = \frac{MPD \, g_t}{1 - e^{-\lambda_e 50}} \left[1 - \frac{1 - e^{-\lambda_e}}{\lambda_e}\right] , \tag{7}$$

where

$g_t = \dfrac{\bar{X}}{MPC_w}$, the fraction of MPC_w in water during a particular year, t.

After the exposure period t the critical organ will continue to be irradiated by the radionuclide retained from the exposure period. The length of time for such

residual exposure depends on the effective half life of the radionuclide. The dose after exposure is

$$D(A)_{t\tau} = \frac{MPD\ g_t \lambda_e}{1 - e^{-\lambda_e 50}} \int_0^t e^{-\lambda_e t'} dt' \int_{\tau-1}^{\tau} e^{-\lambda_e t''} dt'' , \quad (8)$$

where

t'' = a time variable.

Integration of Eq. (8) over an exposure period of 1 year and post exposure period, τ, gives

$$D(A)_{t\tau} = \frac{MPD\ g_t \left[1 - e^{-\lambda_e}\right]}{\lambda_e \left[1 - e^{-\lambda_e 50}\right]} \left[e^{-\lambda_e (\tau - 1)} - e^{-\lambda_e \tau}\right]. \quad (9)$$

The total dose received by a particular critical organ due to a particular radionuclide after a number of years of exposure is then the sum of Eqs. (7) and (9). A dose-correction factor must be applied to Eqs. (7) and (9) to account for differences in the intake and organ size of the individuals under consideration. The dose correction factor is

$$h_\gamma = \frac{R_\gamma / M_\gamma}{R_{sm} / M_{sm}} ,$$

where

R_γ = the rate of water intake of an individual of age, γ,

R_{sm} = the rate of water intake of standard man,

M_A = the weight of the critical organ of an individual of age, γ, and

M_{sm} = the weight of the critical organ of standard man.

For an individual of age, $\gamma = 10$, who began to consume contaminated water at the beginning of year, $t = 1$, the dose received each year for a period of 3 years would be determined as follows:

Period

$$t = 1 \qquad h_{10}\, D(I)_1$$

$$t = 2 \qquad h_{11}\, D(I)_2 + h_{10}(M_{10}/M_{11})\, D(A)_{11}$$

$$t = 3 \qquad h_{12}\, D(I)_3 + h_{10}(M_{10}/M_{12})\, D(A)_{12} + h_{11}(M_{11}/M_{12})\, D(A)_{21} \qquad (11)$$

A code has been developed for Data Control 1604 that permits machine computation of critical-organ burdens and dose received. It will be instructive to compare the critical-organ burden and dose received by the so-called "standard" man and that of individuals of various age groups who hypothetically begin consuming Clinch River or Tennessee River water at various times.

7.5 Desorption of Radionuclides from River Sediments

T. Tamura W. P. Bonner

To ascertain the conditions under which the radionuclides associated with the Clinch River sediments might be desorbed, several leaching agents were applied to a contaminated sediment sample. The sediment was obtained at the mouth of White Oak Creek (CRM 20.8) with a Petersen dredge; a count exceeding 100,000 counts/min when measured with a Geiger-Mueller counter gave reasonable assurance that sufficient activity was present for detecting radionuclides removed by the treatments. The collected sediment was thoroughly mixed and kept in a tightly closed jar in its original moist state prior to use.

The radiochemical analysis of the sediment is (dis/min/50 g, oven dry basis): Ce^{144}, 4145; Sr^{90}, 2405; TRE, 24,190; $Ru^{103-106}$, 129,000; Cs^{137}, 118,000; Co^{60}, 16,600. Cesium-137 and ruthenium-103 and -106 are the principal contributors to the activity. The relative order of contribution by the radionuclides agree in general with earlier results obtained in the vicinity of CRM 20.8. The exception is ruthenium, which, in this sample, is present in higher concentrations than in the earlier samples.

For desorption, duplicate samples of the wet sediment equivalent to 25 g of oven-dry weight were weighed and contacted with 200 ml of solution. The pH of the solution was adjusted prior to contact and immediately thereafter; another adjustment followed 4 hr later. After 24 hr standing, the samples were centrifuged. The supernatant from the duplicate samples was combined after preliminary tests had shown that the desorbed activity was extremely low. The combined volume was acidified with HNO_3 and reduced in volume by heating prior to radiochemical analysis.

In Table 25, leaching results by acid, salt, and basic solutions are given. Up to 1 M solutions of salts, such as NaCl, KCl, and $CaCl_2$ between pH 6 and 8, removed less than 10% of the Co^{60}, Ru^{106}, and Cs^{137}. This behavior suggests that these ions

Table 25. Removal of Cobalt, Cesium, and Ruthenium from Clinch River Sediment by Various Solutions

50 g - oven dry equivalent - CRM 20.8; 400 ml solution; 24 hr standing

Reagent	Concentration (M)	pH	Co^{60}	Cs^{137} (% removed)	Ru^{106}
HNO_3		6	2.8	---[a]	3.0
HNO_3		2	64.6	---	3.1
HNO_3		1	78.1	3.3	5.5
HCl		6	---	---	3.5
HCl		2	65.6	---	4.1
$NaHSO_2$	0.1	6	16.8	---	9.8
$K_2Cr_2O_7$	0.1	5.6	5.9	1.7	4.7
$CaCl_2$	0.1	7	6.4	---	4.1
$CaCl_2$	1.0	7	4.7	---	4.4
NaCl	0.1	6	3.5	0.8	4.1
NaCl	0.1	8	---	5.7	6.8
NaCl	1.0	6	---	0.7	3.9
NaCl	1.0	8	---	0.6	5.1
KCl	0.1	6.2	---	0.7	2.8
KCl	1.0	6.2	3.0	1.7	2.5
NaOH		8	---	0.4	5.9
NaOH		12	16.5	3.1	46.6
NH_4OH		8	---	0.7	8.2
NH_4OH		11.8	17.2	4.5	45.1
Tap Water		7.7 (natural pH)	---	---	4.5
Ethyl Alcohol			---	---	0.9
Acetone			---	---	1.0

[a] Refers to concentrations below detectable limits.

are not held in the sediment by simple ion exchange. The higher value of 5.7% of cesium desorbed by 0.1 M NaCl at pH 8 was not confirmed by later tests. In acid systems of HNO_3 or HCl, ruthenium is not removed from the sediment but cobalt is released. If ion exchange fixation was responsible for cobalt retention and the acid treatment destroyed the clays responsible for the fixation, cesium would be expected to have been higher in the supernatant. The cobalt was suspected to be in a colloidal form.

In basic media, cobalt is only moderately leachable; ruthenium removal is highest in NaOH or NH_4OH media. It may be noted in passing that the pits into which ruthenium is released is highly basic; the river sediment pH is approximately 7.5; and the presence of ruthenium in the sediment may be due to the reduction in pH in the river. Note that cesium is not removed from the sediment by salts, acids, nor bases after 24 hr contact. The extremely high affinity exhibited by certain clay minerals for cesium have been demonstrated and is likely the reason for the nonremovable nature of this element in the sample.

Although strontium analysis is not available, it is believed that it is desorbable by neutral salt solutions since previous laboratory tests have shown this ion to be easily exchangeable when sorbed on sediments.

Behavior of Cobalt in Demineralized and Tap Water. Solutions containing Co^{60} at approximately 10^{-7} M were prepared with demineralized and tap water. The water was first acidified to prevent possible cobalt hydroxide precipitation when the cobalt tracer was added. The amount of cobalt removed from the solution was calculated by dividing the activity of the centrifuged sample after overnight contact by the initial activity of the solution at pH 2.0 after 15 min of stirring. The results of these tests are shown in Fig. 33 for contact times of 16 and 18 hr. With increasing pH up to 9, both demineralized and tap water solutions show a gradual decrease in cobalt content in the liquid. Above pH 9, the demineralized water sample shows a slight increase, whereas the tap water solution continued to decrease in cobalt content in the liquid phase.

Observation of the tap water sample showed definite flocculated colloids in the bottle above pH 9. Due to the composition of tap water (hardness), it is believed that the precipitate is calcium carbonate; the disappearance of cobalt from solution is likely caused by coprecipitation. At the concentration of cobalt added to the water, no precipitation of cobalt hydroxide is expected until the pH is at least above 9.5. A possible explanation of the removal of cobalt from demineralized water is adsorption on the glass sides. The apparent lower removal from tap water may be an argument for this type of removal, since the tap water contains dissolved ions, such as calcium and magnesium, which could substitute for cobalt adsorption on the sides.

In Table 26, the influence of adding Clinch River sediment to the tap water solutions at three different pH's are shown. Since the pH of Clinch River water is approximately 7.5, the results at this pH may be most meaningful. The large removal at pH 7.5 may explain the high concentration of cobalt in the sediment very near the mouth

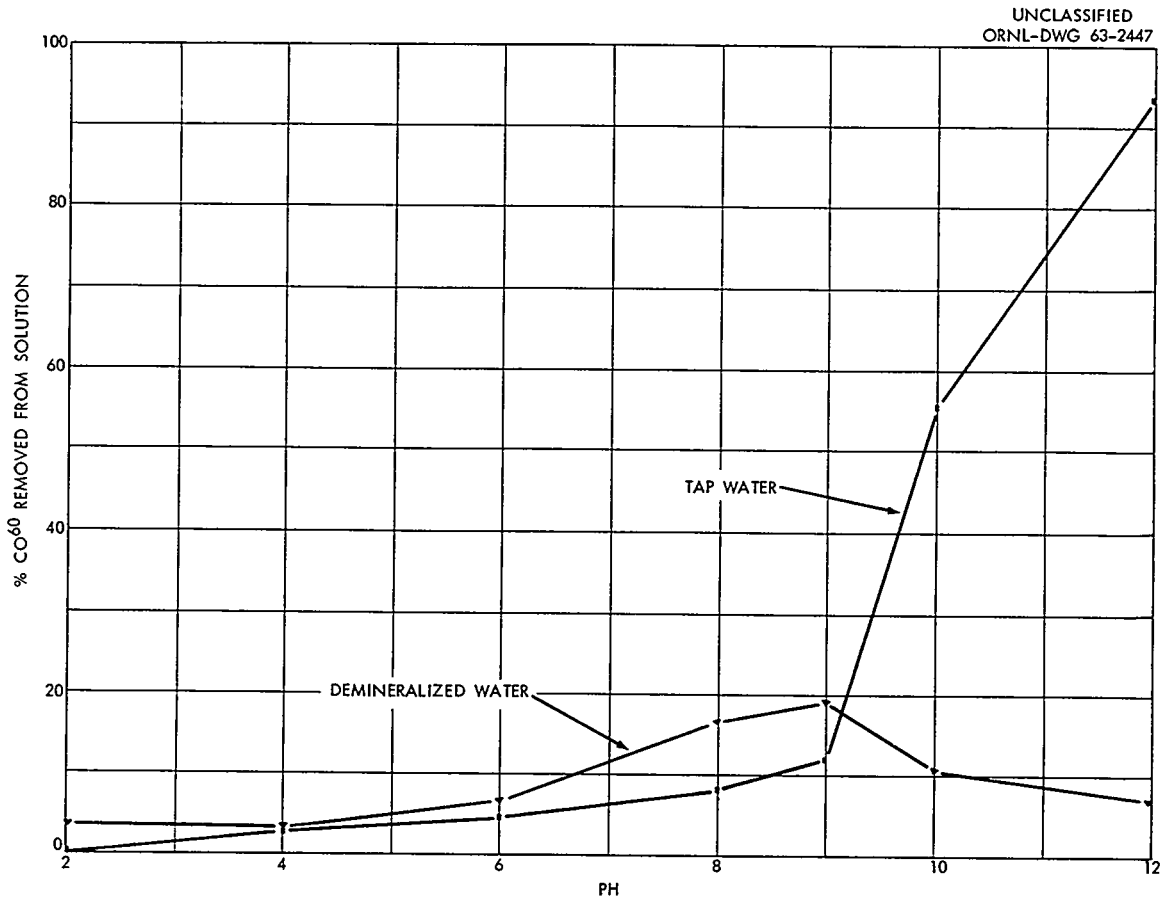


Fig. 33. Removal of Cobalt from Tap and Demineralized Water as a Function of pH.
50 ml Tap Water + Co^{60} - 16 hrs Standing
50 ml Demineralized Water + Co^{60} - 18 hrs Standing

of the White Oak Creek in the Clinch River. Much work remains to be done before the behavior of cobalt is understood, and work is still in progress to elucidate the mechanism of cobalt reaction with Clinch River sediment.

Table 26. Uptake of Cobalt by Clinch River Sediment at pH 4, 6, and 7.5

Solution: 50 ml tap H_2O + Co^{60}

	pH 4		pH 6		pH 7.5	
Time	% Cobalt Removed from Solution	pH Range	% Cobalt Removed from Solution	pH Range	% Cobalt Removed from Solution	pH Range
40 min	39.9	3.98-5.01	73.0	5.98-6.30	91.0	7.50-7.52
1 hr	38.5	3.98-4.34	74.4	6.00-6.13	93.5	7.52-7.58
22 hr	38.2	4.00-4.41	79.3	6.00-6.51	94.6	7.50-7.71
4 hr	38.2	3.98-4.16	80.8	5.95-6.21	95.2	7.51-7.68
24 hr	45.9	3.98-5.30	84.8	6.00-6.78	96.8	7.50-7.82
48 hr	39.7	4.00-4.37	87.0	6.00-6.48	97.8	7.48-7.72

8. MINERAL EXCHANGE STUDIES

8.1 Cesium Exchange by Potassium-Treated Vermiculite

D. G. Jacobs

Previous studies showed that potassium treatment of Zonolite BO-4 (hydrobiotite obtained from American Zonolite Company, Travelers' Rest, South Carolina), an interlayered hydrobiotite of approximately 40% biotite and 60% vermiculite lattices with a particle size range of 20 to 65 mesh, results in an increase of the distribution coefficient for trace cesium exchange from high-sodium-salt systems by a factor of 2.7 when determined by slurry techniques.[23] This increased sorption is attributed to the increased number of collapsed (10-A) lattices which provide exchange sites at the edges of the basal spacings which are sterically favorable for cesium, compared with sodium. However, when column techniques are employed to measure sorption of trace quantities of cesium from 0.5 M $NaNO_3$, the continued leaching action of the sodium nitrate is effective in removing the interlayer potassium. As a result, the lattices collapsed to 10-A by potassium treatment rehydrate upon sodium saturation and expand to 14-A; thus the exchange sites at the edges of the basal spacing lose their specific attractiveness for cesium, and the beneficial effects of potassium treatment are negated.

Zonolite BO-4 was treated with 1 M KCl to induce lattice collapse. The excess salt was removed by elutriation with ethanol (95%). The treated Zonolite had a sharp x-ray diffraction maximum at 10 A and an exchange capacity of 5.9 meq/100 g. Eight

liters of 0.5 M $NaNO_3$ containing traces of cesium (1.7×10^{-7} M) were passed through columns filled with 10 g of the treated vermiculite. Various amounts of potassium were added to the influent to maintain the collapsed lattice structure. The results (Table 27) show that optimum cesium removal was obtained with an influent potassium concentration of 0.0005, which gave a Cs K_d of 366 ml/g and a final exchange capacity of 46.8 meq/100 g. Higher concentrations of potassium were more effective in maintaining collapsed lattices, as indicated by a lower final exchange capacity; but the increased numbers of favorable exchange sites were not sufficient to counteract the increased competition caused by the greater concentration of potassium.

8.2 Strontium Exchange by Vermiculite with Potassium Added to the Influent

Addition of potassium to 0.5 M $NaNO_3$ influent to raise the potassium concentration above 0.01 M results in collapse of vermiculite lattices and the interlayer fixation of trace concentrations of cesium by physical entrapment of the cesium held at exchange sites on the basal surface of the vermiculite.[26] No appreciable quantities of strontium could be fixed in this manner, however (Table 28). The uptake of strontium was reduced by increased concentrations of potassium, although the reduction was not proportional to the reduction in final exchange capacity. In addition, the major portion of the strontium remained in an exchangeable form.

Table 27. Effect of Addition of Potassium to the Influent on the Sorption of Cesium by Potassium-Treated Vermiculite from 0.5 M $NaNO_3$ Containing the Mass Equivalent of 2 μc of Cs^{137} per ml

Potassium Concentration (M)	Cesium K_d (ml/g)	Cesium Leached (%)	Final CEC (meq/100 g)
0.0000	252	15.0	67.0
0.0001	311	16.2	63.7
0.0002	352	10.5	56.2
0.0005	366	9.8	46.8
0.001	358	10.8	37.9
0.002	262	9.5	16.7
0.005	180	10.2	9.1
0.01	147	9.6	10.0
0.05	65	10.2	9.0

Table 28. Effect of Addition of Potassium to the Influent on the Sorption of Trace Quantities of Strontium by Vermiculite from 0.5 M $NaNO_3$

Potassium Concentration (M)	Strontium K_d (ml/g)	Strontium Leached (%)	Final CEC (meq/100 g)
0.00	43.8	84.1	86.0
0.01	46.9	76.2	65.5
0.02	36.0	86.1	44.6
0.04	24.1	70.7	22.8

9. WHITE OAK CREEK BASIN STUDY*

9.1 Distribution and Transport of Radionuclides in the Bed of Former White Oak Lake

T. F. Lomenick

A series of core samples was taken in the bed of former White Oak Lake to determine the quantity and distribution of radionuclides within the area.[4] In general, it is observed that most of the Cs^{137} is associated with the relatively thin layer of recent lacustrine sediment that covers the lake bed. Thus, in areas near the shore line where the sediment is thinnest, the smallest quantities of activity are found. Maps showing concentrations of Cs^{137} for the 0- to 6-in. and 6- to 12-in. layers of lake bed soil are presented as Figs. 34 and 35. For the first 6 in. of soil (Fig. 34) it is noted that concentrations vary from less than 1×10^{-3} μc/g to 77×10^{-3} μc/g, and the areas of maximum concentrations lie roughly adjacent to the course of White Oak Creek through the bed and in the present impoundment area behind the dam. The greatest depth of lacustrine sediment in the lake bed is also found in these areas.[4] In the soil section 6 to 12 in. below the surface, it is seen (Fig. 35) that the concentrations of Cs^{137} at most of the sample points are much less than those observed in the upper layer of soil. The higher values are restricted to sites where the lake sediment is greater than 6 in. deep.

The concentrations of Sr^{90} for the upper 6 in. of soil over the lake bed are shown in Fig. 36. It is of interest that, with the exception of a few narrow zones parallel to

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

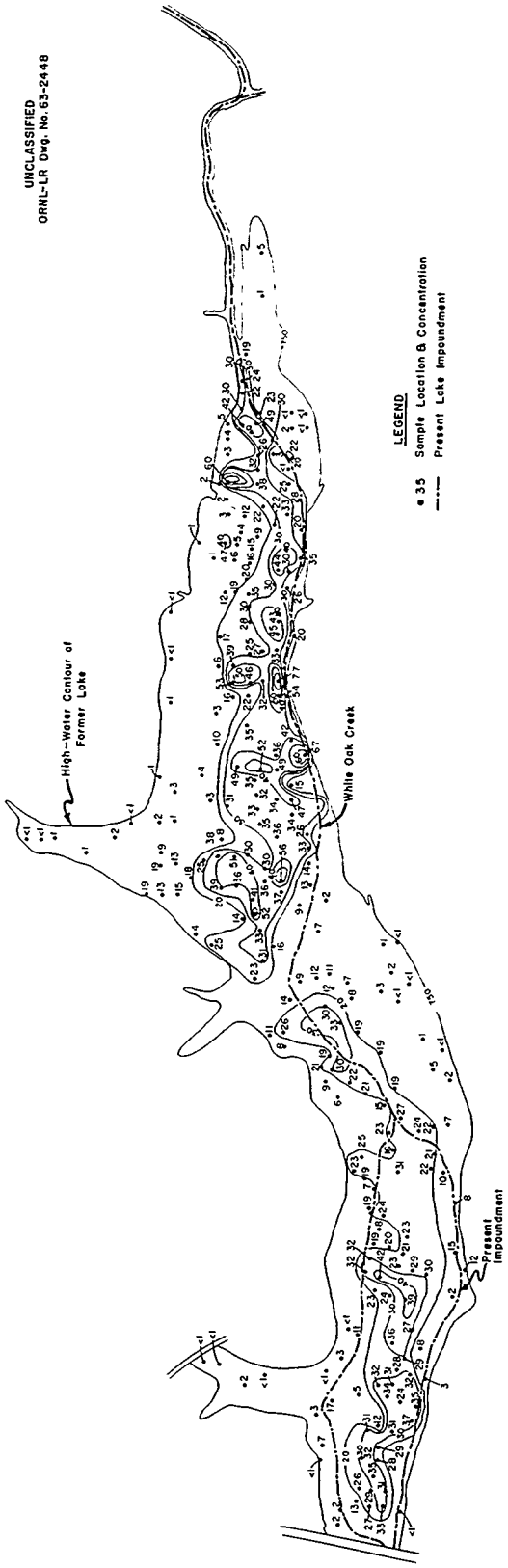


Fig. 34. Map of White Oak Lake Bed Showing Cs^{137} Concentrations in 10^{-3} μc/gm for 0–6 Inches Soil Layer

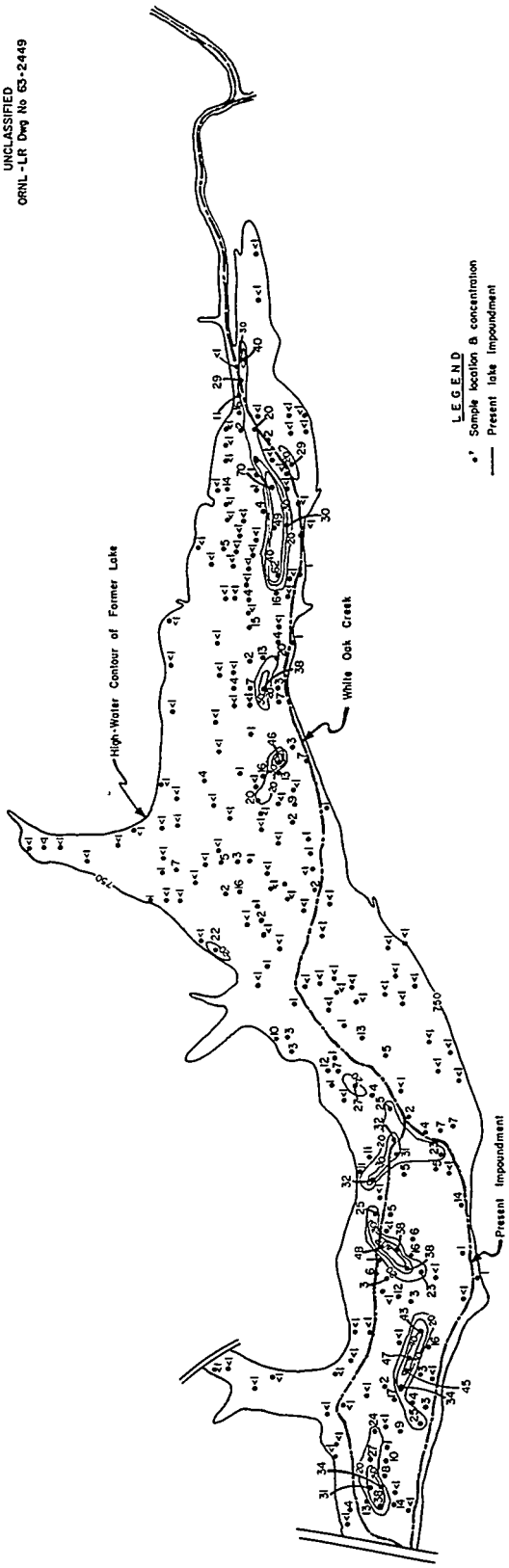


Fig. 35. Map of White Oak Lake Bed Showing Cs^{137} in 10^{-3} μc/gm for 6 to 12 Inches Soil Layer

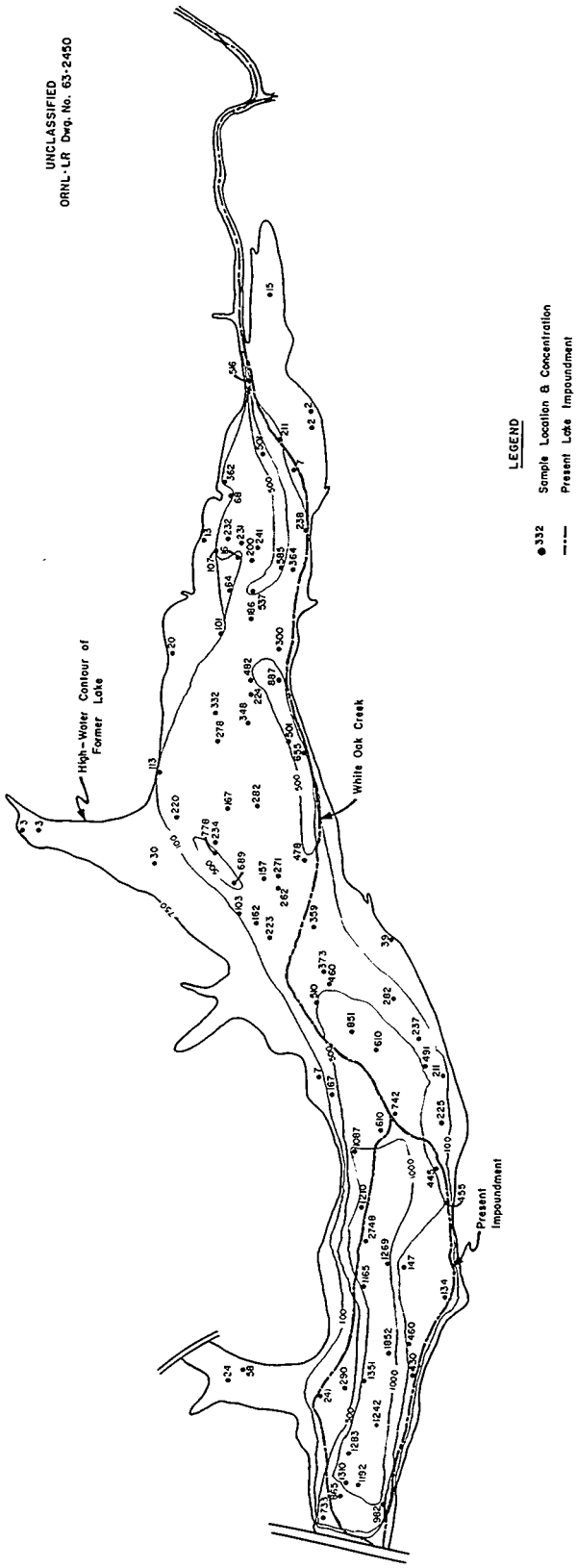


Fig. 36. Map of White Oak Lake Bed Showing Sr^{90} Concentrations in μμc/gm for 0-6 Inches Soil Layer

the creek in the upper part of the bed, the highest concentrations of Sr^{90} are found within the inundated area behind the dam. This indicates that strontium is presently being removed from the lake water and is accumulating in the bottom sediments. It is also observed that the concentrations of Sr^{90} in the soil are roughly a hundredth of those of Cs^{137}.

9.2 Movement of Radionuclides in White Oak Creek

A preliminary investigation of the bed of White Oak Creek and its flood plain revealed that bottom sediments to a depth of 18 in. at mile 2.3 contain Sr^{90}, Cs^{137}, Co^{60}, and the rare earths (exclusive of Y^{90}) in concentrations that range from 100 to 3450 μμc/g, 4000 to 76,900 μμc/g, 290 to 2200 μμc/g, and 0 to 14,100 μμc/g, respectively. In general, for Sr^{90} and the rare earths the highest concentrations occur in the uppermost few inches of the sediment; whereas, for Cs^{137} and Co^{60} the higher concentrations were found at a depth of 6 to 12 in. The concentrations of radionuclides found in the flood plain along the bank of the creek are roughly the same as those observed in the creek bed.

9.3 Geology and Hydrology of White Oak Creek Basin

W. M. McMaster* R. M. Richardson*

Heavy rains occurring on March 5 and again on March 11-12 caused extensive flooding in White Oak Creek basin. On March 5, when 2.68 in. of rain fell at ORNL according to the U. S. Weather Bureau, discharge measurements were made at most of the White Oak Creek basin gaging stations, and water samples were collected at each station for chemical quality and sediment analyses. Sediment samples collected at gaging stations on White Oak Creek were taken continuously at closely spaced intervals as the stream stage changed. Results of analyses of these samples will add to the knowledge of stream discharge-sediment transport relations in White Oak Creek basin.

On March 11 to 12, when 4.47 in. of rain fell at ORNL, a flood time-of-travel study was made in White Oak Creek at a time near the peak discharge, which was about 200 cfs at the gaging station White Oak Creek below ORNL. Two liters of 40% Rhodamine β dye was poured into the stream at a point about 500 ft above the main laboratory area, and samples were collected for measurement of fluorescence at three stations during passage of the dyed water. Results of this flood time-of-travel study are shown in Fig. 37 for stations White Oak Creek at ORNL and White Oak Creek below ORNL. No data were obtained at the station, White Oak Creek at White Oak Dam, due either to dilution of the dye or failure to sample during passage of the dye.

---

*On loan from Water Resources Division, U.S. Geological Survey.

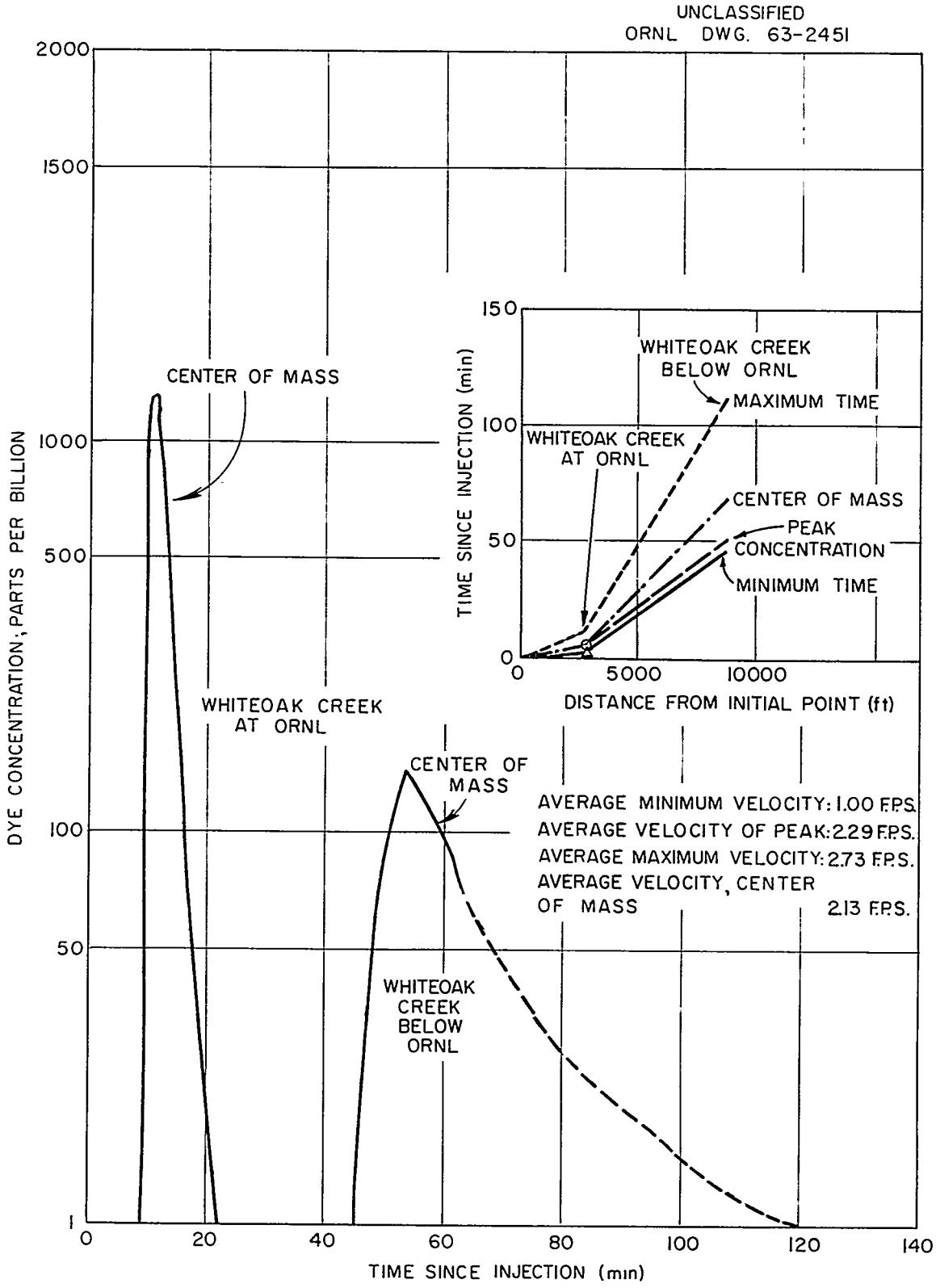


Fig. 37. Time of Travel Study White Oak Creek, March 15, 1963.

The results of this flood time-of-travel study contrast markedly with results obtained from studies made under base flow conditions. When discharge was 4.7 cfs, in October, about 3.5 hr was the minimum time required for water to travel from the Laboratory area to the station, White Oak Creek below ORNL. However, only 37 min were required during the March 15 flood.

During the week of March 18 to 22, water levels were measured in most of the permanent wells in White Oak Creek basin. A water-table contour map, drawn on the basis of the nearly 250 wells measured, was constructed, representing the water-table high for the 1963 water year.

REFERENCES

1. Unit Operations Section Monthly Progress Report for February 1963, ORNL-TM-581 (in press).

2. Unit Operations Section Monthly Progress Report for March 1963, ORNL-TM-586 (in press).

3. Unit Operations Section Monthly Progress Report for April 1963 (in press).

4. Waste Treatment and Disposal Progress Report for November 1962-January 1963, ORNL-TM-516 (June 12, 1963).

5. Chemical Technology Division Monthly Progress Report for Chemical Development Section B, March 1961, ORNL-CF-61-4-108.

6. J. T. Roberts and R. R. Holcomb, A Phenolic Resin Ion-Exchange Process for Decontaminating Low-Radioactivity-Level Process Water Wastes, ORNL-3036 (May 22, 1961).

7. R. R. Holcomb, Low-Radioactivity-Level Waste Treatment. Part I. Laboratory Development of a Scavenging-Precipitation Ion-Exchange Process for Decontamination of Process Water Wastes, ORNL-3322 (in press).

8. R. E. Brooksbank, et al., Low-Radioactivity-Level Waste Treatment. Part II. Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Wastes by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349 (May 13, 1963).

9. P. Hamer, J. Jackson and E. F. Thurston, Industrial Water Treatment Practice, pp. 22-37, Butterworths in association with Imperial Chemical Industries Limited, London, 1961.

10. E. Schonfeld, R. Sanford, G. Mozella, D. Ghosh, and S. Mook, The Removal of Strontium and Cesium from Nuclear Waste Solutions by Foam Separation, NYO-9577 (July 26, 1960).

11. E. Rubin and E. Schonfeld, Foam Separation, Quarterly Progress Report, October 1, 1962 to December 31, 1962, Radiation Applications, Inc., RAI-110 (March 15, 1963).

12. R. M. G. Boucher and A. L. Weiner, "Sonic Defoaming - It's Present Status," Food Processing (October 1962).

13. R. M. G. Boucher, "Ultrasonics in Processing," Chemical Engineering, p. 83-100 (October 2, 1961).

14. Anonymous, "Defoaming by Sound Waves Explained," Chem. Engr. Prog., 57, No. 11, p. 169-70 (November 1961).

15. American Petroleum Institute, Oil-Well Cementing Practices in the United States, API, 50 West 50th Street, New York 20, New York (1959).

16. L. M. Epstein, Formation of Chemically Free Halogen by Radiolysis of Solid Potassium Chloride, Westinghouse Electrical Corporation Research Laboratories, Pittsburg, Pennsylvania, WERL-0100 (June 1962).

17. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

18. Report of Committee II on Permissible Dose for Internal Radiation, International Committee on Radiological Protection, Publication 2, Pergamon Press, London (1959).

19. E. C. Albritton, Standard Values in Nutrition and Metabolism, W. B. Saunders Company (1954).

20. Department de la Protection Sanitaire Contrat de' association, C.E.A./Euratom, Donnees Biologiques de Base pour l'etude des Niveaux de Contamination Applicables aux Enfants, Supplied to ICRP by Dr. Jammet (February 1962).

21. William S. Spector (ed.), Handbook of Biological Data, Wright Air Development Center (October 1956).

22. Harry Levin, "Some Aspects of Inhalation Dose Calculation from Single Exposures," Health Physics. 9, 41-44 (1963).

23. D. G. Jacobs, "The Effects of Collapse-Inducing Cations on the Cesium Sorption Properties of Hydrobiotite," to be published in the Proceedings of the 1963 International Clay Conference, August 12-16, 1963, Stockholm, Sweden.

2005

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ORNL-TM-757
15

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

MAY-OCTOBER 1963

F. L. Parker
R. E. Blanco

This document has been approved for release to the public by:

Donald R Hamm 7/28/95
Technical Information Officer Date
ORNL Site

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM-757

HEALTH PHYSICS DIVISION

CHEMICAL TECHNOLOGY DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

MAY-OCTOBER 1963

F. L. Parker R. E. Blanco

APRIL 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level-Waste Calcination. Two rising-level glass-making tests were made in the vertical 8-in.-diam calciner, using TBP-25 waste to which monosodium phosphate and lead nitrate were added to form the glass mix. The average feed rate was about 5 to 6 liters/hr. Accumulation of dust in the off-gas line required frequent flushing with nitric acid to prevent plugging.

A scouting test for continuous glass making in a horizontal vessel (8 in. in diameter and 40 in. long) heated with a 25-kw furnace was successful. The aqueous waste solution containing phosphate and lead was evaporated on the surface of a shallow pool of molten glass that flowed continuously from the vessel through a jack leg to maintain a fixed pool depth. The maximum feed rate was 20 liters/hr.

High-Level-Waste Disposal - Vapor-liquid equilibria and solution densities of FTW-65 waste solutions were determined for concentrations up to 9 times normal concentration. Ceramic solids for fixation of this waste type were developed; they melted in the range 700 to 800°C and lost 5% or less of their sulfate when heated 100°C above their melting temperatures. The one chosen for demonstration of semi-engineering scale, semi-continuous fixation was satisfactorily stable with respect to sulfate loss and was noncorrosive under the usual fixation conditions but produced a large amount of dust high in iron which tended to plug the off-gas line. Sparging with nitrogen during fixation resulted in loss of about 23% of the sulfate and in catastrophic container corrosion.

A series of solid products were made from fixation of non-sulfate Purex waste. Some of these melted as low as 500 to 600°C. Two of the series were glasses.

Calcination of sulfate-deficient Purex waste (essentially $NaNO_3$ with minor amounts of SO_4^{2-} and Fe^{3+}) was shown to be practical on addition of aluminum. In the absence of any additive there was gross displacement of solids from the fixation container and volatilization of both Na^+ and SO_4^{2-}.

A column packed with copper shot removed 99.4% of the mercury from 510 bed volumes of FTW-65 (low acid) waste solution. A column packed with

aluminum turnings removed 99% of the mercury and 30 to 35% of the ruthenium from 162 bed volumes of FTW-65 waste concentrated by a factor of 3. Both copper and aluminum were attacked too rapidly by Purex 1WW waste to be effective in removing mercury from this (high acid) waste.

Type 304L stainless steel corroded at rates ≤ 0.3 mil/month in FTW-65 evaporator environments both in the presence and absence of expected additives; corrosion rates of titanium were negligible. Coupling the two metals had no appreciable effect on the corrosion of either. Tests on 304L stainless steel during calcination and fixation (melt-down) cycles for FTW-65 wastes resulted in total penetrations of about 10 and 15.3 mils/month, respectively. Maximum rates for 304L stainless steel in salt (simulating waste storage) at 300°C were about 0.03 to 0.04 mil/month.

Low-Level Waste Treatment: Scavenging-Precipitation - Ion Exchange. Pilot plant equipment and piping changes were completed. When the weak-acid strong-acid fixed-bed ion exchange system was operated for a week with waste from the ORNL equilization basin as feed, algae passed through the anthracite filter and the ion exchange beds. Further tests in the system were stopped pending completion of radiochemical analysis of stream samples. Tests with tap water feed were started in the modified scavenging-precipitation equipment.

In the laboratory-scale tests, cesium eluted from the cation exchange column with nitric acid in the Scavenging-Precipitation Ion-Exchange process was sorbed on grundite clay and the slurry recycled to the process feed stream, thus eliminating the need for an evaporation step. The optimum pH range for sorption of cesium on grundite was quite narrow, about 11.8. Sorption is essentially independent of the particle size of the grundite over the range from about 50 mesh to < 200. Addition of grundite prior to pH adjustment favors higher sorption. An alumina column removed about half the phosphate from 10,000 bed volumes of raw ORNL waste. Addition of a column of Dowex 21-K anion exchange resin following the Scavenging-Precipitation Ion-Exchange process resulted in removal of about half of the gross activity but was ineffective in removing all the ruthenium.

Foam Separation: Laboratory Development - The foam separation process to remove cesium, strontium, and other radioactive nuclides from low-radioactivity-level process waste water consists in a scavenging precipitation

by caustic-carbonate followed by countercurrent foam separation. By making the waste 5 to 10 ppm in Fe^{3+}, a coagulant, before adding caustic-carbonate, the deleterious effects of high concentrations (5 to 15 ppm) of phosphates in the water on the extent of precipitation of calcium carbonate are greatly reduced, provided that these high concentrations are only of a few hours' duration. Removal of cesium in the precipitation chamber (sludge column) by sorption on grundite clay (at approximately 0.5 lb/1000 gal water) is increased (from a DF of 8 to a DF of 15) if the clay is first baked at 600°C for 20 min. Operating conditions of the foam column, including concentrations of surfactant in inlet and exit streams, were determined with sodium dodecylbenzene sulfonate as surfactant for linear foam flow rates of 32 to 46 cm/min and at gas-to-liquid flow-rate ratios of about 10. Cesium removal in the foam column was poor when either dodecylbenzene sulfonate or any of three surfactants (RWA-100, dichlorophene, and hexachlorophene) containing an active phenolic group were used.

Foam Separation: Engineering Development - Experimental results show that foams are easily condensed while passing through an orifice with upstream/downstream pressure ratios of two or greater. The 0.015-, 0.100-, and 0.250-cm-diam orifices all gave residual foam volumes of about 0.001 the inlet volumes for foams of 0.05 to 0.08 cm mean diameters. As compared to impingement on a Teflon sheet 2 to 3 in. from the orifice, the amount of uncondensed foam was slightly decreased by placing the sheet 24 in. from the orifice, and it was slightly increased by use of a glass wall in place of the Teflon sheet. The 24-in.-diam foam column (the proposed LLW pilot plant column diameter) was operated at flows up to 80 liters/min of foam and 13 liters/min of liquid. The amount of channeling appeared acceptable when an improved liquid feed distributor was used. From foam-stability tests, it appears that the low-level-waste column should have a stable foam with 25 ppm DBS in the liquid. A proposed design and equipment flow sheet for the Foam Pilot Plant is presented.

Engineering, Economics, and Safety Evaluation. Costs of permanent storage of calcined radioactive wastes in concrete vaults and in rooms mined out of granite formations were estimated. In comparison with previously estimated costs of storage in salt mines, costs of storage in concrete vaults were five to seven times as much, and costs of storage in

granite were about twice as much. This economic advantage, as well as the greater safety it is believed to offer, makes salt the preferred choice.

Vaults for the storage of calcined solid wastes would be similar in their gross features to many of the concrete secondary containments used for tanks built for storage of liquid radioactive wastes, in that they would be underground structures of reinforced concrete with about 10 ft of earth cover and a floor-to-ceiling height of about 15 ft. For maximum safety, they would be sealed completely from the surface; space requirements were calculated by assuming dissipation of the heat of radioactive decay by conduction through the earth cover. Two types of concrete were considered: ordinary concrete, capable of withstanding 400 to 500°F, and "high-temperature concrete," capable of withstanding 1000°F.

Space requirements for the storage of calcined wastes in rooms in granite formations are about the same as those for storage in salt formations. However, excavating costs are higher for granite because heavier equipment is required, drilling is more difficult and slower, and costs of explosives are higher.

Estimations were made of the movement of Sr^{90}, Ru^{106}, and Cs^{137} in Conasauga shale following a hypothetical release of reactor fuel-processing waste from a tank. Computations were based on hydrologic and exchange characteristics of the local formation that had been obtained previously. Although the absolute values for radionuclide movement that have been calculated and presented should not be considered to be precise, since the estimates were based on a rather inadequate description of the site, the procedure used in making these calculations could be applied for any proposed site. The reliability of the estimates could be improved by improving the quantitative description of the geological formation involved.

In Conasauga shale, Sr^{90} would apparently move quite rapidly in an acid waste system, even upon neutralization of the acid by calcite ($CaCO_3$) in the formation. Movement of Sr^{90} in an alkaline waste solution would be much slower due to the formation of insoluble compounds, in addition to holdup due to ion exchange. Ruthenium-106 would be expected to move rapidly in either acid or neutralized waste systems, but it presents little long-term hazard due to its relatively short half-life. The movement of

Cs^{137} would be expected to be slow because of its fixation by the illite of the Conasauga shale (ion exchange).

Disposal in Deep Wells. Detailed logging of wells 1 and 2, before and after the casings were installed, showed that (1) the dip of the beds between the wells is unexpectedly low, (2) that there are zones of sheared or broken rock in the approximately 50 ft of shale immediately above the Rome sandstone, and (3) that there may be a few faults filled with tight clay gouge up to as high as 860 ft in the red shale into which waste mixtures are to be injected.

Four water injections, with and without fluid-loss additives, were made into slots in the injection well (well 1) at 986 ft and 966 ft, respectively. Although the recovery from the last injection is still continuing, there appears to be sufficient similarity between the injections, with and without fluid-loss additives, to suggest that there is little incentive to use such additives in setting or nonsetting mixes. The results obtained from the slotting operations that were performed for the water injection tests indicate that the well casing was not completely severed by the normal operating technique. Some modification of this method will be necessary.

The main emphasis on mix development during this period was on cheap mixes that, although not as strong as previously developed mixes, would be pumpable, would set, and would have no phase separation. The mineral attapulgite 150 is far superior to bentonite as a suspending agent for solutions with a high ionic content. Several retarders have been investigated and glucono-d-lactone (CFR-1) seems particularly effective. The density of these "low solids" mixes is greatly affected by entrained air. This phenomenon is of concern because, during an injection, the relative amounts of solids and liquids fed to the mixer will be controlled by the density of the slurry. Some means of eliminating air entrainment must be found.

A hazards analysis of the fracturing experiments was completed. It was concluded that the waste solution to be used in the first series of injections will be so low in specific activity that no significant hazard would result from its use. The other principal hazard involved in the experiments - that of working with high-pressure equipment - has been

minimized where possible by installing the pumping and mixing equipment in cells.

The experimental program for the first series of injections will consist of four injections, each of 40,000 gal.

1. An injection of a synthetic concentrated waste solution mixed with attapulgite to form a nonsetting slurry.

2. An injection of the same synthetic waste solution mixed with a cheap setting mix.

3. An injection of actual waste solution mixed with additional chemicals to increase the concentration to the same value as that in injections 1 and 2. This will be mixed with sufficient cement to form a strong setting mix.

4. An injection of actual waste solution mixed with a strong setting mix.

An estimate of the probable operating cost of the shale fracturing plant shows that the cost of the mix and the well life are the significant variables. The well life can be significantly extended by making the batch size large. For this reason it seems probable that the direction of future work will be toward larger batch sizes than it is currently planned to inject.

Construction is proceeding on phase 2 of the surface plant. The bulk storage tanks have been erected; the majority of underground lines have been installed; and foundations for the cells have been poured.

Disposal in Natural Salt Formations. Operation of the heated model room continues, and the closure rates are now less than ten times higher than the closure rates before heating. At this time it is not known if the closure rate during heating will remain above the ambient temperature rate, approach it asymptotically, or fall below it.

Design and construction of the Lyons demonstration experiment continues. A contract was let to replace the headframe, foundations, and cages to allow lowering of 7-ton loads into the mine. New power cable and hoisting cables were delivered to the Lyons site. A critical path schedule of the over-all experiment was prepared as an aid to expediting and scheduling all phases of the experiment. A contract was let for the fabrication of the trailer for the waste disposal transporter. The prime

mover (Caterpillar model 619C) for this unit was purchased. Design of other experimental components is underway.

Tentative conclusions on the radiolytic production of chlorine from irradiated rock salt indicate that the amount of oxidizing power created within the salt is independent of the size and surface area of the crystals per unit weight, but the oxidizing power can be increased by stresses and strains in the salt.

Clinch River Studies. The expected summer pulsed releases of water from Melton Hill Dam were simulated by flow through the gates during August 1963. The purpose of the experiment was to determine the dilution in the Clinch River under the changed flow regime. Rhodamine B dye was used to simulate radioactive releases. The minimum dilution was 50, in comparison with the previous median dilution of 570.

Cores taken from the bottom sediments of the Clinch River in 1962 were analyzed and showed that the major portion of the contaminated sediments has been deposited on the sides of the original stream channel.

Desorption of the nuclides from bottom sediments showed that acidified water is more effective in removing Sr^{90} from the sediments than highly salted solutions.

Analyses of fish taken from the Clinch River show that a maximum of 2.5% of the maximum permissible intake (MPI) will be received from eating 37 lb of fish per year from East Tennessee rivers. Radiation levels near filter beds in water plants upstream and downstream of the point of entry of White Oak Creek into the Clinch River are at background.

Fundamental Studies of Minerals. Cesium was desorbed from six representative clay minerals containing trace levels of Cs^{137}. The cesium on both kaolinite and montmorillonite was completely desorbed by 1 M sodium acetate after contact for 1 hr. When 1 M HNO_3 was used, the hydrobiotite and biotite released all their cesium; both illite and muscovite retained 75% and 85% of the cesium even after 24 hr of contact with the nitric acid. Since acids decompose the clay minerals, the difference in release by the minerals reflects the ease of their decomposition.

Three possible types of cesium sorption response are illustrated by the vermiculite, depending on the original cation on the exchanger. With increasing cesium concentration, the K_d for cesium can increase due to

collapse induced by the cesium replacing the magnesium ion, can decrease if the vermiculite is presaturated with potassium ion, which precollapse the layers, or can remain relatively constant if the cesium isotopically exchanges with other cesium ions. One of these three types of responses described responses observed by the other clay minerals, including montmorillonite, kaolinite, and illite.

White Oak Creek Basin Study. A series of preliminary core samples were taken in and around two of the earlier "open" type of intermediate-level waste seepage pits that were recently abandoned and filled. Radiochemical analyses of segmented sections of these cores indicate that most of the activity is associated with the sludges and precipitates that have accumulated in the pits and on the first few inches of weathered shale that comprises the side walls and bottoms of the pits. On a dry-weight basis, concentrations of Cs^{137} and Sr^{90} were observed to be as high as 96 μc/g and 17 μc/g, respectively, in the sludge, and 3 μc/g and 0.2 μc/g in the weathered shale on the side walls and bottoms of the pits. The sludge in the pits was also quite variable in thickness and distribution.

7. CLINCH RIVER STUDY

7.1 Dispersion Due to Power Releases

P. H. Carrigan, Jr.* B. J. Frederick* F. L. Parker

During the recent summer months a series of tracer tests were conducted to study the effects that the peaking power releases of water from Melton Hill Reservoir will have on the dispersion in the Clinch River of radioactive releases originating from White Oak Lake. The electric-generating equipment is not yet fully installed at Melton Hill Dam, and, as a consequence, the variation in flow for the tests was simulated by releases through the spillway gates at the dam.

The first tracer test with steady releases from Melton Hill Dam was preliminary in order to determine the quantity of tracer needed in succeeding tests and to assess the reliability of instruments under field conditions. Subsequent tests were run with the typical pattern of summer water releases. The discharge hydrograph for a week of such releases is shown in Fig. 43.

The regulated flow through the gates of Melton Hill Dam was obtained through the co-operation of A. J. Cooper and M. A. Churchill of the Tennessee Valley Authority.

The three tests made under summer power release conditions differed largely in the procedure of injecting the tracer. In the first of three tests, the fluorescent dye tracer, "Rhodamine B," was injected instantaneously in a line across the Clinch River at the mouth of White Oak Creek. In the second test, the dye was injected continuously for 24 hr into the nappe at White Oak Dam. In the third test, the dye was injected continuously for 1 week into the nappe at White Oak Dam.

The dispersion with time which occurred in the Clinch River during the latter two tests was very similar to the expected dispersion of radioactive wastes from White Oak Creek when power generation begins at Melton Hill Dam. At the time that flow suddenly began in the river, a rapid rise

---

*On loan from Water Resources Division, U.S. Geological Survey.

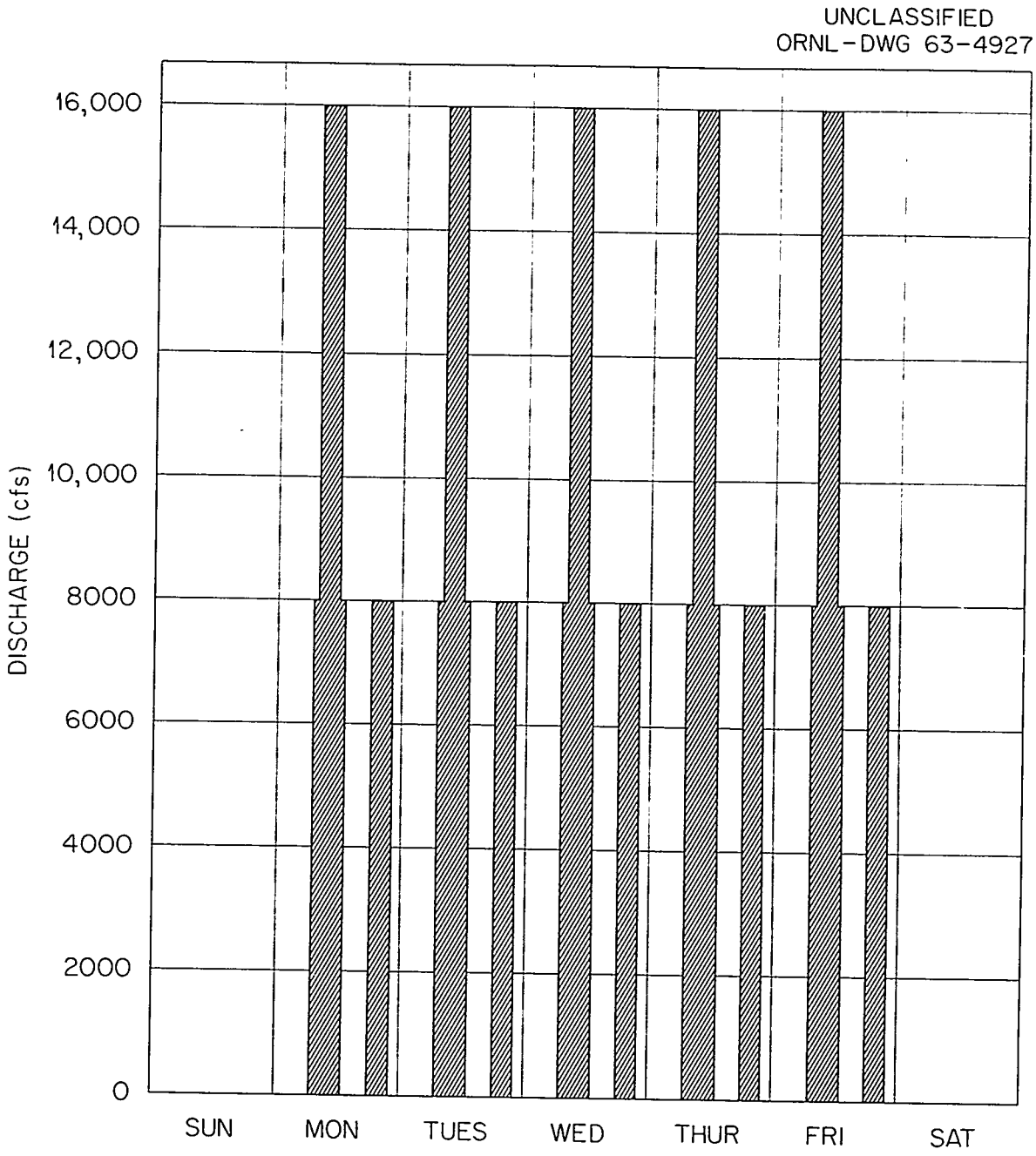


Fig. 43. Estimated Summer Discharge Pattern for Melton Hill Dam.

in river water level occurred at the mouth of White Oak Creek. As a result of the increased water level at the creek mouth, an adverse hydraulic gradient was created in the creek from its mouth to White Oak Dam; and an upstream flow occurred. For a considerable part of the time that water was being released through Melton Hill Dam, there was little flow from the creek into the river. At the cessation of the release, the water level in the river suddenly dropped, and a sudden rush of water from White Oak Creek embayment took place. A discrete pulse of dye accompanied this rush of water from the creek. Because there was no flow in the river, the dye mass remained close to the mouth of the creek.

The progressive spreading of the dye pulse in the stilled river was observed by means of aerial photography. In Fig. 44 the extent of visible dye after the cessation of water release is shown.

At the beginning of the next water release, the slug of dye in the river was swept downstream as a reasonably intact mass, and flow up White Oak Creek again occurred.

Two pulses of dye were injected into the river each weekday. For at least their first 6.4 miles of travel downstream from the mouth of White Oak Creek, the individual pulses of dye could be identified.

The ebb and flow of water in White Oak Creek embayment due to the power releases is much the same as flow in a tidal estuary. With techniques of tidal flow analysis, it was possible to compute the maximum magnitude of concentration of the dye pulse at downstream sections in the river and to determine the travel time of the pulse to these sections. A comparison of predicted and actual times of arrival are shown in Fig. 45.

The last test of the series, in which dye was released for 168 hr, began at 0100 hr on August 21. At 2100 hr on Friday, the week-end shutdown of water releases occurred. The shutdown, with no flow in the river, continued for 58 hr until 0700 hr on the following Monday. Flow of water and dye from the creek into the stilled river commenced soon after the shutdown began. The release of dye continued until startup of flow on Monday morning. On Sunday afternoon, at about 1500 hr, aerial observation of dye spreading was made. It was observed that a continuous mass of dye extended from CRM (Clinch River Mile) 20.0 to CRM 22.5; the mouth of White Oak Creek is at mile 20.8. It was also observed that another discrete

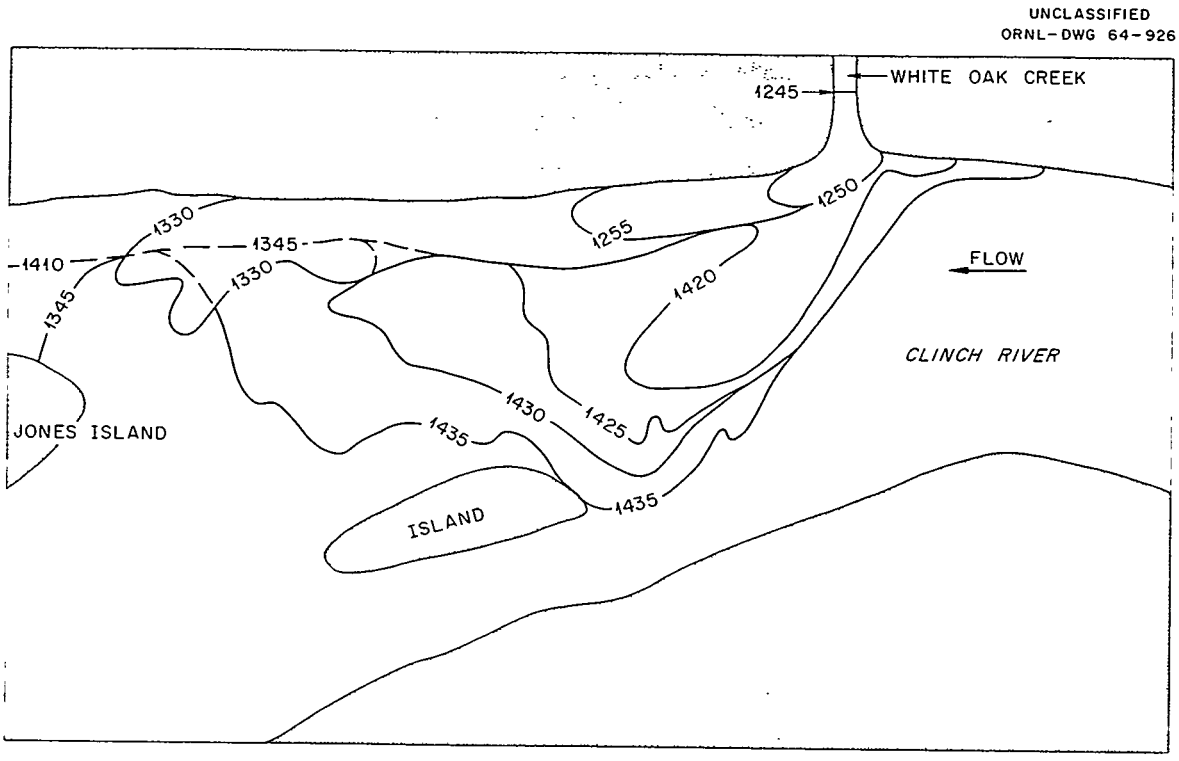


Fig. 44. Sketch of Time Development of Dye Front At and After the End of a 16,000-cfs Release in Clinch River at Mouth of White Oak Creek.

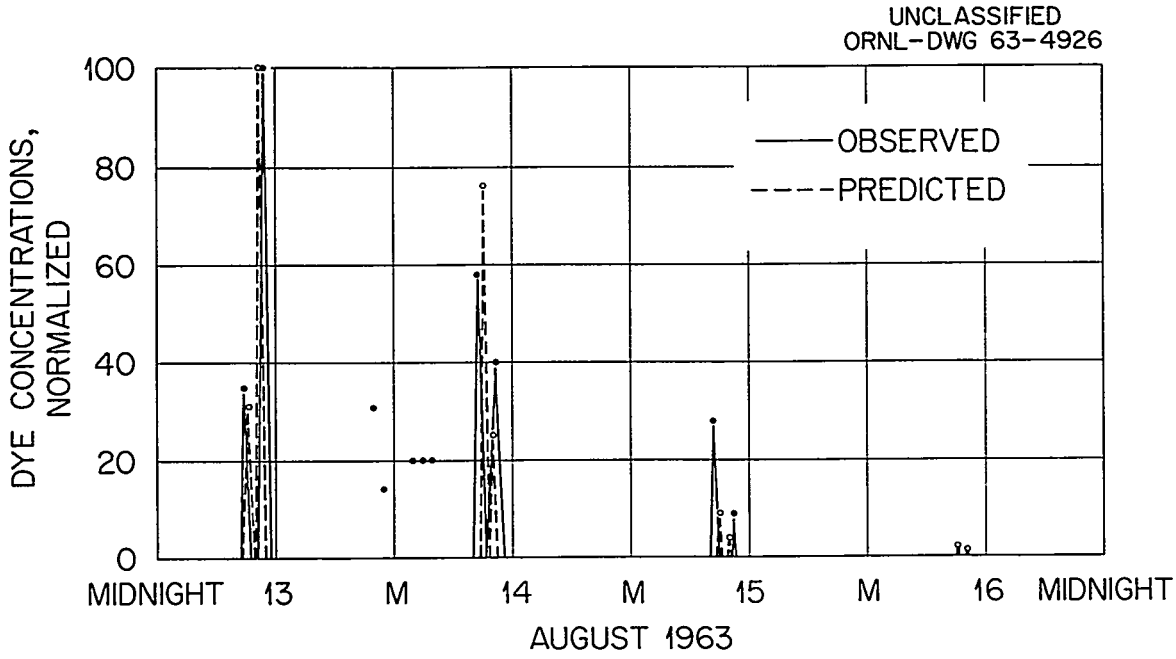


Fig. 45. Dye Concentrations at Clinch River Mile 16.2.

mass of dye was centered about mile 18.5. The mass at mile 18.5 was the pulse created by the first release of water on Friday.

As a result of the large-scale release of dye on the week end, considerably greater concentrations were observed on Monday of the second week at an observation section at Gallaher Bridge sampling site, 6.4 miles downstream from the mouth of White Oak Creek. The variation in dye concentration with time at this sampling site for the test period is shown in Fig. 46.

The twice-daily pulses of dye from the creek occurred on several weekdays during the test period of about 1000 and 1145 hr at the Gallaher Bridge observation station. Increased concentrations began at this station on Sunday afternoon. When there is no release from Melton Hill Reservoir, upstream flows could occur because of river control operations in the Tennessee River, re-establishment of thermal stratification in the Clinch River, or as a result of a combination of both processes. These upstream flows, though minor, could move a mass of dye short distances. It is believed that the mass of dye that passed the section at Gallaher Bridge at 1145 hr on Friday of the first week was slowly moved upstream during the week end and remained almost stagnated at the sampling site, beginning on Sunday afternoon. During the second week of the test, the mass of dye passing the site at 1145 hr stagnated about 2 miles downstream because of cessation of release from Melton Hill Reservoir.

The peak concentration that occurred on Monday of the second week of the test represents the critical condition in so far as dispersion of radioactive wastes are concerned. On the basis of the concentration of tracer injected at White Oak Dam and the peak concentration observed on Monday, the effective dilution at the Gallaher Bridge sampling site is computed to be 50. The median dilution of White Oak Creek releases by Clinch River water for the period of 1950 to 1960 has been 570 (ref 37). At the Gallaher Bridge station the radionuclide concentration in river water during the last few years has been less than 1% of the maximum permissible occupational concentration. On the basis of the dye tracer test, the dilution due to power release will be decreased by a factor of 11. It is thus tentatively concluded that the radionuclide concentrations at Gallaher Bridge would remain below MPC_w during the summer months when power releases from Melton Hill Reservoir are begun.

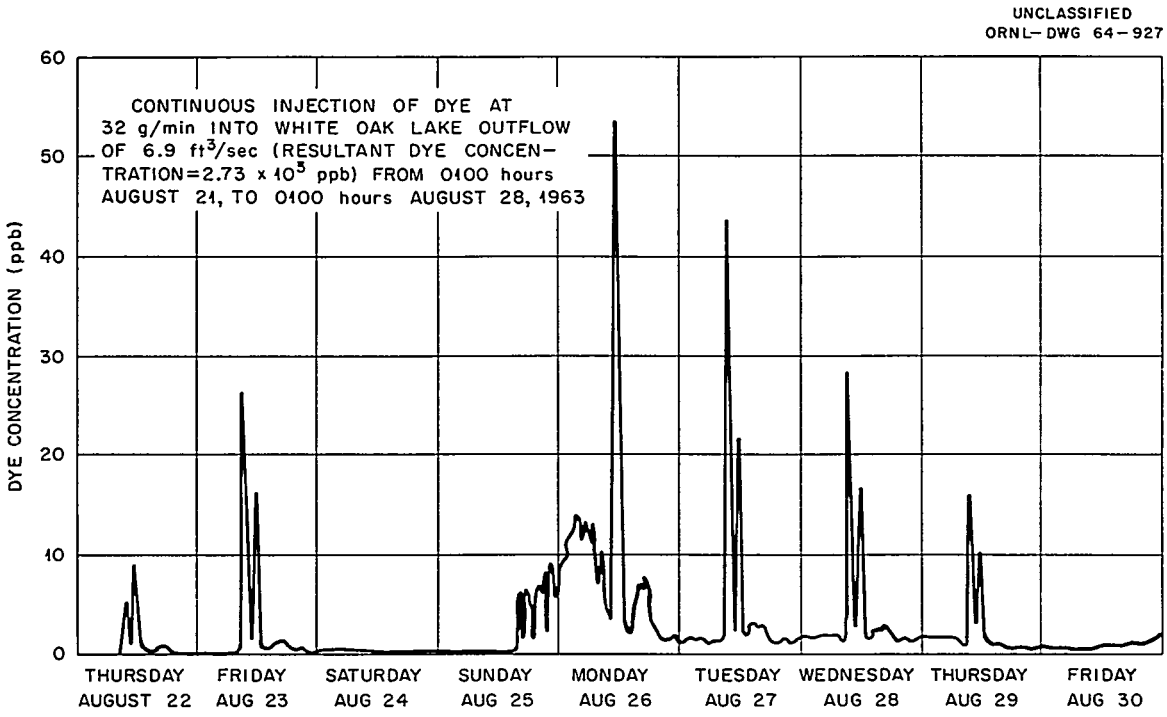


Fig. 46. Variation in Rhodamine B Concentration with Time During Period August 22-30, 1963, at Clinch River Mile 14.4.

7.2 Analysis of Clinch-River-Bottom Sediment Cores Collected in 1962

R. J. Pickering* P. H. Carrigan, Jr.*

Scanning of Clinch-River-bottom sediment cores collected during June, July, and August, 1962, for gross-gamma radioactivity was completed. The scans demonstrate that the greatest thicknesses of radioactive sediments occur in the lower reaches of the river, downstream from CRM 14. The single core showing the greatest thickness of radioactive sediment, 8.7 ft, was obtained at CRM 7.5. Sampler penetration, core recovery, and variations in gross-gamma radioactivity with depth at that cross section are shown in Fig. 47.

It can be seen from Fig. 47 that most of the radioactive sediment has been deposited on the more gently sloping side of the stream channel (note the vertical exaggeration). A recurring general pattern of variation of radioactivity with depth can be observed in several of the cores from CRM 7.5. The same general pattern is exhibited by a number of cores from other cross sections in the lower portion of the river. It is believed that certain features of this general pattern may be correlated with past events in waste-disposal operations at the Laboratory. However, additional data on the distribution of individual radionuclides with depth in the sediments are needed before such correlations can be established positively.

The radioactive portion of each core, as determined from the gross-gamma scans, will be mixed and sampled for radionuclide analysis to determine the total content of each of the major radionuclides in Clinch River bottom sediments.

Spectra of each 2-in. increment of the radioactive portion of selected cores will be obtained to determine the distribution with depth of the gamma-emitting radionuclides in the bottom sediment and to provide information on which to base correlations of their distribution in the cores with past events in waste-disposal operations.

---

*On loan from the Water Resources Division, U.S. Geological Survey.

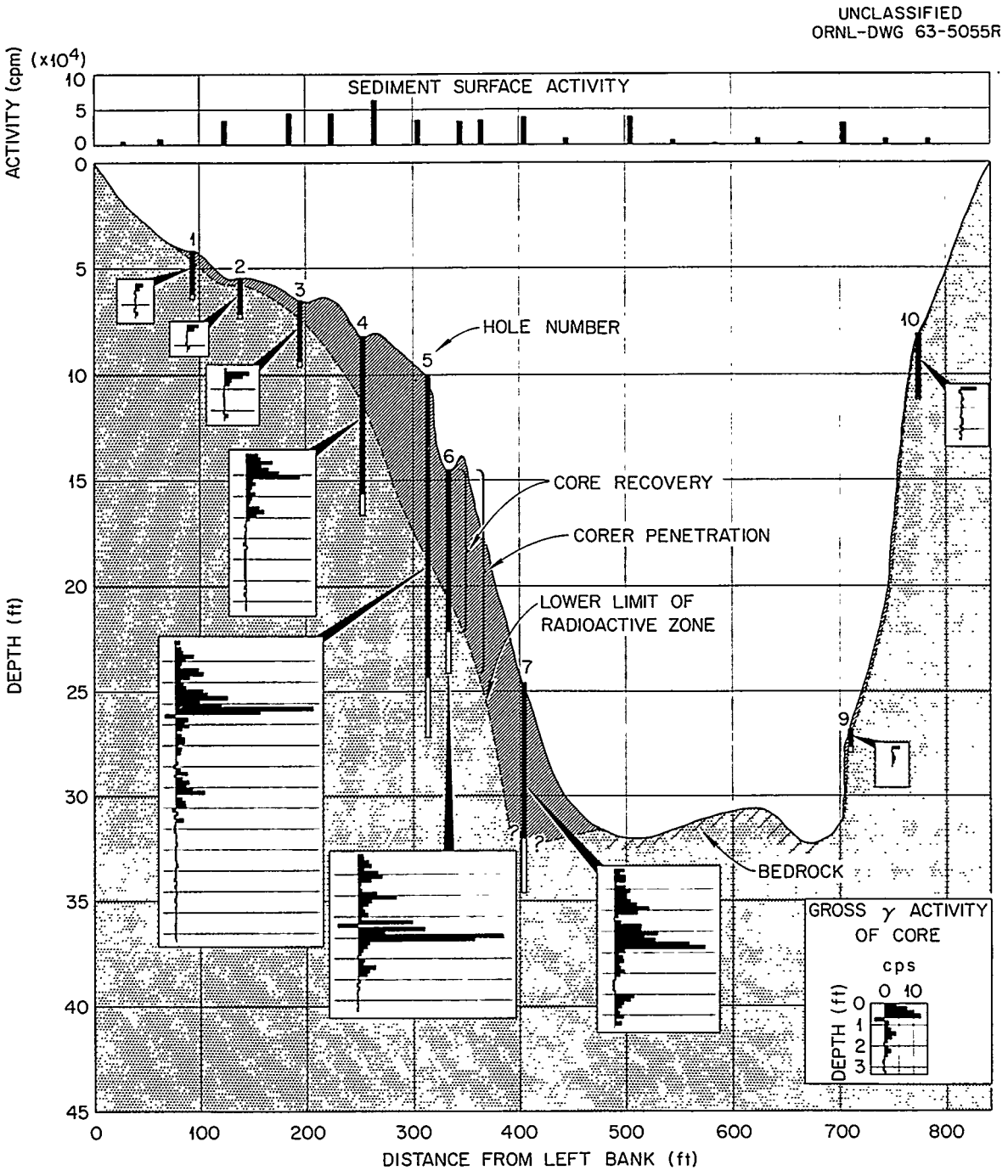


Fig. 47. Shape of Section and Radiation Levels at Clinch River Mile 7.5.

The primary purpose of the geochemical study of the cores is to determine the chemical forms in which the radionuclides exist and, thereby, the mechanisms by which they are incorporated in the bottom sediments.

The particle-size distribution, mineralogy, and cation-exchange capacities of the samples will also be measured. The interstitial water contained in the sediments will be extracted, and the distribution of stable and radioactive chemical constituents between the liquid and solid phases will be determined.

A diagrammatic representation of core-processing plans is shown in Fig. 48.

7.3 Radionuclide Desorption from Clinch River Sediments

T. Tamura W. P. Bonner

To understand the behavior and the mode of retention of radionuclides associated with sediments in the Clinch River, desorption studies were made with naturally contaminated, as well as artificially contaminated, sediments. The results of desorption tests of sediment from the mouth of White Oak Creek (CRM 20.8) were reported earlier for the radionuclides of cobalt, cesium, and ruthenium.[38] Desorption results for Sr^{90} on aliquots from the same sample have been obtained, and the results are shown in Table 25. The sediment contained 2400 dis/min/50 g, based on the oven-dried weight of Sr^{90}.

As shown in Table 25, 11.0% of the strontium was removed by tap water; this corresponds to a K_d of 65, which may be compared with K_d's ranging from 62 to 145 for sediment samples from different sections of the Clinch River. Of the solutions used, the most effective desorbing agent is tap water acidified to pH 2 with HNO_3 or HCl; the acid solution is even more effective than 1 $\underline{M}$ $CaCl_2$, KCl, or NaCl at near neutral pH. It should be pointed out that removal of 30 to 75% of the strontium by the different salt solutions is higher than the removals observed for Co^{60}, Cs^{137}, and Ru^{106} by these same solutions. It is also apparent from the data that pH has a very important influence on the desorption of strontium; the more acid solutions remove more strontium both in highly salted solutions and in tap water systems than do less acid solutions.

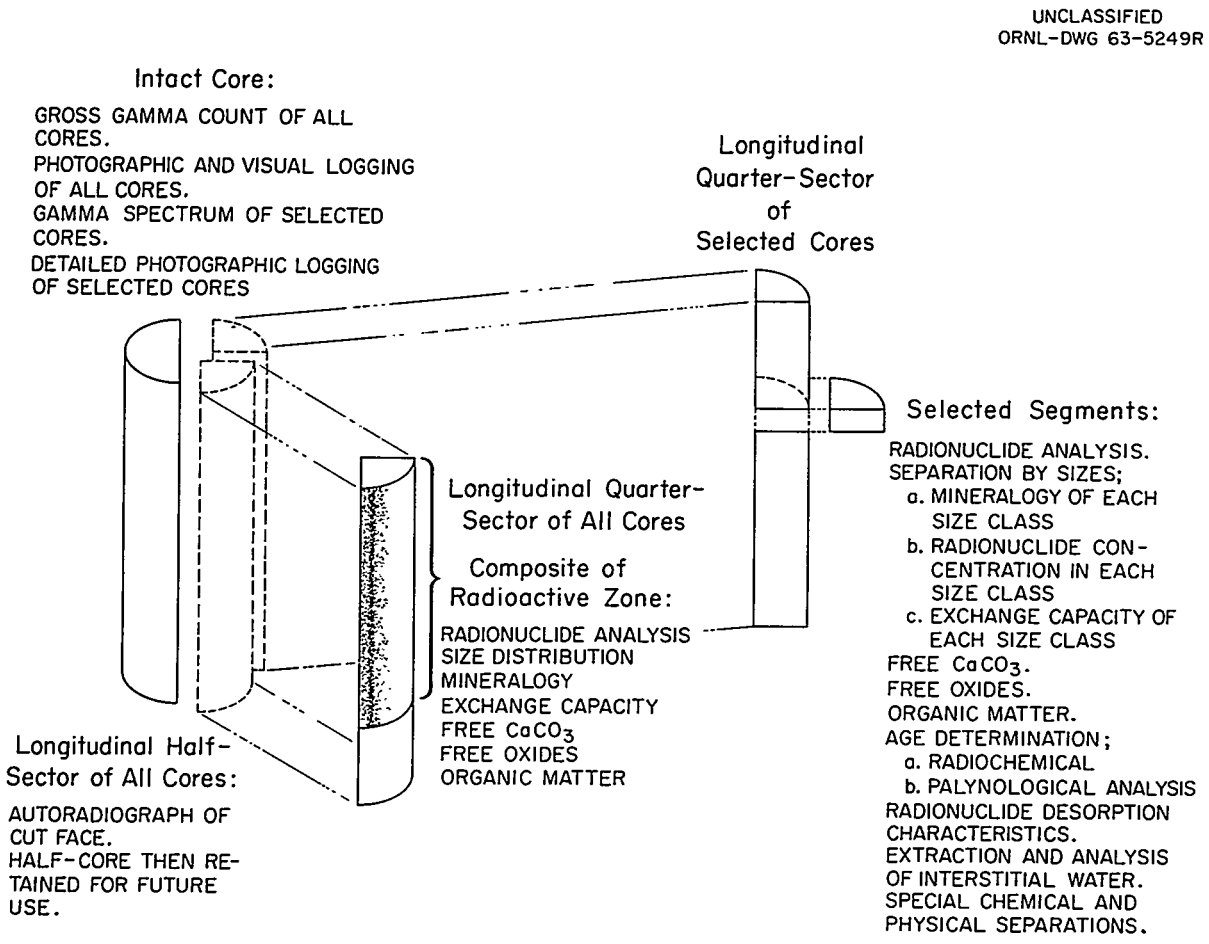


Fig. 48. Diagram of Plan for Analysis of Cores Taken from Clinch River Bottom Sediment During 1962.

Table 25. Removal of Strontium from Clinch River Sediment By Various Solutions Prepared from Tap Water

50 g (oven dried) CRM 20.8
400 ml solution
24-hr contact

Reagent	Concentration	pH	Percentage Strontium Removed
Tap water		6 (HNO_3)	21.3
Tap water		2 (HNO_3)	80.9
Tap water		6 (HCl)	19.4
Tap water		2 (HCl)	89.9
Tap water		7.7 (Natural pH)	11.0
$NaHSO_3$	0.1 M	6	37.7
$K_2Cr_2O_7$	0.1 M	5.9	73.1
$CaCl_2$	0.1 M	7	58.6
$CaCl_2$	1.0 M	7	76.9
NaCl	0.1 M	6	39.2
NaCl	0.1 M	8	30.1
NaCl	1.0 M	6	63.1
NaCl	1.0 M	8	56.0
KCl	0.1 M	6.2	53.0
KCl	1.0 M	6.2	68.7
NaOH		8	6.0
NaOH		12	4.9
NH_4OH		8	20.0
NH_4OH		11.8	3.5
Ethyl alcohol			< 1.0

7.3.1 Strontium Desorption from Artificially Contaminated Sediment

To better understand the nature of the retention of strontium by sediments, desorption studies were made by contaminating sediments artificially in the laboratory. A sample from CRM 15.3 was first contaminated with Sr^{85} in tap water at pH 8. About 46% of the strontium was sorbed; this gives a K_d of 85, a reasonable approximation of the K_d of Sr^{90} on the naturally contaminated sediment. The sample was leached with the solutions listed in Table 26. The desorption characteristics of the strontium sorbed at pH 8 is similar to the behavior observed with the naturally contaminated sediment; a slight difference is the greater effectiveness

Table 26. Equilibrium Sorption and 45-hr Desorption of 1.0 g of CRM 15.3 Sediment in 100 ml of Tap Water at Indicated pH

	Sorption pH			
	8	10.8	10.2[a]	10.1[b]
Sorption (%)	46.2	93.2	94.1	68.4
Desorption (%)				
Tap H_2O; pH 2 (HNO_3)	96.3	95.3	100	89.3
Tap H_2O; pH 12 (NaOH)	14.7	5.1	3.6	
1 M $CaCl_2$, pH 7	97.8	68.8	61.2	5.8
1 M NaCl, pH 8	90.2	83.0	100	85.3

[a] 95 ml tap water + 5 ml simulated waste + Sr^{85}.

[b] 95 ml tap water + 5 ml simulated waste + Sr^{85} (no sediment added).

of $CaCl_2$ over pH-2 tap water in removing strontium from the artificially contaminated material.

Sorption from a tap water system at pH 10.8 revealed that a much larger percentage of the strontium was sorbed (93%). The K_d for strontium at this pH is about 1300, compared with a K_d of about 220 or about 155 for the naturally contaminated system at pH 12, using the data for either NH_4OH or NaOH presented in Table 25. This suggests that another mechanism

is likely operative at this pH for removing strontium; and from observations and considerations of the system, it is apparent that $CaCO_3$ was being formed and was responsible for the much higher removals. The removal may be illustrated by the following equation:

$$Ca(HCO_3)_2 + 2\ OH^- \rightarrow CaCO_3 + 2\ H_2O + CO_3^{=} .$$

In desorption tests for strontium, $CaCl_2$ was not as effective as pH-2 tap water and even 1 M NaCl solution (Table 26).

Almost identical sorption and desorption responses were noted for the sediment when placed in a simulated waste solution containing dissolved ions normally found in intermediate-activity wastes.

Data on the removal of strontium simply from diluting simulated waste with tap water is shown in Table 26. No sediment is present and the pH is 10.1. The removal of strontium by the fine colloidal precipitate averaged 68.4%. Calcium chloride is an ineffective desorbing agent for this precipitate. An explanation of the different behavior of strontium sorbed at pH 8 and 10 from tap water systems may be given by considering the following reactions:

$$Ca^{2+} + \text{Sr-Clay} \rightleftarrows Sr^{2+} + \text{Ca-Clay} , \qquad (1)$$

$$\text{Sr-}CaCO_3 \rightleftarrows Sr^{2+} + Ca^{2+} + CO_3^{2-} . \qquad (2)$$

Since the pH of the tap water was about 8, sorption of the strontium by the sediment was primarily by ion exchange since the $Ca(HCO_3)_2$ is not affected and no $CaCO_3$ is expected at this pH. When calcium or other cations are introduced to the Sr-clay system, the exchange of ions occurs and the sorbed strontium is desorbed, as shown in reaction (1). At the same molarity concentrations, calcium would be expected to be more effective than sodium, as evidenced by the response shown in Table 26, column 1.

When sorption of strontium occurred at pH 10, strontium was sorbed not only by the clay but on the precipitate of calcium carbonate. When $CaCl_2$ salt solution at neutral pH was added, the strontium on the ion-exchange complex was displaced (reaction 1); but the strontium on the precipitate was not. The ineffectiveness of the $CaCl_2$ can be explained

by reaction (2), whereby release of strontium is associated with the dissolution of $CaCO_3$. The dissolution of $CaCO_3$ is repressed by the high Ca^{2+} concentration from the $CaCl_2$, which drives reaction (2) to the left, even though the pH had been decreased from 10 to 7. However, with sodium chloride solution, it would not repress the solubility by the common ion effect; and the reduction in pH would be expected to result in the redissolution of $CaCO_3$.

The use of these desorbing agents may provide a basis for identifying strontium sorbed on $CaCO_3$ and on clay exchange sites in sediments. Thus the results shown in Table 25 suggest that a portion of the strontium is associated with $CaCO_3$ in the naturally contaminated sediment. This tentative conclusion is reached, since less strontium was removed by $CaCl_2$ than by pH-2 tap water when the naturally contaminated sediment was tested. If all the strontium had been in ion exchange sites, more of the strontium would have been removed by the $CaCl_2$.

7.4 Hazards Analyses

K. E. Cowser

The discharge of radioactive solutions to the Clinch River may result in exposure of man to ionizing radiation. Calculations have been made of likely dose received due to exposure pathways deemed to be most important.[39,40] This report includes additional calculations of the internal and external exposure due to consumption of contaminated fish and exposure to the buildup of radionuclides in Clinch River water systems.

7.4.1 Contaminated Fish

Fish that feed in the Clinch River and Tennessee River downstream from White Oak Creek assimulate some of the radionuclides released to the river system. Since fish is a dietary staple, radionuclides in the fish will contribute to the total dose received. Parker showed that a catastrophic release of radionuclides from the biota of the Clinch River system is quite unlikely; the total inventory of radionuclides in the biota is estimated to be less than 1 curie.[41]

The data on radionuclide concentration in fish, used to estimate the dose that man may receive, was developed by the Subcommittee on Aquatic Biology, Clinch River Study Steering Committee.[42-47] Fish were collected during various seasons for the period, 1960 to 1962, and were processed to approximate, in so far as possible, normal human utilization.[43,47] Bottom feeders (carp, carpsucker, and buffalo) were processed either by grinding the flesh and bones together (total analyses) or by removing the flesh after cooking (flesh analyses). Sight feeders (white crappie, bluegill, white bass, largemouth bass, sauger, drum, and catfish) were processes by removing the flesh after cooking. For this analysis, catfish are included with the sight feeders, since only the flesh of the catfish was processed. Another fish sampling program was completed May 1963, but analytical results were not available for inclusion in this report.

Not all species of bottom feeders and sight feeders were collected with each sampling program; the number of a particular species collected varied. Therefore, for this analysis, all bottom feeders are assumed to be a single sample collected at one time; sight feeders were handled similarly. This assumption precludes any differences in fish due to the time of collection. That is, information on seasonal variation of such factors as feeding rates and water content of the flesh and their effect on radionuclide concentrations is unavailable and cannot be considered in the calculations.

Results of analyses of fish collected from the Clinch and Tennessee rivers are listed in Tables 27 and 28, respectively. Average values are given for the four principal nuclides detected (Sr^{90}, Cs^{137}, Ru^{106}, and Co^{60}); variation of the averages is indicated by the standard error of the mean. Standard errors do not appear where fish were composited before analyses. Bottom feeders are listed by species, since information is available on the quantities of these fish harvested commercially from Watts Bar Reservoir and from East Tennessee (Table 29). Information on sight feeders harvested is meager in comparison and does not warrant analyses by species. Only sport fishing routinely takes place on the Clinch River.

Table 27. Concentration of Radionuclides in Clinch River Fish
($\mu\mu$c/kg, fresh weight)

Fish Species	Sr^{90}		Cs^{137}		Ru^{106}		Co^{60}	
	Flesh	Total[a]	Flesh	Total[a]	Flesh	Total[a]	Flesh	Total
Carp	(17)[b] 500 ± 140	(40) 5100 ± 1700	(71) 510 ± 57	(39) 560 ± 79	(69) 170 ± 18	(39) 290 ± 78	(67) 66 ± 6.1	(39) 49 ± 9.9
Carpsucker	(18) 540 ± 190	(39) 940 ± 120 (39) 4800[d]	(122) 1200 ± 460	(37) 640 ± 67	(22) 120 ± 30	(37) 56 ± 16	(22) 120 ± 19	(37) 32 ± 6.8
Buffalo	(3) 240 ± 89	(30) 830 ± 110	(5) 480 ± 94	(30) 590 ± 92	(5) 110 ± 32	(30) 150 ± 38	(5) 78 ± 21	(30) 32 ± 6.8
Sight feeders[c]	(109) 180 ± 83		(126) 680 ± 120		(127) 120 ± 32		(127) 22 ± 11	

[a]Total fish consists of flesh and bone.

[b]Parenthetical values are numbers of fish analyzed.

[c]Sight feeders include white crappie, bluegill, white bass, largemouth bass, sauger, and drum; catfish also included.

[d]Includes four carpsuckers (composited) collected at CRM 19.6.

Table 28. Concentration of Radionuclides in Flesh of Tennessee River Fish (μμc/kg, fresh weight)

Fish Species	Sr^{90}	Cs^{137}	Ru^{106}	Co^{60}
Carp	(13)[a] 120 ± 33	(14) 180 ± 55	(14) 80 ± 27	(14) 71 ± 17
Carpsucker	(10) 99 ± 28	(10) 130 ± 27	(10) 69 ± 23	(10) 62 ± 18
Sight feeders[b]	(24) 250	(24) 170	(24) 48	(24) 66

[a]Parenthetical values are number of fish analyzed.

[b]Sight feeders include white crappie, bluegill, white bass, largemouth bass, sauger, and drum; catfish also included.

Table 29. Commercial Fish Harvest from Watts Bar Reservoir and East Tennessee

(pounds, fresh weight)

Location	Carpsucker	Carp	Smallmouth Buffalo
Watts Bar Reservoir	15,600	23,700	161,000
East Tennessee	61,700	135,000	327,000
Fish dilution factor[a]	3.95	5.70	2.03

[a]Fish dilution factor = $\frac{\text{pounds of East Tennessee fish}}{\text{pounds of Watts Bar fish}}$.

Average values are observed to vary by factors ranging from about 2 to 5 between fish types from the same river; similar variations occur between fish of the same type but from the two rivers. A peculiar difference is noted in Sr^{90} concentrations in sight feeders; the average concentration in Tennessee River fish is about 50% larger than Clinch River fish. At present there is no explanation for these differences. Four carpsuckers, collected at CRM 19.6, contained sufficient radionuclides to audioradiograph. This is typical of fish that have spent considerable time in White Oak Creek (or White Oak Lake).[48] Inclusion of these fish in the analysis can be seen to increase significantly the average concentration of radionuclides.

An estimate is made of man's intake of radionuclides by assuming an annual rate of fish consumption of 37 lb.[49] This rate of fish consumption applies to commercial fishermen and, as a result, would estimate the intake of an admittedly high-exposure group. Data on the quantity of specific types of fish consumed and method of preparation is not available. Thus calculations made are based on the annual consumption of 37 lb of bottom feeders, considering both the total fish and the flesh, and consumption of 37 lb of sight feeders, considering only the flesh. The fraction of the various species of bottom feeders caught is assumed to be distributed according to commercial harvests from Watts Bar Reservoir. Estimates of the annual intake of specific radionuclides by consuming Clinch River or Tennessee River fish are given in Tables 30 and 31, respectively. A very noticeable increase in Sr^{90} intake is observed when consumption of bottom feeders (total fish) is considered. This significantly larger intake is due to the concentration of Sr^{90} by the bones of the fish, all of which are assumed to be eaten. Consumption of 37 lb of "fishburgers" each year is certainly an overestimate and unnecessarily conservative. However, without better data of fish consumption, it is impossible to arrive at a more reasonable value of intake.

Radionuclide intake by the general population is likely to be influenced by all fish harvested in East Tennessee, in addition to the differences in radionuclide content among species of bottom feeders. Applying the fish dilution factor (bottom feeders) for East Tennessee fish (Table 29), annual intakes were recalculated, and results are given in Tables 30 and

Table 30. Estimated Annual Intake of Radionuclides by Assumed Consumption of Clinch River Fish (10^{-3} μc/year)

	Sr^{90}		Cs^{137}		Ru^{106}		Co^{60}	
	Flesh	Total[a]	Flesh	Total[a]	Flesh	Total[a]	Flesh	Total[a]
Bottom feeders[b]	4.9 ± 1.3	23 ± 3.7 (28)[e]	9.0 ± 1.4	10 ± 1.3	2.0 ± 0.44	2.7 ± 0.54	1.3 ± 0.28	0.58 ± 0.094
Bottom feeders[c]	1.9 ± 0.60	7.6 ± 0.83 (8.9)	3.7 ± 0.64	4.4 ± 0.19	0.81 ± 0.21	1.1 ± 0.25	0.58 ± 0.044	0.24 ± 0.061
Sight feeders[d]	3.0 ± 1.4		11 ± 2.6		2.0 ± 0.54		0.38 ± 0.19	

[a]Total fish consists of flesh and bone.

[b]Bottom feeders include carp, carpsucker, and buffalo.

[c]Intake adjusted by fish dilution factor, Table 29

[d]Sight feeders include white crappie, bluegill, white bass, largemouth bass, sauger, and drum; catfish also included.

[e]Parenthetical values include four carpsuckers (composited) collected at CRM 19.6.

31. A significant reduction in radionuclide intake is observed, ranging from factors of about 2 to 4.

Table 31. Estimated Annual Intake of Radionuclides by Assumed Consumption of Flesh of Tennessee River Fish
(10^{-3} μc/year)

Fish Species	Sr^{90}	Cs^{137}	Ru^{106}	Co^{60}
Bottom feeders[a]	1.9 ± 0.38	2.7 ± 0.59	1.3 ± 0.31	1.1 ± 0.21
Bottom feeders[b]	0.39 ± 0.075	0.53 ± 0.11	0.26 ± 0.062	0.23 ± 0.043
Sight feeders[c]	4.3	2.8	0.81	1.1

[a]Bottom feeders include carp and carpsucker.

[b]Intake adjusted by fish dilution factor, Table 29.

[c]Sight feeders include white crappie, bluegill, white bass, large-mouth bass, sauger, and drum; catfish also included.

A maximum permissible intake (MPI) is calculated by assuming a daily intake of 2.2 liters of water containing the maximum permissible concentration (MPC) of the radionuclide of interest. Values used for MPC are discussed at length elsewhere.[50] All MPC_w values used for data relating to the Clinch River are taken as one-tenth of the occupational MPC_w values for continuous exposure recommended by ICRP and NCRP. To obtain MPC_w values relating to the Tennessee River, the MPC_w for continuous occupational exposure has been reduced by a factor of one-hundredth for whole body as critical organ and by one-thirtieth with thyroid, bone, and gastrointestinal tract as the critical organs. Using the estimated intakes (Tables 30 and 31), it is possible to calculate the fraction of MPI attained for the various critical organs as a result of eating contaminated fish (Tables 32 and 33). Estimates indicate that bone of the postulated high-exposure group may receive the largest dose; on the average, 28 to

Table 32. Estimated Percentage of Maximum Permissible Intake That Man May Attain by Consuming Clinch River Fish

Fish Species	Critical Organ			
	Bone	Total Body	GI Tract	Thyroid
Bottom feeders[a] (flesh)	6.1 ± 1.6	1.5 ± 0.39	0.072 ± 0.0081	0.38 ± 0.072
Bottom feeders[a] (total)	28 ± 4.5 (34)[e]	7.1 ± 1.2 (8.6)	0.14 ± 0.014 (0.15)	1.4 ± 0.19 (1.6)
Bottom feeders[c] (flesh)	2.4 ± 0.75	0.61 ± 0.19	0.03 ± 0.0039	0.16 ± 0.034
Bottom feeders[c] (total)	9.5 ± 1.1 (12)	2.4 ± 0.33 (2.9)	0.053 ± 0.0047 (0.0058)	0.48 ± 0.051 (0.57)
Sight feeders[d] (flesh)	3.8 ± 1.7	1.0 ± 0.44	0.071 ± 0.012	0.31 ± 0.080

[a]Bottom feeders include carp, carpsucker, and buffalo.

[b]Total fish consist of flesh and bone.

[c]Intake adjusted by fish dilution factor, Table 29.

[d]Sight feeders include white crappie, bluegill, white bass, largemouth bass, sauger, and drum; catfish also included.

[e]Parenthetical values include four carpsuckers (composited) collected at CRM 19.6.

34% of the MPI may be attained as a result of consuming bottom feeders (total fish) from the Clinch River. Strontium-90 is responsible for almost the entire bone dose.

Table 33. Estimated Percentage of Maximum Permissible Intake That Man May Attain by Consuming Flesh of Tennessee River Fish

Fish Species	Critical Organ			
	Bone	Total Body	GI Tract	Thyroid
Bottom feeders[a]	7.2 ± 1.4	6.2 ± 1.2	0.11 ± 0.014	0.55 ± 0.084
Bottom feeders[b]	1.5 ± 0.28	1.3 ± 0.24	0.021 ± 0.0026	0.11 ± 0.017
Sight feeders[c]	16	14	0.11	0.83

[a]Bottom feeders include carp and carpsucker.

[b]Intake adjusted by fish dilution factor, Table 29.

[c]Sight feeders include white crappie, bluegill, white bass, largemouth bass, sauger, and drum; catfish also included.

Considerably more information would be required to estimate the dose received due to past events. For example, desired information would include at least: (1) rate of transfer of radionuclides from water to fish (flesh and bone) as a function of radionuclide and stable element concentration, fish age, and season of the year; (2) rate of transfer of radionuclide from bone to flesh while cooking; and (3) type and quantity of fish consumed, method of fish preparation, and dietary habits of individuals as a function of age. Current research suggests that the concentration of Sr^{90} in the flesh of white crappie reaches equilibrium rapidly with the water.[51] Such information lends itself to answering in part the questions raised by (1) above and extension of these studies will enhance the ability to estimate doses to man due to past events.

An interesting calculation is made based on the Sr^{90} content of the four carpsuckers previously mentioned. The combined weight of flesh and

whole fish (flesh and bone) for the four carpsuckers was 0.51 kg and 0.83 kg, respectively; the Sr^{90} concentration of flesh was 500 μμc/kg and of whole fish was 43,000 μμc/kg. An individual eating the four fish could have attained 0.3% of the MPI (bone) from the flesh and 44% of the MPI (bone) from the whole fish. Although such an event is unlikely, it seems appropriate to reduce further the probability of its occurrence. Such reduction is possible by preventing fish from leaving the controlled area of White Oak Lake and preventing fish from feeding in the stretch of White Oak Creek extending from White Oak Dam to the Clinch River.

7.4.2 Radionuclide Concentration in Water Systems

The presence of radionuclides in the raw water entering a water treatment plant may create, through processes of concentration, an external or internal dose problem. Three water systems that use Clinch River water as a source of supply were investigated. The Oak Ridge Water Plant has its raw water intake at CRM 41.5, well above the confluence of White Oak Creek and the Clinch River. The other two water treatment plants - the Sanitary Water Plant serving the Oak Ridge Gaseous Diffusion Plant (ORGDP) and that serving the Kingston Steam Plant - have water intakes at CRM 14 and on the Emory River near CRM 4.4, respectively. The water treatment plants are basically similar, differing only in design details. Treatment processes include: prechlorination for algae control; coagulation with alum, soda ash (as dictated by raw-water alkalinity), and occasionally coagulant aids, for turbidity removal; settling; filtration (either sand or anthracite); and postchlorination for disinfection. Activated carbon is used when undesirable taste and other problems occur. Water used in boilers is treated further by zeolite softeners.

The investigation consisted of external radiation surveys, with a scintillation-type survey meter (calibrated with radium), and collection of samples of sludge from settling basins, condensers, hot water heaters, boilers, air conditioners, and an elevated tank; samples of sediment from filters and cores of filter media; and samples of zeolite softener regenerant and the softener media. Results of the analyses are incomplete and will be reported later.

At the time of the surveys, various amounts of water had been treated since the settling basins had last been cleaned or filters backwashed (Table 34). Thus, there was variation in the amount of sludge accumulated in the settling basins or sediment accumulated on the filters. Results of the external radiation survey are summarized in Table 35. Generally, there was little difference noted in dose rates at different units of the plants. Any increase in dose rate above background levels (referenced to the Oak Ridge Water Treatment Plant) was, with one exception, undetectable. At a distance of 2 in. above a partially drained filter at the Kingston Steam Plant supply, a dose rate of 0.021 mr/hr was detected. The dose rate remained the same after the filter was backwashed. It is likely that the anthracite filter is to some extent concentration radionuclides by ion exchange; this is currently being investigated by laboratory studies. The dose rate above the filters (0.015 mr/hr) of this supply is also influenced by the natural radioactivity present in the shale block used for construction of the building walls.

Table 34. Operational Data of Water Treatment Plants

System	Volume Through[a] Flocculator and Settling Basin (gal)	Volume Through[a] Filter (gal)	Sludge in Settling Basin (ft^3)	Plant Capacity (gal/day)
Oak Ridge water plant	1.1×10^9	1.8×10^6	2×10^4	22×10^6
ORGDP	5.4×10^8	4.5×10^6	6×10^3	4×10^6
Kingston steam plant	1.9×10^6	3.7×10^5	----	5.7×10^5

[a]Volume through flocculator, settling basin, and filter since last cleaned.

Table 35. Measurements of Ionizing Radiation In Water Treatment Plants (mr/hr)[a]

System	Ground Surface	Flocculator	Settling Basin	6 in. Above Water in Settling Basin	Filter
Oak Ridge water plant	0.016	0.013	0.012	0.0097	0.0095
ORGDP	0.017	0.011	0.012	0.0092	0.0092
Kingston steam plant	0.015	0.0083	0.0087	----	0.015

[a]All measurements (except as noted) were made 3 ft above the walking surface of the particular component of the treatment plant.

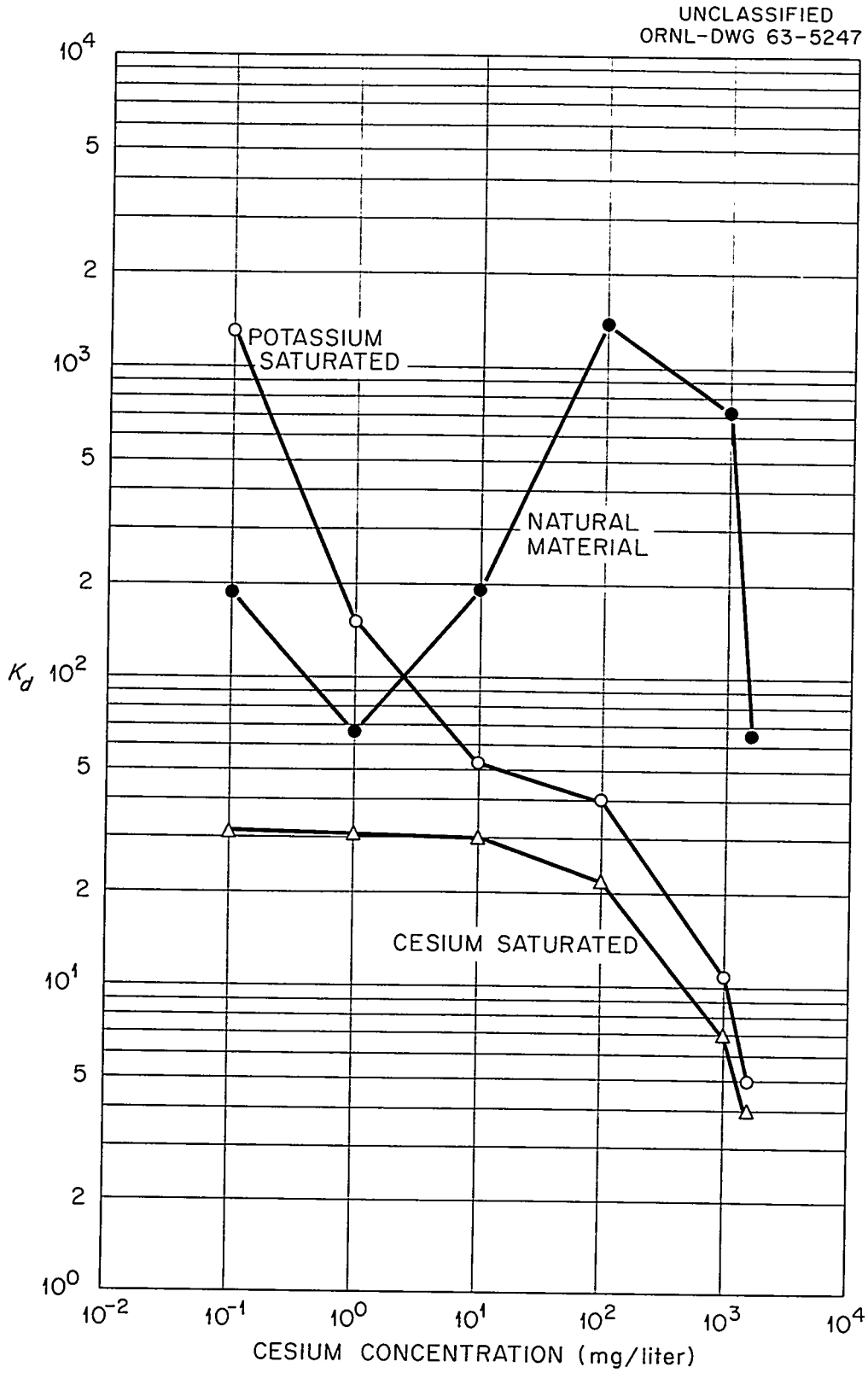


Fig. 49. Sorption of Cesium by Hydrobiotite.

9. WHITE OAK CREEK BASIN STUDY*

9.1 Evaluation of Fission-Product Distribution and Movement In and Around Chemical Waste Seepage Pits 2 and 3

T. F. Lomenick

9.1.1 General

The area in and around the million-gallon chemical waste seepage pits 2 and 3 contains an estimated 180,000 curies of Cs^{137}, 40,000 curies of Sr^{90}, about 10,000 curies of Ru^{106}, and lesser amounts of the rare earths, Ru^{103}, Sr^{89}, Co^{60}, Cs^{134}, and $Zr\text{-}Nb^{95}$. Previous investigations described the movement of ruthenium in and around the site;[54] however, little is known about the behavior of cesium and strontium in the pit area, except that it is apparently concentrated relatively close to the pit walls, since such small amounts have been found in the monitoring wells about the area. The recent abandonment and subsequent filling of the pits provided an opportunity to investigate, in much greater detail, the nature and extent of fission-product migration from the pits, especially of Sr^{90} and Cs^{137}. The study of migration was not possible earlier because of the high-radiation field in the area. The primary objectives of this study are (1) to determine the quantity and distribution of the various radionuclides within the area, (2) to determine the degree of fixation of the activity on the shale that underlies the site and in the sludge and precipitates within the pits, and (3) to predict the future effects of ground water on the waste.

At ORNL, intermediate-level liquid waste is disposed of through a system of seepage pits dug in the Conasauga shale formation. This method of disposal allows the waste solution to seep slowly through the ground, while most of the radioactive materials are retained by the shale. The

---

*This project, entitled, "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin " (AEC Activity 060501), is supported by the U. S. Atomic Energy Commission"s Division of Biology and Medicine. All other projects covered in this report are supported by the Division of Reactor Development (AEC Activity 04640011).

discharge of large quantities of contaminated waste water to seepage pits began in 1952 with the construction of waste pit 2. Three years later waste pit 3 was put into operation, and eventually four additional ones were opened. Pits 2 and 3 formerly had the shape of a frustum of an inverted rectangular pyramid, with dimensions of 200 ft by 100 ft by 15 ft in depth. To prevent animals from getting to the waste water, the pits were covered with a galvanized iron screen. In addition to the several million gallons of liquid waste pumped to these pits, large quantities of sludge or precipitate of illitic clay and calcium carbonate from the low-level waste treatment plant were routinely dumped into pit 3 and to a lesser extent into pit 2.

With construction of covered seepage pits 5, 6, and 7, waste pits 2 and 3 were abandoned and subsequently filled in 1962. Weathered shale containing many thin limestone lenses was the principal fill material. However, a few hundred steel barrels of solid waste were dumped into each pit, and, in addition, the galvanized iron screen that covered the pits and their supporting posts were pushed into the holes. During filling of the pits, it was observed that the soft sludges and precipitates in the bottom of the pits were not being covered by the fill, but were being squeezed into the still uncovered portion of the pit. It was necessary to use wooden siding and other debris to cover the sludge and thus prevent its upward movement.

9.1.2 Quantity and Distribution of Radionuclides in the Area

Due to the nature of the waste pit environment, some unique problems were encountered in obtaining representative samples of the contaminated materials. The metal drums, wire mesh nets and their supporting posts, lumber, and other miscellaneous fill debris in the pits pose special drilling problems. It is also difficult to obtain cores with a single sampling device from the weathered and unweathered portions of the Conasaugs shale, as well as from the loose, fill material in the pits, sludge from the low-level waste water treatment plant, and accumulated precipitates from the waste water. The high degree of contamination of the sludge and weathered shale further complicates the sampling.

A preliminary series of cores was taken in and around the two waste pits to determine the effectiveness of conventional sampling equipment and methods for obtaining representative samples of the various types of rock and fill materials. In addition, a sufficient number of cores were taken and analyzed to grossly delineate radioactivity concentrations on the soil and materials in and around the pits. A sketch map of a portion of the waste pit area, showing the sample locations, is presented in Fig. 50. Due principally to the still relatively high radiation field in the vicinity of waste pit 2, which reduced considerably the allowable working time, fewer samples were taken in that area. The depth of sampling at the various locations varied from 6 to 32 ft. Split-barrel assemblies were used to recover samples of the fill material and weathered shale, while thin-wall tubes were used to sample the soft sludges and precipitates. A series "m" core barrel with diamond bit, with water as a drilling fluid, was used for coring the deeper unweathered shale. Some difficulty was experienced with collapse of the side walls of the holes in the fill material and soft sludges, but the greatest disadvantage to this method of sampling was the very poor core recovery obtained by the series "m" core barrel in zones of alternating hard and soft shale.

Radiochemical analyses of sections of the cores indicate that apparently most of the activity which is largely cesium and strontium is associated with the soft sludges and precipitates and the first few inches of weathered shale on the side walls and bottoms on the pits. Also, the sludges and precipitates are not evenly distributed over the bottoms of the pits but have accumulated in irregular shaped pockets. A cross sectional view of waste pit 2, showing the areas of high activity concentrations and the distribution of sludge within the pit, is presented in Fig. 51. It is noted in well 3 that the sludge is about 10 ft thick and is within 4 ft of the ground surface, while no sludge was found in hole 11 in the center of the pit. This is due to the highly mobile state of the sludge, which allowed it to be pushed ahead of the fill material until it was confined by timbers and eventually covered. On a dry-weight basis, concentrations of Cs^{137} and Sr^{90} were as high as 96 μc/g and 17 μc/g, respectively, in the sludge, and 3 μc/g and 0.2 μc/g in the weathered shale on the side walls and bottoms of the pits. There appears to be little difference in the

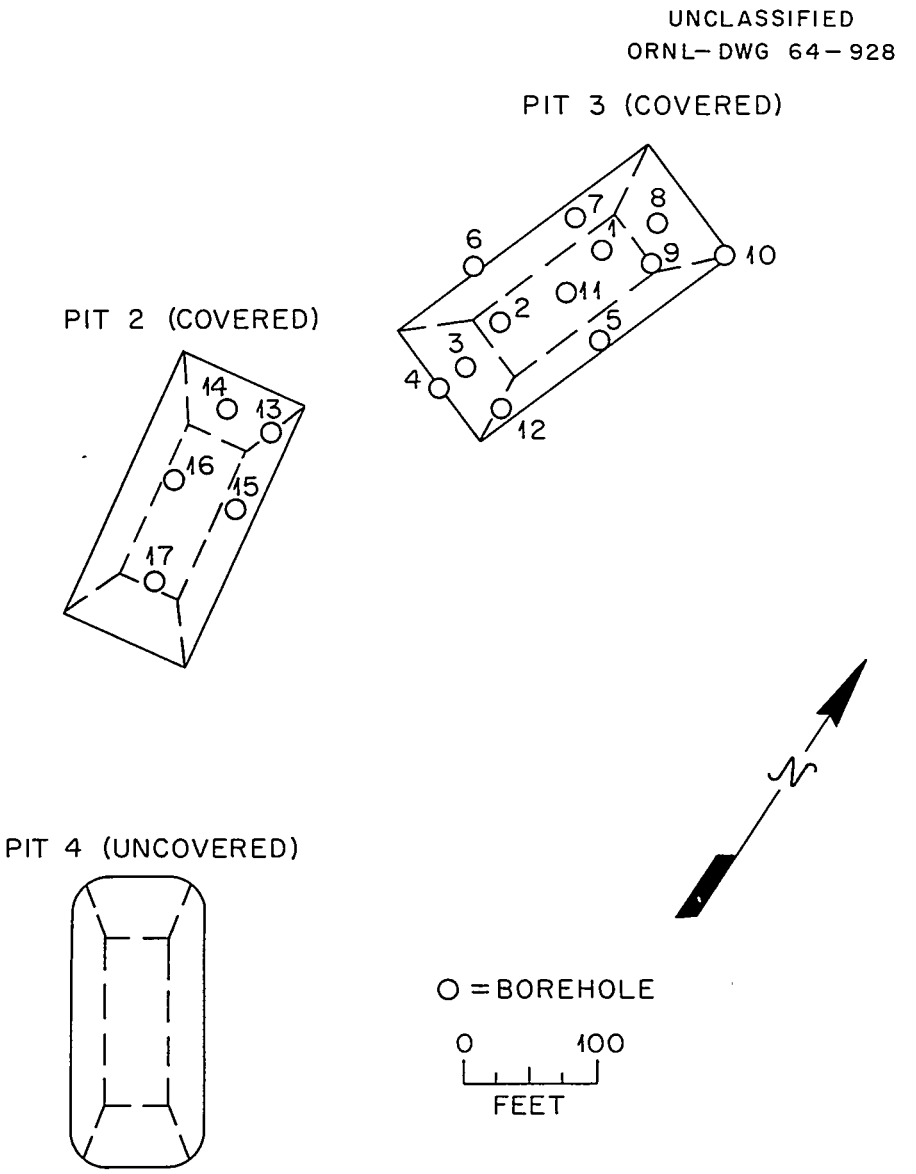


Fig. 50. Sketch Map of a Portion of the Waste-Pit Area, Showing Locations of the Preliminary Series of Boreholes.

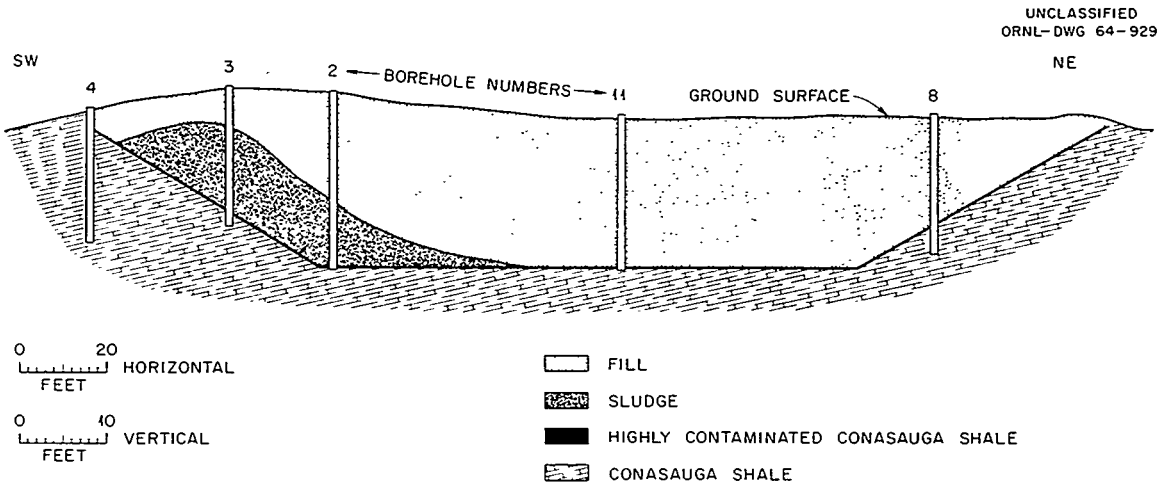


Fig. 51. Longitudinal Cross Section Through Waste Pit 3.

concentrations of activity found on the sludge and weathered shale in the two pits, although the quantity of sludge in waste pit 2 is considerably less than that in pit 3.

The alternating hard and soft shale sequence immediately below the bottom of the pits could not be cored satisfactorily with the drilling equipment used, and, as a consequence, incomplete data was obtained on the quantity and distribution of activity beneath the pits. However, some information on the downward migration of the radionuclides was obtained from boreholes that penetrated the softer and more easily sampled side walls of the pits. For boreholes 10 and 14 it was found that the concentrations of cesium and strontium on the shale were about 100 times greater at the former surface of the wall than at distances of 2 ft below the former surface of the wall.

9.2 Hydrology of White Oak Creek Basin

W. M. McMaster * R. M. Richardson*

A series of water samples was collected from White Oak Creek and from sources contributing radioactive contaminants directly to the stream on September 19, 1963, in order to measure gains or losses in specific radionuclide load as a labeled mass of water moved downstream. The sampling was done during a period of low base-flow conditions.

A mass of White Oak Creek water was labeled for identification by pouring a quantity of dye directly into the stream about 200 ft above the outfall of the effluent from the Process Waste Water Treatment Plant (PWWTP). This procedure was repeated at each source on the accompanying map (Fig. 52) and at other downstream points as the mass of dyed water passed.

As shown in Fig. 53, the stream load of each radionuclide changed considerably as the water moved, increasing downstream to the old intermediate-pond dike, then decreasing by the time it reached sampling point 7. At point 8, water content of total rare earths, Sr^{90}, and Co^{60} increased significantly. This increase is probably due to seepage into White Oak

*On loan from Water Resources Division, U. S. Geological Survey.

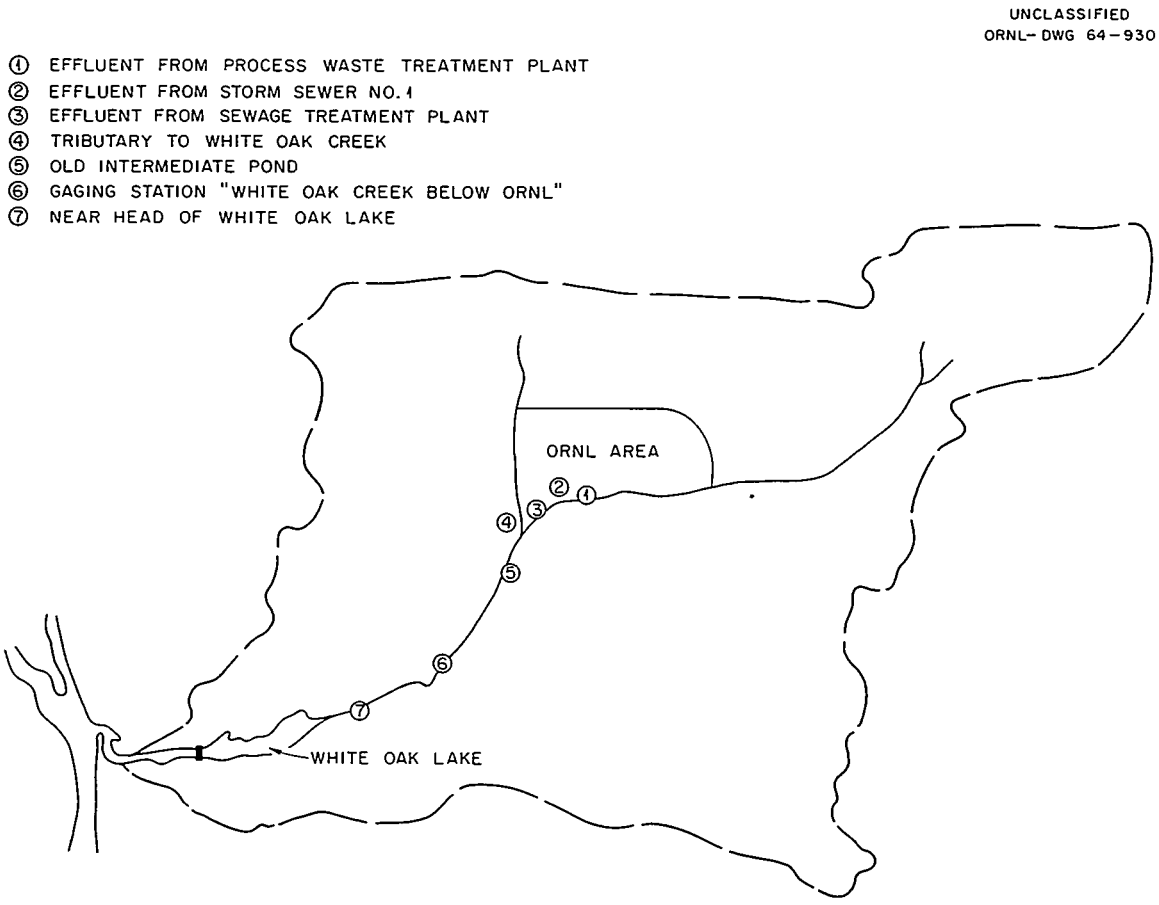


Fig. 52. Map of White Oak Creek Basin, Showing Sources of Contamination Samples and Stream Sampling Sites, September 19, 1963.

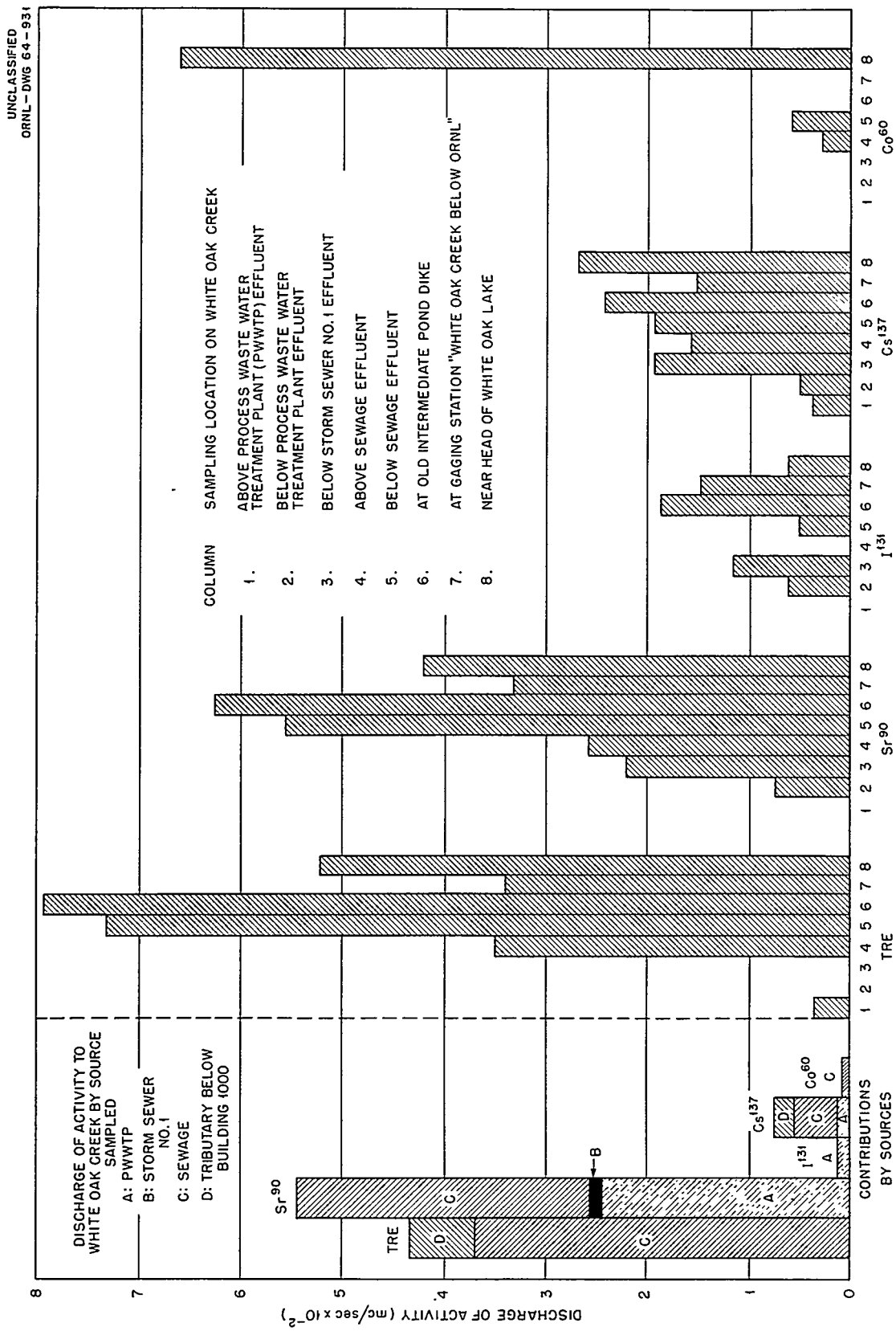


Fig. 53. Discharge of Activity to White Oak Creek According to Sources Sampled.

Creek of contaminated ground water originating at the east drainage stream of the chemical waste pits.[55]

Results of analyses of the samples collected from the PWWTP effluent and from the sewage treatment plant effluent showed that the sewage effluent was contributing more Sr^{90} than the process waste water effluent. On the basis of a discharge of 100,000 gal per day, the sewage effluent would have contributed a total of 542 μc/day, whereas the PWWTP, on the same basis, would have contributed 460 μc/day. Lomenick[56] found during an eight-month study in 1961 that the mean concentration of Sr^{90} in the sewage treatment plant effluent was 1.7×10^{-6} μc/cc, slightly higher than the concentration sampled September 1963.

Prior to the test, an attempt was made to measure small increments of discharge in White Oak Creek for the purpose of accurately computing radionuclide loads at points in the stream. The dilution method was used with Rhodamine B dye as a tracer. The dye was injected into the stream at a constant rate at a point about 200 ft upstream from the PWWTP effluent for a total of 3.5 hr, in order to allow a plateau of dye concentration to become established throughout the stream. Near the end of the injection period, water samples were collected at several points along the channel; dye concentration was then read by fluorometer, and the discharge was computed for each sampling site by the dilution formula. Discharge values obtained from samples collected between the injection point and the sewage effluent were acceptable, but below the sewage effluent computed discharge values became increasingly too large with distance. Later, a short experiment showed that Rhodamine is extremely sensitive to free chlorine. It is thought that sufficient free chlorine enters White Oak Creek in the sewage effluent because of decomposition of part of the dye, precluding the use of dyes in the stream for quantitative measurements. The discharges on which the radionuclide loads were based were interpolated between points of known discharge in the stream.

During the week of October 21, water-level measurements were made in the wells in White Oak Creek Basin, during the period of lowest water surface for the 1963 water year, for the purpose of constructing a low-water-surface map of White Oak Creek Basin.

REFERENCES

1. A. M. Platt, Hanford Atomic Products Operation, private communication.

2. R. E. Blanco, F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

3. Letter, I. R. Higgins to R. E. Blanco, January 1963.

4. R. E. Blanco, F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report for November-December 1962 and January 1963, ORNL-TM-516 (June 12, 1963).

5. R. R. Holcomb, Low-Radioactivity-Level Waste Treatment, Part 1 - Laboratory Development of a Scavenging-Precipitation Ion-Exchange Process for Decontamination of Process Water Wastes, ORNL-3322 (June 25, 1963).

6. R. E. Brooksbank et al., Low-Radioactivity-Level Waste Treatment Part II - Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Wastes by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349 (May 13, 1963).

7. G. B. Hatch and O. Rice, "Surface Active Properties of Hexametaphosphate," Ind. Eng. Chem. 31, p 51 (1939).

8. E. Schonfeld, Effect of Some Impurities on the Precipitation of Calcium and Magnesium from Process Waste Water, ORNL-TM-505 (April 25, 1963).

9. Chemical Technology Division Annual Progress Report for Period Ending May 31, 1963, ORNL-3452.

10. R. E. Blanco, F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

11. R. M. G. Boucher and A. L. Weiner, "Sonic Defoaming - Its Present Status," Food Processing (October 1962).

12. P. A. Haas, Engineering Development of a Foam Column for Countercurrent Surface-Liquid Extraction of Surface Active Solutes, ORNL-3527 (in preparation).

13. R. E. Blanco, E. G. Struxness, Waste Treatment and Disposal Progress Report for February and March 1962, ORNL-TM-252, pp 39-43 (Sept. 10, 1962).

14. L. C. Watson, H. K. Rae, R. W. Durham, E. J. Evans, and D. H. Charlesworth, Methods of Storage of Solids Containing Fission Products, CRCE-736 (June 1958).

15. E. Doud, Design of Underground Storage Tanks for Radioactive Wastes, HW-57282 (March 1959).

16. R. E. Blanco, E. G. Struxness, Waste Treatment and Disposal Progress Report for October and November 1961, ORNL-TM-133, pp 33-39 (Mar. 13, 1962).

17. Paul L. Russell, Bureau of Mines, U. S. Dept. of the Interior, personal communication, May 16, 1963.

18. Bedrock Waste Storage Concept and Cost Appraisal, du Pont Company Report, DPE-2210 (May 1962).

19. M. L. Jackson, Soil Chemical Analysis, Prentice-Hall, Englewood Cliffs, New York., 1958.

20. D. G. Jacobs, "Ion Exchange in the Deep Well Disposal of Radioactive Wastes," International Colloquium on Retention and Migration of Radioactive Ions in Soils, Centre d'Etudes Nucleaires de Saclay, France, October 16, 17, and 18, 1962, pp 43-35 (1963).

21. R. L. Blanchard, B. Kahn, and G. G. Robeck, Laboratory Studies on the Ground Disposal of ORNL Intermediate-Level Liquid Radioactive Wastes, ORNL-2475 (Mar. 15, 1958).

22. W. J. Lacy, Radioactive Waste Disposal Report on Seepage Pit Liquid Waste-Shale Column Experiment, ORNL-2415 (Nov. 1, 1957).

23. D. G. Jacobs and T. Tamura, Proc. 7th Int. Conf. Soil Sci. 2, 206 (1960).

24. D. G. Jacobs, Health Physics 4, 157 (1960).

25. R. J. Morton (ed.), Status Report No. 3 on Clinch River Study, ORNL-3370 (Nov. 21, 1962).

26. K. E. Cowser, W. de Laguna, and F. L. Parker, Soil Disposal of Radioactive Wastes at ORNL (to be published as an ORNL-TM report).

27. E. Glueckauf, Trans. Far. Soc. 51, 34 (1955).

28. Y. Inoue and W. J. Kaufman, Ground Disposal of Radioactive Wastes, TID-7628, p 303 (1962).

29. E. Glueckauf, Ion Exchange and Its Applications, p 34, Society of Chemical Industry, London (1955).

30. G. N. Savin, Stress Concentration Around Holes, Pergamon Press, New York, 1961.

31. S. Serata, Development of Design Principles for Disposal of Reactor Fuel Waste Into Underground Salt Cavities, Technical Report of University of Texas to Atomic Energy Commission (Jan. 1, 1959).

32. P. LeComte, Creep and Internal Friction in Rock Salt, doctoral dissertation, Division of Geological Sciences, Harvard University, Cambridge, Mass. (May 1960).

33. Corps of Engineers, Project Dribble Petrographic Examination and Physical Tests of Cores, Tatum Salt Dome, Mississippi, Technical Report No. 6-614, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss. (Jan. 1963).

34. J. Handin and R. V. Hager, Jr., "Experimental Deformation of Sedimentary Rocks Under Confining Pressure: Tests at High Temperature," Bulletin of The American Association of Petroleum Geologists 42(12), pp 2892-2934 (Dec. 1958).

35. S. Serata, Michigan State University, personal communication.

36. L. Obert, Applied Physics Laboratory, U. S. Bureau of Mines, personal communication.

37. R. J. Morton (ed.), Status Report No. 3 on Clinch River Study, ORNL-3370, p 106 (Nov. 21, 1962).

38. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

39. K. E. Cowser, W. S. Snyder, and M. J. Cook, "Preliminary Safety Analysis of Radionuclide Release to the Clinch River," Proceedings of Conference on Transport of Radionuclides in Fresh Water, January 30, 31, and February 1, 1963, Austin, Texas, U. S. Atomic Energy Commission, Washington, D. C., p 17-39, TID-7664 (July 1963).

40. K. E. Cowser, "Clinch River Study: Hazards Analyses," Waste Treatment and Disposal Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

41. F. L. Parker, "Clinch River Studies," Proceedings of Conference on Transport of Radionuclides in Fresh Water, January 30, 31, and February 1, 1963, Austin, Texas, U. S. Atomic Energy Commission, Washington, D. C., p 161-181, TID-7664 (July 1963).

42. A. G. Friend et al., Fate of Radionuclides in Fresh Water Environments: Progress Report No. 2, Clinch and Tennessee Rivers, February 9-15, 1960, interim report to Clinch River Study Steering Committee, Sept. 1960 (multilithed, 1962).

43. A. G. Friend et al., Fate of Radionuclides in Fresh Water Environments: Progress Report No. 5, Clinch and Tennessee Rivers, May 15-30, 1960, interim report to Clinch River Study Steering Committee, Oct. 1961 (multilithed, 1962).

44. A. G. Friend et al., Fate of Radionuclides in Fresh Water Environments: Progress Report No. 6, Clinch and Tennessee Rivers, September 19-30, 1960, interim report to Clinch River Study Steering Committee, Oct. 1961 (multilithed, 1962).

45. D. B. Porcella, Data on Fish Collected in June and December 1961 and March 1962 (personal communication, May 8, 1963).

46. S. I. Auerbach, Chairman, et al., Progress Report No. 1, Subcommittee on Aquatic Biology, copies submitted to Clinch River Study Steering Committee, April 26, 1962 (unpublished).

47. S. I. Auerbach, Chairman, et al., Progress Report No. 2, Subcommittee on Aquatic Biology, copies submitted to Clinch River Study Steering Committee, Feb. 6, 1963 (unpublished).

48. R. E. Martin, S. I. Auerbach, and D. J. Nelson, Growth and Movement of Smallmouth Buffalo, Ictiobus Bubalus (Rafinesque), in Watts Bar Reservoir, Tennessee (ORNL report in press).

49. P. Bryan and C. E. White, "An Economic Evaluation of the Commercial Fishing in the T.V.A. Lakes of Alabama During 1956," Proceedings of the Twelfth Annual Conference Southeastern Association of Game and Fish Commissioners, 128-132 (1958).

50. C. P. McCammon, Chairman, et al., Progress Report No. 2, Subcommittee on Safety Evaluation, copies submitted to Clinch River Steering Committee, Feb. 6, 1963 (unpublished).

51. R. J. Morton (ed.), Status Report No. 4 on Clinch River Study, Clinch River Study Steering Committee, ORNL-3409 (Sept. 11, 1963).

52. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

53. J. S. Wahlberg and M. J. Fishman, Adsorption of Cesium on Clay Minerals, Geological Survey Bulletin 1140-A, U.S. Government Printing Office, 1962.

54. K. E. Cowser, W. de Laguna, and F. L. Parker, Soil Disposal of Radioactive Liquid Wastes at ORNL, ORNL-2996 (in press).

55. T. F. Lomenick, "Movement of Ruthenium in the Bed of White Oak Lake," Health Physics 9, 835-845 (1963).

56. T. F. Lomenick, "Accumulation and Movement of Radionuclides in White Oak Creek Basin" in Status Report No. 4 on Clinch River Study, ORNL-3409, pp 15-32 (Sept. 11, 1963).

ORNL MASTER COPY

2005

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ORNL - TM - 830

15

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT

NOVEMBER 1963-JANUARY 1964

R. E. Blanco
F. L. Parker

This document has been approved for release to the public by:

David R. Hamrin 7/28/95
Technical Information Officer, ORNL, Site — Date

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

ORNL-TM-830

CHEMICAL TECHNOLOGY DIVISION
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT NOVEMBER 1963-JANUARY 1964

R. E. Blanco F. L. Parker

AUGUST 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level-Waste Calcination: Engineering Development. Development of a continuous melting system for conversion of aqueous waste to glassy solids was continued with emphasis on equipment development using simulated TBP-25 waste with lead and phosphate additives. A feed rate of up to 20 liters/hr was obtained during initial operation, but this was reduced to 10 liters/hr after three days of operation.

A "rising level" fixation test (R-82) using simulated FTW-65 Purex waste with lithium phosphate and calcium nitrate additives was made with an average feed rate of 8.2 liters/hr. General operation was satisfactory. The resulting solid had a bulk density of 1.9 g/cc and a residual nitrate content of 130 ppm. Corrosion in the upper portion of the pot averaged 80 mils with 120-mil pits. Part of this corrosion was attributed to a deficiency of lithium in the feed. Although this high rate of corrosion will probably be tolerable for a single-use container with 320-mil walls, further work is required to produce less-corrosive melts.

High-Level-Waste Calcination: Laboratory-Scale Development. More than 99% of the mercury was removed from Purex FTW-65 waste solution by passing the solution through a column packed with copper. Gentle agitation of the column or imposition of a small anodic current on the copper increased the volume of waste that could be effectively treated (i.e., 99% mercury removed) from 76 column volumes to about 425 and 800 column volumes, respectively. This method of removing mercury appears to be applicable to all waste types where the acidity is less than about 1.0 M.

Volatilization of cesium during calcination of sulfate-deficient Purex waste to 900°C was reduced to entrainment values less than 0.02% by addition of aluminum in amounts equal to or greater than the chemical equivalents of alkali metal present in the waste.

A long-range program was initiated to define the compositional limits of desirable solid products from fixation of non-sulfate and of sulfate-bearing Purex wastes in phosphate media. Data from preliminary experiments are reported.

Welded type 304L stainless steel exposed in boiling simulated Darex waste solution corroded at rates that increased slowly with time up to 14.7 mils/month for 336 hr of exposure. Coupling the steel to titanium decreased the corrosion rate to 7.6 mils/month. Attack on the titanium was negligible in every case.

Low-Level-Waste Treatment: Laboratory Development. Two micro-pilot plant runs of a modified Scavenging-Precipitation Ion-Exchange process show that grundite clay is effective for sorbing cesium activity present in cation exchange regenerant waste (decontamination factor of 11). Thus, by metering this slurry into the untreated low-level waste (pH 7 to 8) and by retaining the solids in the sludge of the precipitation step (pH 11.8), the radioactive strontium and cesium and other radioactive nuclides are consolidated and disposed of as a solid. Thus there will be no liquid waste stream from the process, only the solid sludge. Grundite clay also improves the decontamination factor for cobalt in the precipitation step from 2 to 7. Illco TAD-1 anion exchange resin is only partially effective in removing the ruthenium and cobalt remaining in the waste after precipitation and cation exchange.

Two methods are being considered for the clarification of raw low-level waste to replace the caustic-copperas treatment. In jar tests, with tap water, visually clear water was obtained either by the addition of 5 ppm of copperas followed by 70 ppm of lime or by the addition of 10 to 20 ppm of alum. These specifications are for waste that has a pH of 7 to 8, an initial total hardness of 125 ppm, and a specific conductivity of 250 micromhos/cm.

Low-Level-Waste Treatment: Scavenging-Precipitation Ion-Exchange: Pilot Plant. The 4-ft-diam agitated clarifier was modified, and the Scavenging-Precipitation head-end flowsheet using the modified clarifier was tested on tap water feed. The lowest values of total hardness in the clarifier effluent for 10 gpm and 5 gpm tap water feed rates were 11.8 ppm and 4.1 ppm (as $CaCO_3$ equivalent), respectively.

Foam Separation. A method for direct, rapid radiochemical analyses by resolution of complex gamma-ray spectra using the method of least squares was developed. The spectra obtained by scanning process solutions with a multichannel analyzer are compared with those of prepared standards. Computations are done on a CDC-1604 computer.

Sludge bed studies under conditions of total foam recycle indicated that the surfactant, dodecylbenzene sulfonate (DBS), accumulates in the solid phase. An increase in the entrainment of calcium-rich solids in the sludge-bed effluent was also noted along with poorer strontium decontamination in the foam column.

Sludge-bed density values, useful in equipment design and the selection of sludge withdrawal rates, were determined to be an inverse function of both the feed flow rate and the sludge-blanket depth.

Tests of a laboratory model of the proposed pilot plant foam column indicated that smooth operation can be expected.

Low- and Intermediate-Level-Waste Disposal in Asphalt. Asphalt, tar, and cement were studied as media in which to disperse simulated waste-evaporator concentrates. Volume reduction factors (volumes of waste solution per volume of product) were as high as 2 for products prepared from emulsified asphalt, while they were usually less than 1 for products prepared from Portland cement. The leach rates of ^{137}Cs and sodium from an asphalt product were 2×10^{-4} and 3×10^{-4} g cm^{-2} day^{-1} at the end of ten weeks, whereas the rates from a cement product were about 100 times greater.

The Tritium Problem in Fuel Processing Wastes. Tritium, a fission product of very low yield, may merit special consideration from the standpoint of its management in wastes from fuel processing. For present solvent extraction plants, at least 75% of the tritium in the irradiated fuel is discharged to the environment in low-level aqueous wastes. Future plants situated less remotely may be restricted in the quantity they can release to their immediate environs.

It is estimated that, under present regulations, relatively little tritium could be released to surface streams, but plants processing fuel at rates equivalent to as much as 100,000 thermal megawatts of reactor power might disperse the tritium safely to the atmosphere. Larger plants must consider containment of the tritium by internal recycle of aqueous streams. Additional work is needed, however, to establish environmental tolerances for tritium as well as the feasibility of recycling the necessary process streams within the plants.

Disposal in Deep Wells. The relative behavior of tritiated water and chloride ions as water tracers was investigated by using columns of hydrobiotite. Repulsion of the chloride ion by the negatively charged surfaces of the hydrobiotite (negative sorption or anion exclusion) can be described on the basis of electric-double-layer theory. In the case of the vermiculite-type layers of hydrobiotite the successive layers are close enough (5.55 A) so that Donnan membrane theory can be used to estimate interlamellar anion exclusion. The response of anion exclusion to the expansion and collapse of hydrobiotite makes this method useful for obtaining data on the distribution of surface charge density. Surface charge density is apparently quite important in determining the ease of lattice collapse of the clay minerals.

Mix development work during this period was directed at the development of mixes to be used in the injections scheduled for February. The outstanding characteristics of these mixes is their low cost. The mix for the first injection is a nonsetting slurry of attapulgite; the mix for the second injection has the lowest cement concentration deemed practical.

Type II cement is superior to Type I as a basis for all cement mixes because of its greater resistance to deterioration of the set grout by sulfate action.

When concentrated waste solution is mixed with lean cement mixtures, enough air is entrapped with the slurry to reduce the bulk density to virtually that of the waste solution. Under these conditions the control of the solid-to-solution ratio by the Densometer system is not possible. For this reason a suitable defoaming agent was sought. Of the defoamers tested, tributylphosphate (TBP) gave a slurry with the highest bulk density; the necessary plant modifications have been made to add TBP to the waste solution fed to the mixer.

To verify that the Densometer system could be used to control the ratio of solids to liquid in the feed at very low proportions of cement, a mix test was run by the Halliburton Company. The Densometer controlled the density of the slurry to within 0.1 lb/gal of the desired density, which is entirely acceptable. It was found, however, that the density indicated by the Densometer was uniformly 0.8 lb/gal lower than the

true density. This error in calibration can be compensated for by a change in the Densometer setting.

Construction of the injection plant was completed, and the waste pumps and injection pumps were operated to leak-test the system.

On the last water-injection test, the sand-erosion method for slotting the casing of the injection well failed to cut the casing at the first attempt after 20 min at 2600-psi jet pressure. To determine, if possible, the reason for this failure, a series of tests was run by the Halliburton Company in their test well. The principal observation made during the tests was that the jetting tool oscillated considerably and that a much wider slot was being cut than experience had suggested. This oscillation was probably responsible for the failure of the slotting operation at Oak Ridge, since more time would be required to erode a wider slot, and no allowance had been made for such a factor. In any case, these tests have shown that the 5-1/2-in. casing of the injection well can be cut despite the oscillation if a jet pressure of 4000 psi and a cutting time of 30 min are used.

Disposal in Natural Salt Formations. Stressmeter tests in the flatjack calibration block, made in the Hutchinson mine by the U.S. Bureau of Mines' Applied Physics Laboratory under contract to us, showed that the photoelastic gage is not suitable and that the solid inclusion gage, oil-filled hydraulic cells, and the borehole deformation gage appear to have worked satisfactorily. Potts' gages were also installed under test conditions in the Hutchinson mine.

Work on the renovation of the Lyons mine is underway on the new headframe, cages, and shaft collar. The structural steel in the headframe is complete. The mining equipment has been received at the mine.

Design of the underground transporter shield is complete, and the contract was let to the Athey Products Corporation.

Prototypes of the fuel element cannister were received. The hole liner was redesigned to permit removal of the liner and reaming of the salt in the lower portion of the hole. A contract was let for a prototype hole liner.

Clinch River Study. Diffusion coefficients based on a one-dimensional convective solution of the transport equation were obtained from the tracer tests run in the Clinch River. The diffusion coefficient at 20,000 cfs is higher than the one at 8000 cfs. The ratios of velocities to diffusion coefficients also decrease in the downstream direction.

A special computer program was developed to analyze the gamma spectrum scans of the bottom-sediment cores. The program strips the background from the spectrum, resolves the nuclides, and corrects for the contribution from adjacent sections of the core due to imperfect collimation.

Surveys of large sloughs in the Clinch River indicate that the radioactivity is within the range of radioactivity in the main river channel.

Mineral Exchange Studies. Mass-action equations predict that in the sorption of tracer concentrations of a cation in a medium containing a high concentration of a competing cation, the distribution coefficient (K_d) of the tracer ion is inversely proportional to the concentration of the competing ion. In ideal situations, the log-log plot of the K_d vs competing cation concentration yields a straight line whose slope is dependent on the ratio of the charge of the cations, and, for the exchange of tracer levels of strontium in sodium nitrate solutions, the line should have a slope of -2.

Plots obtained with trace-level strontium in sodium nitrate solutions at pH 7 show near-ideal response with sodium-saturated forms of Wyoming montmorillonite, South Carolina hydrobiotite, and Wisconsin illite. Sodium-saturated Illinois illite, which is generally regarded as a reference illite sample, showed lines whose slope was less than -2. Activated alumina did not show an appreciable decrease in sorption with increasing sodium nitrate concentrations, which suggests that activated alumina sorbs strontium by a different mechanism.

In dilute sodium nitrate concentrations, the highest K_d was found for the hydrobiotite sample; in the highest concentration (1.0 M $NaNO_3$) activated alumina gave the highest K_d. Of the clay minerals investigated, Illinois illite had the highest K_d in the concentrated solution but had only a moderate K_d in dilute solutions.

White Oak Creek Basin Study. A slug of tritiated water was injected into the ground water within the waste pit area, and after 3 months, it had spread in a southwestwardly direction and broadened into a tract of contamination that is at least 8 ft wide and more than 10 ft long. The tritium is observed to be moving at different velocities within the zone.

readings, the lower liner will be removed (after removal of the fuel canister), and the lower section of the storage hole will be reamed and the salt removed. The liner and fuel canister can then be replaced and the demonstration continued.

The new design has other advantages over the previous one. In the event of heater or thermocouple failures, the liner can be removed for replacement of these components. The liner can also be withdrawn for inspection of the corrosion attack by the salt. The annulus also provides a closed cavity for gases released from the salt by the effect of heat and radiation and provides a region in which gas-sample probes may be used. Plugging of gas sample lines is also minimized as provisions are made to insert lines from the surface during any time during the demonstration period.

Drawings of the hole liner were completed, and outside bids for the fabrication of a prototype were received from three companies, the low bid being $3260. The low bidder, Visioneering Bunell Company (a division of Curtis Manufacturing Company), Cleveland, Ohio, was also asked for a preliminary price for 21 units and quoted a unit price of $3150. The ORNL shops made a rough estimate of 200 man hours plus $600 material costs or a total of about $1800. A more detailed estimate is being made by the shop estimating group to determine the major cost items in the fabrication. If possible, design changes will be made to effect a cost savings.

Fuel Shipment and Hazards Analysis. — The carrier and shipping-rack drawings have been modified to strengthen regions which were calculated to be less than required for structural acceptability to meet the provisional rules for shipping irradiated fuel elements (Title 10, Code of Federal Regulations, Part 72). The changes were relatively minor. A report prepared by the Plant and Equipment Division stress-analysis group covers the calculations in detail (Engineering Document No. 10161-N-001R, dated November 20, 1963, Stress Analysis of Carrier and Shipping Rack, Radioactive Waste Disposal in Salt).

Installation drawings for the shipping rack and railroad gondola are nearing completion. The Plant and Equipment report on the stress analysis of the carrier and shipping rack is being edited to conform to the revised drawings and for use in the consolidated hazards analysis report on the fuel shipment which is in preparation.

6.2.3 Experimental Design (W. J. Boegly, Jr. and R. L. Bradshaw)

Further layout work and design has been completed on the experimental area. Based on a preliminary layout of the instrumentation, a cost estimate was prepared to assist in the preparation of a detailed instrument design. The major changes in the instrumentation design during this period have been the substitution of multiconductor cables to transmit thermocouple signals to the recorders instead of individual cables and the substitution of fiberglas covered thermocouple wire for the metal-sheathed thermocouples in the salt. These couples will be inserted in plastic sheaths to protect the wire from corrosion.

With the completion of the topside electrical design, emphasis was switched to the mine electrical system and the power circuitry to the experiment. It is planned to provide a system flexible enough to allow the use of most of the components required for the experiment to also be used for the operation of the mining equipment.

7. CLINCH RIVER STUDY

7.1 Dispersion Due to Power Releases

P. H. Carrigan, Jr.*

It has been shown that reasonable prediction of the effects of a sequence of power releases from Melton Hill Reservoir could be made if the dispersion characteristics of these releases were known.[37] A more general method of predicting dispersion due to these power releases is being sought. One possible method of prediction is to assume that factors influencing variations in the dispersion characteristics are the same for the unsteady nonuniform flow occurring in the Clinch River as for steady uniform flow.

In steady flow, no variation in flow or in velocity occurs with time. In uniform flow, no change in velocity occurs with distance; that is to say, there is no convective acceleration either in the direction of flow or in the direction normal to the flow.

---

*On loan from the U.S. Geological Survey, Water Resources Division.

Laboratory studies by Carrigan and Parker[38] indicated that the dispersion process for nonuniform flow is much the same for unsteady flow, due to power releases, as for steady flow. Their work indicates that if the diffusion coefficient for steady flow can be predicted, the general method desired may be developed.

The diffusion coefficient D for steady uniform flow is implicitly expressed in the following equation:

$$C = \frac{M}{A\sqrt{4\pi Dt}} \quad \exp - \frac{(x - vt)^2}{4Dt} , \tag{1}$$

in which

C = concentration of tracer (lb/ft^3),

M = quantity of tracer injected (lb),

A = cross-sectional area of flow (ft^2),

D = eddy diffusion coefficient (ft^2/sec),

t = time after injection (sec),

x = distance downstream from injection (ft), and

v = mean velocity in river (ft/sec).

Using Eq. (1), the diffusion coefficient was computed for many points at which observations were made during the tracer studies in August 1961 and February 1962 (refs 39 and 40). The flows during these studies were steady. The variation of the coefficient with Clinch River Mile for both tests is shown in Fig. 25.

The convective acceleration in the longitudinal direction, a measure of the nonuniformity of flow, during the February 1962 test was about 0.001% of the gravitational acceleration. The convective acceleration (longitudinal) α_x has been approximated by:

$$\alpha_x = v_x \frac{\partial v_x}{\partial X} \approx v_x \frac{\Delta v_x}{\Delta X} , \tag{2}$$

in which

v_x = mean velocity at section (ft/sec),

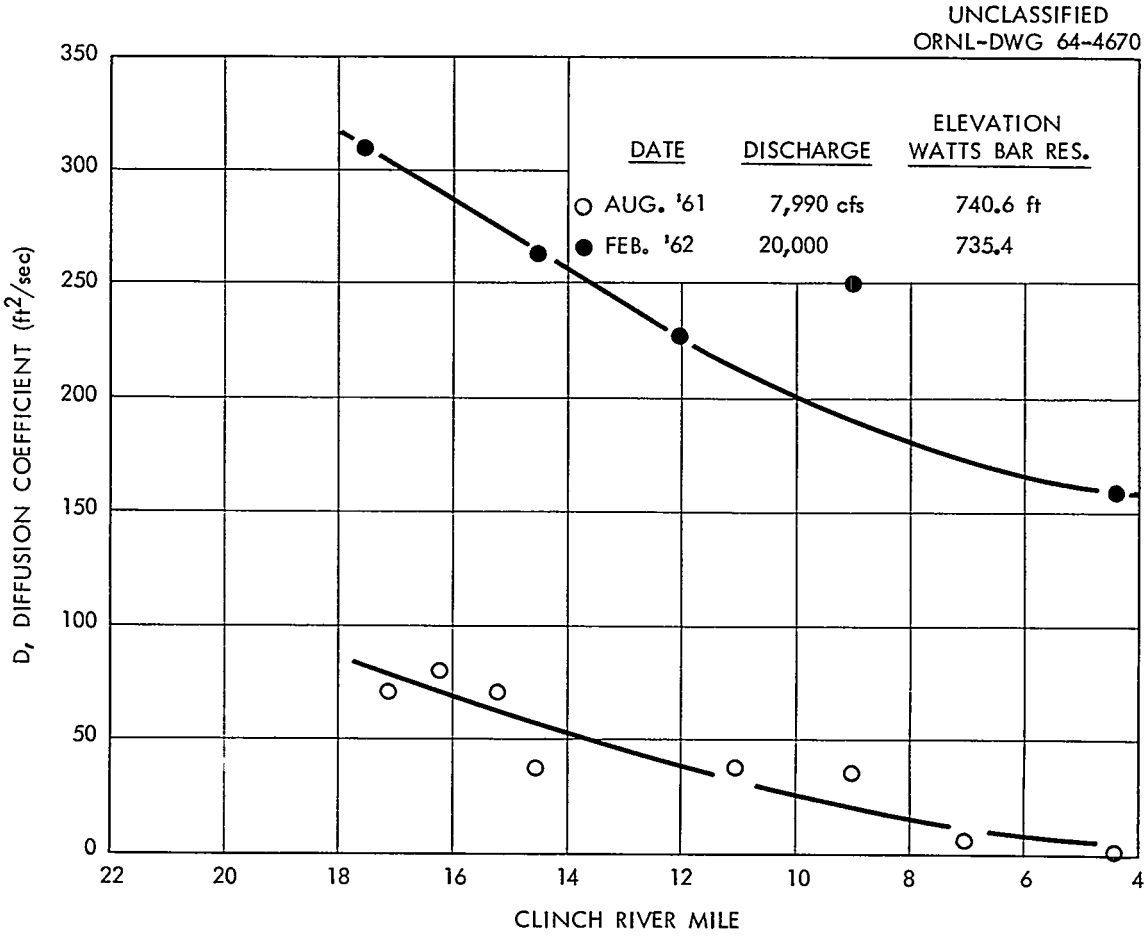


Fig. 25. Longitudinal Variation in Diffusion Coefficient for Two Conditions of Steady Flow in the Clinch River.

Δv_x = change in mean velocity between adjacent sections (ft/sec), and

ΔX = distance between adjacent sections (ft).

For steady flow in a straight pipe, G. I. Taylor found that the variation in diffusion coefficient could be simply defined in terms of the pipe radius and the shear velocity:[41]

$$D = 10.1\, r\, v_* , \tag{3}$$

in which r is the radius of pipe (ft), and v_* is the shear velocity (ft/sec).

Equation (3) may be transformed for flow in open channels to:

$$D = 2(10.1)\, R\, v_* , \tag{4}$$

in which R is the hydraulic radius (ft). The hydraulic radius is the ratio of the cross-sectional area to the wetted circumference (or perimeter) of the channel. In pipe flow, R = r/2.

Except for the rather restricted case of extremely uniform pipes, the virtual diffusion coefficient, D/rv_* or $D/2Rv_*$, is greater than the theoretical value of 10.1. In light of this experience it would be fortuitous if the theoretical value were approached in the Clinch River.

In the application of Eq. (3) to problems in open channels, the following substitution for shear velocity, v_*, is appropriate:

$$v_* = \frac{v\sqrt{g}}{C_1} , \tag{5}$$

in which g is the acceleration due to gravity (ft/sec^2), and C' is Chezy's coefficient (ft$^{1/2}$/sec). Substituting Eq. (5) and Eq. (4) and replacing 10.1 with a variable, ϕ,

$$D = 2\phi R \frac{v\sqrt{g}}{C_1} . \tag{6}$$

The variation of D with v is shown in Fig. 26. For both sets of data shown in the figure, D generally increases as v increases, as would be expected on the basis of Eq. (6).

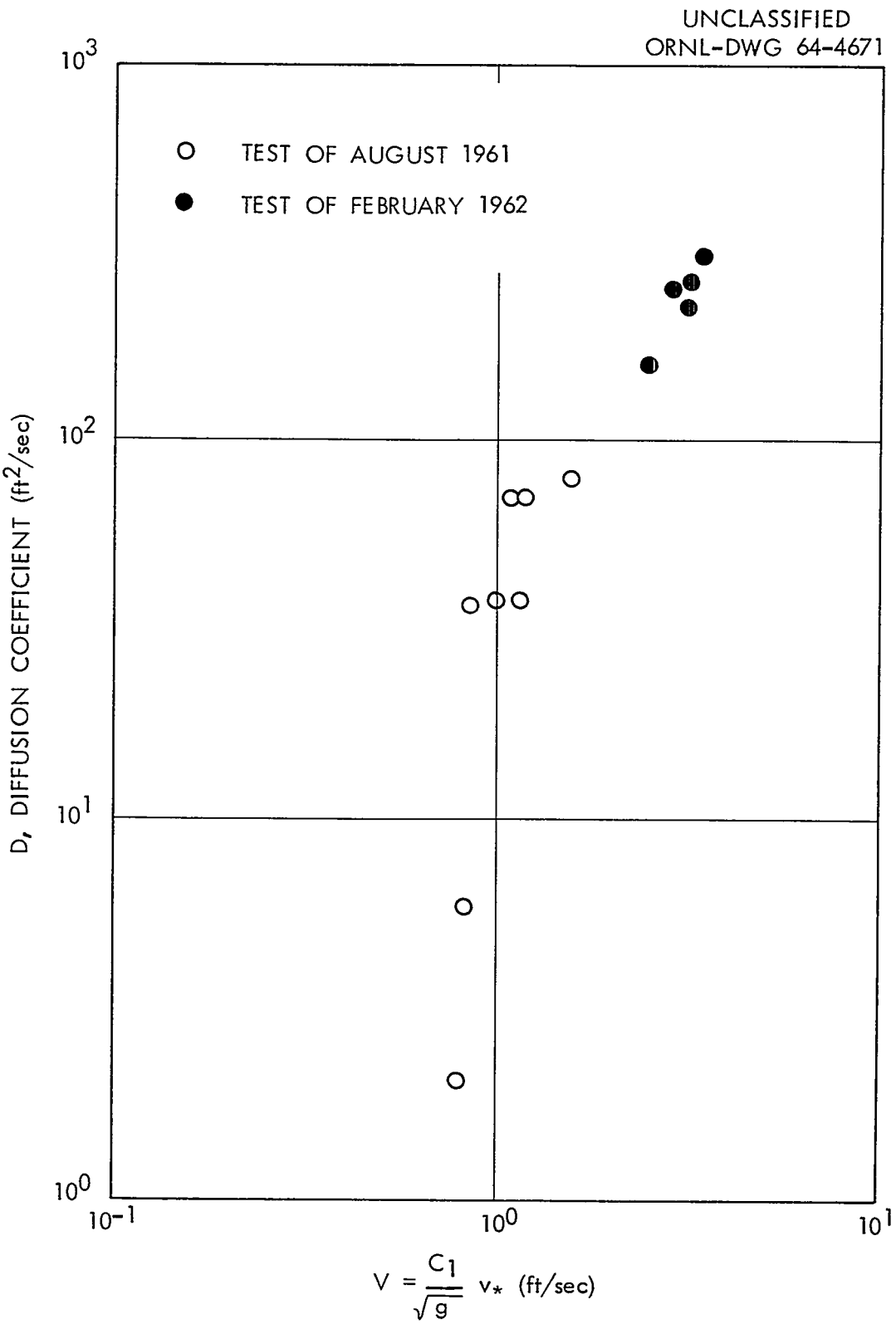


Fig. 26. Relation of Diffusion Coefficient to Mean Velocity.

Only limited data is available to evaluate the other variables, R and C_1 in Eq. (5). Study of this data does indicate that D generally decreases as R increases. The influence of C_1 has not been considered as yet because of these limitations in data. By definition,

$$C_1 = \frac{v}{\sqrt{RS}} , \qquad (7)$$

in which S is the energy gradient (ft/ft). Hence, better evaluation of C_1 requires not only additional information for R but also for S.

With the development of better information for the determination of R and S, it may be possible to show that $\emptyset$ in Eq. (6) is a constant for the Clinch River, though not equal to 10.1. If $\emptyset$ is constant for steady but nonuniform flow in the Clinch River, the extension of Eqs. (1) and (6) to problems of power releases appear feasible.

7.2 Procedure for Analysis of Gamma Spectrum Scans of Clinch River Bottom Sediment Cores

R. J. Pickering*

A procedure for the processing and analysis of gamma-spectrum scans of Clinch River bottom-sediment cores was developed for use with the Radioactive Waste Disposal Section's 512-channel pulse-height analyzer. Upon completion of a scan of a 2-in. increment of core, the resulting gamma spectrum is automatically punched out in digital form on paper tape. The counts in each energy range of the spectrum are transferred from the paper tape to magnetic tape and then to punch cards by means of a computer program which examines the paper tape for mechanical punching errors. The punch cards are then processed through a second computer program which subtracts the background from each spectrum. The resulting "net" spectrum is then analyzed by means of a third computer program which determines the concentration of the various suspected gamma-emitting radionuclides present in the 2-in. increment through a comparison of the unknown spectrum with standard spectra of known radionuclide concentrations. This computer program provides an estimate of how complete the spectrum analysis has been and a general indication of the accuracy of the results.

*On loan from the U.S. Geological Survey, Water Resources Division.

The contents of the various gamma-emitting nuclides in each of the 2-in. core increments, as determined by means of the spectrum analysis program, are processed through a fourth computer program that corrects the analyses for the effect of adjacent portions of the core. This "adjacent increment" effect is the result of imperfect collimation in the "core scanner" in which the cores were counted. The values obtained from this fourth computer program represent the true radionuclide concentrations in each of the 2-in. core increments analyzed.

Outputs of all four computer programs can be plotted automatically to permit visual inspection of the spectra at different stages in the analysis. By this means, the presence of unsuspected gamma-emitting elements can be detected.

Two tests were developed by which the performance of the multi-channel analyzer can be assessed. The first test consists of the analysis of a standard containing ^{51}Cr, ^{137}Cs, and ^{60}Co. These three elements cover a large portion of the gamma-spectrum energy range and, through observation of the channels in which the photopeaks of the three appear, any undesirable shift in gain in the analyzer can be detected and corrected. The second test consists of a computer program for application of the "Chi Square" test to a series of duplicate spectrum analyses. In this test, the computer determines the amount of deviation of each count in each channel of the analyzer from the average of all the counts in that channel, and indicates the channels in which the deviation is great enough to cast doubt on the performance of the analyzer with respect to those channels.

Most of the computer programs described above can be used for analyzing samples other than cores, and will be used for determining the content of gamma-emitting elements in composites of bottom sediment cores. The results of these analyses will be used in the computation of the total radionuclide content of Clinch River bottom sediments.

7.3 Survey of Bottom Sediment Radioactivity in Clinch River Sloughs

R. J. Pickering*

During May 1963 a survey of bottom sediment radioactivity was made in six large sloughs (drowned tributary-stream mouths) of the Clinch River and one slough of the Emory River (Fig. 27). The primary purpose of the survey was to determine whether the sloughs represent repositories of fine sediment with higher surface radioactivity than that in the main channel of the river. Radioactivity readings were made with the ORNL Applied Health Physics Section's "Flounder." The results of the survey are shown in Table 24.

The results of the survey indicate that the radioactivity of sediment in the sloughs surveyed is within the range of radioactivity in the main river channel and is in places several times the "background" (surface soil) radioactivity, but in none of the sloughs surveyed was the maximum radioactivity as high as that in adjacent portions of the main channel.

Plots of bottom sediment radioactivity vs depth of water indicate that in several of the deeper sloughs a direct relationship exists between these two variables. Although the causes of this relationship are not definitely known, the following two erosional processes are probably largely responsible: (1) exposure of the portions of the sloughs less than 6 ft deep to subaerial erosion during winter low water in Watts Bar Lake and (2) washing of sediment down the sides and into the deeper portions of the sloughs during periods of high rainfall and high surface runoff.

---

*On loan from the U.S. Geological Survey, Water Resources Division.

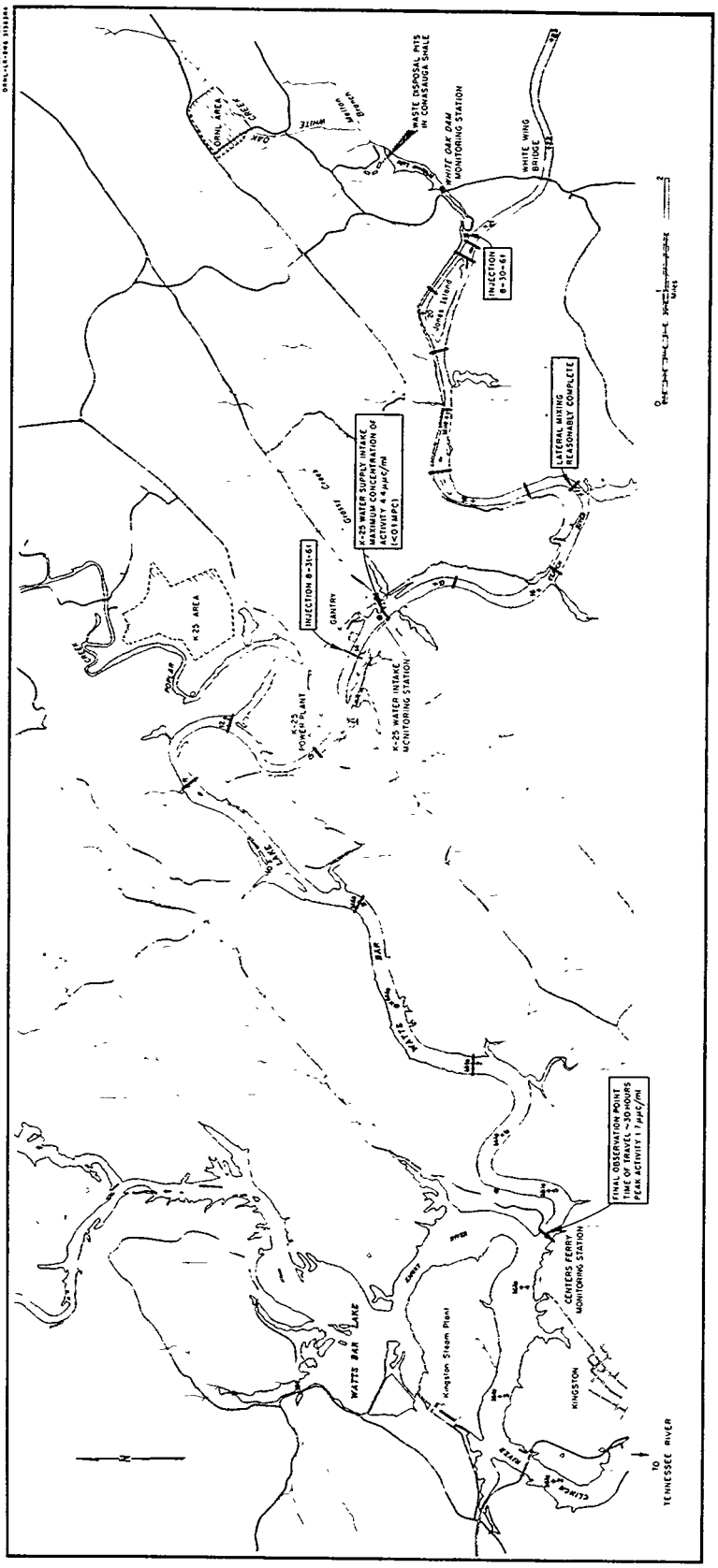


Fig. 27. Location Map, Survey of Bottom Sediment Radioactivity in Clinch River Sloughs.

Table 24. Bottom Sediment Radioactivity in Sloughs

River Mile	Section	Radioactivity (counts/sec) Average	Maximum	Minimum	Background[a]
Clinch 17.0	A	13.0	17.2	9.7	7.8
	B	7.9	9.4	5.1	ND[b]
Clinch 14.6	A	16.0	42.0	7.9	6.5
	B	15.2	26.9	6.9	6.6
	C	15.3	20.8	10.6	ND
Clinch 14.4	A	28.6	54.4	11.1	ND
Clinch 13.6	A	34.5	53.3	11.1	6.5
Clinch 6.5	A	21.3	32.8	4.1	6.2
Clinch 2.7	A	19.8	38.1	5.8	ND
Emory 0.9	A	15.0	20.8	8.2	7.2

[a]Background determined on surface of soil at bank of slough.

[b]ND - not determined.

8. MINERAL EXCHANGE STUDIES

T. Tamura

The sorption of strontium by the clay minerals has been considered to be an ion exchange reaction; on the other hand, sorption of this element by activated alumina and the hydrous sesquioxides is believed to be by a different mechanism than that for the clay mineral. To get a better understanding of the nature of the reaction of strontium, comparisons were made of the sorption of strontium with several sorbents, and mass-action theory was used to depict ideal ion exchange behavior.

8.1 Ion Exchange Equilibria

Mass-action expressions have been used by several investigators to describe ion exchange equilibria. For the exchange of strontium on a sodium clay, one may write:

$$Sr^{2+} + Na_2C \rightleftharpoons SrC + 2Na^{+} \quad , \qquad (1)$$

and the equilibrium expression as:

$$K = \frac{[SrC]\,[Na^{+}]^2}{[Sr^{2+}]\,[Na_2C]} \quad , \qquad (2)$$

where

K = equilibrium constant,

C = clay, and

[] = activity.

In a system where the strontium is present in tracer quantities and the clay is almost saturated with sodium, the activity coefficients of the sodium clay, strontium clay, and strontium ion may be considered to be constant. One can rewrite Eq. (2) in the form:

$$K' = \frac{(SrC)\,[Na^{+}]^2}{(Sr^{+2})(Na_2C)} \quad , \qquad (3)$$

where

K' incorporates the constant activity coefficients and the ( ) denotes concentrations.

By definition, the distribution coefficient (K_d) for strontium is defined as:

$$K_d = \frac{(SrC)}{(Sr^{+2})} \quad , \qquad (4)$$

and one may combine Eq. (3) and (4) to form

$$K_d = K' \frac{(Na_2C)}{[Na^+]^2} \quad . \tag{5}$$

Since the clay remains nearly sodium saturated, Na_2C is a constant, and a log-K_d-vs-log-$[Na^+]$-plot should yield a straight line. The slope of the line is a function of the exponent of Na^+ and K_d, and, in this case, the slope is -2.

If one varies the sodium ion concentration over a wide range, the activity coefficient for the sodium ion changes, and activity should be used in the plot. With clay-size particles, dispersion of the material is observed below approximately 0.01 M sodium nitrate; and accurate measurements of (Sr^{2+}) is difficult to obtain below this concentration. For a more complete treatment of mass-action equilibria in ion exchange reactions, see the paper by K. A. Kraus.[42]

8.2 Strontium Sorption by Clay Minerals

The log-K_d-vs-$[Na^+]$-plot for montmorillonite and hydrobiotite is shown in Fig. 28. Note that in less than 0.02 M sodium ion concentration, the K_d appears constant for the montmorillonite sample; this behavior is believed to be due to the dispersion of the very fine particles of montmorillonite in the low salt concentration. On the other hand, particles in the hydrobiotite sample are between 35 to 70 mesh, and very little dispersion was noted. These two materials represent the more classic examples of clays that exhibit ion exchange characteristics by isomorphic substitution, and they exhibit a slope of -2, as calculated. It is interesting to note that the K_d is greater for the hydrobiotite with about 70 meq/100 g of cation exchange capacity than for the montmorillonite, with 90 meq/100 g.

In Fig. 29 similar data is given for two illite samples. Tests show that the sample from Wisconsin differs from the one from Illinois in degree of crystallinity and exchange capacity. The former material gives a strong, sharp diffraction maximum at 10A, in contrast to a weak, diffuse maximum for the latter. The ion exchange capacity is about 22 meq/100 g for the Wisconsin sample and 17 meq/100 g for the Illinois sample. The

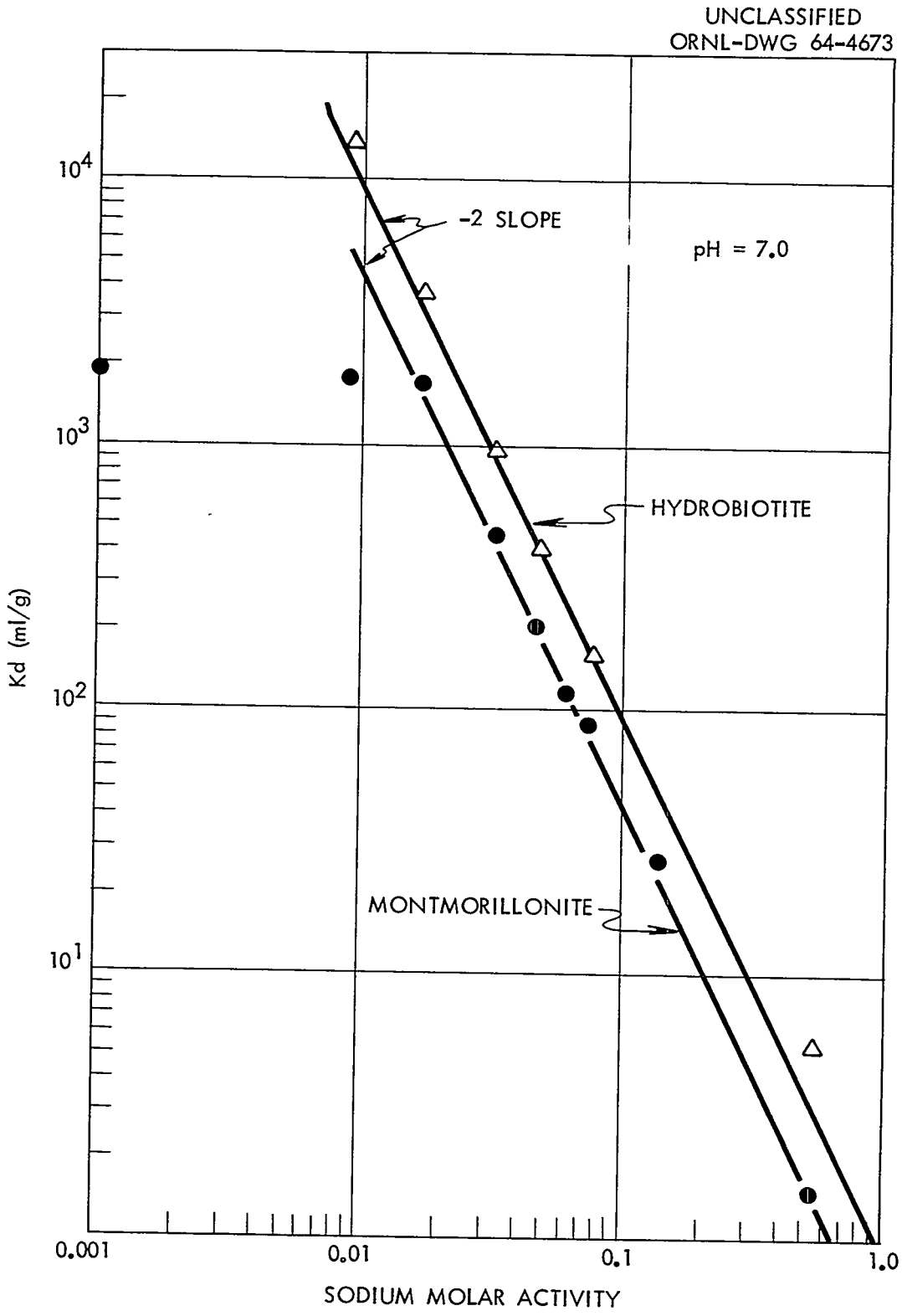


Fig. 28. Influence of $NaNO_3$ Concentration on Strontium Sorption by Montmorillonite and Hydrobiotite.

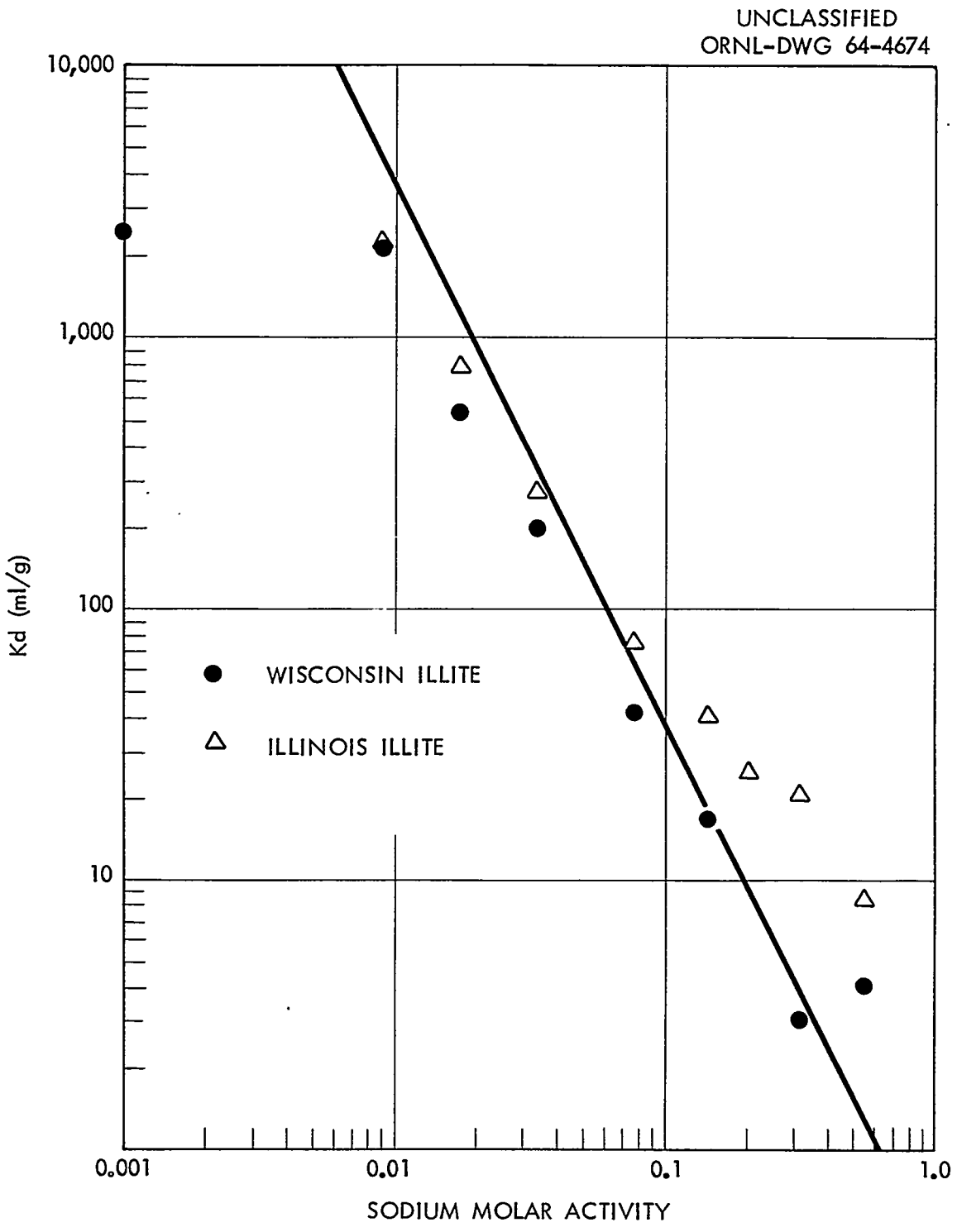


Fig. 29. Influence of Sodium Nitrate on Strontium Sorption by Illites.

data in Fig. 29 show that Wisconsin illite's response is similar to that of montmorillonite and hydrobiotite and that the response follows the predicted mass-action reaction. The slope obtained for the Illinois sample is less than that predicted for ideal exchange; the reason for this difference in behavior is not yet known. It is interesting to note that despite a lower exchange capacity for the Illinois illite, the K_d is higher than the Wisconsin illite at all levels of sodium nitrate concentration.

8.3 Strontium Sorption by Alumina

When activated alumina (F-20 grade) from the Aluminum Company of America was similarly tested, the response curve differed greatly from that observed with clays. The K_d remained nearly independent of the sodium ion concentration (Fig. 30). This type of response might be expected for a precipitation reaction whereby strontium aluminate or similar type of compound is formed.

Although it is premature to postulate a mechanism for the reaction between strontium and the alumina, several interesting applications of the data to waste solutions can be mentioned. In tracer-level strontium solutions, whose sodium nitrate concentration exceeds 0.04 M, alumina is a more effective sorbent than even hydrobiotite, and, as the sodium nitrate concentration increases, alumina as a sorbent is even more favored. Tests with aluminum oxide powder, which has much lower surface area than activated alumina, show a similar type of curve, and, at pH 9, the K_d is higher than that observed at pH 7. Hence it is expected that the activated alumina will also show a much higher K_d in alkaline systems; a K_d as high as 30,000 has been measured using heated gibbsite, which is a powdered form of activated alumina.

8.4 Strontium Sorption by Conasauga Shale

Tests with Conasauga shale show excellent agreement between the predicted and the experimental slope at pH 7. After removing the free iron oxide with sodium dithionite, the shale showed only a slight increase in K_d, especially at the lower sodium concentrations. At pH 7 the sesquioxides were not expected to influence the slope significantly, especially since the material contained about 8% Fe_2O_3.

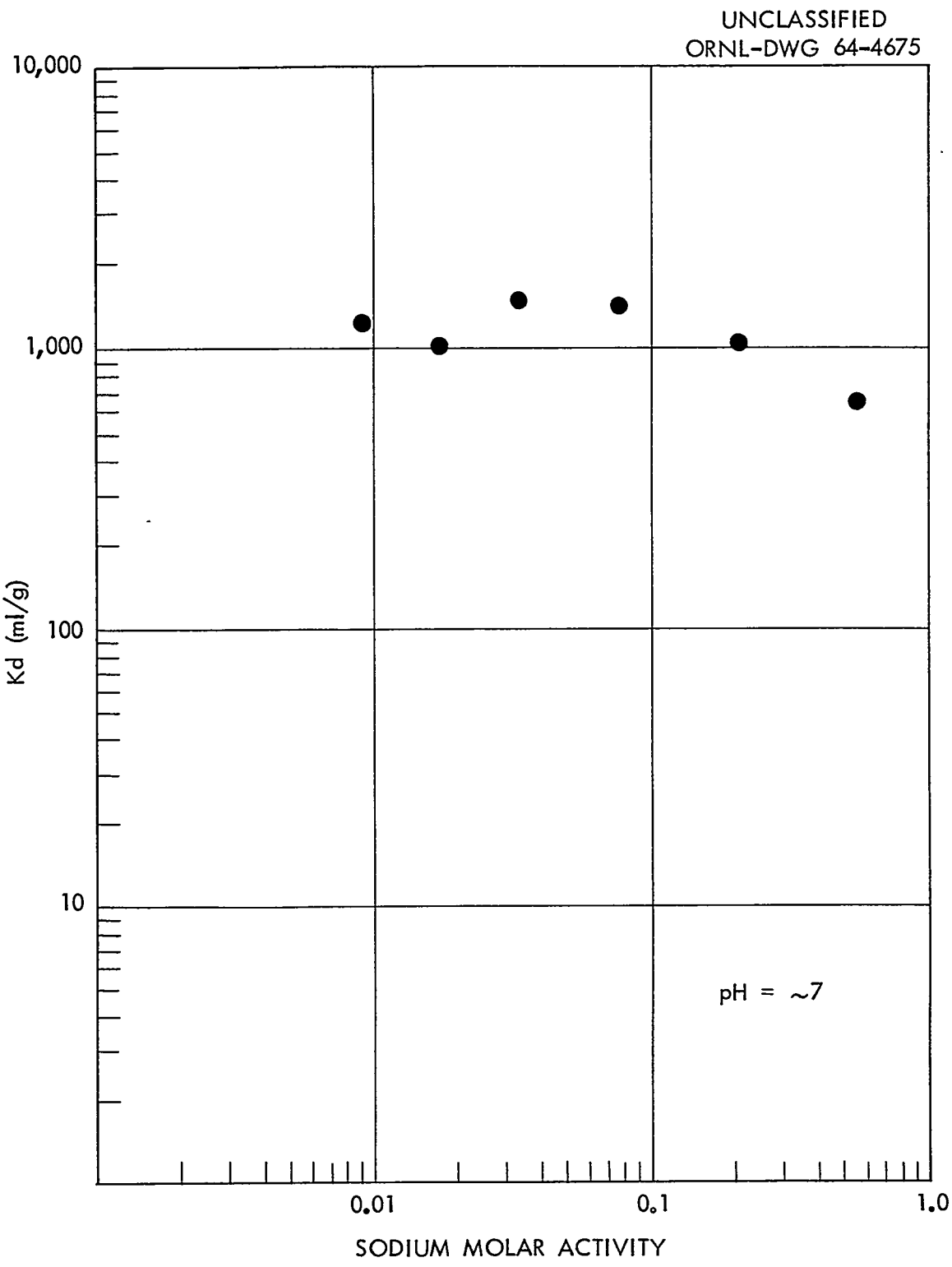


Fig. 30. Influence of Sodium Nitrate on Strontium Sorption by Activated Alumina.

Since Conasauga shale is used at ORNL to sorb waste whose sodium ion concentration is about 0.1 M or higher and whose pH is greater than 7, it was deemed highly desirable to test the material at a higher pH. The data obtained at pH 9.0 are shown in Fig. 31. Prior to removal of the iron oxide, the shale shows a slope which is less than -2. The slope which approaches -2 suggests that the residual clay, when the iron oxides are removed, sorbs according to the law of mass action. Note that at 0.08 M activity (0.1 M) of sodium the K_d is nearly halved after the treatment; it therefore seems likely that the hydrous iron oxide can play an important role in the sorption of strontium from ORNL waste. Ion exchange capacity cannot be a factor in this change since the measured value of the capacity increased after the removal of the iron oxide.

These studies suggest that hydrous sesquioxides can play a significant role in waste disposal under certain conditions; further work is continuing, using this relationship of mass action equations, to define the reaction of other minerals and natural materials, including soils.

9. WHITE OAK CREEK BASIN STUDY*

9.1 Evaluation of Fission-Product Distribution and Movement in and Around Chemical Waste Seepage Pits 2 and 3

T. F. Lomenick F. Gera**

In evaluating the effects of ground water on the various radionuclides in and around waste pits 2 and 3, it is essential that the directions and rates of subsurface-water movement be known. To aid in defining the movement of ground water in the waste pit area, a tracer test, using tritium, was initiated. In general, the test consisted

---

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

**NATO Postdoctoral Fellow from Italy.

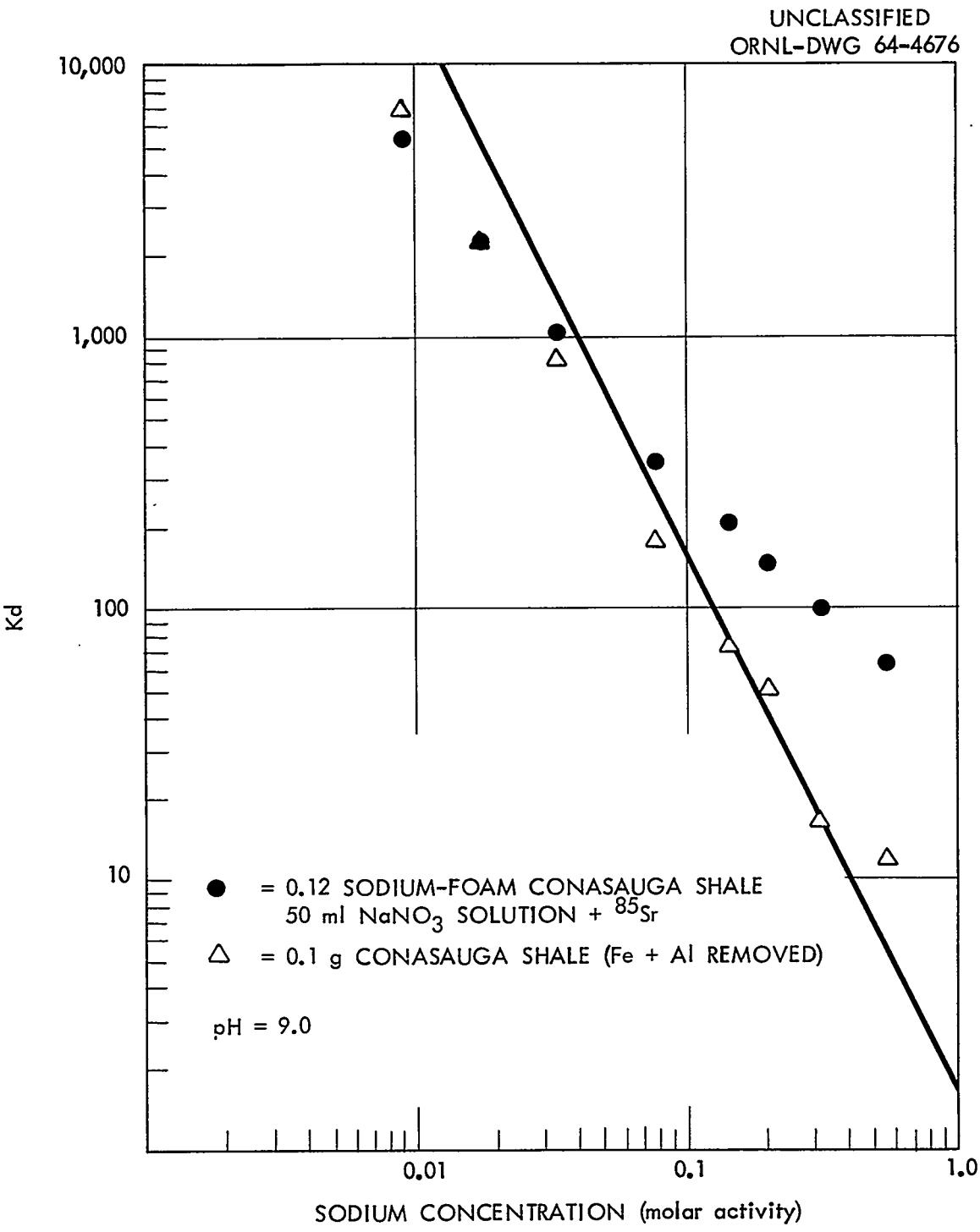


Fig. 31. Influence of Sodium Nitrate Concentration on Strontium Sorption by Conasauga Shale.

in injecting tritiated water into five 40-ft-deep holes, drilled on 1-1/2-ft centers, along a line estimated to be at right angles to the strike of the geologic formation (Conasauga shale) that underlies the area (Fig. 32). By periodic sampling and analysis of the water from a series of observation wells, the rates and directions of movement of the tracer are being determined. From previous geologic and hydrologic studies of the area, we felt that the tracer would move in a southwestwardly direction away from the injection wells or along the strike of the formation. Thus, most of the observation wells were located in that direction. However, a few wells were located in other directions to intercept the tracer should it move in a direction other than along the path that was predicted. As the tritium is detected in the existing observation wells and the direction or directions of movement are determined, additional wells are drilled along the most likely avenues of movement toward surface streams.

About 21 curies of tritiated water was used for the test. The seemingly large amount is necessary to ensure detectable quantities of the material in the observation wells at distances up to 200 ft from the points of injection. The significant quantities of ^{106}Ru and some tritium in the ground water due to pit operations causes a relatively high "background" count in water from the wells. Thus, the detection of small quantities of tracer tritium is extremely difficult. A Packard "Tri-Carb" liquid scintillation counter was used to determine the concentrations of activity in samples from the observation wells.

At this time, 3 months after injection, it is certain that the slug of tritiated water has moved in a southwestwardly direction and has broadened into a tract of contamination that is, out to a distance of 10 ft, at least 8 ft wide (Fig. 32). At the 10-ft-distant observation points, tritium was detected in wells 10 and 11 at a much earlier date than at well 6. Thus, it is apparent that there is some variation in the rates of movement of the tracer within the contamination zone. Additional information on the rates of movement of the tracer can be observed from Fig. 33, which is a plot of the concentration of tritium in various wells with time. For well 5, located 5 ft from the injection points, the first traces of the tritiated water were detected within 24 hr after injection. The concentration of activity in the well rises rather rapidly to a peak concentration after

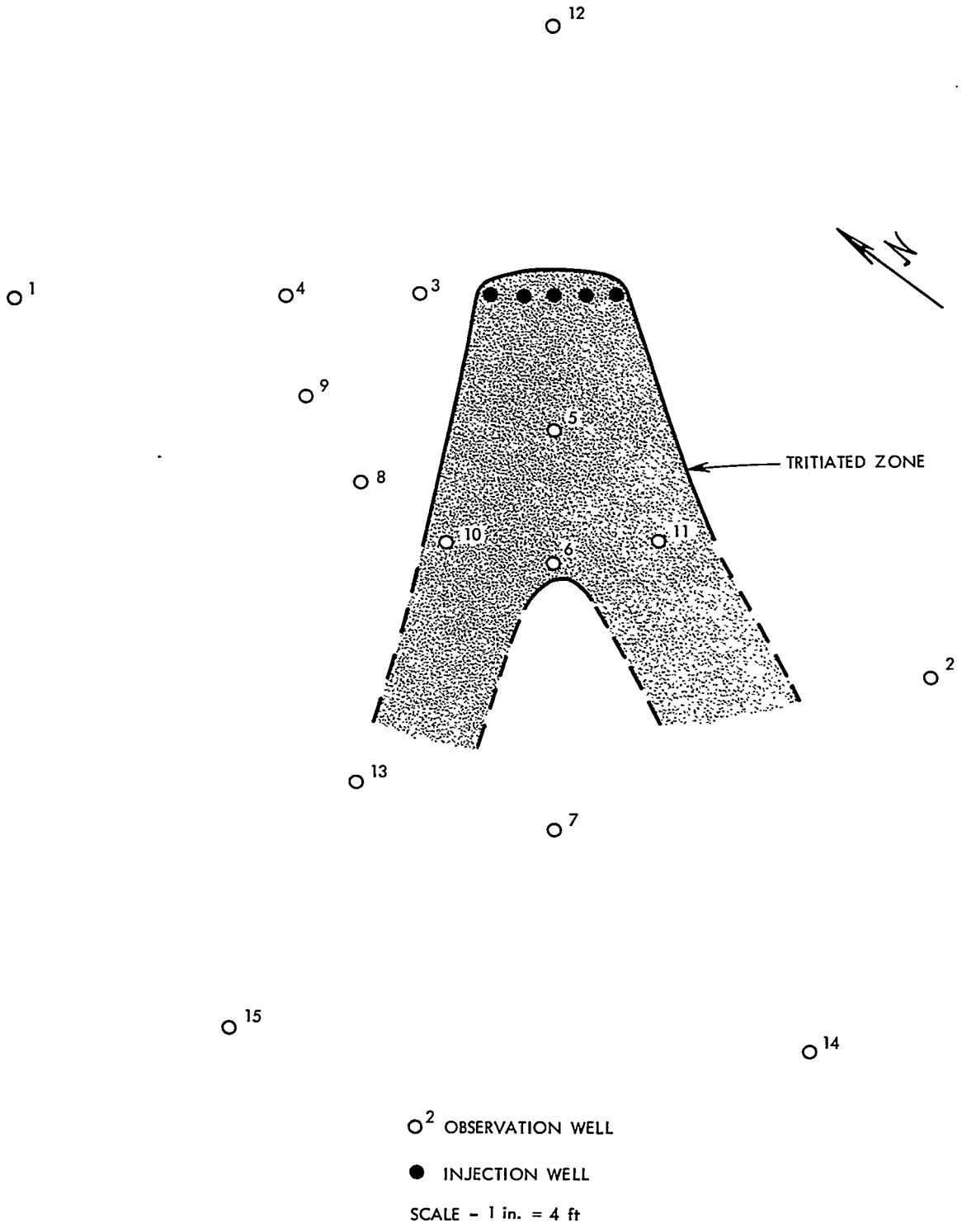


Fig. 32. Plan Showing Extent of Subsurface Migration of Tritium in Waste Pit Area Approximately 3 Months After Tracer Injection.

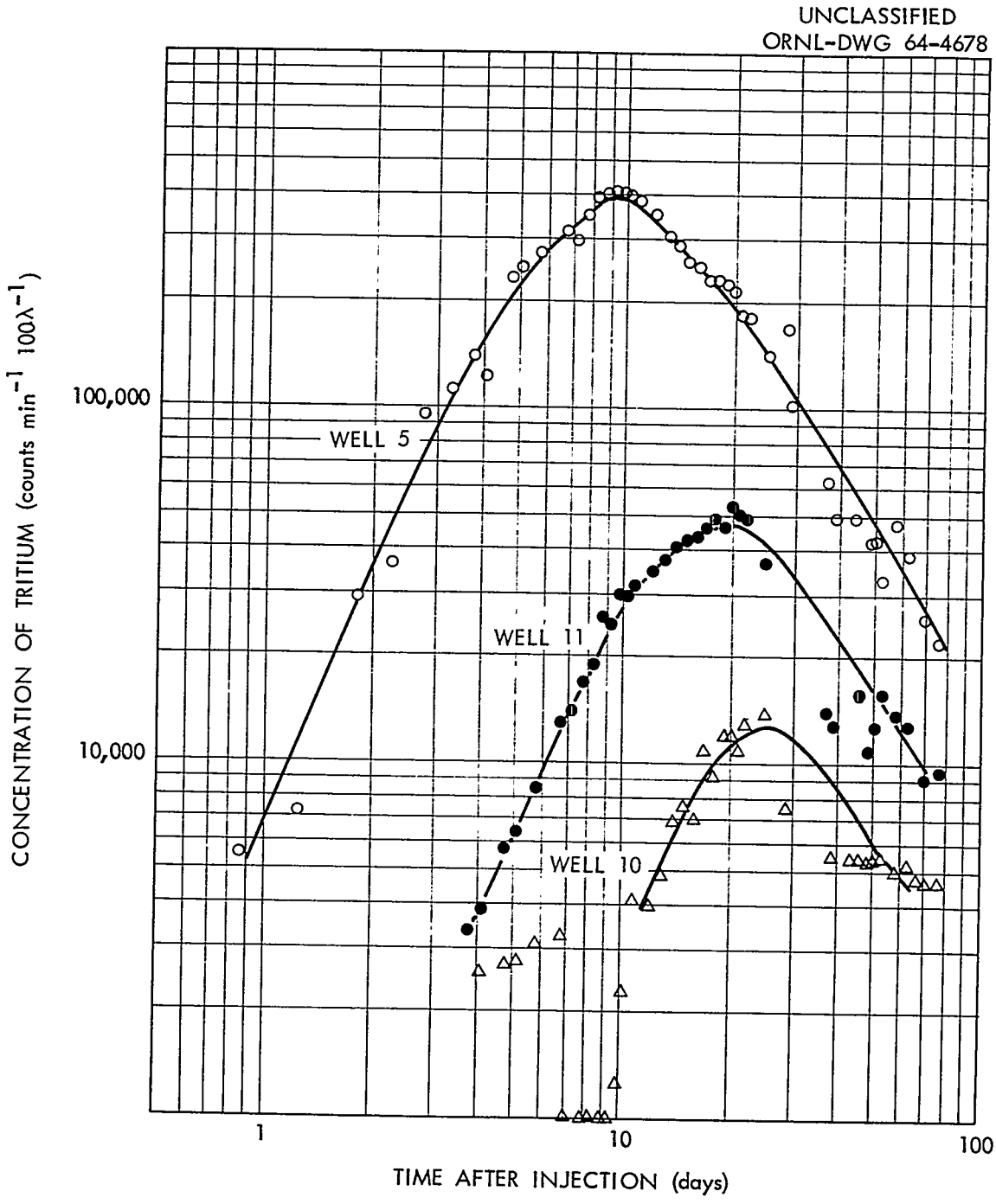


Fig. 33. Movement of Tritium Slug Through Observation Wells in Waste Pit Area.

about 9 days. The decline in the amount of tritium in the well is much slower than the buildup. Tritium was first detected at wells 11 and 10, located at a distance of 10 ft from the injection wells, after about 5 days, and the peak concentrations occurred after about 20 and 25 days, respectively. The break in the increase in concentration for well 10, after about 7 days, was due to an artificial recharge of the water table in that area as a result of drilling a nearby observation well. The temporary disturbance of the water-table gradient is also believed to be responsible for the lag in the peak concentration of the tritium in that well behind that occurring in well 11. The low concentrations of tritium observed in many of the well samples on the downslope portion of all three curves is due to a dilution of the tritium in the wells by recharging rainfall to the aquifer and by the leaking of surface water into the hole around the well casings. These low values were mainly disregarded in fitting the curves to the plotted points. All the curves closely resemble curves that would be expected from flow through a chromatographic column. The decrease in the concentration of tritium in the wells at 10 ft, compared with the decrease at the 5-ft-distant observation wells, reflect dispersion of the tracer. The rate of flow of the peak concentration of the tritium, which may be referred to as the modal velocity of the water, was, for the first 5 ft, about 0.56 ft/day, while it was only slightly less for the flow out to a distance of 10 ft in the direction of wells 10 and 11.

9.2 Hydrology of White Oak Creek Basin

W. M. McMaster* R. M. Richardson*

Eleven channel sediment ranges were established in White Oak Creek for (1) measuring changes in channel configuration caused by scour and fill, (2) measuring variation in sediment movement with stream flow conditions at the different sites, and (3) for sampling to determine sediment characteristics and their variations with time and place and the quantity and distribution of associated radionuclides.

Eleven samples from the upper 2 in. of White Oak Creek bottom sediments were collected on February 3, 1964, between White Oak Creek Mile (WOCM) 1.1 and 2.8,

---

*On loan from U.S. Geological Survey, Water Resources Division.

and seived to obtain the material less than 63 μ in diameter (silt and smaller) for analysis for ^{137}Cs, ^{106}Ru, and ^{60}Co. Results showed, for ^{137}Cs, an average concentration, in micromicrocuries pre gram, of 3.93, x 10^3 and a range from 6.75 x 10^2 to 8.23 x 10^3; for ^{106}Ru, an average concentration of 7.54 x 10^2 and a range from 1.47 x 10^2 to 3.32 x 10^3; and for ^{60}Co, an average concentration of 4.82 x 10^2 and a range from 0 to 1.08 x 10^3. The highest concentration of ^{137}Cs was found at WOCM 2.4; of ^{106}Ru, at WOCM 2.55; and of ^{60}Co, at WOCM 2.73.

10. REFERENCES

1. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Progress Report May-October 1963, ORNL-TM-757 (April 1964).

2. W. E. Clark and C. L. Fitzgerald, Proposed Methods for the Removal of Mercury from Radioactive Waste Solutions, ORNL-TM-827 (Mar. 31, 1964).

3. K. Takahashi, "Advances in Glass Technology," VI Intern. Cong. on Glass, Washington, D. C., July 8-14, 1962, pp 366-76 in Plenum Press, New York, 1962.

4. R. E. Brooksbank, et al., Low-Radioactivity-Level Waste Treatment. Part II. Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Waste by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349 (May 20, 1963).

5. R. R. Holcomb, Low-Radioactivity-Level Waste Treatment. Part I. Laboratory Development of a Scavenging-Precipitation Ion-Exchange Process for Decontamination of Process Water Wastes, ORNL-3322 (July 10, 1963).

6. R. E. Brooksbank, L. J. King, and J. T. Roberts, Pilot Plant Demonstration of the Removal of Radioactivity from Low-Level Process Waste Water by a Scavenging-Precipitation Ion-Exchange Process, Symposium on Radionuclide Exchange on Soils, Minerals and Resins, sponsored by the Nuclear Technology Division of the American Chemical Society, Philadelphia, Pennsylvania, April 10, 1964.

7. E. Schonfeld and W. Davis, Jr., Head-End Treatment of Low-Level Waste Prior to Foam Separation, ORNL-TM-260 (May 1962).

8. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report for August-October 1962, ORNL-TM-482 (Mar. 25, 1963).

9. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Progress Report for November-December 1963 and January 1964, ORNL-TM-516 (June 12, 1963).

10. R. R. Holcomb, Low-Radioactivity-Level Waste Treatment. Part I. Laboratory Development of A Scavenging-Precipitation Ion-Exchange Process for Decontamination of Process Water Wastes, ORNL-3322 (June 25, 1963).

11. R. E. Brooksbank et al., Low-Radioactivity-Level Waste Treatment. Part II. Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Wastes by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349 (May 13, 1963).

12. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Progress Report May-October 1963, ORNL-TM-757 (April 1964).

13. E. Schonfeld and W. Davis, Jr., Softening and Decontaminating Waste Water by Caustic-Carbonate Precipitants and Filtration in a Slowly Stirred Sludge-Blanket Clarifier: Laboratory Development and Semi-Pilot-Plant Testing, ORNL-TM-835 (Sept. 13, 1964).

14. L. Salmon, Computer Analysis of Gamma-Ray Spectra from a Mixture of Known Nuclides by the Method of Least Squares, AERE-M1140, Atomic Energy Research Establishment, Harwell, England (1963).

15. E. Schonfeld, unpublished data.

16. P. Dejonghe et al., Insolubilization of Radioactive Concentrates by Asphalt Coating; Final Report No. 2, 1st Part, concerning Proposal 167, April 1, 1961, to March 31, 1963; EURAEC-695.

17. C. D. Watson, A. J. Hoiberg, and G. A. West, "Asphalt Lining of Radiochemical Waste Storage Basins," Ind. and Eng. Chem. 50, 87A-90A (1958).

18. E. L. Albenesius, Phys. Rev. Letters 3, 274 (1959).

19. E. L. Albenesius and R. S. Ondrejcin, "Nuclear Fission Produces Tritium," Nucleonics 14, 100 (Sept. 1960).

20. E. N. Sloth et al., "Tritium in the Thermal Neutron Fission of U-235," J. Inorg. Chem. 24, 237-41 (1962).

21. U. S. Dept. of Commerce, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," NBS Handbook 69 (1959).

22. W. A. Haney et al., Fission Product Tritium in Separations Wastes and in the Ground Water, HW-74536 (Aug. 1, 1962).

23. J. H. Horton and D. I. Ross, "Use of Tritium from Spent Uranium Fuel Elements as a Ground Water Tracer, Soil Science 90 (5) 267-71 (1960).

24. W. A. Haney, Fission Product Tritium in Fuel Reprocessing Wastes, HW-SA-3303 (Dec. 30, 1963).

25. Civilian Nuclear Power, Appendices to a Report to the President - 1962, U.S. Atomic Energy Commission, Washington 25, D. C.

26. F. L. Culler, The Effect of Scale-Up on Fuel Cycle Costs for Enriched Fuel and Natural Uranium Fuel Systems, ORNL-TM-564 (Apr. 16, 1963).

27. Federal Register, Vol. 25, pp 8591-8664 (Sept. 7, 1960).

28. W. H. Farrow, Jr., Radiochemical Separations Plant Study Part II - Design and Cost Estimates, DP-566, Appendix II (March 1961).

29. C. E. Guthrie and J. P. Nichols, Theoretical Possibilities and Consequences of Major Accidents in U-233 and Pu-239 Fuel Fabrication and Radioisotope Processing Plants, ORNL-CF-63-10-34.

30. Procedures and Practices for Radiation Protection, Health Physics Manual, Oak Ridge National Laboratory, Oak Ridge, Tennessee (Aug. 4, 1961).

31. E. R. Irish, Description of Purex Plant Process, HW-60116 (May 19, 1959).

32. J. M. Skarpelos, Progress in Treatment of a Radioactive Condensate Waste, HW-79174 (October 1963).

33. W. J. Kaufman and G. T. Orlob, J. Amer. Water Works Assoc. 48(5), 559 (1956).

34. H. R. Kruyt, Colloid Science 1, 129, Elsevier, Amsterdam (1952).

35. R. K. Schofield and O. Talibuddin, Dis. Far. Soc. 1948 (3), 51 (1948).

36. R. E. Grim, Clay Mineralogy, p 74, McGraw-Hill, New York, 1953.

37. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Progress Report, May-October 1963, ORNL-TM-757 (in press).

38. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, August-October 1962, ORNL-TM-482 (Mar. 25, 1962).

39. R. J. Morton (ed.) et al., Status Report No. 3 on Clinch River Study, ORNL-3370 (Nov. 21, 1962).

40. R. J. Morton (ed.) et al., Status Report No. 4 on Clinch River Study, ORNL-3409 (Sept. 11, 1963).

41. G. I. Taylor, "The Dispersion of Matter in Turbulent Flow Through a Pipe," Proceedings, Royal Soc. of London 223 (1155), p 446 (May 20, 1954).

42. K. A. Kraus, "Ion-Exchange," Trace Analysis, John Wiley & Sons, New York, pp 34-101 (1957).

ORNL
MASTER COPY

2005

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ORNL - TM - 1081

15

WASTE TREATMENT AND DISPOSAL SEMIANNUAL PROGRESS REPORT

JULY-DECEMBER 1964

This document has been approved for release to the public by:

Daniel R Hamrin 7/28/95
Technical Information Officer ORNL Site — Date

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

ORNL-TM-1081

HEALTH PHYSICS DIVISION

CHEMICAL TECHNOLOGY DIVISION

WASTE TREATMENT AND DISPOSAL SEMIANNUAL PROGRESS REPORT

JULY-DECEMBER 1964

F. L. Parker R. E. Blanco

MAY 1965

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

Solidification of Highly Radioactive Waste. Five tests have been completed with the 150-kw induction furnace. Two were calcination tests using a 16-in.-diam pot; these tests were terminated because holes developed in the pots due to local overheating. The average feed rates for these two tests were 25 and 15 liters/hr, as expected from previous calcinations in a 8-in.-diam pot.

One 8-in. pot-calcining test and two 8-in. rising-level glass tests were completed; a 15-in. susceptor in the induction furnace was used to smooth the heat flux, and local overheating was not observed. The average feed rate for the rising-level glass tests were 8 and 9 liters/hr, respectively. This is equivalent to the waste from about 2.0 tons of uranium processed per day. There was some difficulty in monitoring the heights of liquid and solid zones.

The 20-in.-diam, continuous, horizontal melter operated successfully for 250 hr until a hole formed in the melter as the result of corrosion. The average feed rate for the continuous melter was between 30 and 45 liters/hr for extended times.

High-Radioactivity-Level Waste Disposal: Laboratory Development. A computer code was developed for retrieving and correlating the mass of data generated in the program for developing glassy melts for the fixation of high-level waste. Initial read-out was obtained on 356 ORNL melt compositions. Melts have been prepared which contained up to 32% total waste oxides, including simulated fission products expected from fuel burned to as much as 35,000 megawatt days/metric ton (Mwd/tonne). These materials melt at about 800°C and are sufficiently fluid at 850°C or 900°C to permit their use in a continuous melting process.

Melts containing simulated fission products from a fuel burnup of 10,000 Mwd/tonne were successfully run in semiengineering-scale continuous melters. In these tests, phosphate volatility was generally $< 0.5\%$, and sulfate volatility $< 5.0\%$. There were, however, some anomalous results with these constituents as well as with iron and ruthenium.

Of a number of candidate materials of construction exposed in a continuous melter at 950°C, only platinum was unattacked. A 50% Cr-50% Ni

alloy was relatively resistant and might prove usable in a melter operating at a lower temperature. Inconel ranked third. Stainless steel types 304L, 310, 347, and Carpenter 20SCb, Hastelloys B, C, and F, Ni-o-nel, Nichrome and BM1-HAPO 20 were the other materials tested.

The measured viscosity of a melt incorporating solids from a Purex waste was 11.4 poises at 800°C. The viscosity was measured by a restrained-sphere apparatus, which employs a comparative method to determine viscosity. An advantage of this method is that density as well as viscosity can be determined as a function of temperature. The density of the melt was 2.06 g/ml at 800°C. The melt used in these studies contained 20 wt % oxides from Purex FTW-65 (without simulated fission products). The additives used in its formation were H_3PO_4, LiOH, NaOH, and $Al(NO_3)_3$.

Foam Separation: Laboratory Development. Several aspects of the application of foam separation to the decontamination of low-radioactivity-level process waste water (LLW) were studied. First, general studies were made of (1) the analysis of solutions having radionuclides in the very low range - 500 to 50,000 μμc/liter, (2) the rapid determination of alkylbenzene sulfonate in LLW, and (3) the screening of biodegradable surfactants. Studies in support of the ORNL foam-separation pilot plant included an evaluation of various gas distributors and an analysis of the dynamics of a foam column having a square cross-section. Other experiments were performed to observe the effects of operating variables, such as chemical concentrations, contact time, and volume reduction, on the one-step process for LLW decontamination.

Final results obtained with the two-step process are also presented, including an evaluation of grundite clay for cesium removal and decontamination factors for Ca, ^{85}Sr, ^{137}Cs, ^{60}Co, ^{106}Ru, and ^{144}Ce.

Foam Separations: Pilot Plant Test. The pilot plant work on the scavenging-precipitation foam-separation process has been terminated. The objective was to decontaminate very slightly radioactive, yet voluminous, process waste water sufficiently well to allow its return to the environs. It was demonstrated that the equipment is capable of treating the water at a rate of 2 gpm and of achieving a strontium decontamination factor of over 1000. The activity concentration of the treated waste was only 2.3%

of the MPC_w (occupational) for a 168-hr week. Analyses for other radionuclides have not been completed. The capacity of the system was limited by the present air-supply equipment and the capacity of the centrifugal foam breaker now in use.

Water-Recycle Process. Mixed phosphates present in raw low-radioactivity-level waste (LLW) inhibited calcium precipitation in the scavenging step of the Scavenging-Precipitation Ion-Exchange process. Use of the most economical, commercial activated alumina tested, ALCOA F-1, removed more than 99% of four phosphates tested for more than 3000 bed volumes (BV) (equivalent to 15,000 BV for a feed 1 ppm in phosphate) in downflow operation through a packed bed of solid. The ortho form had the least capacity on F-1 alumina and therefore was the form which is controlling. The capacities were 9, > 30, > 30, and > 25 mg as PO_4^{3-} per gram of F-1 alumina for the ortho-, pyro-, tripoly-, and hexametaphosphates, respectively, after about 5×10^4 BV had been processed (based on a feed concentration of 1 ppm). The less efficient method of upflow through a fluidized bed of solid is used for treating raw low-level waste (LLW) because of the presence of suspended solids. In this manner, a maximum of only 80% of the mixed phosphates in LLW were removed by a fresh bed of F-1 alumina. After about 40,000 BV (1-ppm basis), the total amount of mixed phosphates removed was about 20 mg as PO_4^{3-} per gram of F-1 alumina. Regeneration of the alumina was accomplished with 12 BV of reagent, which included 1 M NaOH and 1 M HNO_3. The liquid-waste volume-reduction factor was estimated to be 5000 (1-ppm basis).

Initial evaluation of a water-recycle flowsheet was made consisting of (1) batch clarification of LLW using zeta-potential-controlled additions of coagulant and coagulant aid, (2) demineralization of the supernatant through a mixed cation-anion ion exchange column, and (3) treatment with a column of activated carbon. Overall decontamination factors at 10% conductance breakthrough or 200 BV were estimated to be: > 200 for ^{106}Ru, > 1300 for ^{60}Co, 300 for ^{137}Cs, 1000 for ^{90}Sr, > 600 for ^{144}Ce, and > 25 for ^{95}Zr-Nb. Demineralization was accomplished for 175 BV with waste water and with tap water, 210 BV. Thus, with the use of recycle water, where the salt content would be expected to be about 20% of that

in present LLW, the volume of waste processed for demineralization and decontamination could probably be as high as 1000 BV.

Incorporation of Intermediate-Level Waste in Asphalt. Asphalt products containing 20 to 60 wt % solids from simulated ORNL waste-evaporator bottoms have been leached with water for periods of up to 9 months. The product containing 60 wt % solids from waste reaches an apparent steady-state leach rate that corresponded to a penetration of 3×10^{-4} g cm^{-2} day^{-1}. The product containing 20 wt % solids reaches an apparent steady-state leach rate of 1.5×10^{-4} g cm^{-2} day^{-1} or half that of the 60% product. The difference between leach rates determined by gamma counting of ^{137}Cs and flame-photometric determination of sodium in the same leachate was negligible. The leach rate of an asphalt product containing 60 wt % solids was not effected by irradiation to an absorbed dose of 10^8 rads.

Engineering, Economic, and Safety Evaluations. A detailed estimate of the costs of "perpetual" tank storage of wastes is being undertaken to establish a basis for comparison with costs for alternative waste-management schemes. In this study, the concept of double containment of radioactivity is applied throughout; and in all instances, the design and operation of the facility emphasizes safety over any potential savings in cost.

Storage of Purex and Thorex solvent extraction raffinates as both acid and alkaline solutions is considered, and storage of Zirflex and Sulfex decladding wastes in alkaline form is postulated. In each case the volumes are adjusted to the smallest values consistent with efficient removal of decay heat. As acid solutions, Purex wastes are stored at a concentration of 0.1 gal per kg of fuel processes, and Thorex wastes are stored at 0.2 gal/kg. Under alkaline conditions, the wastes are stored at 0.6 and 1.2 gal/kg, respectively. Zirflex wastes are stored at 1.8 gal/kg, and Sulfex wastes at 2.0 gal/kg.

In this study, the tanks are enclosed in steel-lined concrete vaults for secondary containment and are similar to those at Savannah River. Decay heat is removed by circulating water through banks of coils submerged in the waste. Costs are being developed for use in a computer code that calculates the total storage costs based on the optimal tank size for a given filling rate and return on investment.

Disposal in Deep Wells. Solution-dispersion coefficients were measured in Berea sandstone as a function of flow rate. The experimental values of the dispersion coefficients varied with the 1.22 power of the solution velocity. This agrees more closely with the power of 1 expected on the basis of a statistical model than with the power of 2 expected on the basis of a capillaric model. Molecular diffusion contributes negligibly to the total dispersion except at very low flow rates.

At the site of the hydrofracture experiment four wells were cored to obtain grout samples for analysis. No grout sheets were found in the wells 100 ft north and 100 ft northwest of the injection well. Samples of grout from injection 5 and probably from injection 1 were obtained from the well 100 ft northeast. A sample of grout from injection 5 was obtained from the well 100 ft south; coring of this well is continuing. No leakage of water or activity from any grout sheet was observed.

Disposal in Natural Salt Formations. Preparations for Project Salt Vault (demonstration of disposal of highly radioactive solid wastes in a salt mine) are on schedule. Most of the topside facility and mine renovations are complete, and the waste-charging shaft has been installed. Mining of the experimental area is about 67% complete.

The underground waste transporter passed acceptance tests in the mine. The surface shipping carrier is being tested at ORNL. Design of most auxiliary equipment and experimental instrumentation is complete and is either on hand, on order, or out for bids.

Phase I of the prototype test (one hole) was completed after 48 days of operation. Operation was essentially as expected, although some changes in design were made as a result of the test. The test was restarted (Phase II) on November 9 to obtain long-term corrosion data. Phase I confirmed the sensitivity and adequacy of the plastic-flow instrumentation planned for the demonstration.

A degassed ceric sulfate dosimeter appears to be best suited for measuring the radiation dose to the salt at elevated temperatures.

A series of creep tests of up to several thousand hours' duration is underway on model salt pillars. Tests have been run at ambient temperatures, 60°C, and 100°C. An empirical equation which gives a reasonable fit to the creep-rate data is: $\dot{\epsilon} = 3.2 \times 10^{-36} T^{10.9} \sigma^{3.2} t^{-0.65}$.

Clinch River Study. In the lower 21 miles of the Clinch River, an inventory showed that about 200 curies of radioactivity are in the bottom sediments. Over three-quarters of it is ^{137}Cs. Other principal radionuclides found in the sediment are ^{60}Co, ^{106}Ru, ^{90}Sr, and rare earths. Comparison of the inventory to quantities of these radionuclides released over White Oak Dam seems to indicate that only the retention of cesium (about 20%) is important.

By use of mathematical models coded for Data Control 1604 computer, calculations were made of dose received by the skeleton, total body, and thyroid of individuals of various ages due to ingestion of contaminated water and contaminated fish. Of the organs anlyzed, the skeleton of the male receives the largest dose. In all cases the dose to the critical organ of the potentially critical groups is significantly smaller than permissible levels.

White Oak Creek Basin Study. About half of the 70-acre site of proposed burial-ground 6 in Melton Valley is believed to be suitable. The remainder is either too steep for convenient operations, has unsuitable ground-water conditions, or lies beneath power wires.

Disposal of Gases. The desorption of iodine from Clinch River Floodplain sediment with either water or air gives a rapid initial desorption of the loosely bound iodine (probably iodine that is condensed in the pores of the sediment). This is followed by a slower desorption of the more tightly bound iodine (probably iodine that is adsorbed onto surfaces of the sediment). The amount of bound iodine is a function of the temperature of the system.

For the results of the tests to date at ORNL (13 samples, total) the following empirical equations give reasonable fits for times from 10 hr on:

$$\dot{\epsilon} = 3.2 \times 10^{-36} T^{10.9} \sigma^{3.2} t^{-0.65} ,$$

$$\epsilon = 9.2 \times 10^{-36} T^{10.9} \sigma^{3.2} t^{0.35} + A ,$$

where

$\dot{\epsilon}$ = strain rate (vertical convergence, μin. in.$^{-1}$ hr^{-1}),
ϵ = cumulative deformation (μin. in.$^{-1}$),
T = absolute temperature (^{o}K),
σ = average pillar stress (psi),
t = time (hr),
A = total deformation at 10 hr.

At ambient temperature these equations give approximately the same results as the ones derived from the APL tests. (It should be noted that $\dot{\epsilon}$ is in units of "per hour," whereas in the previous report the units used were "per day.") Although the data are still too sparse to attempt a statistical analysis, the results appear to corroborate the hypothesis that the effect of elevating the temperature is essentially the same as that of increasing the average pillar stress.[31] That portion of the hypothesis involving the ultimate strength of the salt has not been tested yet due to the difficulty of establishing an ultimate strength value for salt at ambient temperature in a pillar model with a 4-to-1 width-to-height ratio. One attempt failed when the 5/8-in.-thick steel restraining rings yielded at a pillar stress of 14,000 psi, while the pillar itself showed no signs of having reached its ultimate load.

7. CLINCH RIVER STUDY

7.1 Inventory of Radioactivity in Bottom Sediments of the Clinch River

P. H. Carrigan, Jr.

An inventory of radionuclides associated with the bottom sediments in the lower Clinch River was made. The reach included in the inventory extends from the mouth of White Oak Creek to the mouth of the river, 21.0 miles.

The source of the radionuclides in these sediments, as shown by Cottrell,[32] was the release of low-radioactivity-level radioactive waste waters from the Oak Ridge National Laboratory into White Oak Creek basin and, thence, into the river through White Oak Dam.

Results of the inventory indicate that the following quantities of radioactivity are associated with the bottom sediments: 154.6 curies of ^{137}Cs, 17.5 of ^{60}Co, 15.5 of ^{106}Ru, 10.2 of rare earths, and 2.9 of ^{90}Sr, totaling 200.7. Cesium-137 constitutes 77% of the total radioactivity. The following percentages of the total activity were found for the other radionuclides: ^{60}Co, 8.7; ^{106}Ru, 7.7; ^{90}Sr, 1.5; and rare earths, 5.1.

Most of the radioactivity was found to be downstream from Mile 15; approximately 95% of the identified radioactivity was in this downstream reach. At least 50% of the identified radioactivity was downstream from Mile 8.7.

Comparison of the quantities of radionuclides associated with the bottom sediments to the quantities of these radionuclides released through White Oak Dam (allowing for decay) indicate that about 21% of the ^{137}Cs released has been retained in the sediments, about 9% of the ^{60}Co, about 0.4% of the ^{106}Ru, and about 0.2% of the ^{90}Sr. It is difficult to estimate the percentage retention for the rare earths because of the variety of half-lives involved in trying to compensate for the decay of releases.

The total volume of radioactive sediments in the 21-mile reach is 84.8 million ft^3 (1946 acre-feet); the total weight of radioactive sediments in the reach is 4.08 million tons (wet weight).

The longitudinal variations of mean concentrations of the radionuclides, of radioactive sediment area, and of radioactive sediment thickness are shown in Figs. 7.1, 7.2, and 7.3.

7.2 Methods of Computing Inventory

First, the mean concentration of the radionuclides in the radioactive portion of each core was determined. The procedure for making these determinations was as follows:

After the distribution of gross gamma radioactivity in the cores had been determined with the core scanner, each core was cut, longitudinally, into one-half and two-quarter sectors. The radioactive length of one of the quarter sectors was selected for compositing so as to provide samples for determination of the mean concentrations of the radionuclides. The volume and wet weight of the radioactive quarter-sector was measured, and then the sediment was thoroughly mixed with a household-type electric mixer to obtain a homogeneous composite. The composite was dried and weighed. Aliquots of 100 g and 50 g were split (with a Jones splitter) from the dry composite for radiochemical analysis. The 100-g aliquot was used for gamma-spectrum analyses of the composites. Determination of the concentration of gamma-emitting radionuclides was made through computer analysis of the spectra, using a ten-standard base for comparison. The 50-g aliquot was sent to the Low Level Counting Facility (Analytical Chemistry Division, ORNL) for determination of the concentrations of ^{90}Sr and the rare earths by wet-chemical methods.

Of the 105 cores used in making this inventory, there were 17 for which the thickness of the radioactive zone was not known. By a core-correlation computer program,[33] the thickness of the radioactive zone for the nine gross-gamma-scanned cores could be estimated. For the remaining eight cores, the depth of the radioactive zone was estimated to be at the depth of penetration of the coring tool, on the basis of data from adjacent cores. For the dredge samples, the thickness of the sample was estimated on the basis of the volume of sample collected and geometry of the dredge.

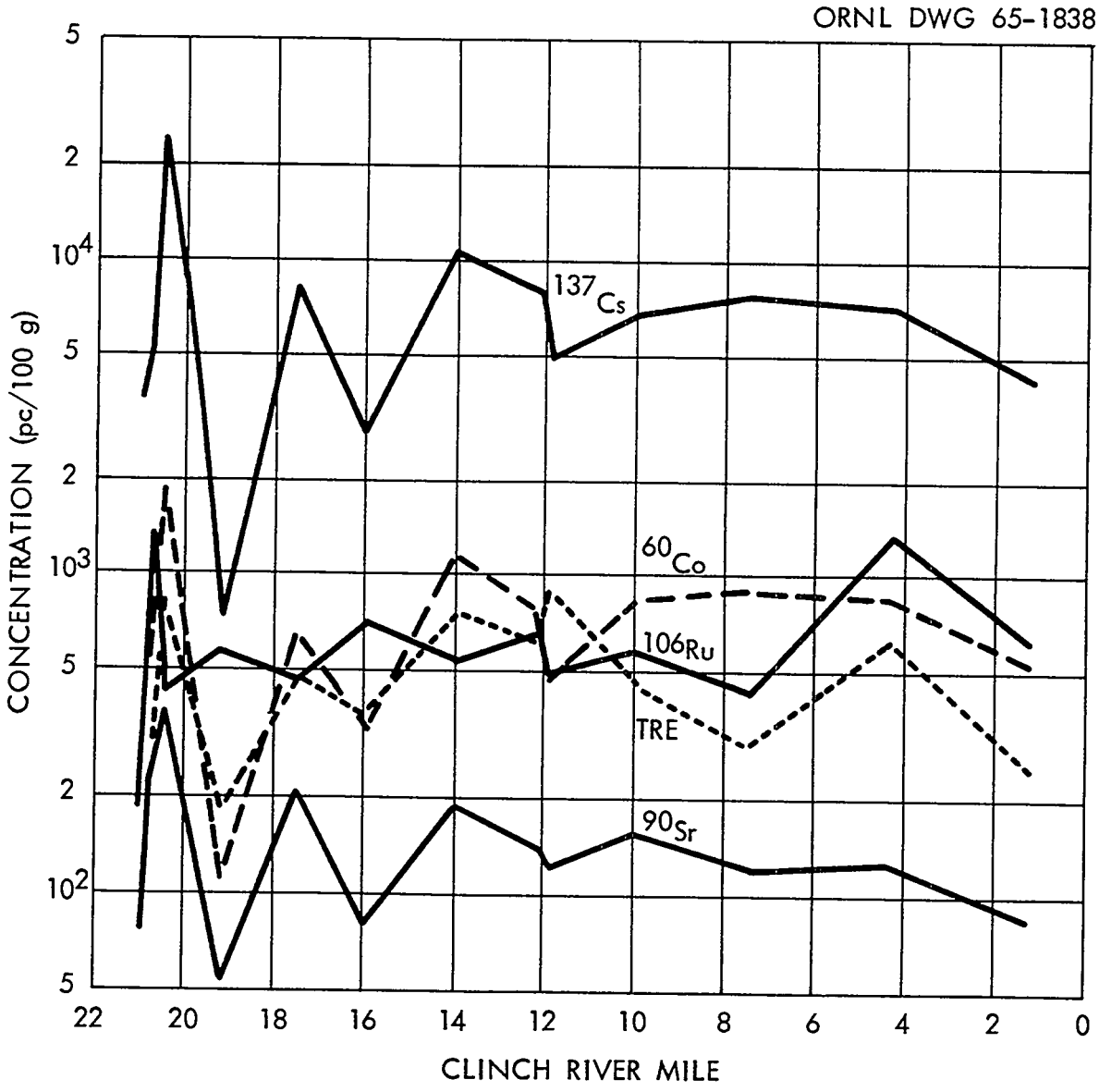


Fig. 7.1. Longitudinal Variation in Mean Concentration of Principal Radionuclides in Bottom Sediments of Clinch River.

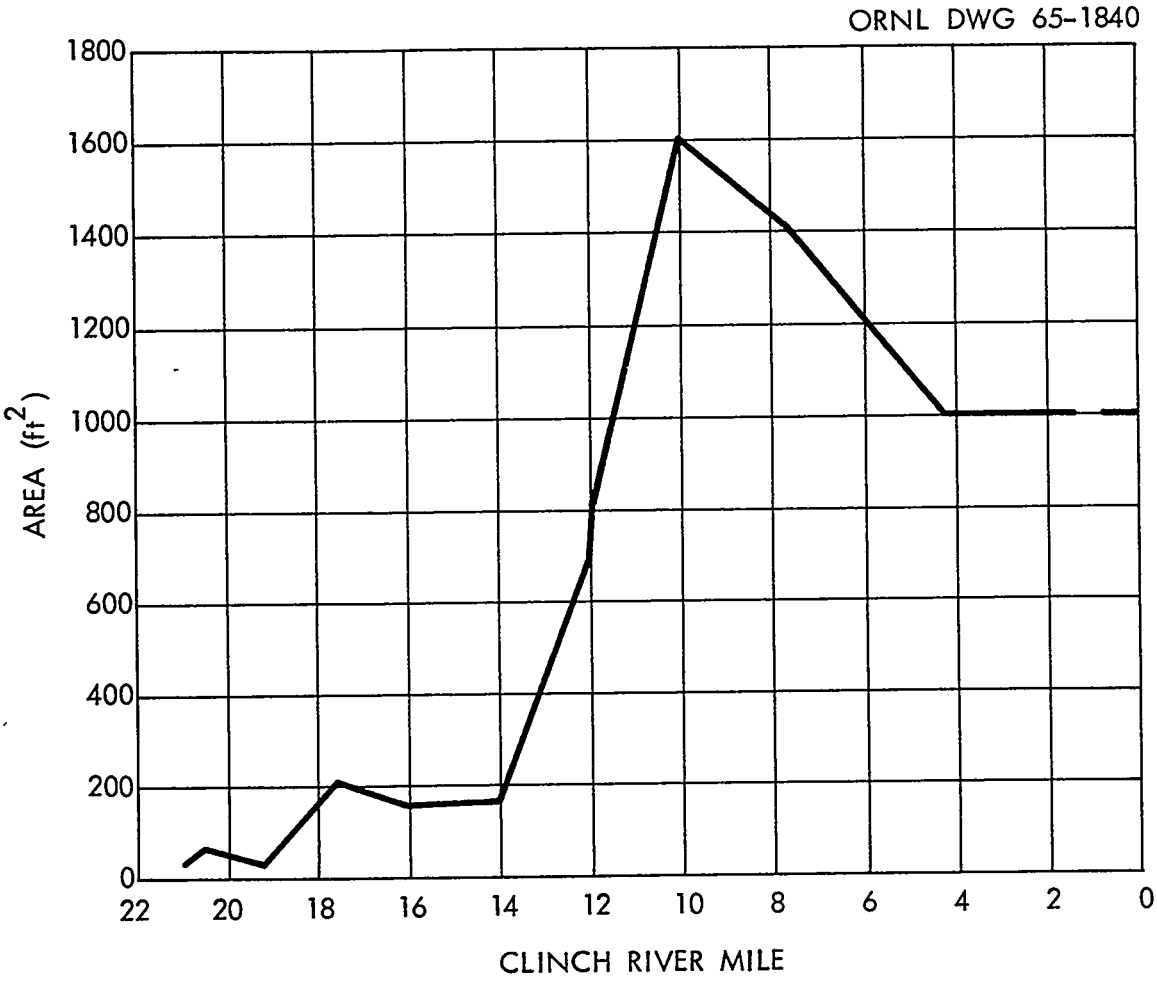


Fig. 7.2. Longitudinal Variation in Cross-Sectional Area of Radioactive Bottom Sediments of Clinch River.

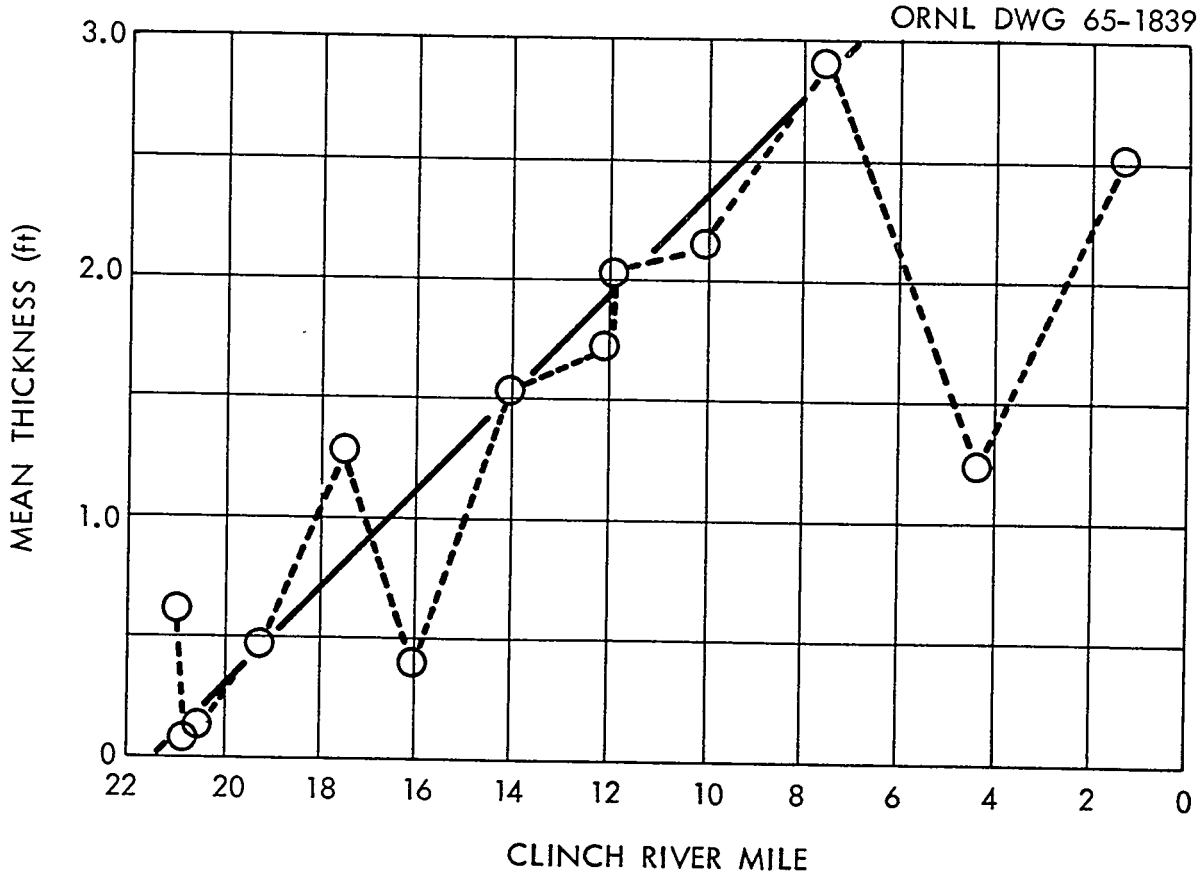


Fig. 7.3. Longitudinal Variation in Mean Thickness of Radioactive Bottom Sediments in Clinch River.

The concentration of radionuclides in the composite was considered representative of the concentration in a prism of sediment whose length was equal to half the distance between adjacent sampling sections, whose thickness was equal to the thickness of the radioactive portion of the core, and whose width was equal to half the distance between adjacent cores in the sampling section. At each section, the radioactive zones were estimated on the basis of the thickness of the nearest radioactive core, the shape of the cross section, penetrometer determinations of zones of bedrock, and the lateral variations in radiation levels at the surface of the sediments.

After the prism volume had been determined, the dry weight of sediment in the prism was computed by using the specific wet weight of the quarter sector and the wet-to-dry weight ratio of the composite.

The total radioactivity for each radionuclide was equal to the sum of the products of the concentration of the radionuclide, in curies per gram (dry weight), and dry weight of the prism.

Most of these computations having to do with the total quantities of the radionuclides, and with other information such as the radioactive cross-sectional areas and mean thicknesses of the radioactive sediments, were made using the CDC-1604 digital computer at ORNL.

7.3 Hazard Analyses

K. E. Cowser

Mathematical models that permitted machine computations of critical organ burdens and dose due to ingestion of known concentrations of radionuclides were devised and coded for the Data Control 1604 computer.[34] The MPC_w values follow the recommendations of ICRP, Publication 2. Due to the recent change in ^{90}Sr values recommended by ICRP, Publication 6, the calculations of dose to the total body and skeleton from ingestion of ^{90}Sr are overestimated by a factor of 2 and 4, respectively. Correction factors were included to take into account differences in rate of intake and organ size as a function of the age of the individuals. Calculations were performed by assuming that individuals of ages 0 (newborn infant) through 45 and standard man begin in 1944 to drink untreated water from the Clinch River (mile 14.5) and from the Tennessee River (mile 471). They continue to drink water from these sources through 1963,

following which water is obtained from an uncontaminated supply. It was also assumed that all water taken into the body in food or other form is equally contaminated and that intake and organ mass vary with age.

An example of the computed annual dose received by the skeleton of males drinking Clinch River water is shown in Fig. 7.4. At the end of 1963, the dose rate to the skeleton of the potentially critical population group, the 14-year-old, is about twice that of standard man. The dose rate received by the male skeleton of other age groups is less than the 14-year-old (see Table 27). The differences in dose rate are attributed to differences in intake and size of the skeleton. Strontium-90 is responsible for more than 99% of the skeleton dose; thus, smaller releases of this radionuclide in 1950 to 1952 and 1960 to 1964 are reflected by a reduction in annual dose received by the skeleton. Notice that the dose rate to the skeleton of the potentially critical group is smaller than 2.8 rems per year; that is, smaller than 1/10 of the continuous occupational levels that ICRP recommends not be exceeded. Dose rate to the total body and thyroid of the potentially critical groups in 1963 is about 50% larger than that of standard man. Similar differences are found for the Tennessee River (Table 27), but in all cases, the dose rates to the critical organ of the potentially critical groups is at least one order of magnitude smaller than permissible levels. The dose rate received by males is larger than that received by females for all age groups and critical organs considered.

Another interesting comparison is the total dose received by individuals during the period in which Clinch River and Tennessee River water is consumed. As shown in Table 28 the skeleton of a 14-year-old male may receive a total dose of 10.8 rems by use of Clinch River water and 1.4 rems by use of Tennessee River water - about twice that of standard man. The total body of the 14-year-old attains a 50% larger dose than standard man. About 99% of the total body dose is due to ^{90}Sr, and fluctuations in dose rate reflect changes in ^{90}Sr release, as well as differences in intake and organ mass. The thyroid of the newborn infant receives the largest dose, which is about twice that of standard man. Strontium-90 and iodine-131 are responsible for 70% and 30% of the total thyroid dose, respectively. A large release of ^{131}I and the short effective half-life of this radionuclide result in a sizable increase in thyroid dose during

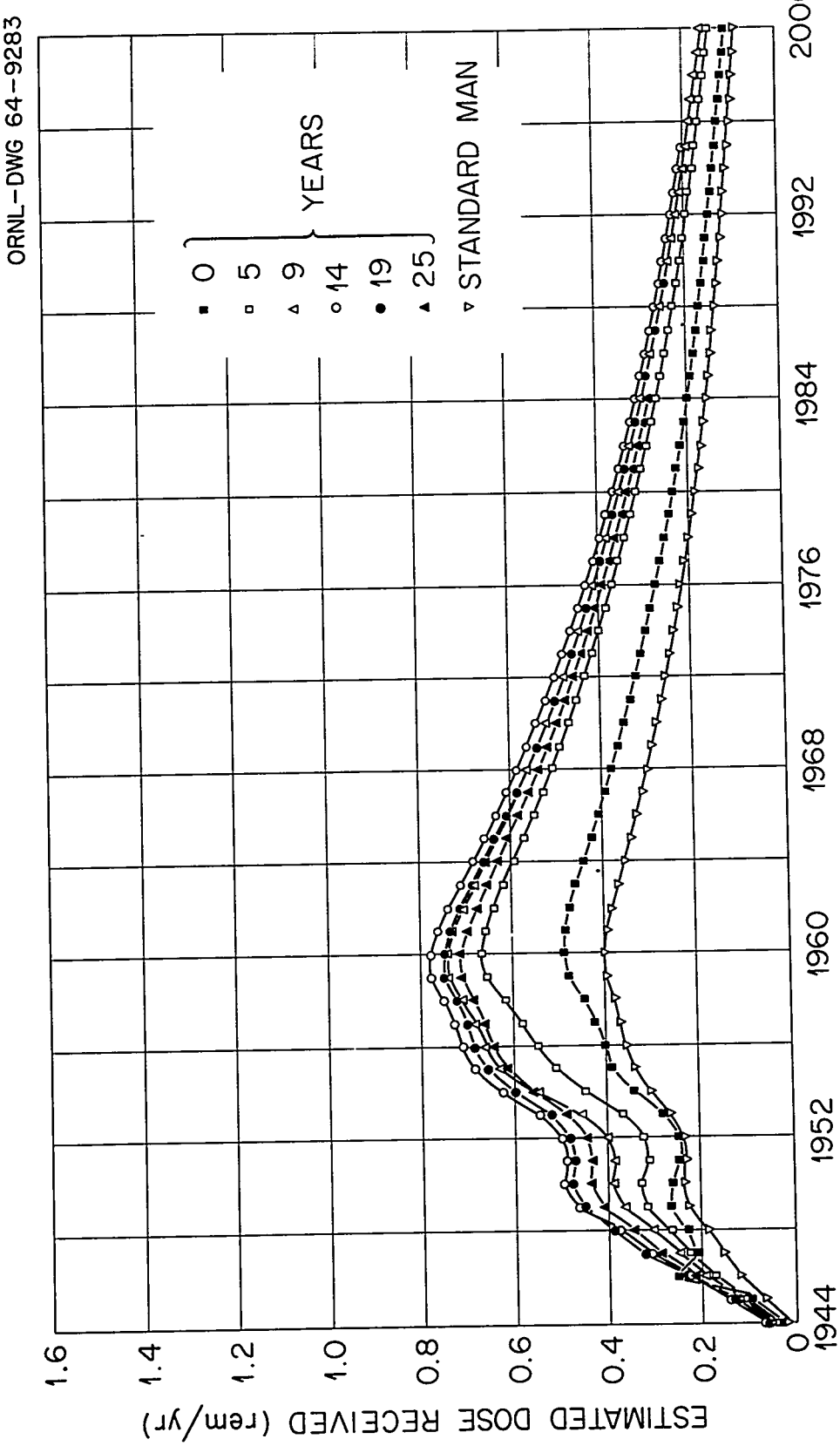


Fig. 7.4. Estimated Dose Received by Skeleton of Males from Drinking Clinch River Water.

Table 27. Dose Rate (rems/yr) to Critical Organs of Males from Drinking Water[a]

Age at Start of Exposure	Clinch River Water			Tennessee River Water		
	Skeleton	Total Body	Thyroid	Skeleton	Total Body	Thyroid
0	0.59	0.017	0.023	0.063	0.0024	0.0032
5	0.62	0.022	0.027	0.085	0.0031	0.0038
9	0.68	0.024	0.029	0.092	0.0033	0.0039
14	0.71	0.025	0.028	0.095	0.0033	0.0039
19	0.69	0.024	0.027	0.092	0.0032	0.0037
25	0.65	0.022	0.025	0.087	0.0030	0.0034
Standard man	0.37	0.017	0.017	0.049	0.0023	0.0024
Maximum permissible dose[b]	2.8	0.5	3.0	0.94	0.05	1.0

[a]The cumulative dose rate at the end of 1963.

[b]According to recommendations of the ICRP publication 2 where values of MPC_w for continuous occupational exposure are reduced to 1/10 and applied to the Clinch River and are reduced to 1/30 for skeleton and thyroid as critical organ and to 1/100 for whole body as critical organ and applied to the Tennessee River.

Table 28. Dose (rems) Received by Critical Organs of Males from Drinking Water[a]

Age at Start of Exposure	Clinch River Water			Tennessee River Water		
	Skeleton	Total Body	Thyroid	Skeleton	Total Body	Thyroid
0	6.5	0.36	0.65	0.85	0.046	0.087
5	8.4	0.39	0.61	1.1	0.051	0.082
9	9.7	0.40	0.60	1.3	0.051	0.079
14	10.8	0.41	0.59	1.4	0.052	0.078
19	10.5	0.37	0.53	1.3	0.049	0.070
25	9.8	0.35	0.48	1.2	0.045	0.063
Standard man	5.5	0.26	0.32	0.70	0.034	0.042

[a]The cumulative dose for the period 1944 to 1963.

1949. Of the organs analyzed, the skeleton of man receives the largest dose. After 1963 any dose received by the critical organs is due to radionuclides that have accumulated during the period that contaminated water is consumed. This dose commitment must be considered in any assessment of future exposure likely to be received.

The dose received by the skeleton, total body, and thyroid of man, due to consumption of contaminated water and fish, is also calculated by use of the models. In addition to the assumptions previously listed for contaminated drinking water, it is also assumed that 37 lb per year of the flesh of bottom feeders is consumed by standard man during the period 1960 to 1963. A recent survey of 80 fishermen by the Tennessee Fish and Game Commission lends support to the thesis that consumption of "fishburgers" is at most uncommon. Although the number of fishermen interviewed is small, not one indicated even occasional use of a mixture of flesh and bone. Without information on the actual rate of fish consumption as a function of age, it is further assumed that the intake of fish is distributed as the intake of water. Another way to state this assumption is that the ratio of fish eaten by an individual to that of standard man is equal to the ratio of water consumed by the individual to that of standard man.

Figure 7.5 shows the computed annual dose to the skeleton due to the consumption of contaminated water and fish. By comparison with Fig. 7.4, it is seen that the net increase in dose rate to the skeleton of individuals is small. This is due to inclusion of only 4 years of data (1960-1963) in the calculations, to the long effective half-life of the critical radionuclide ^{90}Sr, and to the reduction in ^{90}Sr released to the river. It is likely that findings of current studies by the Radiation Ecology Section will eventually permit an estimate to be made of ^{90}Sr in processed fish flesh (and the consequent dose to man) for periods in which fish data is lacking. The net increase in total dose received through 1963 by the organs of interest is given in Table 29. The cumulative dose over the 4-year exposure period is not excessive, with the skeleton receiving the largest increase, about 100 millirems. Consumption of fishburgers could result in a five- or tenfold increase of the cumulative dose. However, available information does not justify such a pessimistic assumption but does emphasize the need to define the habits of individuals living near the river system.

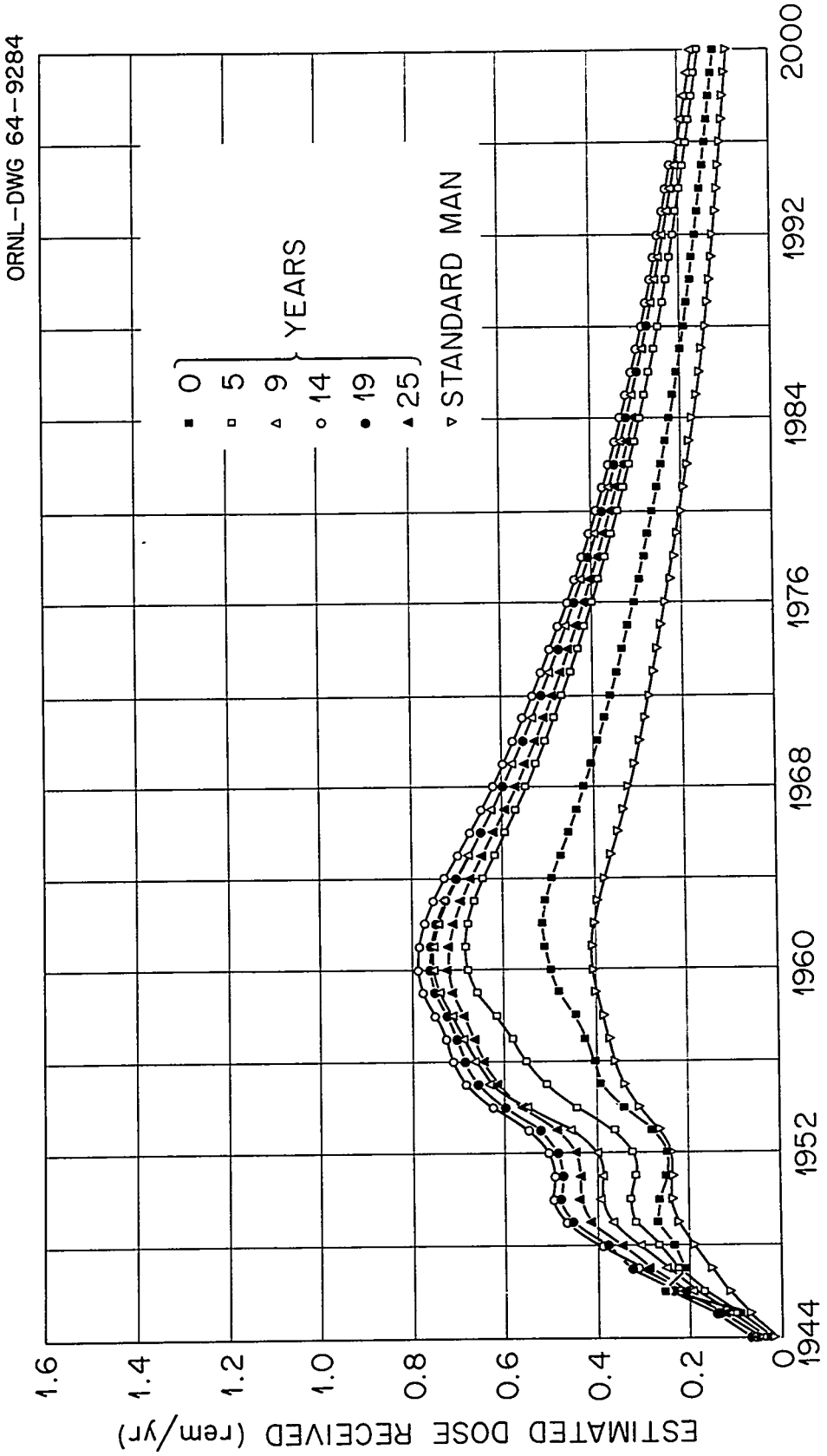


Fig. 7.5. Estimated Dose Received by Skeleton of Males from Drinking Clinch River Water and Consuming Contaminated Fish.

Table 29. Dose (rems) Received by Critical Organs of Males from Consuming Fish[a]

Age at Start of Exposure - 1944	Clinch River Water			Tennessee River Water		
	Skeleton	Total Body	Thyroid	Skeleton	Total Body	Thyroid
0	0.12	0.0063	0.011	0.048	0.0023	0.0037
5	0.12	0.0055	0.0089	0.045	0.0021	0.0031
9	0.11	0.0051	0.0078	0.042	0.0019	0.0027
14	0.11	0.0049	0.0072	0.041	0.0019	0.0025
19	0.10	0.0048	0.0069	0.040	0.0018	0.0024
25	0.10	0.0045	0.0066	0.039	0.0017	0.0023
Standard man	0.058	0.0036	0.0047	0.026	0.0014	0.0016

[a]The cumulative dose for the period 1960 to 1963.

8. WHITE OAK CREEK BASIN STUDY*

8.1 Solid-Waste Disposal

T. F. Lomenick

The proposed burial ground 6 is located in Melton Valley, immediately southwest of the Oak Ridge National Laboratory liquid-waste seepage-pit area and northwest of White Oak Lake. (See Fig. 8.1.) The area includes about 70 acres of gently to moderately sloping land, divided into several smaller sections by natural surface cuts. The site is underlain by the Conasauga shale formation of Cambrian age, consisting mainly of multicolored calcareous and noncalcareous shales interbedded with limestone lenses and resistant siltstones. In general, there is an increase in the amount of limestone and a decrease in silty layers toward the southeast. Weathering persists generally to depth of 5 ft or less in areas of low topography, and in excess of 20 ft in areas of high topography. In the extreme southern portion of the area, well-rounded pebbles and cobbles of quartzite and other resistant materials, along with sands, silts, and clay, are found immediately overlying the shale. The pebbles and cobbles, which are not representative of the surrounding bedrock, are believed to be remnants of an ancient flood plain in the nearby Clinch River.

Water-level measurements are being made periodically in a series of 40 shallow observation wells that were only recently completed within the proposed burial area, along with several existing deep churn wells, to determine seasonal variations in the depth to ground water and to define water-table configurations.

From the available information, it appears that in areas of high elevations within the burial site the weathered shale should be easily

---

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

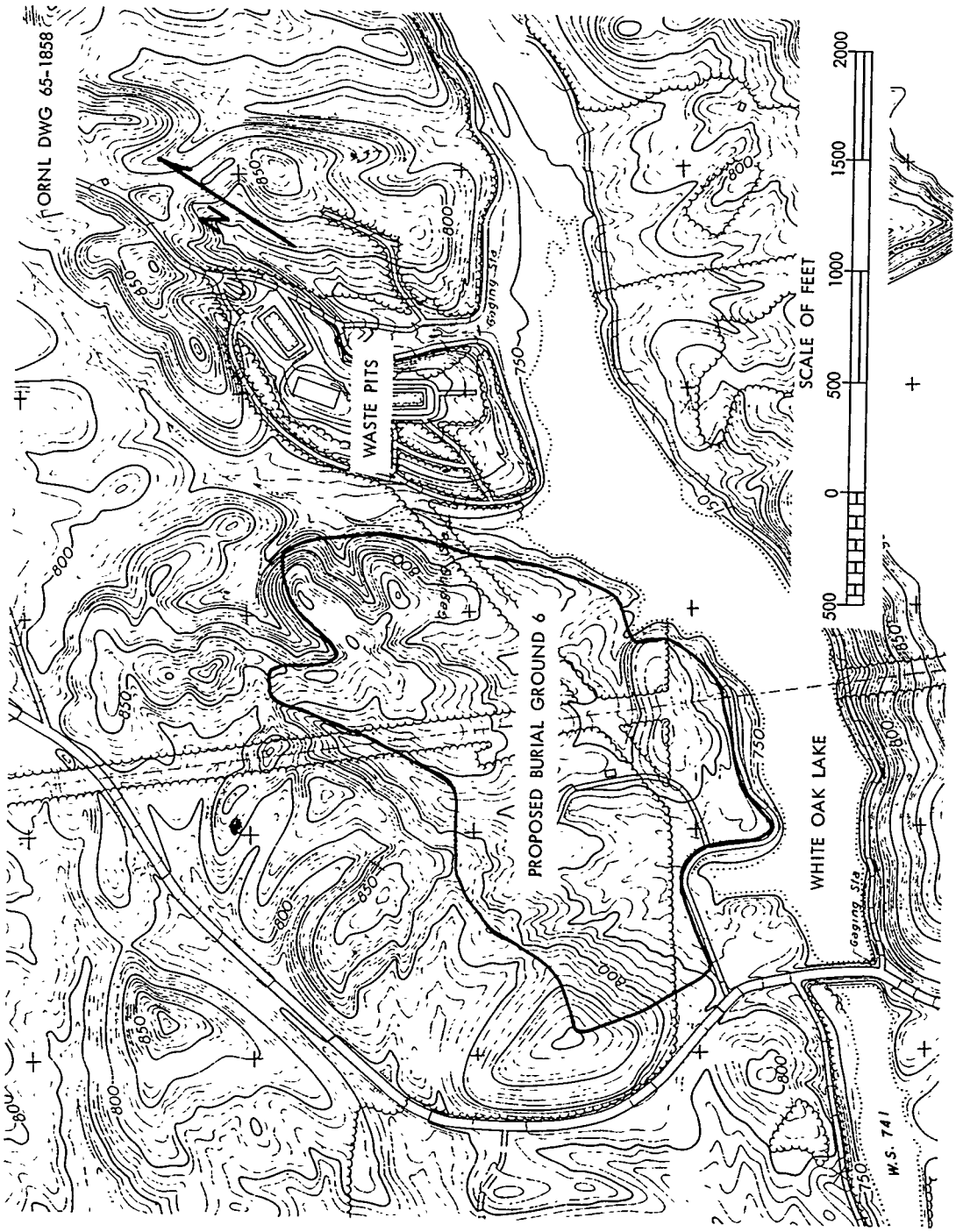


Fig. 8.1. Map of a Portion of Melton Valley Showing Location of Proposed Burial Ground 6.

excavated, and the depth to ground water is sufficient to allow the waste to be suspended a considerable distance above the water table. However, about half of the 70-acre area is believed to be unsuitable, because it is either too steep for convenient operations, has a "high" water table, or lies beneath power wires.

9. DISPOSAL OF GASES

D. G. Jacobs O. M. Sealand

9.1 Desorption of Iodine from Conasauga Shale

Sediment from the Clinch River floodplain was contaminated with iodine vapor from the oxidation of tagged KI with $FeNH_4(SO_4)_2$ to a level of approximately 0.004 mmole of I_2 per gram of sediment. The surface area of the sediment sample, determined by the Analytical Chemistry Division, was about 4 m^2/g. Thus the original iodine loading of the sediment was about 10^{-7} mmole of I_2 per square centimeter.

9.1.1 Desorption with Air

One-gram samples of the sediment were weighed into glass sample tubes equipped with ground, tapered joints to accommodate inlet and outlet fittings. The assemblies were placed in small ovens for temperature control, and air was passed through the samples at a rate of 120 ml/min. The outlet lines led into scrubbers containing 1 M NaOH. At various times the desorption process was halted and the samples counted in an NaI(Tl) well-type crystal with a single-channel analyzer.

The results (Fig. 9.1) show that desorption occurs in two phases. The initial desorption is quite rapid with the rate dependent on temperature, apparently because the iodine is loosely bound. The rate of desorption is probably controlled by the vapor pressure of the iodine at the various temperatures. After the mobile iodine has been removed, the "bound" iodine is desorbed very slowly. After 300 hr, more than 30% of the iodine remained on the samples desorbed at room temperature. Experimentally, no relationship was found between temperature and the rate of desorption of the bound iodine. Extrapolation of the second portion of the desorption curves to zero time gives a measure of the bound iodine at each temperature. These values are listed in Table 30.

An attempt was made to determine the activation energy for the desorption process from the desorption velocities at various temperatures.[35] The data were fitted to the equation:

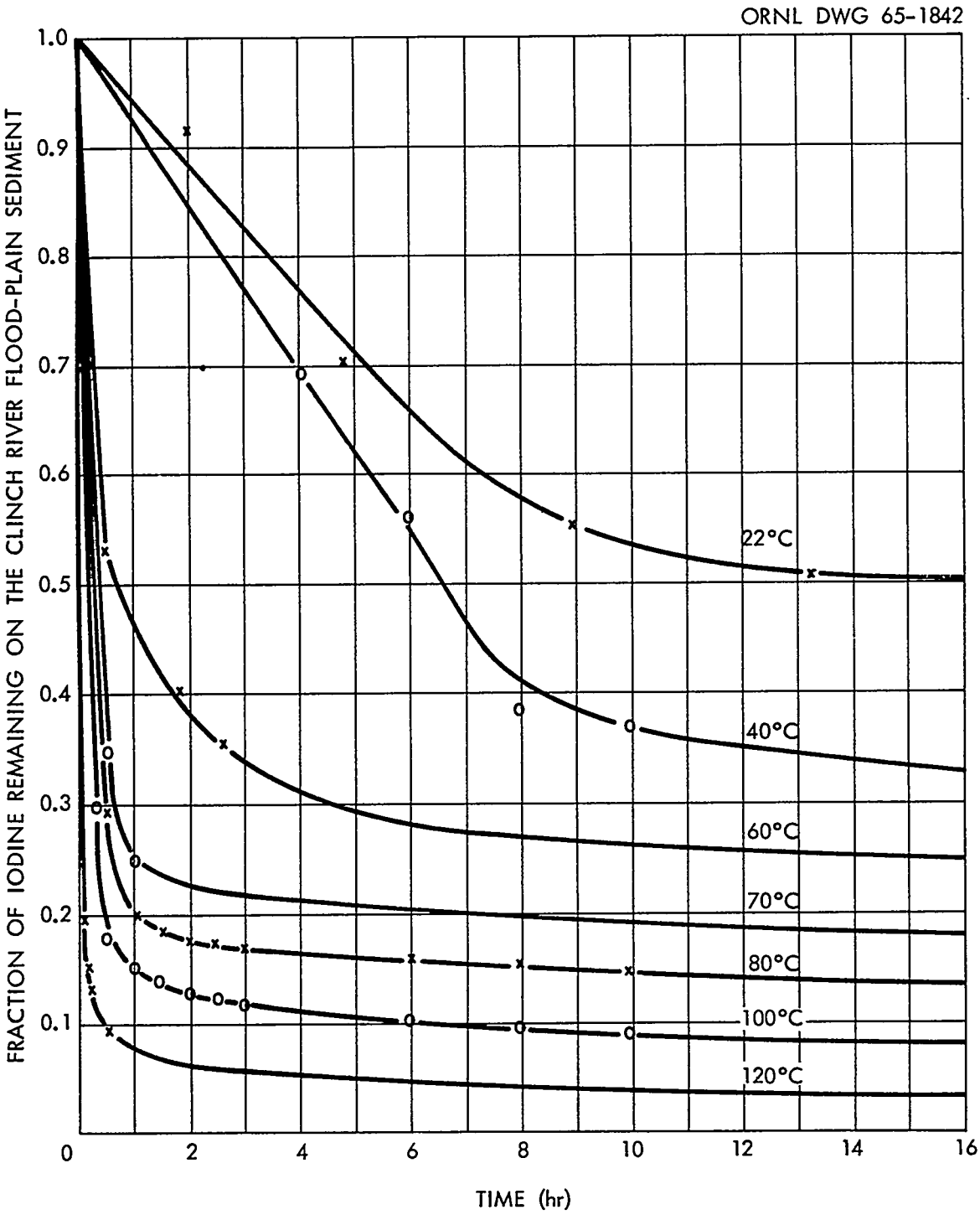


Fig. 9.1. Effect of Temperature on the Desorption of Iodine (I_2) from Clinch River Floodplain Sediment Using Air.

Table 30. Effect of Temperature on the Amount of Slowly Desorbable Iodine on Clinch River Floodplain Sediment

Temperature (°C)	Amount of Slowly Desorbable Iodine (moles/cm^2)
22	4.3×10^{-11}
40	3.3
60	2.6
70	1.9
80	1.4
100	0.88
120	0.34

$$\ln u = a - E/RT ,$$

where

a = a constant,

u = the desorption velocity (moles cm^{-2} sec^{-1}),

E = the activation energy (cal/mole),

R = the gas constant,

T = the absolute temperature.

The values of E and a were obtained from the fit of the data and are shown in Table 31. The value of a remains constant with loading, but the activation energy increases with a decrease in loading. This indicates, as mentioned above, that two desorption processes are involved. About 9.3×10^{-11} mole/cm^2 of the iodine is loosely bound, with an apparent activation energy of 6.5 kcal/mole; and 0.7×10^{-11} mole/cm^2 are more tightly held, with an apparent activation energy of 16.7 kcal/mole.

Recalculation of the desorption curves, using the extracted activation energies, indicates that the desorption equations used are too simple. The experimental curves have a greater initial desorption velocity and change more abruptly than the recalculated curves. This

Table 31. Desorption of Iodine from Clinch River Floodplain Sediment

Q^a (mole/cm^2)	a	E (kcal/mole)	β^b (mole/cm^2)
9×10^{-11}	-21.0	7.31	6.85×10^{-12}
8	-21.0	7.45	7.16
7	-21.1	7.54	6.90
6	-21.1	7.67	6.72
5	-21.9	7.98	7.12
4	-18.7	8.39	7.30
3	-20.1	8.95	7.13
2	-21.4	10.5	7.80
1	-20.8	13.5	6.85
0	--	(16.7) est.	

[a] Q is the loading of iodine on the sediment.

[b] β is the quantity of bound iodine.

suggests that the quantity of "bound" iodine, as well as the rate of desorption of the iodine, is a function of temperature.

9.1.2 Desorption with Water

Two 10-g samples of the contaminated sediment were weighed into centrifuge tubes and leached with 25-ml increments of tap water for time intervals of 30 min. The supernatant was decanted, and an aliquot removed for counting.

Most of the iodine was readily removed by the tap water (Fig. 9.2), but again it was noted that about 10% of the iodine is removed at a much slower rate than the initial 90%.

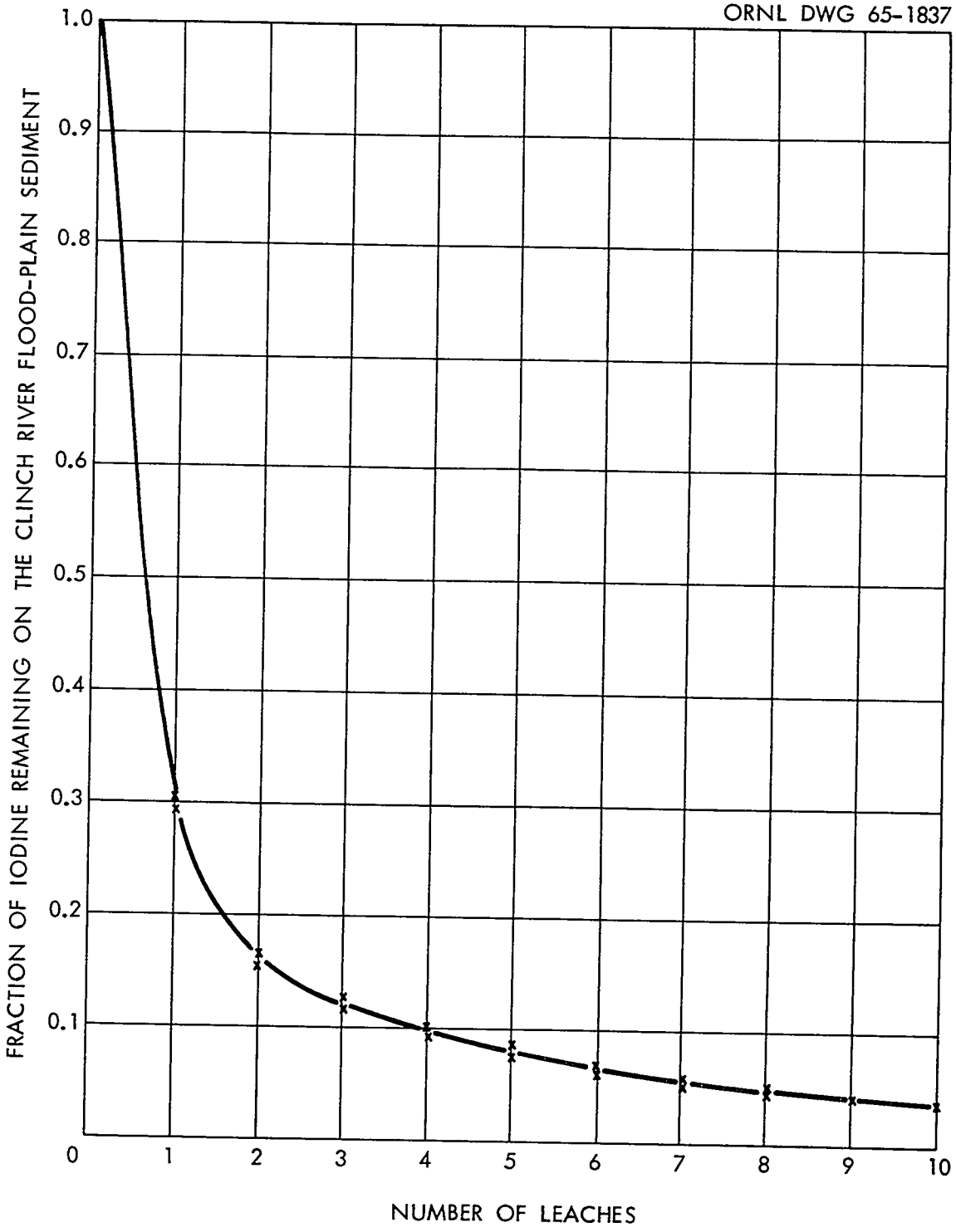


Fig. 9.2. Desorption of Iodine from Clinch River Floodplain Sediment with Tap Water.

10. REFERENCES

1. F. L. Culler et al., Chem. Technol. Div. Ann. Progr. Rept. May 31, 1964, ORNL-3627 (October 1964).

2. M. E. Whatley et al., Unit Operations Section Monthly Progress Rept. April 1964, ORNL-TM-886.

3. M. E. Whatley et al., Unit Operations Section Monthly Progress Rept. May 1964, ORNL-TM-937.

4. H. W. Godbee and W. E. Clark, Conversion of Simulated High-Level Waste Solutions to Glassy Solids in a Pot by a Rising Liquid Level Method: The RL-Potglass Process, ORNL-3629 (August 1964).

5. F. L. Culler et al., Chem. Technol. Div. Ann. Progr. Rept. May 31, 1964, ORNL-3627 (October 1964).

6. C. W. Hancher, J. C. Suddath, and M. E. Whatley, Engineering Studies on Pot Calcination for Ultimate Disposal of Nuclear Waste: Formaldehyde-Treated Purex Waste for 1965 (FTW-65), ORNL-TM-715 (Jan. 6, 1965); see also, C. W. Hancher and J. C. Suddath, Pot Calcination of Simulated Radioactive Waste with Continuous Evaporation, ORNL-TM-117 (Dec. 26, 1961).

7. R. E. Burns, R. F. Maness, D. C. Drennen, and C. L. Peterson, "Material for Nuclear Power Reactor Fuel Dissolvers," Ind. Eng. Chem., Product Research and Development 2, 163-7 (1963); see also, R. F. Maness, HW-68426 (Feb. 1961) and C. L. Peterson et al., BMI-1459 (Aug. 8, 1960).

8. Leo Shartsis and Sam Spinner, J. Res. Nat'l Bur. Standards 46, 176 (1951).

9. J. M. Holmes, Survey of Nuclear Fuel Services, Inc., Waste Compositions, ORNL-TM-1013 (Dec. 1964).

10. J. J. Weinstock, The Removal of Metallic Ions by Foaming Agents and Suspensions: Laboratory and Engineering - Interim Progress Report, July 1964, RAI.

11. E. Rubin, E. Schonfeld, and J. J. Weinstock, The Removal of Metallic Ions by Foaming Agents and Suspensions: Laboratory and Engineering Studies, RAI-116 (Dec. 1963).

12. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Quarterly Report for November 1963 through January 1964, ORNL-TM-830 (Aug. 1964).

13. E. Rubin and E. Schonfeld, Foam Separation: Quarterly Progress Report, October-December 1962, RAI-110 (Mar. 15, 1963).

14. J. J. Weinstock, The Removal of Metallic Ions by Foaming Agents and Suspensions: Laboratory and Engineering Studies, RAI-117 (Jan. 10, 1964).

15. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Progress Report for May through October 1963, p 71, ORNL-TM-757 (April 1964).

16. R. E. Brooksbank et al., Low-Radioactivity-Level Waste Treatment. Part II. Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Wastes by a Scavenging-Precipitation Ion-Exchange Process, ORNL-3349 (May 27, 1963).

17. R. R. Holcomb, Low-Radioactivity-Level Waste Treatment. Part 1. Laboratory Development of a Scavenging-Precipitation Ion-Exchange Process for Decontamination of Process Water Wastes, ORNL-3322 (July 10, 1963).

18. F. L. Culler et al., Chem. Technol. Div. Ann. Progr. Rept. May 31, 1964, ORNL-3627 (October 1964).

19. Personal communication from D. G. Stephan, Advanced Water Treatment Program, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

20. T. M. Riddick, Technical Association of the Pulp and Paper Industry (TAPPI), 47, 171 (1964).

21. T. M. Riddick, The Proceedings of the First Annual Water Quality Research Symposium, sponsored by the New York State Department of Health, New York Water Pollution Control Association, held at New York State Department of Health, Albany, New York, February 20, 1964.

22. H. A. Mahlman, "Hydrogen Formation in the Radiation Chemistry of Water," J. Chem. Phys. 32(2), 601-3 (1960).

23. J. I. Stevens, "Treatment, Processing and Future Disposal of Radioactive Wastes at the Idaho Chemical Processing Plant," 44 483-508 in Disposal of Radioactive Wastes, vol. 1, IAEA, Vienna (1960).

24. A. E. Scheidegger, The Physics of Flow Through Porous Media, p 259, Macmillan, New York, 1950.

25. I. Hashimoto, K. B. Deshpande, and H. C. Thomas, Fundamentals of Industrial and Engineering Chemistry 3(3), 213-218 (1964).

26. R. E. Collins, Flow of Fluids Through Porous Materials, p 209, Reinhold, New York, 1961.

27. M. N. E. Rifai, W. J. Kaufman, and D. K. Todd, Dispersion Phenomena in Laminar Flow Through Porous Media, Progress Report No. 2, Sanitary Engineering Research Laboratory, University of California, Berkeley (July 1956).

28. F. L. Parker et al., Health Phys. Div. Ann. Progr. Rept. June 31, 1964, ORNL-3697, p 26 (October 1964).

29. T. F. Kircher and R. G. Bowman, Effects of Radiation in Materials and Component, p 57, Reinhold, New York, 1964.

30. F. L. Parker et al., Health Phys. Div. Ann. Progr. Rept. July 31, 1964, ORNL-3697, p 28 (October 1964).

31. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, May-October 1963, ORNL-TM-757, p 132 (April 1964).

32. W. D. Cottrell, Radioactivity in Silt of the Clinch and Tennessee Rivers, ORNL-2847 (Nov. 18, 1959).

33. R. J. Pickering, "Vertical Distribution of Radioactivity in Clinch River Bottom Sediments; Results of Core Sampling and Analysis - Summer, 1962," progress report presented to the open session of the December 1964 meeting of the Clinch River Study Steering Committee.

34. R. E. Blanco and F. L. Parker, Waste Treatment and Disposal Quarterly Progress Report, February-April 1963, ORNL-TM-603, p 98 (Dec. 16, 1963).

35. D. O. Hayward and B. M. W. Trapnell, Chemisorption, pp 141-50, Butterworth's, Washington, D.C., 1964.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-1465

15

WASTE TREATMENT AND DISPOSAL SEMIANNUAL PROGRESS REPORT

JULY-DECEMBER 1965

ChemRisk Document No. 2005

Publicly Releasable

NOTICE This document has received the necessary patent and technical information reviews and can be distributed without limitation.

and wa Laborat not repi nature ational e does

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-TM-1465

CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL SEMIANNUAL PROGRESS REPORT

JULY-DECEMBER 1965

R. E. Blanco F. L. Parker

JUNE 1966

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

Solidification of High-Level Wastes: Engineering Development.--Four rising-level potglass tests were made in this report period, two (R-89, -90) with FIW-65 Purex (with sulfate) waste and two with PW 1 Purex waste (R-91, -92). Particular emphasis was placed determining the best method of adding the glass-making additives and evaluating the pot-corrosion problem. Test R-89, in an 8-in.-diam pot at 900°C, showed an excessively high corrosion rate on the pot; but a duplicate test, R-90, at 850°C, was completely successful, with negligible corrosion. A similar test in a 8-in.-diam pot at Pacific Northwest Laboratory also showed negligible corrosion. Test R-91, in an 8-in.-diam pot at 900°C, was also successful, with low corrosion. A similar test in a 12-in. diam pot showed excessive corrosion, up to 239 mils. The proportional feeding of a solution of glass-making additives (LiOH, NaOH, and H_3PO_4) to the waste feed-line is recommended as preferable to mixing directly with the waste in the feed tank.

Solidification of High-Level Wastes: Laboratory Development.--The ORNL work on waste solidification by the pot-calcination and rising-level glass processes was summarized in the ORNL section of the Operating Manual for the Waste Solidification Engineering Prototype (WSEP). Phosphate melts were developed for fixation of Purex-1 and Purex-2 waste types in glassy solids. Fixation in these melts was successfully demonstrated in semiengineering-scale experiments with solutions containing elements simulating the fission products resulting from a burnup of 20,000 Mwd/metric ton of uranium. The solid products obtained had volumes that varied from 11.1 to 17.5 gal per metric ton of uranium processed for Purex-1 waste. The best Purex-2 melt produced 14.3 gal of solid per metric ton. Low-melting-point lead silicate compositions developed for fixation of Purex-1 waste gave solid volumes as low as 9 gal of solid per metric ton of uranium.

Scoping experiments indicated the feasibility of fixing solid alumina wastes from fluidized-bed fuel processing in either phosphate or lead borate glasses at temperatures $\leq$900°C.

Incorporation of Intermediate-Level Waste in Asphalt.--Considerable interest has been shown throughout the world in the use of asphalt as a medium in which waste having an intermediate level of radioactivity can be incorporated. In the process being developed at ORNL, evaporator wastes are introduced into an emulsified asphalt, which contains about 35% water, and the water volatilized by heating to about 160°C to yield a product containing up to 60 wt % salts from waste.

Products containing 60 wt % salts from simulated waste reach a steady-state leach rate for ^{137}Cs or sodium of 3×10^{-4} g cm^{-2} day^{-1}. Hot-cell tests with concentrated actual ORNL intermediate-level waste, containing 5 curies of aged mixed fission products per gallon, confirmed these nonradioactive and tracer tests. After 5 months of leaching, a product incorporating 60 wt % salts from actual waste approached a steady-state leach rate of 2×10^{-4} g cm^{-2} day^{-1}. No radiolytic gas was released from the asphalt product over this period (an internal radiation dose of about 1.2×10^{7} rads).

Initial results with small samples, 1 or 2 g, indicate that the flash point of unirradiated asphalt, approximately 280°C, is not lowered significantly--about 50°C--when the mixture contains 35 wt % nitrate and a total of 60% salts. Further tests are continuing to determine the effect of sample size and radiation dose level.

Water-Recycle Process.--A large inventory of decontaminated and demineralized water is being accumulated from the treatment of low-radioactivity-level waste (LLW) in order to demonstrate the recycle portion of the water-recycle process. During this period, the effects of several variations in the process flowsheet are being studied. In one run, where the nitrate concentration in LLW was 20 times that normally present, low pH (4.9) resulted in poor alum flocculation, and, consequently, there was a 35-fold decrease in the overall decontamination factor (DF) for ^{60}Co. In a second run, another activated-carbon column was added to the system and located between the cation and anion exchangers. This activated carbon altered the chemistry of the ^{60}Co in the cation exchange effluent and resulted in a greater than 100-fold

decrease in the overall DF for ^{60}Co. These runs show that the pH of the raw waste must be in the range of 7 to 8 before treating it in a system that includes activated-carbon treatment after anion exchange.

Engineering, Economic, and Safety Evaluations.--The costs of "perpetual" tank storage of both acid and alkaline wastes were estimated as a function of tank size, tank life, and fission product concentration in the waste for three representative types of financing. For acid wastes, the optimum tank capacity is about a million gallons, and minimum total costs range from 0.0165 to 0.0272 mill/kwhr. For alkaline wastes, the optimum tank capacity is 2.5 million gallons, and minimum total costs range from 0.0177 to 0.0294 mill/kwhr. Reducing the volume of wastes, as stored, by doubling the concentration of fission products reduces the total costs between 15 and 30%.

The total costs for storing cladding wastes ranged from 0.0215 to 0.0398 mill/kwhr. These costs were greater than those for raffinate wastes because of the greater volumes of cladding wastes.

In a study of the safety of tank storage, consideration of the nature and extent of tank failure indicates that the most likely mechanism of release would be through loss of cooling, and that the atmosphere would constitute the major exposure pathway. Two incidents leading to major releases were postulated, and total radiation exposures to neighboring populations at various distances downwind were estimated based on dosage to the lungs resulting from inhalation, subsequent exposure to the fallout from the passing cloud, and exposure to direct radiation from the passing cloud. Exposure due to direct radiation from the passing cloud was found to be only a few percent of that from the other two sources and may be considered to be of negligible importance.

Disposal by Hydrofracturing.--The seventh experimental injection was made in the slot used for the sixth injection. The clumpiness of the solid blend used in the sixth injection was traced to the fly-ash source. The injection proceeded smoothly in spite of several changes in mix ratios demanded by differences in the waste composition. The slurry was too low

in solids, resulting in phase separation of the grout. The injection required 6-1/2 hr to complete and dispose of 78,000 gal of liquid waste.

A theoretical analysis of the uplift due to the injections of the waste-cement matrix has been developed, based on the analysis extraction mining theory.

Disposal in Natural Salt Formations.--All experimental equipment (except for the floor array) for Project Salt Vault was installed and checked out. A number of waste-handling operations were performed with dummy canisters to verify the procedures. Two canisters were loaded with 500 curies each of ^{60}Co each and transferred to Lyons, Kansas, in the shipping carrier. The canisters were lowered into the mine and removed a number of times to obtain experience in handling radioactive canisters and to test the effectiveness of the shielding.

Fourteen fuel assemblies from ETR cycle 73 were selected. The assemblies were sawed to length, loaded into the seven canisters, the canisters welded shut, leak tested, loaded into the carrier, and shipped to Lyons. On November 17-19, the seven cans, containing about one million curies of fission products, were placed in the mine. The maximum radiation dosage received by those involved in the transfers was about 200 millirads. Radiation levels immediately above the array holes are generally less than 10 mr/hr, and unlimited access is allowable everywhere except immediately over the holes.

The rise in salt temperature and the temperatures of the fuel elements are in reasonable agreement with theoretical calculations, although generally running somewhat below the predictions. Thermal expansion of the floor had reached about 1/2 in. in the center of the arrays at the end of the second week. Thermal stresses (but not yet temperature rises) have also been transmitted to the supporting pillars, as indicated by the increased flow rates of the salt in the pillars and in the roof. There have been no indications of any differences in behavior between the radioactive and control arrays, and no indications of chlorine release.

Soil Studies.--Measurement of losses of ^{137}Cs from field plots has been extended to cover 1 year of operation. Comparisons of losses among the three different cover plots are made, and the factors affecting ^{137}Cs loss are discussed.

Unusual desorption of radiocesium from three soils of Southeastern United States was reported in the Health Physics Division Annual Progress Report for 1965. It was shown that 1 M sodium acetate released radiocesium from these soils but that with increasing length of solution:soil contact time, the amount released decreased. The tests were extended to evaluate different desorbing salts and to include reference clay minerals for comparisons.

Behavior of Radionuclides in the Ground.--A computer program was written to describe the transient behavior of radionuclides in the ground when the transporting solution is of a different concentration than the original ground water. Experimental data, obtained on a Berea sandstone for different sets of conditions, confirm the model. The program is based on Glueckauf's model for the passage of a wide band of solute through a chromatographic column, modified for changes in the adsorptive capacity due to changes in the total electrolyte concentration.

Disposal of Gases into Permeable Formations.--In a nuclear incident involving fuel-element meltdown, ^{131}I appears to present the most serious short-term hazard. If the radioactive gases could be pumped underground, the delay time afforded by absorption and physical movement through the soil would allow a reduction in the relative hazard by a few orders of magnitude. Strontium-90 would present the most serious potential for contaminating ground water near the site of discharge.

Laboratory studies have been conducted on the sorption of iodine by clays. The activation energy for the desorption of iodine increases from 14.2 kcal/mole at a loading of 10^{-10} mole of I_2 per square centimeter to 54 kcal/mole at a loading of 10^{-11} mole per square centimeter for Clinch River floodplain sediment. Iodine has a heat of sublimation of 14.66 kcal/mole.

Safety Evaluation.--An age-dependent metabolic model developed by Kulp was used to estimate dose to the skeleton of males from ingestion of Clinch River water. This model yields a slightly larger estimate of dose than the adjusted ICRP model.

CONTENTS

Page

Abstract iii

1. Introduction 1

2. Solidification of High-Level Wastes 3

2.1 Engineering Development 3
2.1.1 FTW-65 Purex Waste 3
2.1.2 FW 1 Purex Waste 5
2.1.3 Conclusions 12

2.2 Laboratory Development 15
2.2.1 Preparation of Operating Manual for WSEP 15
2.2.2 Melt Development Studies 15
2.2.3 Semiengineering-Scale Fixation Tests 15
2.2.4 Ruthenium Volatility Studies 18
2.2.5 Corrosion with Phosphate Melts 20
2.2.6 Conclusions 22
2.2.7 Fixation of Fluidized-Bed Waste in Glass 23

3. Low- and Intermediate-Level Waste Treatment 23

3.1 Incorporation of Intermediate Level Waste in Asphalt . . . 23

3.2 Water-Recycle Process 26

4. Engineering, Economics, and Safety Evaluations 31

4.1 The Cost of Perpetual Tank Storage 31
4.1.1 Raffinate Wastes 31
4.1.2 Cladding Wastes 32

4.2 A Safety Analysis of Tank Storage 35

5. Disposal by Hydrofracturing 42

5.1 Objectives 42

5.2 Plant Modification and Preparation 42

CONTENTS (cont'd)

	Page
5.2.1 Plant Modifications	42
5.2.2 Solids Blending	43
5.3 Injection	44
5.4 Analysis of Data	45
5.5 Mechanical Effects of Hydrofracturing on Nearby Rocks	48
6. Disposal in Natural Salt Formations	51
6.1 Preparation for Project Salt Vault	51
6.1.1 Prototype Test	51
6.1.2 Safety Analysis	51
6.1.3 Equipment Installation	52
6.1.4 Preoperational Tests	52
6.2 Startup of Project Salt Vault	54
6.2.1 ETR Fuel Assemblies	54
6.2.2 Startup	55
6.2.3 Preliminary Results	57
6.3 Pillar-Model Studies	59
6.3.1 Effects of Shale Partings	59
6.3.2 Deformational Behavior	63
7. Soil Studies	65
7.1 Desorption of Cesium-137 from Clays and Soils	65
7.2 Movement of Cesium-137 by Runoff, Erosion, and Infiltration	70
8. Behavior of Radionuclides in the Ground	73
8.1 Nonequilibrium Ion Exchange	73
8.2 Hydroxide Consumption by Conasauga Shale	76

CONTENTS (cont'd)

Page

9. Disposal of Gases into Permeable Formations 76

9.1 Estimation of the Behavior of Radionuclides Discharged to the Ground in a Gas 76

9.2 Adsorption of Iodine by Minerals 82

9.3 Nuclear Safety Pilot Plant Runs 86

10. Safety Evaluation 87

10.1 Clinch River Safety Studies 87

11. References 90

1. INTRODUCTION

This report is the fifteenth of a series* of 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 include those of high, intermediate, and low levels of radioactivity in liquid, solid, or gaseous states.

Under the integrated plan, low-activity wastes, consisting of very dilute salt solution, such as cooling water and canal water, would be treated by scavenging and ion exchange processes or foam separation to remove radioactive constituents, and the water would be discharged to the environment. The retained waste solids or slurries would be combined with the high-activity wastes or incorporated into asphalt or concrete before disposal in concrete vaults, salt mines, or burial pits. Alternatively, the retained solids or the untreated waste could be discharged to the environment in deep geologic formations. The high-activity wastes could be stored at their sites of origin for economic periods to allow for radioactive decay and artificial cooling.

Methods investigated for the permanent disposal of high-activity liquid wastes include conversion to solids by high-temperature "pot" calcination or glass formation in the final storage container (pot) and formation of a glass or ceramic in a continuous melter. High-activity solid wastes from nonaqueous fuel processing method, such as the fluid bed-fluoride volatility process, could be packaged directly as solids or incorporated in a glassy matrix. The solids from either process would be stored in a permanently dry place such as a salt mine. This is undoubtedly the safest method because control of radioactivity can be ensured within present technology during treatment, shipping, and storage.

---

*ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, ORNL-TM-169, ORNL-TM-252, ORNL-TM-376, ORNL-TM-396, ORNL-TM-482, ORNL-TM-516, ORNL-TM-603, ORNL-TM-757, ORNL-TM-830, and ORNL-TM-1081; see also annual reports for 1962-1965, ORNL-3452, ORNL-3492, ORNL-3672, ORNL-3697, ORNL-3830, and ORNL-3849, from the Chemical Technology and Health Physics Divisions.

Tank storage or high-temperature calcination of intermediate-activity wastes may be unattractive because of their large volumes, and other disposal methods will be studied. One method, for example, the addition of solidifying agents prior to direct disposal into impermeable shale by hydrofracturing, has been investigated. Particular attention was given to the engineering design and construction of an experimental fracturing plant to dispose of ORNL intermediate—activity wastes by this method. A second method is incorporation (and dehydration) of intermediate-level wastes in asphalt.

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.

2. SOLIDIFICATION OF HIGH-LEVEL WASTES

The development programs were principally concerned with making the final tests in the development of the rising-level (RL) potglass process, using two new prototype waste compositions, PW 1 and PW 2. These compositions, to be used as new standard wastes for the development program in the U.S., were proposed early in 1965 at a meeting in Washington. These wastes differ considerably from the previous standard waste, FTW-65, because of the high iron content of PW 1 and the increase in the fission product concentration of both wastes to that equivalent to a burnup of 20,000 Mwd/metric ton. This necessitated additional melt-development studies and small-scale rising-level tests in the laboratory to develop a melt with a suitably low melting point and low corrosivity. Additional large-scale tests were also required to define pumping, heat transfer, corrosion, and other engineering variables in 8- and 12-in.-diam pots.

Previous work on high-level wastes has been confined to processing aqueous wastes. A new program was started to develop suitable treatment methods for the solids (alumina, etc.) from the Fluidized-Bed Fluoride-Volatility process. An engineering economic survey is being made to define the parameters for this work, and a topical report will be issued when the survey is completed. It will also be summarized in the 1966 annual report for the Chemical Technology Division (ORNL-3945).

2.1 Engineering Development

J. C. Suddath C. W. Hancher

2.1.1 FTW-65 Purex Waste

A final test (test 90) of the RL potglass process with FTW-65 Purex waste was made in an 8-in.-diam x 96-in.-high pot (Tables 1,2,3). The operating temperature was limited to 850°C since laboratory studies had indicated that the viscosity and corrosivity of the melt were satisfactorily low at this temperature. Also, a previous test at 900°C (test 89) in an 8-in.-diam pot had shown that the corrosion rate was excessive (Table 3). Test R-90 proceeded smoothly, and the corrosion was negligible--

Table 1. Composition of FTW-65-X3 Waste, Tests R-89, R-90

Expressed in moles/liter

Constituent	Type of Waste: FTW-65-X3[a]
H^+	1.5
Na^+	0.9
Al^{3+}	0.15
Fe^{3+}	0.30
Cr^{3+}	0.06
Ni^{2+}	0.03
Hg^{2+}	0.0105
SO_4^{2-}	0.45
PO_4^{3-}	0.015
SiO_3^{2-}	0.03
F^-	0.0015
NO_3^-	~3.1
Fission Products	0.5

[a]The FTW-65-X3 represents the highest concentration of this waste type that can be conveniently simulated by direct makeup from laboratory reagents without heating the solution.

Table 2. Composition of FTW-65-X3 Purex Glass, Tests R-89, R-90

Concentration of additives expressed as g-moles per liter of waste.

Additives	
H_3PO_4	3.6
LiOH	2.4
NaOH	2.7
$Al(NO_3)_3$	0.75
Wt % waste oxides (theoretical)	
10,000 Mwd/metric ton FP's[a]	30
Approximate mp, °C	
10,000 Mwd/metric ton FP's	800

[a]Hanford-BNL simulated-fission-product composition.

Table 3. Corrosion Results in Rising-Level Potglass Engineering-Scale Test

Diameter of pot, 8-in.

Run	Waste Type	Equiv. Fission Product Level (Mwd per metric ton)	Additive[a] per of Liter Waste	Operation Temp. (°C)	Operation Time (hr)	Additive Addition Method	Maximum Corrosion Depth (mils)
R-89	FTW-65-3X	10,000	Type 1	900	45[b]	Pre-mix	320
R-90	FTW-65-3X	10,000	Type 1	850	97	Pre-mix	15[c]
R-91	PW-1	20,000	Type 2	900	67	Pre-mix	<5[d]
R-92[e]	PW-1	20,000	Type 2	900	100	Feed line	239

[a]Type 1: 2.7 moles NaOH, 2.4 moles LiOH, 0.75 mole $Al(NO_3)_3$, and 3.6 moles H_3PO_4.
Type 2: 1.27 moles NaOH, 1.37 moles LiOH, 2.4 moles H_3PO_4, and 0.1 moles NaH_2PO_2.

[b]Failure occurred.

[c]Pot cooled and solids remelted and held at 700 to 800°C for 30 additional hours.

[d]Crushing and remelting caused failure of 28-mil-wall tubing.

[e]Pot diameter, 12-in.

a total of 15 mils. The original wall thickness of the pot was 320 mils. The same melt was also successfully tested at Pacific Northwest Laboratory in a 8-in.-diam pot. In this test, a dense solid product was formed, and there was no evidence of any corrosion.

2.1.2 PW 1 Purex Waste

Purex Waste 1 (PW 1) is a synthetic waste (Table 4) about 5 M in HNO_3 and 1 M in $Fe(NO_3)_3$; it contains simulated fission products equivalent to burnup of 20,000 Mwd/metric ton. Test R-91 was a rising-level potglass test made in an 8-in.-diam pot, using simulated PW 1 waste and lithium and sodium phosphates as glass-making additives (Tables 4 and 5). Phosphite was also added to provide a reductant to decrease corrosion (see Sect. 2.2.3). The waste, additives, and simulated fission products

Table 4. Composition of Purex Waste 1, Tests R-91, R-92

	Desired Molarity	Molarity Found by Analysis
Chemical Constituents		
H^+	5.0	4.9
Fe^{3+}	0.93	0.93
Na^+	0.14	0.16
H_3PO_4	0.003	0.004
NO_3^-	7.8	8.0
Ni^{2+}	0.005	NA[a]
Al^{3+}	0.001	NA
Cr^{3+}	0.012	NA
Fission Products		
Sr^{2+}	0.015	NA
Ba^{2+}	0.019	NA
Rare earths	0.118	NA
Zr^{4+}	0.065	NA
MoO_3	0.065	

[a]NA = no analysis.

Table 5. Composition of Glass-Making Additive Mixture, Tests R-91, R-92

Concentration Expressed as gram-moles of Additive per liter of Original Feed

Additive	Desired Makeup	Found by Analysis: Average of 3 Samples	Percentage Deviation of 3 Samples
NaOH	1.27	1.256	6.5
LiOH	1.37	1.09	11.3
H_3PO_4	2.40	2.105	9.2
NaH_2PO_2	0.10	NA[a]	NA[a]

[a]NA = no analysis.

were combined in the feed tank and fed to the pot as a single stream, as in all previous tests. A precipitate formed in the feed tank, making it difficult to control the flow rate of the resultant slurry to the pot. However, the test was completed, and a satisfactorily dense glassy product was formed. Corrosion was negligible; less than 5 mils (Table 3).

Test R-92 was a duplicate of R-91, with two exceptions: (1) a 12-in.-diam pot was used to determine the effect of pot diameter on processing rate, and (2) the glass-making additives and phosphite were added as a separate, proportionated stream to the waste feed line to the pot. Test R-92, which lasted for 100 hr, was carried out in a 12-in.-diam by 6-ft-high stainless-steel (304LC) pot. The pot was heated in an induction furnace having a 15-in.-diam susceptor.

The glass-forming additives (Table 5) were added to the pot as a separate liquid stream. In the 100-hr test, the total amount of liquid feed was 852 liters of waste and 294 liters of additive; the average feed rates were 8.5 liters/hr for waste and 3 liters/hr for additive. The condensate volume represented the sum of the waste feed, the additive feed, feed-line washings (to remove plugs), and condenser washings (to remove entrained solids). The contributions to the condensate were, in liters:

Feed	852
Additive	294
Washings	260
Total	1406 liters

The waste feed rate was controlled manually, starting at 15 to 20 liters/hr and then decreasing as the test progressed. After 68 hr of operation, the pot became filled with a mixture of glass at the bottom, solid above and on the walls, and a foam-liquid mixture in the center. After this condition was reached, the feed was stopped from time to time to prevent overfilling. The top thermocouples were used as level indicators. During the test, about 100 liters of feed overflowed from the pot to the condensing system as the result of inattention of the operators. The principal overflow occurred in the 44th and 45th hours and caused a general surging of liquid and foam from the pot. During this period,

the feed rate for the waste stream was 5 times that of the average and the ratio of additives flow to the waste flow as 0.1, not the desired ratio of 0.34 (Figs. 2.1 and 2.2).

The glass-making additives (Table 5) were fed through a line teed into the waste feed additive line. The flow rate of the additive was controlled by a volume-ratio feed controller, 0.34 volumes of additive per volume of waste feed.

Both the feed line and the additive line plugged occasionally, although these lines were equipped with water purges to prevent plugging. When either of the feed lines plugged, the plug was removed by applying high-pressure water. The liquid-level-probe line in the additive tank also plugged six or seven times during the test, resulting in a false indication of a high liquid-level in the additive tank. The controller then caused the outlet valve on the additive feed tank to open until the blockage of the dip tube was removed. This malfunction, coupled with the lack of manual control of the waste feed stream, caused the ratio of additive to waste stream to vary from 4.00 to 0 during the test (Fig. 2.2). About 26% too much additive solution was fed to the pot for the first 20 hr of operation. Not until the 44th hour did the additive-to-waste ratio in the pot reach the desired value of 0.34 (Fig. 2.3). This may have caused excessive corrosion in the bottom of the pot, since laboratory experience (Sect. 2.2.5) indicates that excessive phosphate additives of this type frequently lead to excessive corrosion.

Undoubtedly, these variations in flow rates can be controlled and prevented by suitable equipment modification. Otherwise, the feeding operation in test R-92 proceeded smoothly in the absence of significant amount of solid. Consequently, proportional addition of the additives is recommended for the rising-level Potglass process.

The material balance for test R-92 is shown in Table 3. The iron balance was high (151%), probable because of pot corrosion. If the iron from corrosion is included (calculated from corrosion penetration), the material balance for iron is 96%. The balance for phosphate was low (61%).

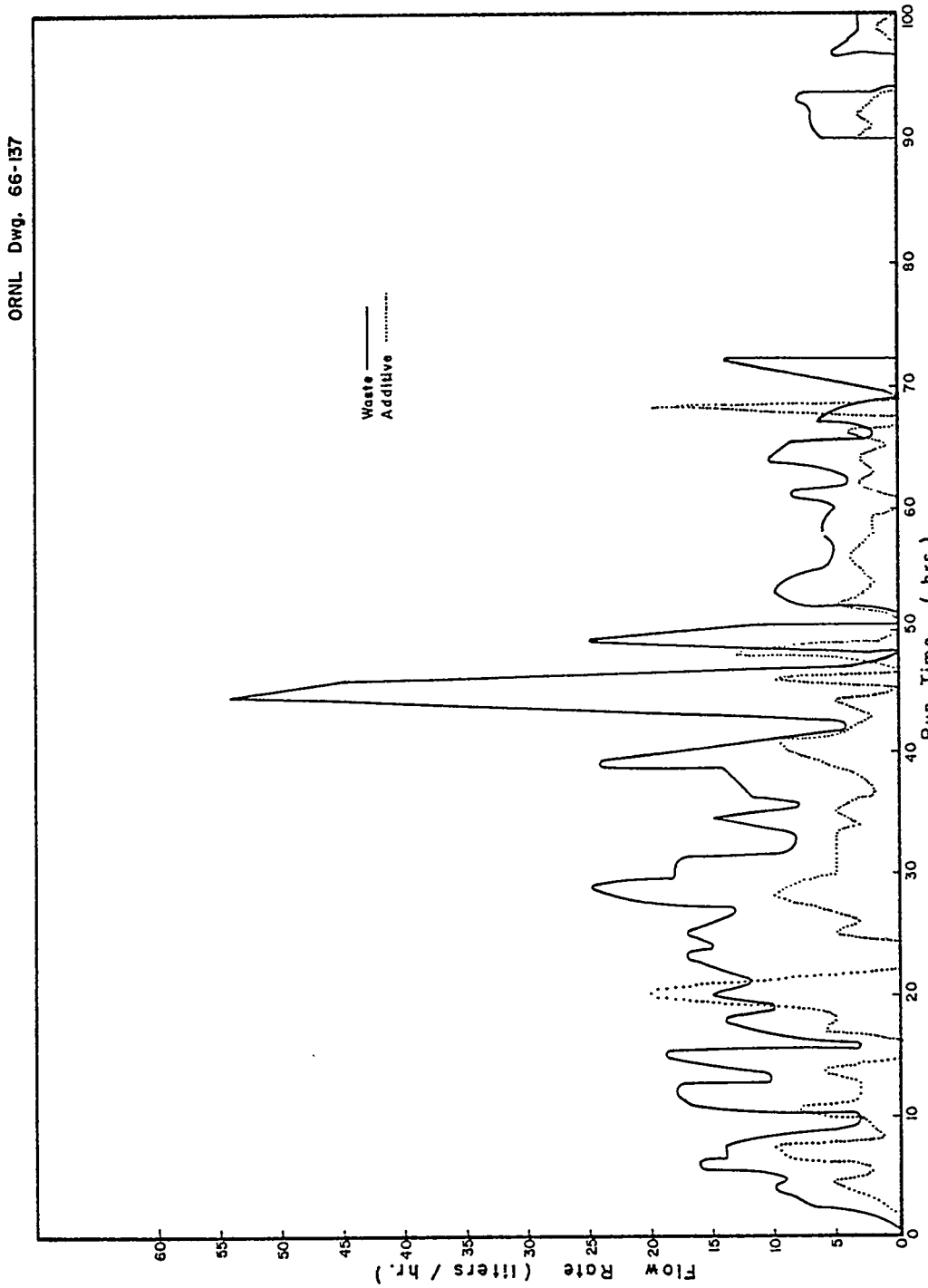


Fig. 2.1 Instantaneous Flow Rates of Additive and Waste Solutions for R-92.

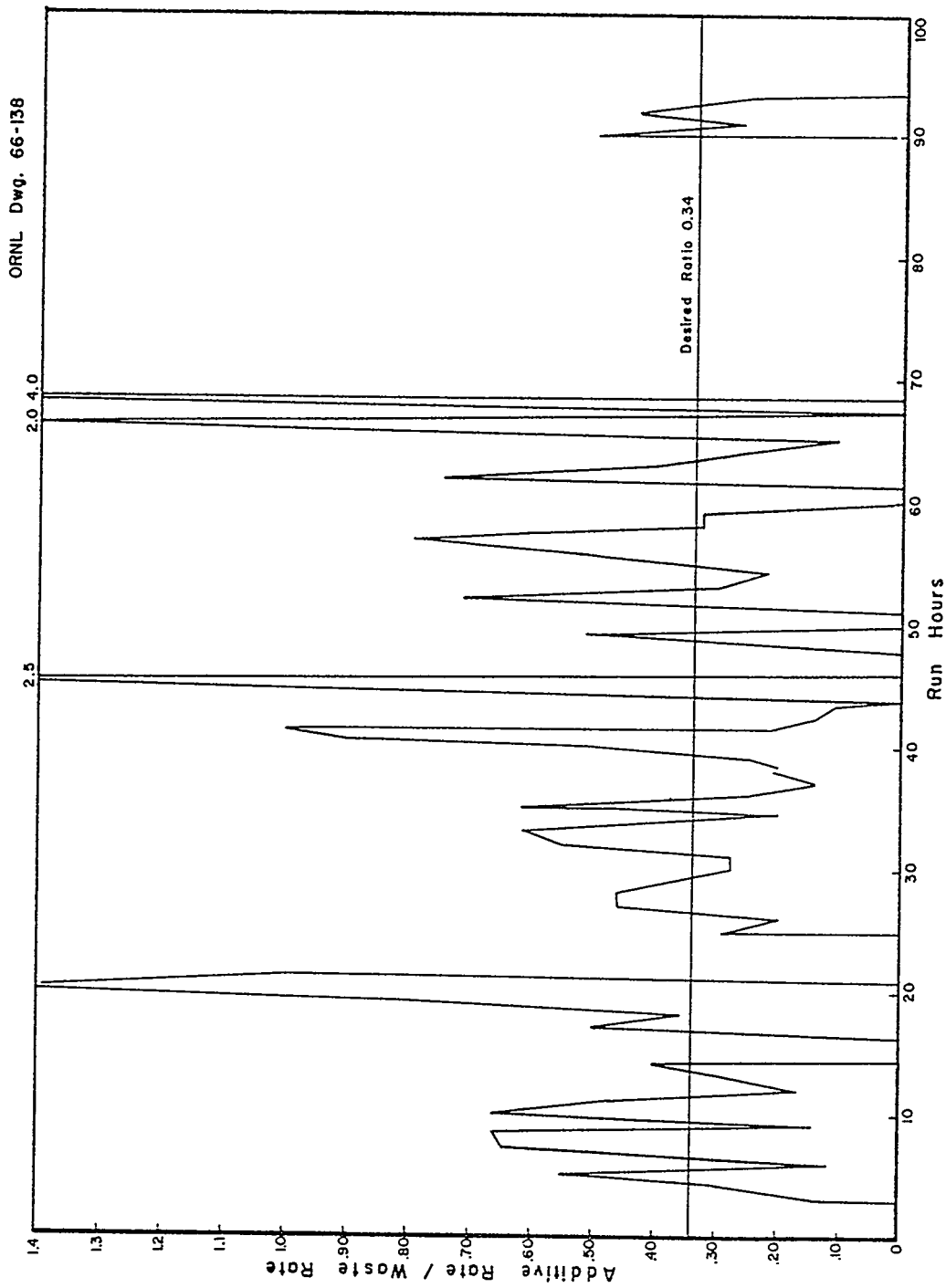


Fig. 2.2 Instantaneous Ratio of Flow Rates for Glass Additive and Waste Solution for R-92.

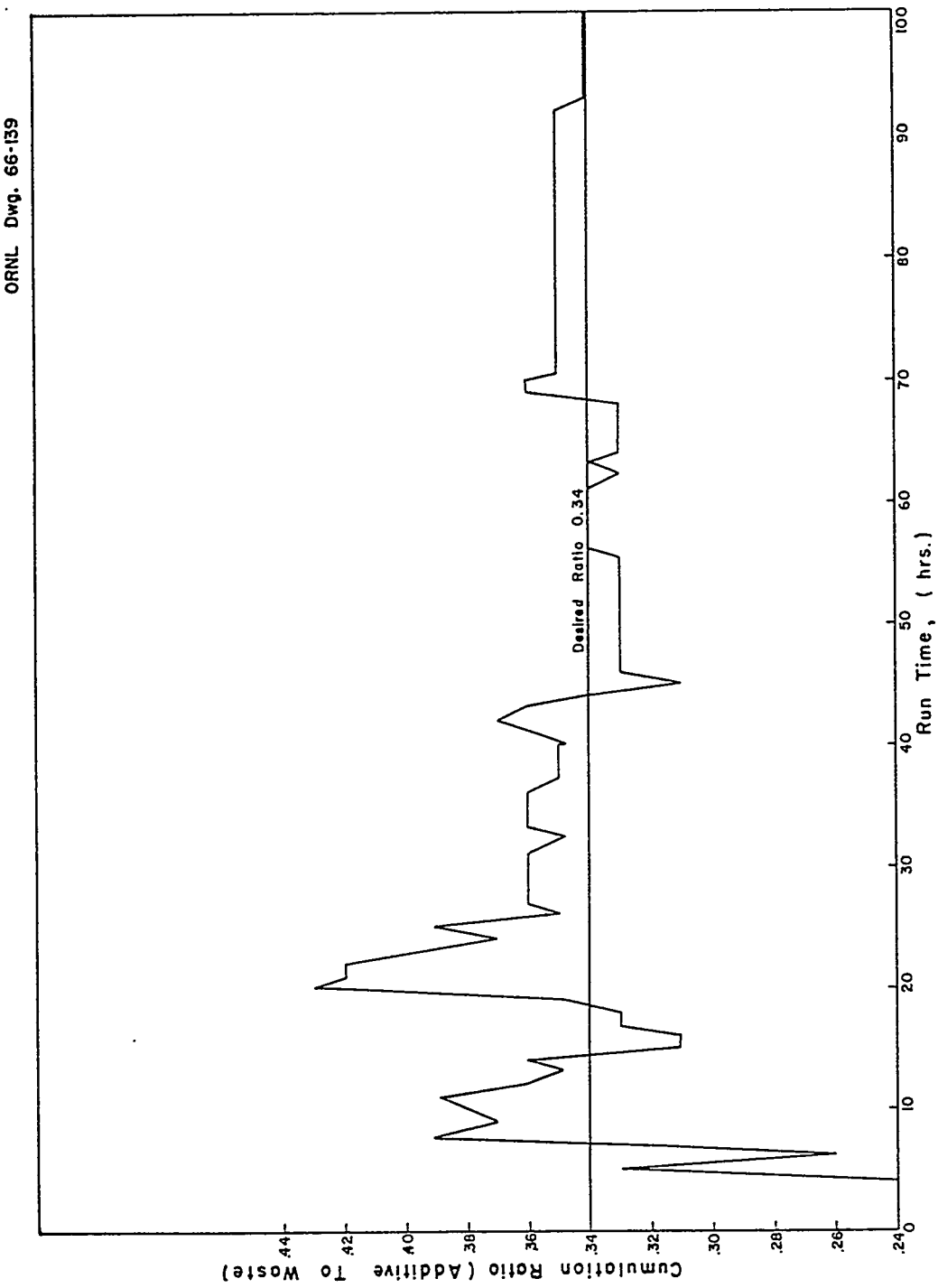


Fig. 2.3 Cumulative Ratio of Total Volumes of Glass Additive to Waste Solutions for R-92.

The large deviation in analyses for the phosphate concentration in the glass additives solution (Table 5) makes an accurate estimate of the amount of phosphate added difficult. Also, the large variation in the ratio of feed to additive solution (Fig. 2.1) makes the uniformity of the product glass suspect. Five samples of glass were taken and the analyses averaged in making the material balance (Table 6). The semi-glassy solid produced in the pot contained the following major ions (wt %):

Fe	Na	PO_4	Li
22.1	9.42	18.2	2.42

The residual nitrate concentration was 45 ppm.

The operating temperature of the pot was 900°C; the maximum temperature was 925°C, but for not over 30 min. After the feed was stopped, the contents were held for 9 hr at 900°C as part of the 100-hr test.

During the last half of the test, zone 1 produced additional heat to heat the overfilled pot. With zone 2 at its control temperature, the large heat output from zone 1 caused zone 2 to overheat. Hence, it was necessary to reduce the temperature of zone 1 to about 800°C.

The pot was 12-in. in diameter by 97-in. long and was made of 304L stainless-steel about 500 mils thick. Thickness was measured before and after the test at 30 places per heating zone by an ultrasonic thickness gauge. After the tests, the bottom zones of the pot were badly corroded (up to 239 mils), and the amount of corrosion decreased to very near zero at the top. Thus, the corrosion in this test appears to increase with the time that the area was covered. The center thermocouple well (109 mils) was completely corroded away at the zone-5 and -6 level (Table 7).

2.1.3 Conclusions

Only a limited number of large-scale tests (ten) have been made in the development of the rising-level process, two on PW 1 Purex waste, five on FTW-65 Purex waste, and three on TBP-25 aluminum waste. In

Table 6. Material Balance for Test R-92

Concentrations Expressed as gram-moles

	Nitrate	Iron	Sodium	Phosphate
Waste feed (852 liters)	6816	792	136	3
Additive (294 liters)	646	--	981	1780
Total	7462	792	1117	1783
Condensate (1404 liters)	8564	252	449	620
Solids (236 kg)	--	938	968	454
Total	8564	1190	1417	1074
Balance, %	115	151	127	61

Table 7. Wall Thickness of 12-in.-diam 304L Stainless-Steel Pot For Test R-92

Average Wall Thickness in inches, Measured Ultrasonically

Zone	Before Glass Test	After Glass Test
1	- 0.007 0.525 + 0.007	- 0.002 0.524 + 0.012
2	- 0.007 0.527 + 0.011	- 0.082 0.515 + 0.021
3	- 0.009 0.532 + 0.008	- 0.046 0.452 + 0.071
4	- 0.008 0.530 + 0.008	- 0.063 0.410 + 0.063
5	-0.007 0.524 + 0.011	- 0.039 0.349 + 0.134
6	- 0.008 0.529 + 0.011	- 0.040 0.338 + 0.072

Maximum penetration - 0.239 in. in zone 6.

addition, both 8-in.- and 12-in.-diam pots were used. Because of the large number of variables, it is difficult to draw firm conclusions or show a definite cause-and-effect relationship. The exact corrosion mechanism is unknown, and, more work, both in the laboratory and in large-scale tests, is required to definitely establish acceptable operating limits.

1. Corrosion: Test R-90 in an 8-in.-diam pot with FTW-65 waste (containing sulfate) and a maximum temperature of 850°C, and a similar run at Pacific Northwest Laboratory in an 8-in.-diam pot, were completely satisfactory. Corrosion was negligible. However, a duplicate run at ORNL, R-89, in an 8-in.-diam pot at 900°C was highly corrosive. This emphasizes the dependence of corrosion on the temperature and indicates the need for operating at the lowest possible temperature. Laboratory-scale tests have also shown a sharp relationship between corrosion and temperature.

Test R-91 with PW 1 waste (no sulfate, but high iron content) at 900°C in an 8-in.-diam pot showed a negligibly low corrosion rate. All glass-making additives were added to the waste feed tank, thus guaranteeing a uniform mixture. Test R-92, with the same chemical system, showed a high corrosion rate, up to 239 mils. The total times for the two tests were 67 and 100 hr, respectively. Operational problems in test R-92 caused a variation in the ratio of additive to waste solutions of 4.0 to 0, in contrast to a desired ratio of 0.34. The exact reason of the high corrosion rate in test R-92, compared with rate for R-91 is unknown but could have been caused by (1) improper mixing of waste and additives (see Sect. 2.2.5), (2) additional length of operating time, or (3) unpredictable corrosivity at high temperatures (see Sect. 2.2.5).

2. Addition of Glass Additives: The addition of phosphate and other glass-making additives can cause considerable precipitation in some kinds of waste. Although most wastes will contain solids as they come to the waste-treatment plant, it would be wise to limit the amount of slurry (solids) which must be pumped to a pot. Hence, the proportional feeding of the additive solution to the waste feed addition line is recommended.

2.2 Laboratory Development

W. E. Clark H. W. Godbee C. L. Fitzgerald

2.2.1 Preparation of Operating Manual for WSEP

The ORNL work on waste solidification has been summarized in the ORNL section of the operating manual for the Waste Solidification Engineering Prototype (WSEP) at Pacific Northwest Laboratories (PNWL). With a few additions and alterations this will be issued as a final report summarizing the ORNL work on solidification of highly radioactive aqueous wastes.

2.2.2 Melt Development Studies

A series of studies was made in which the compositions of melts from FTW-65 Purex waste were varied systematically, and the leach rates of the products were determined. Correlation of this data has not been completed.

The designation by PNWL of two new standard compositions for Purex waste with and without sulfate and both containing simulated fission products from a burnup of 20,000 Mwd/metric ton of uranium (Table 8) necessitated development of modified melt compositions for those particular variations. Reasonably satisfactory phosphate-melt compositions were readily available as a result of past melt-development work recorded in the ORNL melt catalog[1] (Table 9). Some difficulty was encountered with corrosion from Purex-1 waste, which is high in iron (see following paragraph). Lead silicate melts were also developed for this waste type. These were more homogeneous in appearance, had lower softening and operating temperatures, and gave higher volume reductions than the phosphate melts. They have not, however, been tested on a semiengineering scale.

2.2.3 Semiengineering-Scale Fixation Tests

Seven semiengineering-scale rising-level experiments were made, five with Purex-1 and two with Purex-2 waste types. The most satisfactory compositions tested are listed in Table 9.

Table 8. Simulated Purex Waste Types, Including Fission Products

For a burnup of 20,000 Mwd/metric ton at 15 Mw/metric ton, a cooling time of 6 years and a waste volume of 100 gal/metric ton.

Constituent (g-moles/l)	Purex-1	Purex-2	Simulated Fission Products (g-mole/l) Identical for Both Waste Types	
H^+	5.00	5.00	Rb	0.71×10^{-2}
Fe^{3+}	0.93	0.445	Cs	3.45×10^{-2}
Cr^{3+}	0.012	0.024	Sr	1.55×10^{-2}
Ni^{2+}	0.005	0.010	Ba	1.95×10^{-2}
Al^{3+}	0.001	0.001	Rare earths (total)	11.85×10^{-2}
Na^+	0.138	0.930		
Hg^{2+}	<0.001	<0.001	Zr	6.50×10^{-2}
$NO_3^- - NO_2^-$	8.80	6.44	Mo	7.9×10^{-2}
SO_4^{2-}	--	0.870		
PO_4^{3-}	0.003	0.006	Ru	4.66×10^{-2}
SiO_3^{2-}	0.010	0.010	Ag	0.80×10^{-2}
F^-	<0.001	<0.001	Total fission products	39.37×10^{-2} (0.394 M)

Fixation of Purex-1 waste in phosphate ceramics at reasonable rates required a slightly higher operating temperature (900 to 950°C) than the 900°C maximum, which is desirable in a stainless steel pot. At about 950°C, corrosion was fairly severe and resulted in loss of one or more thermocouples in times as little as 5 to 6 hr. Substitution of 0.1 M hypophosphite for an equivalent amount of phosphate in the melt decreased the corrosion markedly, perhaps by reducing Cr(VI) to Cr(III). The optimum amount of reductant to be added was not determined.

Volume reductions obtained from the Purex-1 waste type varied from 5.7 to 9 volumes of liquid waste per volume of solid product and corresponded to 11.1-17.5 gal of product per metric ton of uranium processed. Physical entrainment during operation (determined by lithium carryover

Table 9. Melt Compositions Currently Recommended for Fixation of Purex-1 and Purex-2 Waste Types

Additives (g-moles added to a liter of waste)	Purex-1 Melts		Purex-2 Melt
	A	B	
NaH_2PO_2	0.1	--	0.1
$Pb(NO_3)_2$ or	--		--
PbO	--	0.9	--
H_3PO_4	2.4	--	2.2
$LiOH \cdot H_2O$	1.37	--	1.37
NaOH	1.27	1.0	1.37
$Ca(NO_3)_2 \cdot 4H_2O$	--	--	0.2
H_3BO_3	--	0.8	--
SiO_2	--	0.8	--
Simulated fission products (g-moles/liter waste)	0.397	0.397	0.397
Wt % waste oxides	40.0	30.0	45.03
Approximate softening temperature, °C	750°	770°	750°
Operating temperature, °C	900°-950°	850°[a]	800-850°
Gal product/metric ton U	11.1	9.0	14.3

[a]Estimated. This melt has not been used in any semiengineering-scale test.

into the off-gas) was as low as 0.01% in one experiment. A figure of about 0.2% appears to be more realistic, however, since wide fluctuations in operating conditions during the course of an experiment often result in much higher entrainment values. Ruthenium volatility varied from 24 to 53% of the total present, the lower value representing the case in which a maximum of reductant was present. Molybdenum volatility varied from 0.4% to 1%.

Purex-2 was successfully converted to ceramic phosphate solids in two semiengineering-scale experiments. Previous small batch experiments had shown that volatilization of sulfate can be made almost negligible

if the equivalents of alkali and alkaline earths present overbalance the equivalents of nonvolatile anions (SO_4^{2-}, PO_3^-, BO_2^-, SiO_3^{2-}, etc.). The cation/anion ratio was too low, i.e., 0.95, in the first experimental melt, and 15.2% of the sulfate was volatilized, although the experiment was successful otherwise. Increasing the ratio to 1.05, as in the recommended melt shown in Table 9, resulted in a satisfactory experiment. Sulfate volatility was 11% of the total present vs about 2% for normally satisfactory experiments with other high-sulfate wastes. Both melts produced about 7 volumes of solid per volume of liquid waste, which corresponds to about 14.3 gal of solid per metric ton of uranium processed.

2.2.4 Ruthenium Volatility Studies

The flowsheets developed for all pot processes at ORNL assume that ruthenium volatility will be controlled by recycle of the pot off-gas to the evaporator. In the latter, the nitric acid is steam-stripped from the combined feed and pot condensate to yield a condensate containing very little ruthenium. Although this approach has been successfully tested on an engineering-scale,[2] controlled laboratory experiments were also desirable.

For this purpose, metered streams of water, simulated Purex-1 waste, and simulated pot condensate (9.68 $\underline{M}$ HNO_3) were fed into a glass distillation apparatus at volume ratios of 2:1:1, respectively. The volume ratio of evaporator condensate (about 3.2 $\underline{M}$ HNO_3) to evaporator bottoms (simulated pot feed) was 3:1 (Fig. 2.4). Temperatures in the solution and vapor phases were about 115-116° and 106°C, respectively. Ruthenium content of the simulated waste was 0.0566 $\underline{M}$ (about 5 mg/ml), and the ruthenium concentration of the simulated pot off-gas was varied from 0 to 1 mg/ml to resemble the possible buildup of ruthenium in the off-gas with time. Material balances for ruthenium for each of the three experiments were about 99%.

About 0.99, 0.59, and 0.40% of the ruthenium fed in was volatilized when the concentration of the ruthenium in the simulated pot off-gas was 0, 0.5, and 1.0 mg/ml, respectively. The value predicted from equilibrium-

ORNL Dwg. 66-140

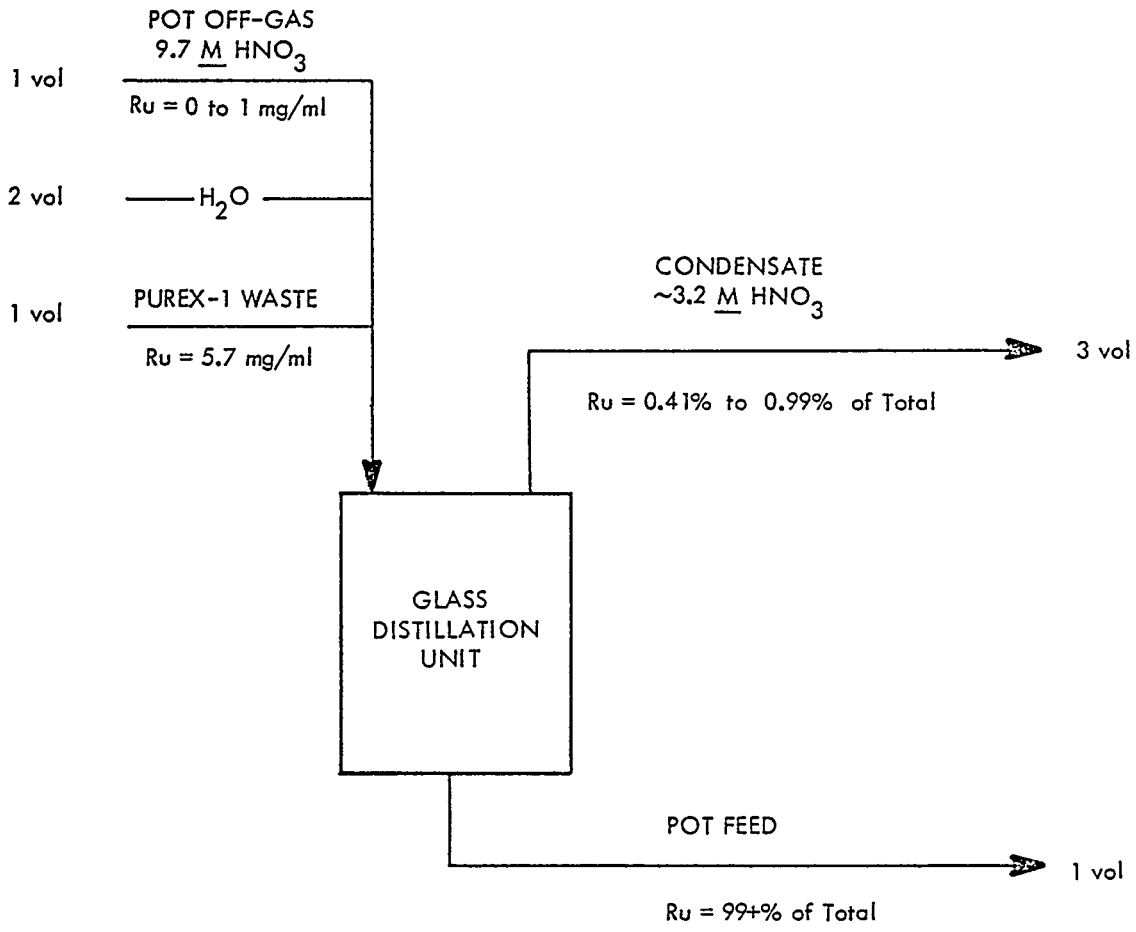


Fig. 2.4 Flowsheet for Laboratory-Scale Experiments Simulating Evaporator Operation.

still studies was $\geq 2\%$.[3] The steam-stripping technique resulted in less ruthenium volatility than predicted. Also the apparently reversed trend of volatility with ruthenium content cannot be real and must be ascribed to either physical entrainment and/or analytical scatter. The results indicate that the ruthenium decontamination factor from the evaporator could be limited by physical entrainment. Small concentrations of a reductant (e.g., NaH_2PO_2) will reduce the "true volatility" of ruthenium by factors which vary between 38 and 2500 (ref 4), depending upon the waste type and the experimental conditions.

2.2.5 Corrosion with Phosphate Melts

The corrosion of test specimens and stainless steel beakers during batch studies on phosphate melts in the laboratory was somewhat erratic. However, there seemed to be some general trends. Usually, corrosivity of the melts increased with increasing ratio of phosphoric acid or phosphoric acid plus alkali metals to waste solution, and decreased with increasing amounts of calcium. Particular studies that lead to such generalizations include melts 398 through 421 (ref 1) with FTW-65 waste, and melts 466 through 477 with Purex-1 in which the additives (expressed as gram-moles added to a liter of waste) were H_3PO_4 (2.5 to 4), LiOH (1.4 to 2.2), NaOH (1.4-2.2), and $Ca(NO_3)_2$ (0 to 0.45).

Summarized below are observations from four laboratory experiments in which phosphate melts were much more corrosive than expected. Most of the glassy melts were taken from large-scale-test pots (see Sect. 2.1).

1. Long-Term Storage Test.--Material from Unit Operations (UNOP) run 91 — Purex-1 plus phosphate, lithium, and sodium (melt 478)[1]— was crushed and ground. A can (7-1/2-in.-OD and 25-in.-long) was filled with powder, and the temperature of the system raised to between 850 and 900°C. The temperature was held constant (for about 4 hr) until sufficient powder could be added to bring the level of molten material to within about 5 in. of the top of the pot. During this time at temperature, the eight thermocouple wells (1/4-in. 304L stainless steel tubing with 28-mil wall) in the can failed and filled with molten material.

2. Thermal Conductivity of Melt 478.--Material from UNOP run 91 — Purex-1 plus phosphate, lithium, and sodium — was crushed and ground. A can (4-in.-OD and 24-in.-long) was filled with powder, and the temperature of the system raised to between 850 and 900°C. The temperature was held constant (for about 2 hr) until sufficient powder could be added to bring the level of molten material to within 4 in. of the top of the pot. The pot was cooled to room temperature. Thermal conductivity measurements were made from 100 to 830°C. The material was at 830°C for about 24 hr. At the end of the tests, the can was taken apart. No severe corrosion was apparent. There was a 1/2- to 1-in. layer of snow-white crystals that had floated to the top of the material in the can.

3. Thermal Conductivity of Melt 2.--The thermal conductivity of a product (melt 2)[1] formed in the laboratory with Purex FTW-65 waste plus phosphate, lithium, aluminum, and calcium was measured in situ. The product was formed in a 4-in.-OD and 24-in.-long pot by the rising-level technique. Conductivity measurements were made from about 100 to 830°C. The material was at 830°C for about 24 hr. During the tests, the material in the pot had corroded through the inner 1-in. tube (1/16-in. wall) that accommodated a central heater. The material filled the tube and completely coated the central platinum heater.

4. Thermocouples as Level Detectors.--In a series of experiments to determine the response of pulse-heated thermocouples in various media, a product from a laboratory continuous-melter experiment was tested. The material was made with Purex FTW-65 waste plus phosphate, lithium, sodium, and aluminum (melt 358).[1] This product was crushed and ground. Sufficient material was put into a 4-in.-OD and 24-in.-long pot so that upon melting the pot was about half full. The material was held at 850°C for 3 or 4 hr on each of two successive days. The central heater (Nichrome) was lost during the second day. The pot was taken apart and it was discovered that the central 1-in. tube (1/16-in. wall) that accommodated the heater had been corroded through at the melt-air interface.

2.2.6 Conclusions

The corrosion observed in the above tests and in the large-scale engineering tests (Sect. 2.1) indicates a serious lack of knowledge regarding the mechanisms and control of corrosion of phosphate melts containing sulfate and multivalent metals such as iron and chromium. Previous work with aluminum—lead phosphate melts from TBP-25 waste had shown low corrosion rates on 304L stainless steel at temperatures up to 950-1000°C once the water and nitrate had been volatilized. Corrosion in the FTW-65 (sulfate) and PW 1 (high in iron) Purex systems in "neutral" glass (suitable balance of cations and anions) at low temperatures also has been negligible in many small- and large-scale tests. However, in other tests, corrosion has been unacceptably high. Comparison of small and large scale tests at 825 to 850°C and 900°C (1 and 2 above) and R-89, R-90, and the PNWL test (see Sect. 2.1) shows a significant decrease in corrosion at lower temperatures. However, excessive corrosion was noted at 830 to 850°C in tests 3 and 4 above. The fact that the material in tests 1, 2, and 4 was ground in air and added to the melt containers may have increased corrosion due to the presence of moisture or as the result of a change in valence of the iron and chromium. The effect of these variables is not known at present but is being determined in additional tests.

Recommendations and conclusions at the present time are:

1. The corrosion mechanism in Purex glassy melts is not sufficiently known at present. Consequently, tests in the radioactive pilot plant at Hanford are not recommended at temperatures above 850°C. A test using FTW-65 Purex waste and the conditions successfully tested at ORNL and PNWL could be considered. A test with TBP-25 aluminum waste could also be considered.

2. The corrosion and other data obtained in small-scale tests (4-in.-diam x 24-in.-high cans) cannot be used to accurately predict the results in large-scale tests. Additional research and development is required on both a laboratory and engineering scale if a dependable and successful rising-glass process is to be developed for Purex wastes. The total of

ten large-scale tests involving three waste types, in addition to other variables, has been too small to provide adequate data for process evaluation or to serve as a guide to laboratory research.

2.2.7 Fixation of Fluidized-Bed Waste in Glass

Preliminary scoping experiments show that the alumina bed plus the fission products that collect in the bed during fluidized-bed volatility processing can be readily incorporated in glass compositions developed for TBP-25 waste. Borophosphate glasses were prepared which contained about 33% by weight (about 29 mole %) of waste oxides (Al_2O_3 plus simulated fission-product oxides). Four different grades of alumina were investigated, and the effects of oxides from cladding materials (e.g., stainless steel, zirconium) were also studied. The 33% melts were sufficiently fluid for fixation at 900°C, although there was some cracking of the glass on cooling, probably caused by entrapped air bubbles. Pouring the glass melts appeared to minimize this problem.

Lead borate glasses provide a second possible type of matrix. One such melt was prepared which contained 37.3 mole % of Al_2O_3 and was completely molten, although very viscous, at 850°C.

The alumina bed was completely dissolved in these initial tests; that is, visual examination indicated only one phase. Further definition of the effects of constituents of the bed, for example, H_2O, F^-, etc., is also required. Dissolution of the alumina may not be required, however, and may be undesirable since the presence of solid alumina would increase the thermal conductivity of the product. Further tests are planned using melts to encapsulate, but not dissolve, the alumina.

3. LOW- AND INTERMEDIATE-LEVEL-WASTE TREATMENT

3.1 Incorporation of Intermediate-Level Waste in Asphalt

H. W. Godbee W. E. Clark J. H. Goode J. R. Flanary

Intermediate-level wastes (ILW's) are generally stored in tanks or incorporated in concrete since their high salt or solids content prevents

efficient treatment by normal water-treatment methods. Incorporation in concrete has not proved entirely satisfactory for several reasons: The operation is dusty, good mixing is difficult to achieve, the product generally represents a volume increase over that of the original waste, and radioactivity can be leached from the product at an unacceptably high rate. Considerable interest has been shown throughout the world in the use of asphalt as a medium in which ILW can be incorporated. Asphalt has good adhesive and coating properties and is insoluble in water, but its sensitivity toward radiation limits the radioactivity of wastes to be treated, and its organic nature limits the temperatures at which it can be used. Plants for incorporating ILW waste in asphalt have been constructed in Belgium and in France.

At ORNL, emphasis is placed on developing a process which can handle both liquid (including nitrates) and solid wastes. Details of the development program at ORNL are reported in refs 5, 6, and 7. In this process, evaporator wastes are introduced into an emulsified asphalt, which contains about 35% water, and the water is volatilized by heating to about 160°C to yield a product containing up to 60 wt % salts from waste (Table 10). Attractive features of the process include: use of emulsified asphalt which flows readily at room temperature; evaporation at low temperatures (120 to 160°C) to minimize entrainment of activity and degradation of the asphalt; low agitation rates (100 to 300 rpm), which provide adequate mixing and keep the heated surfaces of the evaporator clean; operation in batch or continuous manner; and incorporation of soluble as well as insoluble solids with equal effectiveness.

Probably the best measure of how well the waste particles have been coated with asphalt is how resistant the product is to leaching by water. Samples of asphalt products containing 20 to 60 wt % salts from simulated waste were leached with water in the laboratory for periods of up to 16 months. Products containing 20 and 60 wt % salts reach steady-state leach rates for ^{137}Cs (as well as sodium) of 1.5×10^{-4} and 3×10^{-4} g cm^{-2} day^{-1}, respectively. Hot-cell tests with concentrated actual ORNL ILW, containing 5 curies of aged mixed fission products per gallon, confirmed these nonradioactive and tracer tests. After 5 months of

leaching, a product incorporating 60 wt % salts from actual waste approached a steady-state leach rate of 2×10^{-4} g cm^{-2} day^{-1}.

Samples of product containing 60 wt % salts from simulated waste (Table 10) were prepared from an emulsified hard-base asphalt and were irradiated to absorbed doses ranging from 10^6 to 10^8 rads. A dose of 10^6 rads had negligible effect. A dose of 10^7 rads caused the asphalt to swell very slightly, while a dose of 10^8 rads caused the material to increase about 36% in volume. In contrast, similar samples prepared from a soft-base asphalt and irradiated to a dose of 10^8 rads showed only a slight increase in volume. Calculations have shown that the maximum dose absorbed by an asphalt product made from waste containing 5 curies of mixed fission products per gallon will be 10^8 rads. Thus, a product made with this soft-base asphalt will be satisfactory from the standpoint of radiation stability. Leach tests on the irradiated samples indicated that irradiation to a dose of 10^8 rads has no effect on the leach rate. As mentioned above, a product incorporating actual ORNL waste with 5 curies per gallon of mixed fission products had a leach rate after 5 months (an internal radiation dose of about 1.2×10^7 rads) essentially the same as that obtained with nonradioactive products. No radiolytic gas was released during this time.

In addition to the laboratory-scale tests with nonradioactive and radioactive waste in a 4-in.-diam x 6-in.-high evaporator, tests on a pilot-plant scale were carried out with a 12-in.-diam x 16-in.-high Pfaudler wiped-film evaporator with 4 ft^2 of heat transfer surface. The processing rate in the large unit was about 4 gal/hr of nonradioactive product containing 60 wt % salts from waste (Table 10). In all, eight 30-gal drums of asphalt products were prepared with the Pfaudler unit.

The incorporation of inert solids in asphalt does not appear to present any additional hazard to that normally present when processing, storing, or shipping an organic material with a high flash point. However, the hazards involved in incorporating nitrate salts in asphalt are being studied intensively. Specifically, the objectives are to

Table 10. Compositions of Simulated ORNL Intermediate-Level Waste (ILW) Solution and an Asphalt Product Incorporating Solids from ILW

Component	ILW Solution (M)	Asphalt Product[a] (wt %)
Sodium	6.61	18.5
Nitrate	4.64	34.9
Hydroxide	2.06	3.8
Sulfate	0.35	4.1
Aluminum	0.22	0.7
Ammonium	0.19	--
Chloride	0.056	0.2
Asphalt	--	37.8
Density at 25°C	1.34 g/ml	1.5 g/ml

[a]Volume reduction = $\frac{\text{volumes ILW}}{\text{volumes product}}$ = 2.

determine the change in burning rate or flash point with increasing nitrate content and to determine whether the mixture will sustain combustion in the absence of external oxygen. Initial results with small samples, 1 to 2 g, indicate that the flash point of irradiated asphalt, approximately 280°C, is not lowered significantly--about 50°C--when the mixture contains 35 wt % nitrate and a total of 60% salts. The flame was easily extinguished when the air was replaced by nitrogen, even though the solid-phase temperature was in the range of 400 to 500°C. Tests are continuing to determine the effect of radiation-dose level. Further standard safety tests are being carried out by a subcontractor. These tests include drop weight, autoignition, shock sensitivity, and flame propagation tests with small samples, and fire tests with 30-gal drum samples.

3.2 Water-Recycle Process

W. C. Yee W. E. Clark

The conservation of water resources and the minimization of waste pollution of water streams have been the subjects of increasing national concern. The resulting penchant for water reuse has served as the

motivation for developing the water-recycle process for treating low-level-radioactivity waste (LLW). In this process, the waste water of a nuclear installation, containing a low concentration of bulk ions, is completely decontaminated and completely demineralized; the product water is returned to the plant for reuse, thus providing a closed circuit. Fresh water is demineralized before entering the circuit. This approach contrasts with the more traditional "treat and discharge" method, which allows "tolerable" amounts of radioactivity to leak into natural streams and relies on dilution by the stream to maintain radionuclide concentrations at levels below Federal (MPC_w) requirements. Speaking out on stream pollution in general, however, the U.S. Public Health Service maintains that "dilution is no solution."[8]

Promising results have been reported[9,10] for micro-pilot plant tests of the process. Overall decontamination factors (DF's) range from 100 to 10,000 — in the hundreds for ^{144}Ce, ^{131}I, ^{106}Ru, ^{125}Sb, and ^{95}Zr-Nb; in the thousands for ^{137}Cs and ^{90}Sr; and in the ten-thousand range for ^{60}Co and total rare earths (Table 11). The DF's for ^{106}Ru and ^{60}Co were 10 to 1000 times as high as previous values obtained in the ORNL development program. In these tests, LLW had a bulk ionic concentration similar to that of tap water (specific conductance of 200 to 300 μmho/cm). A large inventory of decontaminated and demineralized water is being accumulated by treating low-level waste and by retaining the water so treated in development experiments. This water will subsequently be adjusted to simulate closed-circuit water-recycle conditions (contaminated water of low bulk ionic content) in micro-pilot plant tests.

The flowsheet used for treating LLW includes zeta-potential-controlled (ZP) flocculation-clarification, cation-anion exchange, and sorption by activated carbon (Fig. 3.1). For LLW similar to tap water, 20 to 30 ppm of alum, as $Al_2(SO_4)_3$, and 0.5 ppm of activated SiO_2 was sufficient to neutralize the negative ZP of the suspended solids in the waste (from its original -14 to -17 mv to +2.5 mv) and obtain optimum clarification. Demineralization capacity (0.2% of ionic breakthrough as measured by specific conductance) with separate cation (Dowex 50W) and anion (Dowex 1) exchange columns was about 400 bed volumes (BV) of clarified LLW (total

Table 11. Effects of Variations in the Water-Recycle Process Flowsheet When ORNL LLW Is Used.

A. Changes in the Properties of the Water as it is Processed.

	ORNL Low-Level Waste					Flocculated Water			Demineralized Product Water	
	pH	Specific Conductance (μmho/cm)	Total Hardness (ppm $CaCO_3$)	Nitrate (ppm NO_3^-)	Zeta Potential (mv)	Alum Added (ppm $Al_2(SO_4)_3$)	pH	Zeta Potential (mv)	Specific Conductance (μmho/cm)	Vol. Product Water Per Vol. Cation Resin
Run 6, Normal Waste[a]	7.4	280	130	15	-12.8	20	ND[c]	+2.5	0.67	400
Run 12, High Nitrate Waste[a]	4.9	427	123	264	-15.8	27 to 64	4.4 to 4.7	-7.6 to -2.5	0.90	230
Run 13, Normal Waste,[b] Act. Carb. after cation exchange	8.0	316	123	10	-13.2	37	7.1	+2.7	1.0	270

B. Overall Decontamination Factors.

	^{137}Cs	^{90}Sr	^{60}Co	^{106}Ru	^{144}Ce	Total Rare Earths	^{125}Sb	^{95}Zr-Nb	^{131}I
Run 6, Normal Waste[a]	2600	6300	12,000	610	330	11,000	300	160	430
Run 12, High Nitrate Waste[a]	1000	5500	350	500	110	5,200	250	75	50
Run 13, Normal Waste,[b] Act. Carb. after cation exchange	1000	3000	100	500	70	2,000	250	40	>30[d]

[a]System: Alum-activated silica flocculation-clarification, cation-anion exchange, activated carbon.

[b]System: Alum-activated silica flocculation-clarification, cation exchange, activated carbon, anion exchange, activated carbon.

[c]Not determined.

[d]Decontaminated to background.

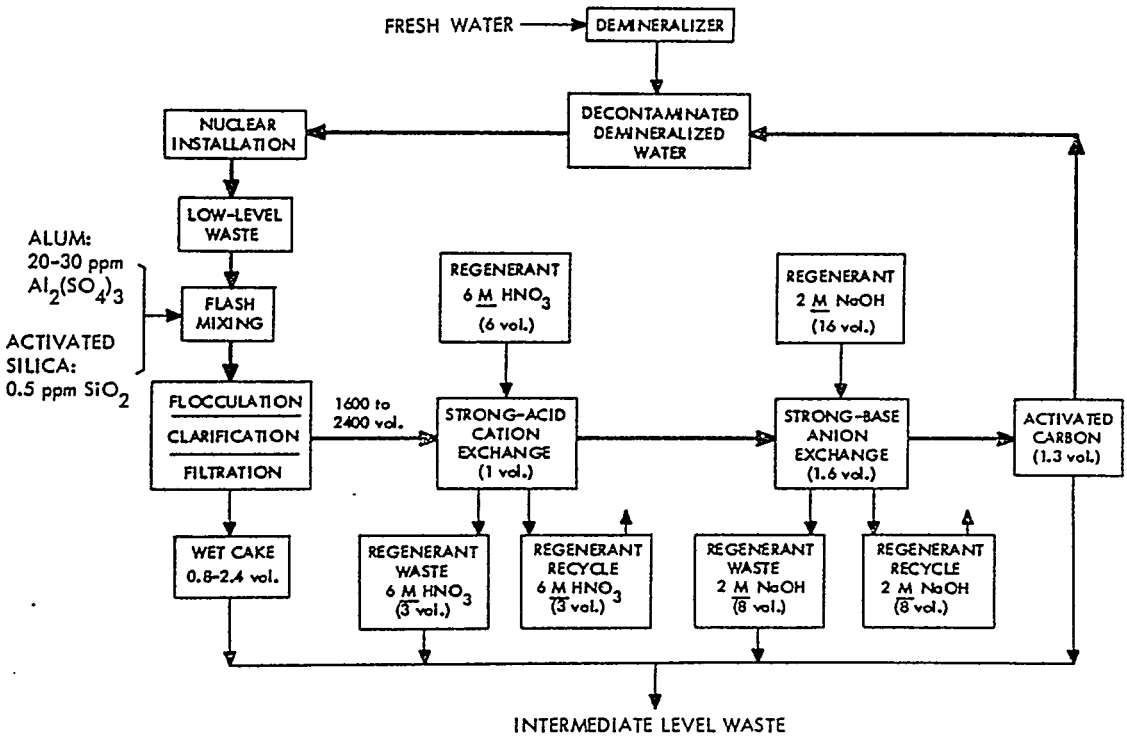


Fig. 3.1 Flowsheet for the Water-Recycle Process.

hardness of 100 to 130 ppm as $CaCO_3$) per volume of cation resin. Bituminous-coal-based activated carbon* removed a significant additional amount of ^{60}Co remaining after ion exchange.

When operating conditions deviate from normal (for example, run 6), high overall DF's for some radionuclides are more difficult to achieve (Table 11). For example, in run 12, the pH and specific conductance of LLW were 4.9 and 427 umho/cm, respectively, due to an abnormal twenty-fold increase in nitrate concentration to 260 ppm. The low pH prevented complete neutralization of the negative ZP charge on the waste colloids even though up to 3 times the normal amount of alum was added. Poor alum-activated silica flocculation resulted in poor upflow clarifier operation and a 35-fold decrease in the overall DF for ^{60}Co (Table 11). Obviously, the pH of this LLW should have been adjusted to 7 to 8 prior to adding the coagulants. The higher concentrations of NO_3^- and SO_4^{2-} also contributed to an early breakthrough in the demineralization step.

Another variation in the flowsheet was the insertion of an additional activated-carbon column into the system, between cation and anion exchange (run 13). This column sorbed ^{106}Ru from the cation exchange effluent (pH 2.5 to 3.0), but the total ^{106}Ru taken out was the same as without this column (run 6); the overall DF for ^{106}Ru was not improved. However, a greater than hundredfold decrease in the overall DF for ^{60}Co was noted. These data suggest that the chemistry of the ^{60}Co remaining after cation exchange treatment was altered by contact with the activated carbon and that activated-carbon treatment should come only after ion exchange.

Gross-beta decontamination is at least twofold greater than Dowex 1 anion resin than with Dowex 21K.

Regeneration and reuse of the activated-carbon column which follows anion exchange is a possible alternative to the disposal of the exhausted material. Elution with 2.75 bed volumes of 1 M HNO_3 reduced the sorbed ^{60}Co activity a hundredfold. There was some gassing in the column.

*Type CAL (12 x 40 mesh), made by Pittsburgh Activated Carbon Company, Pittsburgh, Pennsylvania.

4. ENGINEERING, ECONOMICS, AND SAFETY EVALUATIONS

4.1 The Cost of Perpetual Tank Storage

J. O. Blomeke E. J. Frederick R. Salmon E. D. Arnold

A study of the costs of perpetual storage of power-reactor fuel-processing wastes in tanks has been completed and published as ORNL-2873. In this study, the economics are examined for three representative types of financing: government ownership, private ownership, and a combination of government and private ownership. The case of government ownership includes only depreciation and interest on the investment capital; whereas, for private ownership, costs reflect a 15% return on equity as well as allowances for depreciation, insurance, taxes, and interest. In the third case, private ownership is assumed during a 20-yr period of waste accumulation, after which the government assumes responsibility for perpetual care of the tank farm. In each case, it is assumed that a permanent tax-free fund is established during the filling period of such size that the annual tax-free interest will be sufficient to provide for the periodic replacement of tanks and for the annual operating expense of the facility.

The tank farms were designed for storing high-radioactivity-level wastes in both acid and alkaline forms, and in tanks ranging in capacity from 200,000 to 5,000,000 gal. Capital costs were estimated for each case and then used in a computer code to estimate total costs for each method of financing as a function of tank size, tank lifetime, and fission product concentration in the waste. The basis of this study and the conceptual design of the tank farms were summarized in the previous semiannual report;[11] the final results are summarized below.

4.1.1 Raffinate Wastes

For the raffinate wastes, the initial capital expenditures varied from 8 to 16 million dollars, and the total over the 20-year period of waste accumulation ranged from 22 to 61 million dollars. The annual operating expenses ranged from 0.3 to 0.4 million dollars during the first year, to 0.5 to 2.0 million dollars during the twentieth year.

The size of the permanent fund needed for "perpetual care" ranged from 22 to 72 million dollars; and annual payments of 0.7 to 2.6 million dollars are required to establish this fund. The total costs of perpetual storage of acid raffinate waste, in mills per kwhr of electricity generated, is plotted in Fig. 4.1 against tank capacity for tank lifetimes of 25, 50, and 75 years for the three cases of financing. Minima occur at a tank capacity of about 1 million gallons in all cases. These minima range from 0.0165 mill/kwhr to 0.0184 mill/kwhr for case 1, from 0.0235 to 0.0253 mill/kwhr for case 2, and from 0.0251 to 0.0272 mill/kwhr for case 3. Total costs for alkaline waste storage were generally higher than the equivalent costs for acid storage (Fig. 4.2). For alkaline wastes, the optimum tank capacity is about 2.5 million gallons, and the minimum total costs are from 0 to 15% higher than those for acid wastes.

One of the least certain aspects of the basis used for this study is the degree of fission product concentration that can be tolerated during storage. The concentrations adopted are based on a careful consideration of Savannah River and Hanford experience and are believed to be as high as practical for wastes of this type. To obtain an indication of the effect of fission product concentration on costs, a second set of costs was computed assuming that the wastes were reduced in volume to half those of the original design basis. In this instance, acid Purex and Thorex wastes are stored at 50 and 100 gal per ton of fuel, respectively, and alkaline Purex and Thorex wastes are stored at 300 and 600 gal per ton. This reduction in volumes caused a decrease of between 15 and 30% in total costs. The optimum tank size for acid waste storage remained about 1 million gallons, whereas the optimum size for alkaline waste storage dropped from about 2.5 million to 1.5 million gallons.

4.1.2 Cladding Wastes

The costs of cladding-waste storage were compiled independently of those for the raffinates. The initial capital cost in all cases was 3.5 million dollars, and the total cost over 20 years was 52 million.

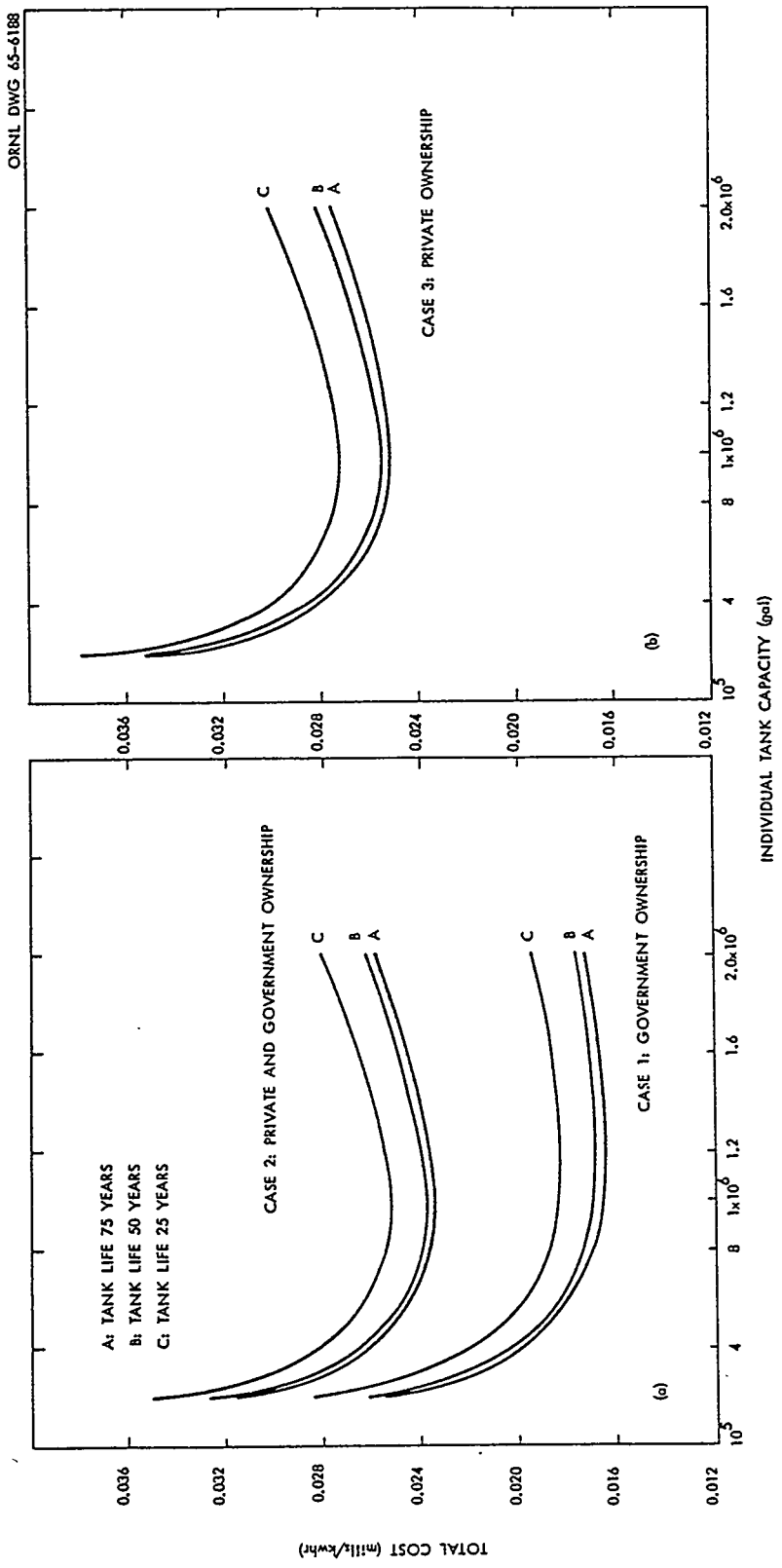


Fig. 4.1 Cost of Acid Waste Storage as a Function of Tank Capacity, Tank Life, and Method of Financing for (a) Case 1, Government Ownership; Case 2, Private and Government Ownership; and (b) Case 3, Private Ownership.

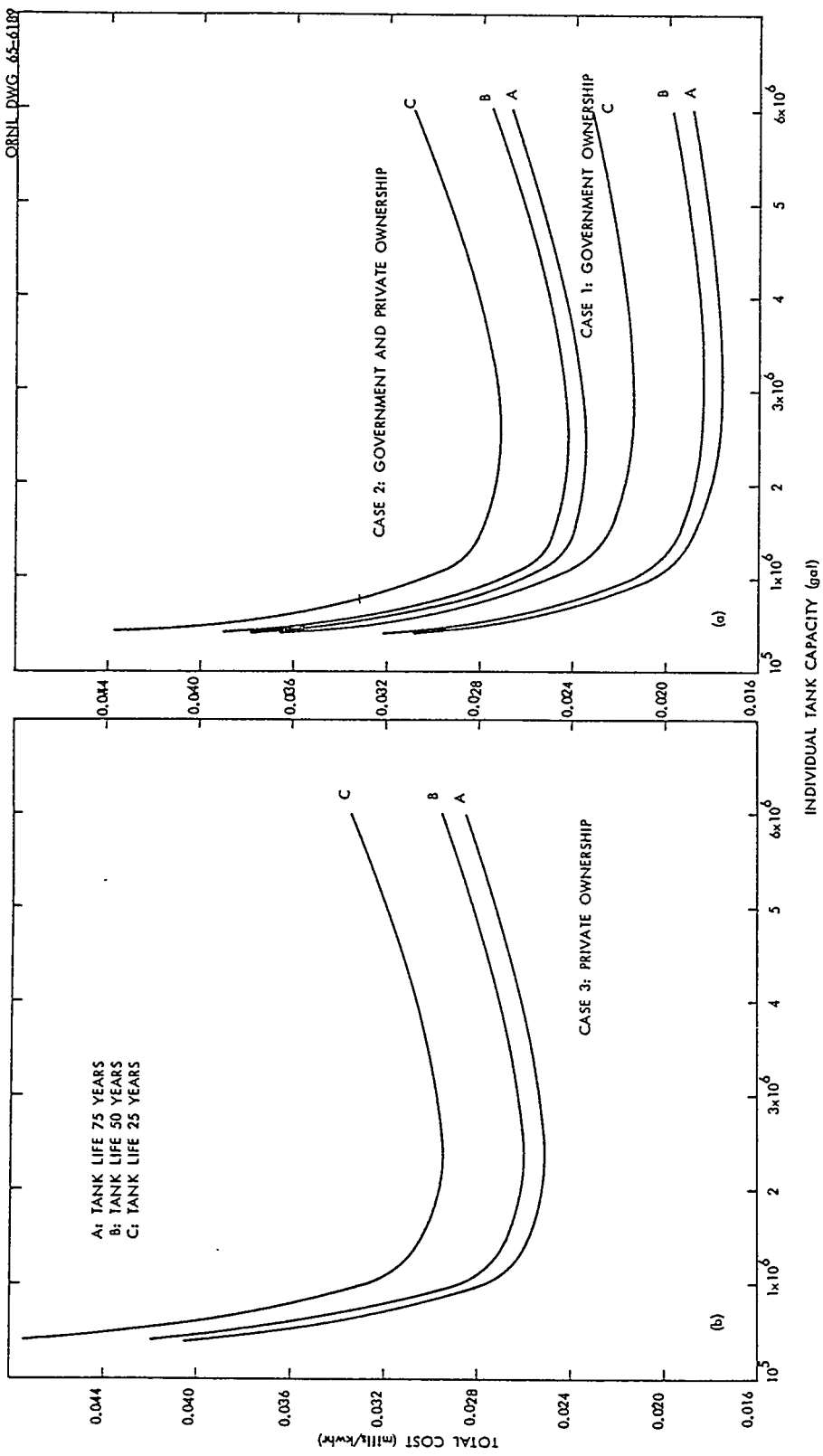


Fig. 4.2 Cost of Alkaline Waste Storage as a Function of Tank Capacity, Tank Life, and Method of Financing for (a) Case 1, Government Ownership; Case 2, Private Government Ownership; and (b) Case 3, Private Ownership.

The annual operating expenses ranged from 19 to 89 thousand dollars for the first year to 82 and 980 thousand for the twentieth year. The permanent fund varied from 17 to 78 million dollars, and required annual deposits of from 0.6 to 2.8 million dollars. Total costs ranged from 0.0215 mill per kwhr for tanks of 75-yr life with government ownership, to 0.0398 mill per kwhr for tanks of 25-yr life with private ownership. The total costs of cladding-waste storage, which are in every instance greater than the comparable costs for raffinate storage, are consequences of their larger volumes.

4.2 A Safety Analysis of Tank Storage

J. O. Blomeke L. C. Emerson

A safety analysis of tank storage of high-level power reactor fuel processing wastes has been undertaken, using the same basis as was adopted for the economic studies of waste management. A hypothetical tank farm is assumed to be located on the ORNL reservation, thus permitting a more detailed study to be made of the movement of accidentally released radionuclides by virtue of an existing thorough knowledge of the local environment. Tanks of Savannah River design with about 1 million gallons capacity are assumed, and when newly filled, contain between 4 and 7 billion curies of fission product activity, depending on whether the wastes are stored as alkaline or acid solutions. Maximum heat generation rates range from about 40 to 70 million Btu/hr.

We believe the most likely mechanism of a major release would be the loss of cooling. The worst possible time for this to occur would be when the tank was newly filled and the heat evolution rate was at its peak. In this event, the wastes would heat themselves to boiling in 10 to 20 hr. An additional 115 hr would be required for evaporation of the acid waste to dryness, and 240 hr would be required to evaporate the alkaline waste to dryness. It is estimated that decomposition of the inert and fission product salts would require 10 hr and 17 hr in the case of acid and alkaline wastes, respectively; and from 24 to 47 hr would be needed for thermal decomposition of the concrete vaults. Assuming continued containment of the fission products at this time,

it is estimated that the maximum in-tank temperature would reach several thousand °F at the end of an additional hour.

Based on these considerations, two incidents are postulated (Table 12). In the first one, it is assumed that cooling is interrupted for a time sufficient for the wastes to self-heat to boiling, and that they boil for 10 hr with both the condenser and the filter out of service. Releases from an acid and an alkaline waste tank are as shown. This type of incident might be such as could be incurred by sabotage of the surface-located cooling and ventilation facilities.

Table 12. Postulated Incidents

	Activity Released to Atmosphere	
	Acid Waste	Alkaline Waste
1. Self-boiling for 10 hr without condenser and filter.	300 curies/min Ru 10^3 curies/min FP's (720,000 curies)	300 curies/min FP's (180,000 curies)
2. Permanent loss of cooling.	90% of Ru, Cs, and Te; 5% other FP's — over 168 hr (1.1×10^9 curies)	50% of Ru; 25% of Cs and Te; 1% other FP's — over 300 hr (1.5×10^8 curies)

The second postulated incident assumes permanent loss of cooling as might result from an explosion of radiolytic hydrogen in the tank. Hydrogen is produced in these tanks at such rates that if the ventilation system failed, the lower explosive limit of 4% H_2 in air would be reached in only 1-1/2 to 3 hr; and our analyses indicate that quantities could accumulate which could explode with force sufficient to rupture the tank and concrete encasement. In this event, if no effective remedial action were taken, atmospheric releases of a major magnitude would be encountered over the ensuing 168 to 300 hr.

Assuming that the fission products (FP's) associate with the normal dust particles in the air, and choosing a typical particle size (i.e., deposition rate), the gamma exposure rate, in r/hr, at the ground from the FP's deposited by fallout, is shown in Fig. 4.3 as a function of the distance downwind from an acid waste tank. This is for incident 1 under conditions of rainfall and dry weather, at night. Here, it is assumed that the activity does not lie directly on the surface but is distributed exponentially throughout the topmost layers as in weapons fallout. Figure 4.4 shows similar curves for incident 2. The ground exposure rates for incident 2 are about 5000 times greater than those for incident 1.

Figure 4.5 shows the ground-level concentration (uc/cm^3) at various distances downwind following the first incident, and the resulting exposure to the lungs from breathing the contamination over the duration of the incident. These dose equivalents are the result of integration over the first year.

Figure 4.6 gives the same information for incident 2. These results are a thousand times higher than those shown in Fig. 4.5.

Similar analyses of incidents 1 and 2 for the case of alkaline waste gave results from 1/5 to 1/2 those of acid wastes.

A third source of exposure to the surrounding population is that which would result from direct radiation from the passing radioactive cloud. This has been found to be only a few percent of that from the two sources already treated and consequently is considered to be of negligible importance.

Another phase of this study, which is still in progress, is a consideration of a large-scale release of activity to the geological environment, and the resultant contamination of the ground and surface waters.[12] From a consideration of all known exposure pathways, and the corrective measures necessary, we expect to estimate the extent of liabilities incurred by these releases.

ORNL DWG 65-3086

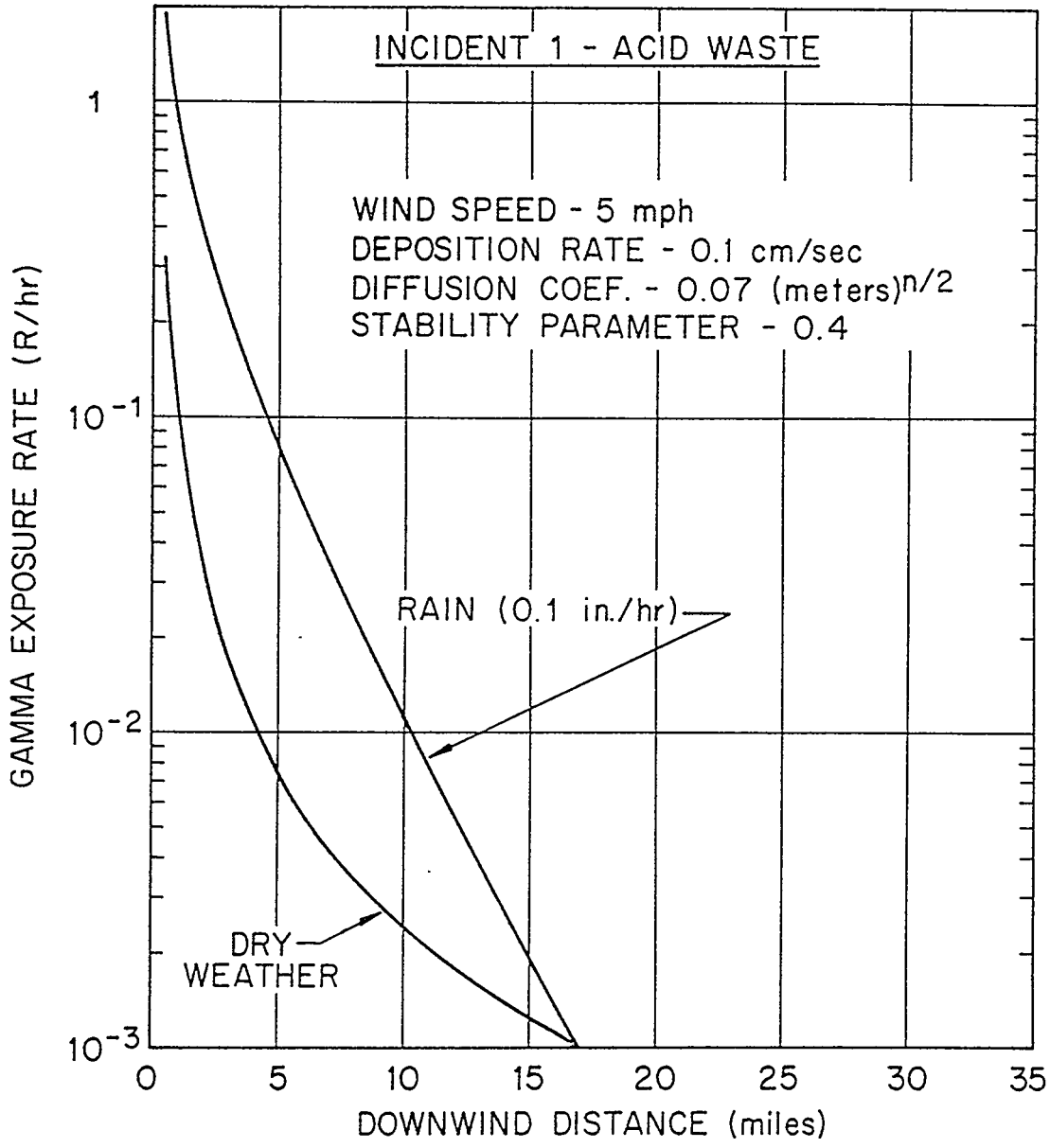


Fig. 4.3 Ground-Level Exposure Rate as a Function of Distance Downwind from an Acid Waste Tank Following Temporary Loss of Cooling.

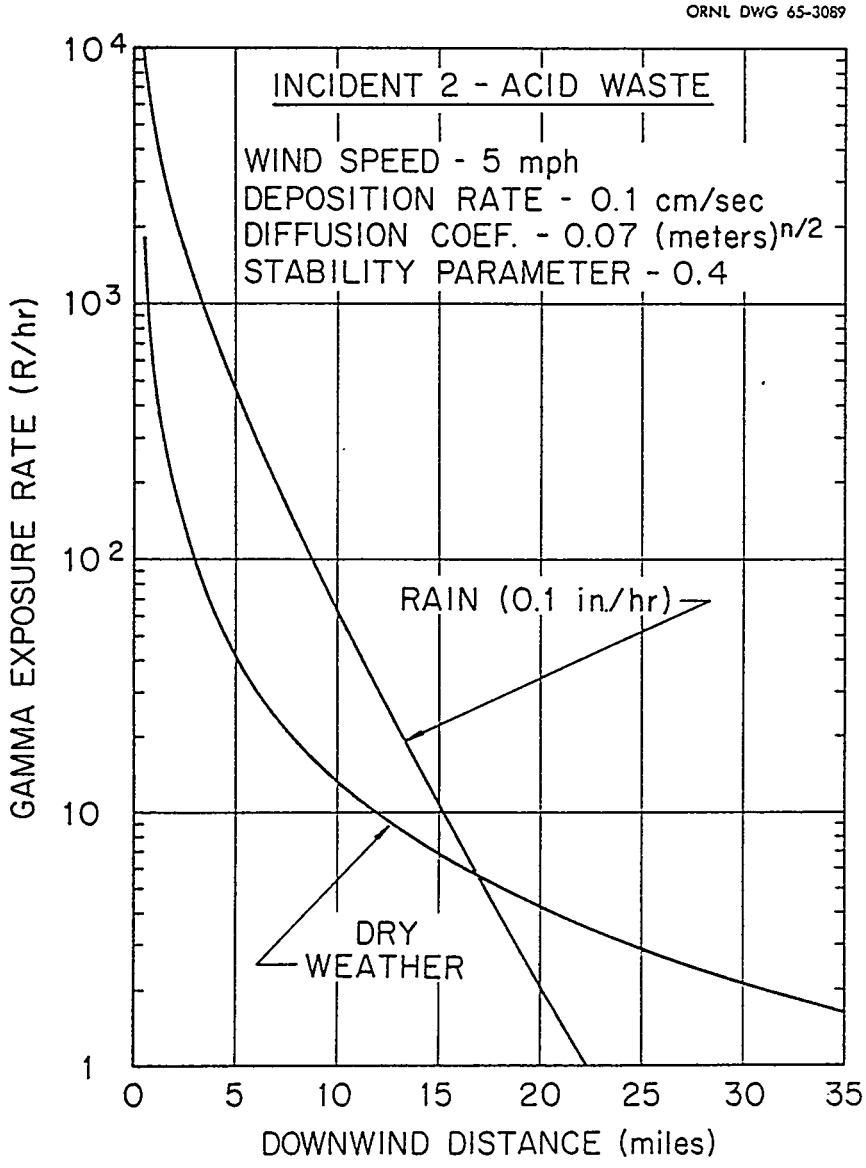


Fig. 4.4 Ground-Level Exposure Rate as a Function of Distance Downwind from an Acid Waste Tank Following Permanent Loss of Cooling.

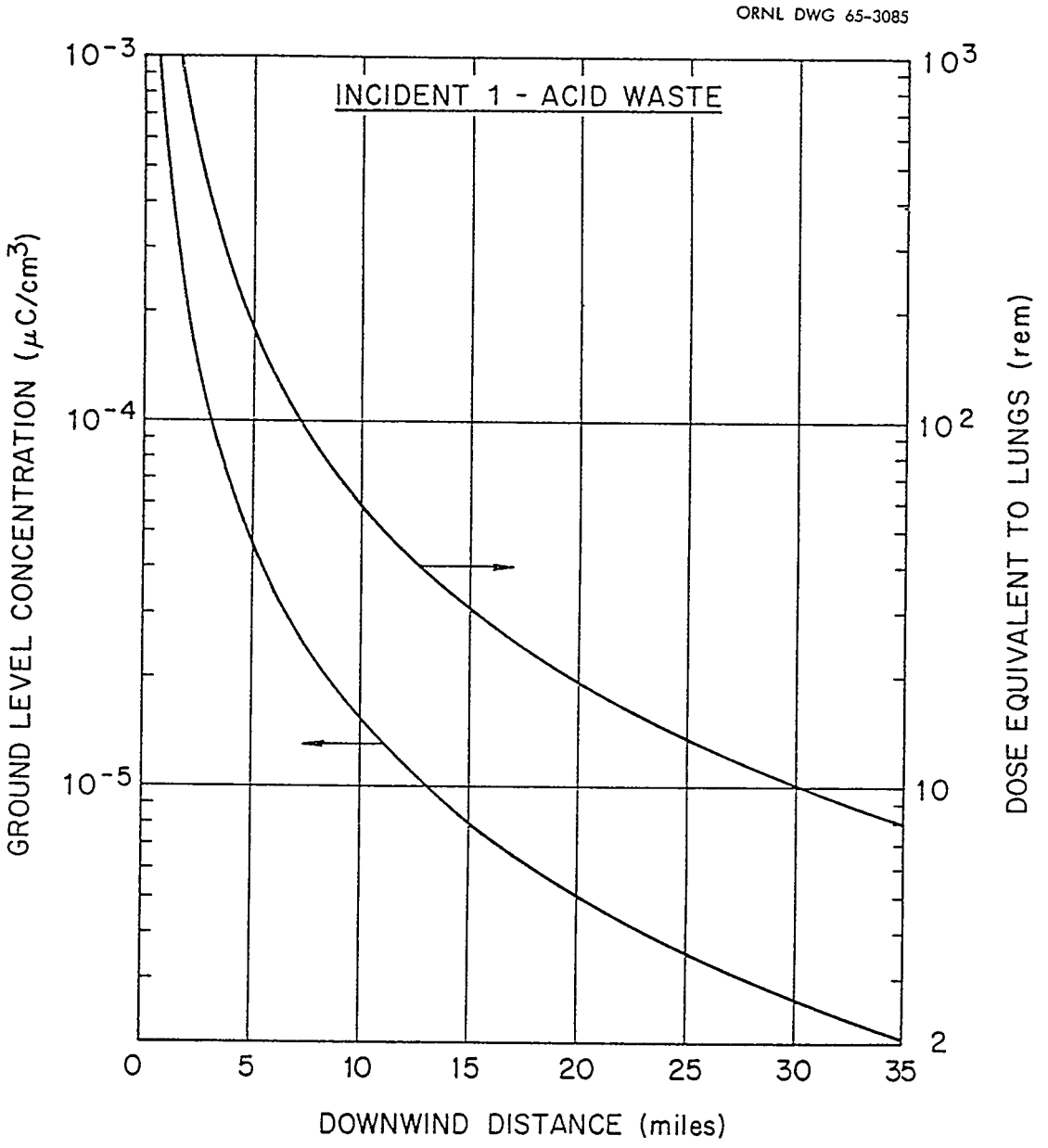


Fig. 4.5 Ground-Level Concentration as a Function of Distance Downwind from an Acid Waste Tank Following Temporary Loss of Cooling.

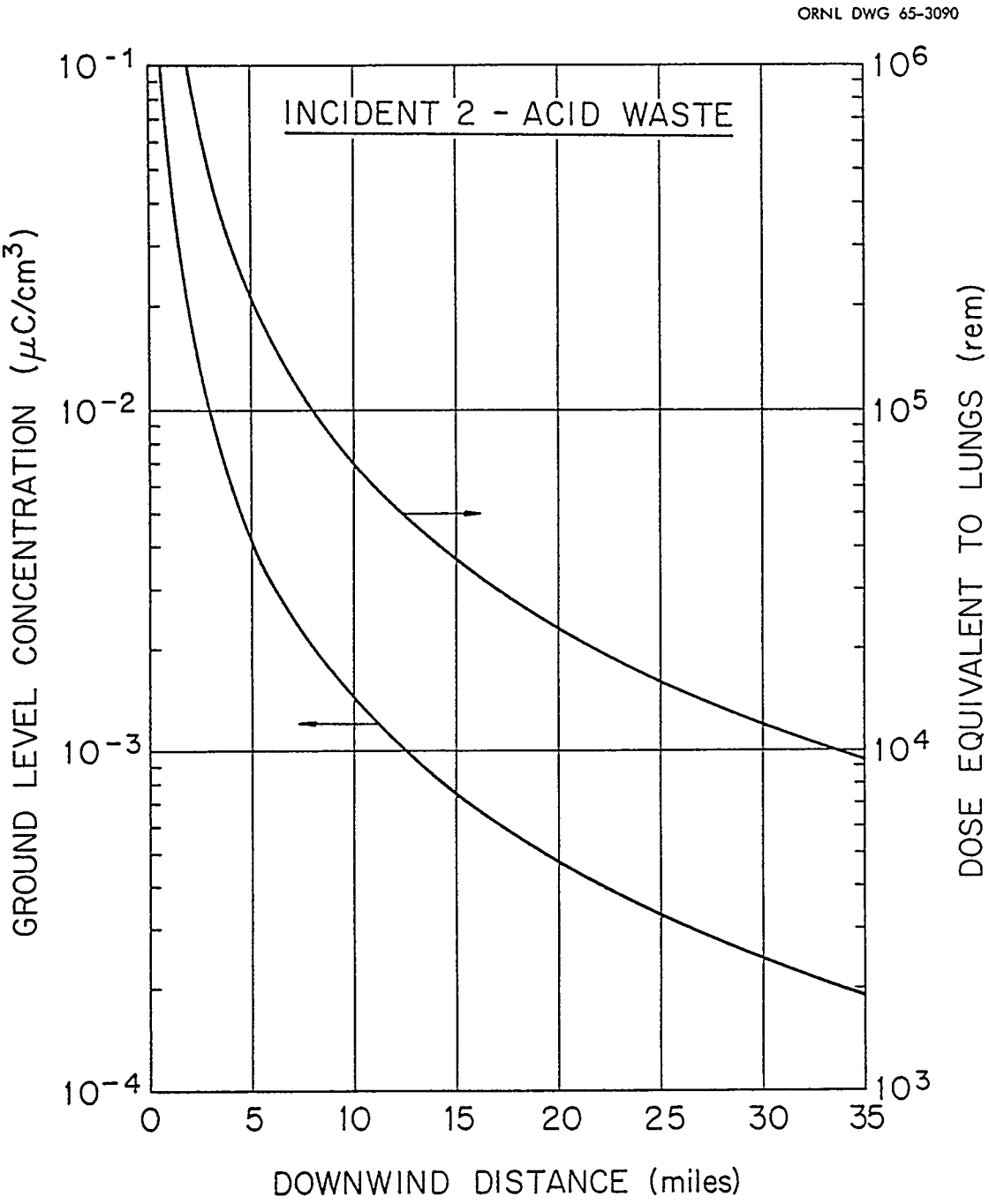


Fig. 4.6 Ground-Level Concentration as a Function of Distance Downwind from an Acid Waste Tank Following Permanent Loss of Cooling.

5. DISPOSAL BY HYDROFRACTURING

5.1 Objectives

The seventh injection in the series of tests with radioactive waste was done (1) to determine the ease with which an injection can be made into the slot used in a previous injection, (2) to evaluate the performance of the mass flowmeter, and (3) to obtain data useful in comparing field mixing of the slurry with laboratory mixing by measuring bleedback of water from the grout. The waste solution had about 1.25 times the concentration of dissolved salts in normal ORNL waste. The activity of the waste solution in the underground tanks average 0.08 curie/gal, mostly due to ^{137}Cs. About 50 curies of ^{60}Co were added to the waste to distinguish it from that used in injection 6 when cores are recovered.

5.2 Plant Modification and Preparation

Tsuneo Tamura
R. C. Sexton[a]
Wallace de Laguna[b]
E. G. Struxness
F. S. Brinkley
H. O. Weeren[c]

5.2.1 Plant Modifications

Following injection 6 considerable concern was expressed by the Halliburton representative about the lumps that had been found in the solid mix. It was theorized that they had been formed by water condensed from the air during blending and aeration. To avoid their formation, a different blower was obtained. It was capable of supplying 450 cfm of air at 30 psig rather than 100 psig. However, it was found that the clumps had formed prior to blending (Sect. 5.2.2).

One of the heads of the injection pump was replaced. The pump was repacked, and new Chicksan fittings were installed on the high-pressure discharge. The sump tub was found to contain set cement (cement that had entered dry and had later become wet). Caked cement was also found

---

[a]Plant and Equipment Division.

[b]Leave of absence.

[c]Chemical Technology Division.

in the tub drain line. The cement was chipped and scraped out of the tub and drain lines, and hydrochloric acid solution was circulated through the system to complete the cleaning.

The concrete waste pit had been filled with cement in the cleanup operations of injection 6. Another pit was made and the suction and drain lines rerouted to the new pit. The suction line from the waste pit to the waste pump was plugged with cement, and this line was replaced. Bin 4 contained solids left from injection 6; all bins and "P" tanks were inspected and cleaned before use in injection 7.

The top of the wellhead cell was removed to simplify decontamination. The cell and the cell top were decontaminated, and the grating on the bottom side of the cell top was covered with welded metal sheets to make any future decontamination easier. The cell top was replaced and the cell was repainted.

5.2.2 Solids Blending

Blending was started on August 2, 1965. The contents of two trucks were blended and stored in bin 1. The third truck could not be fully unloaded because of many large clumps in the bottom. The source of the clumps was traced to its origin, and the blending was suspended until fresh material could be obtained. A screen was made and mounted on the truck for straining out any lumps during delivery.

Blending operations were resumed, and the blended solids were stored in bin 2. However, the clumps were found during delivery of solids, and blending had to be suspended again. Laboratory tests of samples of blended solids from bins 1 and 2 showed evidence of "flash setting", which was not encountered earlier when bagged samples were used. Further tests showed that the synthetic waste stored in the waste pit could be used with this blend without flash setting, and these solids were reserved for use with the synthetic waste. A new mix (second mix) to be used with actual ORNL waste was formulated, and there was no flash setting.

Blending was resumed after 10 days; no further difficulty was encountered, and bins 3 and 4 and the "P" tanks were charged with the new mix. A total of 587,000 lb of solids were stored.

5.3 Injection

Tsuneo Tamura
R. C. Sexton
Wallace de Laguna
E. G. Struxness
F. S. Brinkley
H. O. Weeren

To ensure that the slot used in injection 6 would be capable of accepting fluid, the well was pressurized to 1600 psi, and a minimum of water was used to open the formation and ensure an adequate pumping rate. The injection took place on August 16. As planned, a water-solids mix was injected for the first 20 min to determine that the mass flowmeter was functioning properly. Injection of waste was started after this initial test.

It was soon established that the mass flowmeter readings were too high. Knowing the weight of solids in bin 3 (second mix) and the volume of waste pumped, it was calculated that the mix ratio had been 6 lb/gal instead of the desired 7 lb/gal. A similar error was noted after bin 4 (second mix) was empty. It was later suspected that the high reading was caused by a buildup of solids on the mass flowmeter.

Since the densometer and mud-balance reading had indicated that the solid:solution ratio was too low, the flow of solids was increased. However, the change was made when the waste solution being disposed was the synthetic waste 0.3 times the usual ORNL concentration, and the solids had been designed for a tank waste of 1.25-fold concentration. The lower salt concentration of the waste was caused by further dilution of the waste standing in the waste pit when the volume decreased through seepage. The increase in solids to this solution caused the slurry to be too viscous. This slurry could not be handled by the pumps, hence, the injection was halted, and the slurry was flushed out with water.

The injection was restarted by using a lower solids:liquid ratio for the remaining solids in bin 3, which were the original "P" tank solids (second mix). Although there was some suspicion that the solids in bin 1 (first mix) contained clumps, which might cause flow stoppage, no stoppage occurred. After bin 1, the solids of bin 2 (first mix) were used. Based on the rate of solids consumption and the amount of solids stored in the bin, it was planned to complete the injection by

using water and solids during the last 15 min. The use of water at the end serves to decontaminate the lines and the well. It required 54 min instead of 15 min to use up all the solids, which suggests again that the solids:liquid ratio was below that desired. The injection well was overflushed with water and valved shut rather than plugged; this was done to enable measurement of phase separation by bleed-back measurements.

5.4 Analysis of Data

Tsuneo Tamura
R. C. Sexton
Wallace de Laguna
E. G. Struxness
F. S. Brinkley
H. O. Weeren

Figure 5.1 shows the liquid volume pumped during the injection as measured by waste storage tank volumes and the flow totalizer. Since the tanks were directly calibrated and hence their reading more reliable, the data indicate that the totalizer was reading about 15% high.

Figure 5.2 is a plot of the solids flow rate based on the mass flowmeter readings, on calculations from the densometer readings, and the difference between the two. Comparison of these curves shows a gradually increasing difference for the first 90 min and a nearly constant difference thereafter, except for 30-min period when the mass flowmeter indicated very high flows and the densometer indicated lower than average flows. Integration of the mass flowmeter curve yields a value of 835,000 lb for the total weight of solids consumed; integration of the densometer curve yields a value of 635,000 lb (with no correction for the 3-min when consumption of solids was probably much higher than indicated). Since only 588,000 lb of solids were actually used, the accuracy of both curves is obviously poor.

It was noted during the injection that solids were building up on the mass meter and giving high readings. This would account for the difference in the mass-meter reading and the densometer. The mass-meter curve was therefore corrected by subtracting a fixed quantity from each reading over 90 min and a proportional quantity below 90 min. The amount subtracted was also chosen so that an integration of the corrected curve would give 588,000 lb of solids. With this corrected curve, the solid:

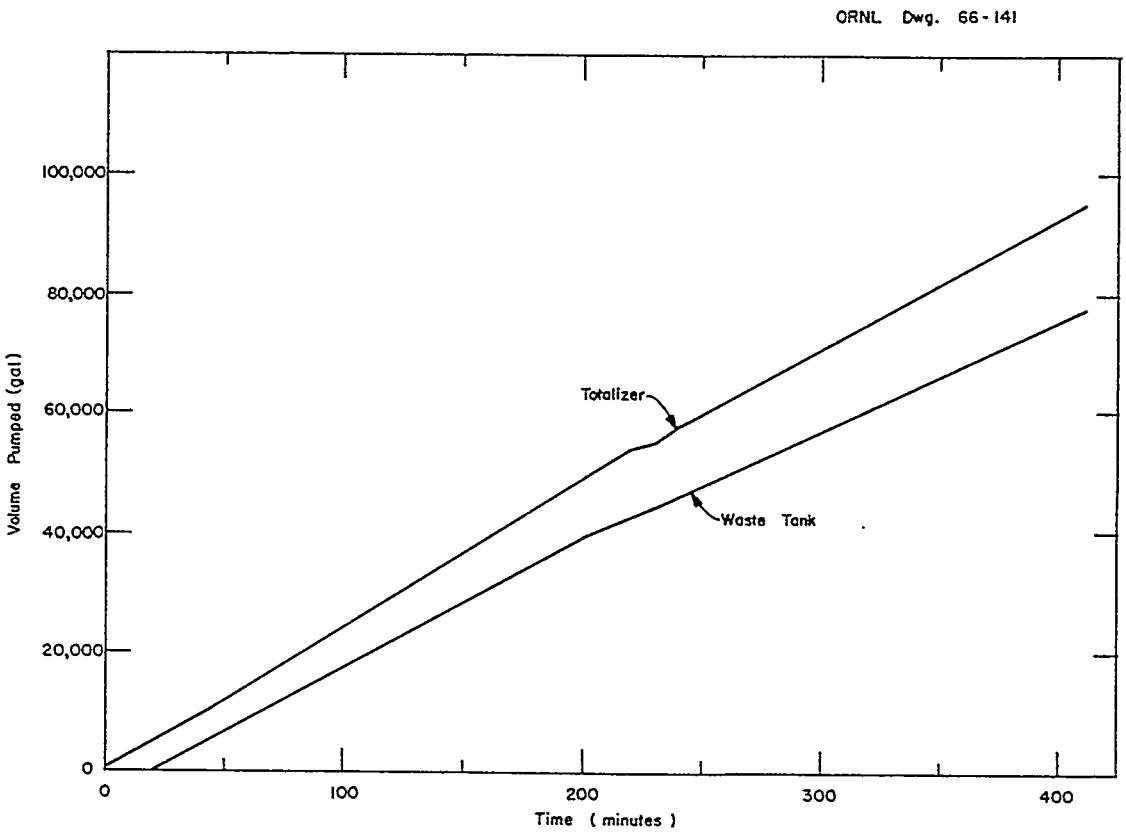


Fig. 5.1 Volume of Waste Pumped According to Readings Taken from the Waste Tank and from the Totalizer.

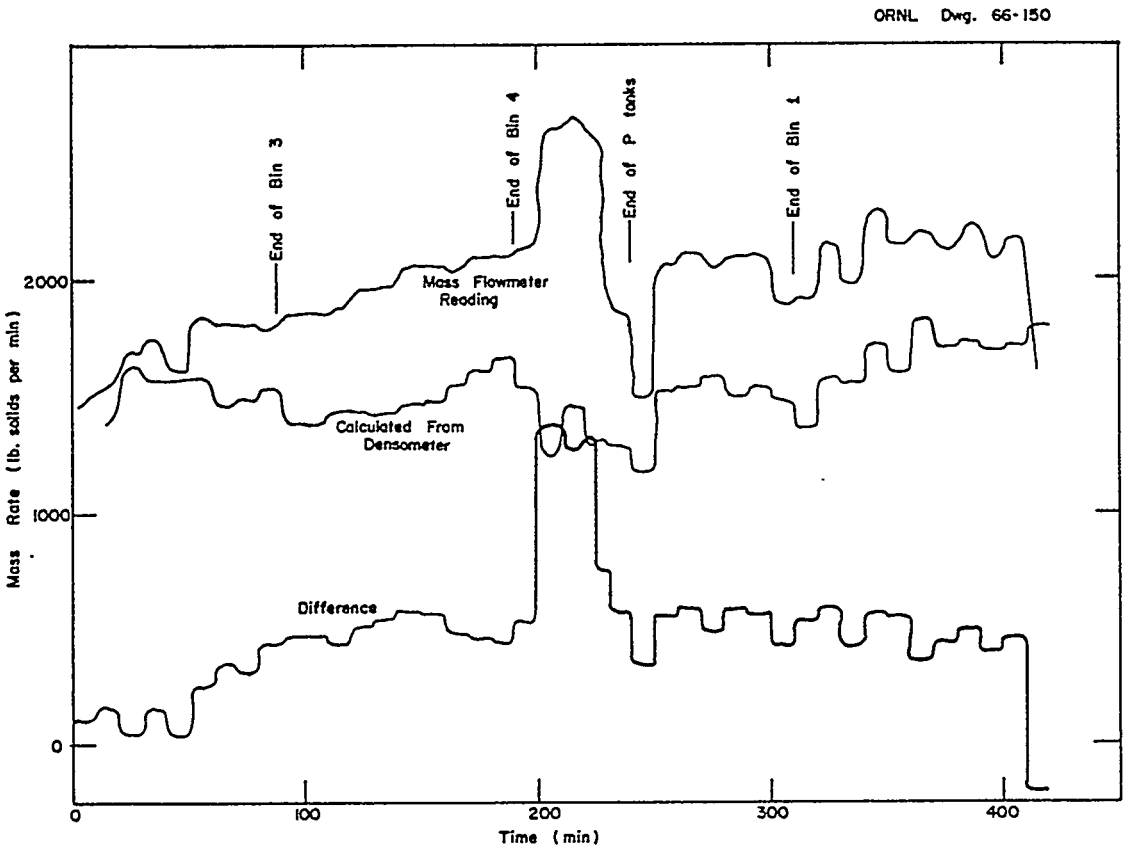


Fig. 5.2 Rate of Solids Feed Based on Mass Flowmeter Reading and Calculated from Densimeter Reading. The difference of the two readings are also shown.

liquid mix ratio was calculated, and the resultant curve is shown in Fig. 5.3. The desired mix ratio is also indicated in the figure. Note that except for a short period, the actual mix ratio was substantially below that desired. With most of the waste containing too little solids, it was suspected that phase separation would occur, and bleedback liquid has been measured during the first 3-1/2 months. These results show that a new mix formulation must be designed to show less phase separation, even with a 10% error in solids:liquid proportioning. Studies are being made, and preliminary results show that formulations with minimal phase separation can be designed.

5.5 Mechanical Effects of Hydrofracturing on Nearby Rocks

W. C. McClain

The effects on the surrounding and overlying rocks caused by injecting grout sheets into the ground at depth are now being studied. This examination seeks to provide information on the optimum sheet spacing and on the maximum number of sheets possible before the overburden fails, resulting in a release of grout to the surface. Better understanding of this subject will also be valuable in the determination of site-selection criteria for other areas.

The situation can be examined theoretically by assuming that the injection of material underground is inversely analogous to removing underground material. Concepts from mining-rock mechanics are then applicable to the problem.

A theoretical analysis developed by Salamon,[13] by which displacements and strains at all points in the rock mass can be calculated, is particularly amenable to the hydrofracture case. The solution involves the evaluation, by computer techniques, of the generalized equation,

$$Q = 1/\pi \iint_A S_z(\xi,\eta)\, f(r^2, z, H)\, d\xi\, d\eta ,$$

where

Q = the desired orthogonal deformational component, such as vertical movement, horizontal strain, or shear strain in a specified plane;

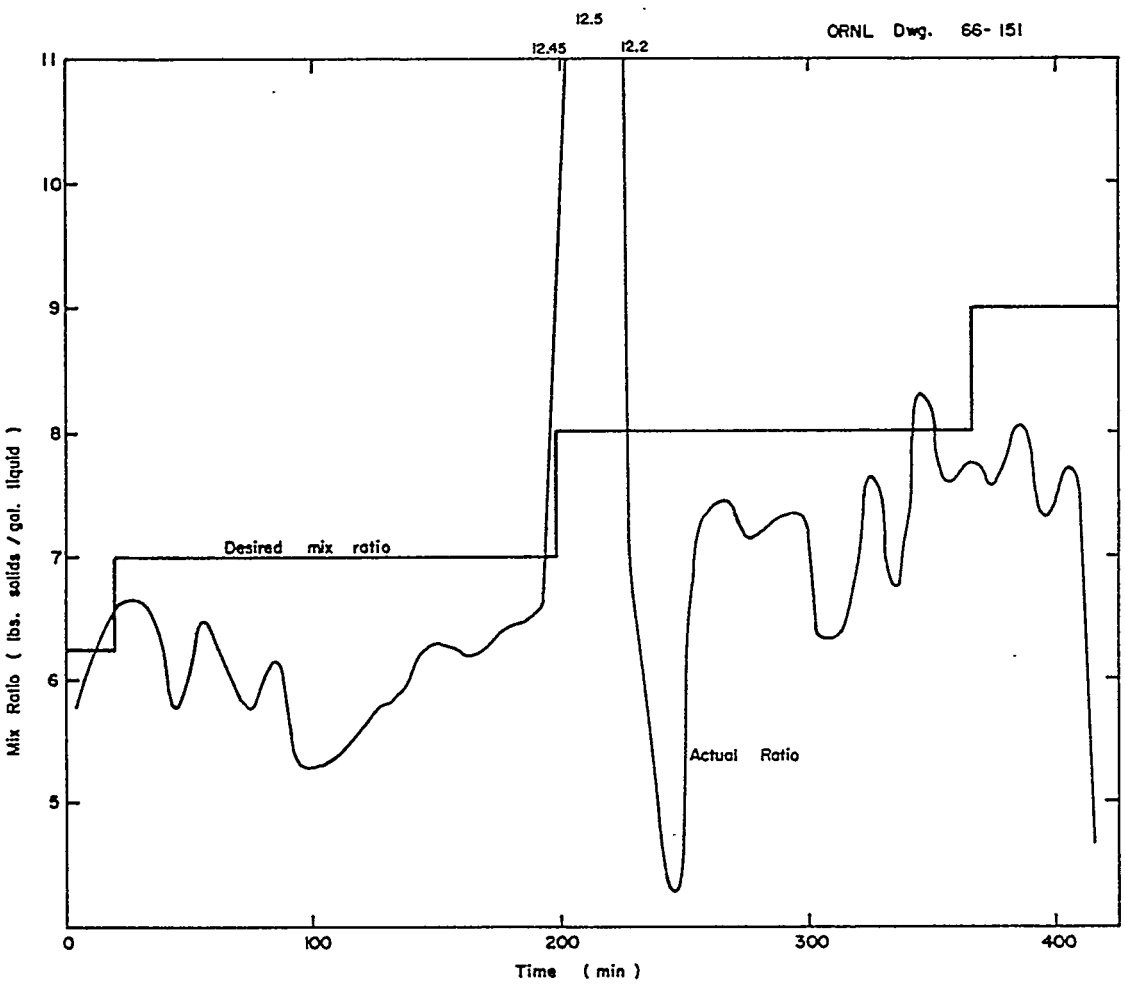


Fig. 5.3 Comparison of the Desired Mix Ratio and the Actual Ratio in Injection 7.

$S_z(\xi,\eta)$ = geometrical expression of the disturbance, in this case, the shape of the injected grout sheet;

$f(r^2Z,H)$ = a functional expression based on (1) the applicable deformational components, (2) the position of the point for which the solution is being made, and (3) the properties of the mathematical model being utilized;

$\iint_A d\xi\, d\eta$ = an integration over the area of the horizontal grout sheet.

The data from the shale-fracturing plant were compared with results of this theoretical evaluation for a number of mathematical models (homogeneous isotropic, homogeneous transversly isotropic, frictionless laminated and multimembrane) approximating the properties of the actual site. Based on the comparisons, a number of conclusions were drawn, contributing to the understanding of the hydrofracture phenomena.

Some of the more important of these conclusions are:

1. For injections similar to those at the shale-fracturing site (1000 ft depth, grout sheet of some few hundreds of feet in areal extent), the maximum surface uplift represents only a small fraction (5 to 20%) of the thickness of the sheet but extends over several times the area.

2. The volume of surface uplift should be equivalent to the injected volume.

3. For a given shape of injected grout sheet of constant horizontal dimensions, the surface uplift is everywhere proportional to the thickness of the sheet.

4. For an ellipsoidally shaped injection of high eccentricity in plan view (ratio of horizontal axes = 1/5), the surface uplift is very nearly circular and does not reflect the eccentricity of the injection.

5. For an injection which is circular in plan and elliptical in section, a region of high tensional strain in the vertical direction exists at the tip of the ellipse, while the maximum shear strains occur above and below the flanks of the injection.

6. DISPOSAL IN NATURAL SALT FORMATIONS

6.1 Preparation for Project Salt Vault

W. J. Boegly, Jr.
R. L. Bradshaw
F. M. Empson
W. C. McClain
F. L. Parker
W. F. Schaffer, Jr.

6.1.1 Prototype Test

Phase IV of the Hole Liner Prototype Experiment was terminated on July 19, after 47 days of operation without off-gas purge. The new bottom section of the lower liner, made at ORNL (type 304L stainless steel) and attached by the Lyons Manufacturing Company, appeared to be in good condition, although there was a bright red coating on the bottom three inches. The off-gas system was operated for 45 min just before shutdown, producing about 50 ml of condensate.

6.1.2 Safety Analysis

A draft copy of the Safety Analysis for the operation of Project Salt Vault[14] was completed, and reviews were held with the ORNL Radiochemical Plant Review Committee[15] and the Kansas State Board of Health.

The maximum credible accident for Project Salt Vault is one in which the canister is dropped down the waste-charging shaft, resulting in the destruction of the canister and failure of the cladding on some of the fuel assembly plates. Since fuel meltdown is not possible, it is assumed that 0.1% of the iodine and 100% of the rare gases contained in 19 fuel plates (each ETR assembly is composed of 19 plates) is released to the shaft. Because air flow is restricted in the shaft during transfers, and the material released is not vented until the waste-shaft fan is turned on, optimum meterological conditions can be selected prior to release. Even if this were not the case, and the activity from the fuel assembly were released during an inversion condition, the following would occur: Released ^{131}I would result in restrictions on mild production on land within a downwind distance of 1050 m, and at a distance of 100 m from the waste shaft an inhalation dose to the thyroid of 1.6 rems would be received; the ^{85}Kr and ^{131m}Xe released would result

in submersion exposures to an individual standing 100 m from the source of 42 and 16 millirems, respectively. Since milk production within 1050 m is negligible, and since it is possible to exclude workers from an area 100 m from the waste shaft, the consequences of a maximum credible accident can be minimized.

6.1.3 Equipment Installation

Procurement and installation of the waste-shaft fan has been completed. The fan will normally draw 5000 cfm of air up the shaft from the experimental area, but in an emergency the air flow can be reversed.

The hoist for handling the canisters has three speeds: 100, 33, and 1.6 ft/min. In normal operation, the slow speeds are used when the canister is being raised or lowered from the shipping carrier. The high speed is used for most of the canister travel in the shaft. The hoist is equipped with standard mine-safety auxiliaries, such as independent dual brakes, slip clutch, and a depth indicator. The capacity of the hoist (2000 lb) is sufficient to handle 12-in. calciner pots and to remove people from the mine in the case of an emergency in the main hoisting shaft.

Figure 6.1 shows room 1 (main radioactive array) during the time that the experimental equipment was being installed. The tops of the hole liners may be seen in this figure, along with the trenches containing heater, thermocouple, and off-gas lines. The large white box on the wall contains the off-gas system flowmeters. In the upper right corner of the picture may be seen the end of the main power-control panel.

6.1.4 Preoperational Tests

A number of operations were performed with empty fuel-assembly canisters to test the procedures, and minor procedural changes followed.

Early in October, two canisters were loaded with 500 curies each of ^{60}Co and shipped to Lyons in the shipping carrier. A fan-shaped beam was found to emanate from one section of the carrier (apparently due to

Fig. 6.1 Room 1, Main Radioactive Array of Waste Storage Canisters.

a gap in the lead shielding), necessitating the addition of an auxiliary shielding ring. The canisters were lowered into the mine, placed in the array holes, and removed a number of times to obtain handling experience with radioactive canisters and to evaluate the shielding calculations. It was also found that a "scatter" shield was needed inside the shot-retainer tubes in the hole liners.

All experimental equipment, such as the off-gas system, fission-product leak-detection system, etc., was put through a shakedown test before startup. The chief difficulty encountered was failure of the "Electrofilm" heaters on the off-gas-system tubes in the upper sections of the hold liners. During the shakedown tests, three of the seven heaters in the electrical array and two of the heaters in the radioactive array failed. There was no apparent reason for this since the units were operating below their rated temperature. Three units were repaired and two were replaced. No additional trouble was encountered with the operation of the electrical-array off-gas heaters, but by the second week after startup, all seven (including the replacements) of the units in the radioactive array had failed. Since there has been no indication of a water problem in these arrays, there are no plans to make any further replacements. However, it will be necessary to obtain more reliable units for installation of the array in the old mine floor, since water problems do exist there.

6.2 Startup of Project Salt Vault

R. L. Bradshaw
F. M. Empson
W. J. Boegly, Jr.
W. F. Schaffer, Jr.
F. L. Parker
W. C. McClain

6.2.1 ETR Fuel Assemblies

The 14 fuel assemblies from the Engineering Test Reactor cycle 73 were canned, the cans leak-tested, decontaminated, and loaded into the shipping carrier at the NRTS in Idaho without any major difficulties. Radiolysis of the coolant (ethylene glycol and water) presented a problem, which was solved by using plain water and installing a demineralizer in the cooling system.

The irradiation history of each of the fuel assemblies was taken into account in calculating the fission-product decay heat, and the assemblies were paired so that the total heat content of each canister would be about the same. The calculated heat generation rate as a function of time is shown in Fig. 6.2. The rates for five of the canisters follow this curve almost exactly, while the other two deviate by less than 10% (lower). Note that on November 18, the heat generation per canister was about 520. On November 1 (the original target date), the heat generation rate would have been about 630 w, compared with the 750 w calculated under the assumptions of the original feasibility study. The total fission-product activity in the seven canisters as of November 18 is calculated to have been about one million curies.

6.2.2 Startup

In order that the peak salt temperature may be raised to the vicinity of 200°C within the duration of the test (2 years) and with the limited number of heat sources, auxiliary heaters are attached to the hole liners. To simplify operation and analysis of data, a fixed power input was chosen. All holes are to be operated with a power input of 1500 w.

On November 15, the electrical (control) array and the main-radioactive-array heaters were turned on at 1500 w each. The heaters were operated two days before the first canister was installed so that the relationships between the temperatures at the prime points of comparison in the arrays could be established. The prime comparison point is the one at the vertical center-plane of the canisters but 1-1/2 ft from the central axis of the canister. Then, as each radioactive canister was placed, the electrical power was cut back so that the sum of the fission product power and electrical power was still 1500 w. Later, as the fission products decay, the electrical power will be increased periodically in accordance with Fig. 6.2.

On November 17-19, all seven of the fuel-assembly canisters were lowered into the mine and placed in the floor. Only one of the seven caused any difficulty. This canister could not be lowered out of the shipping carrier and finally had to be forced out by means of a steel

ORNL Dwg. 66-132

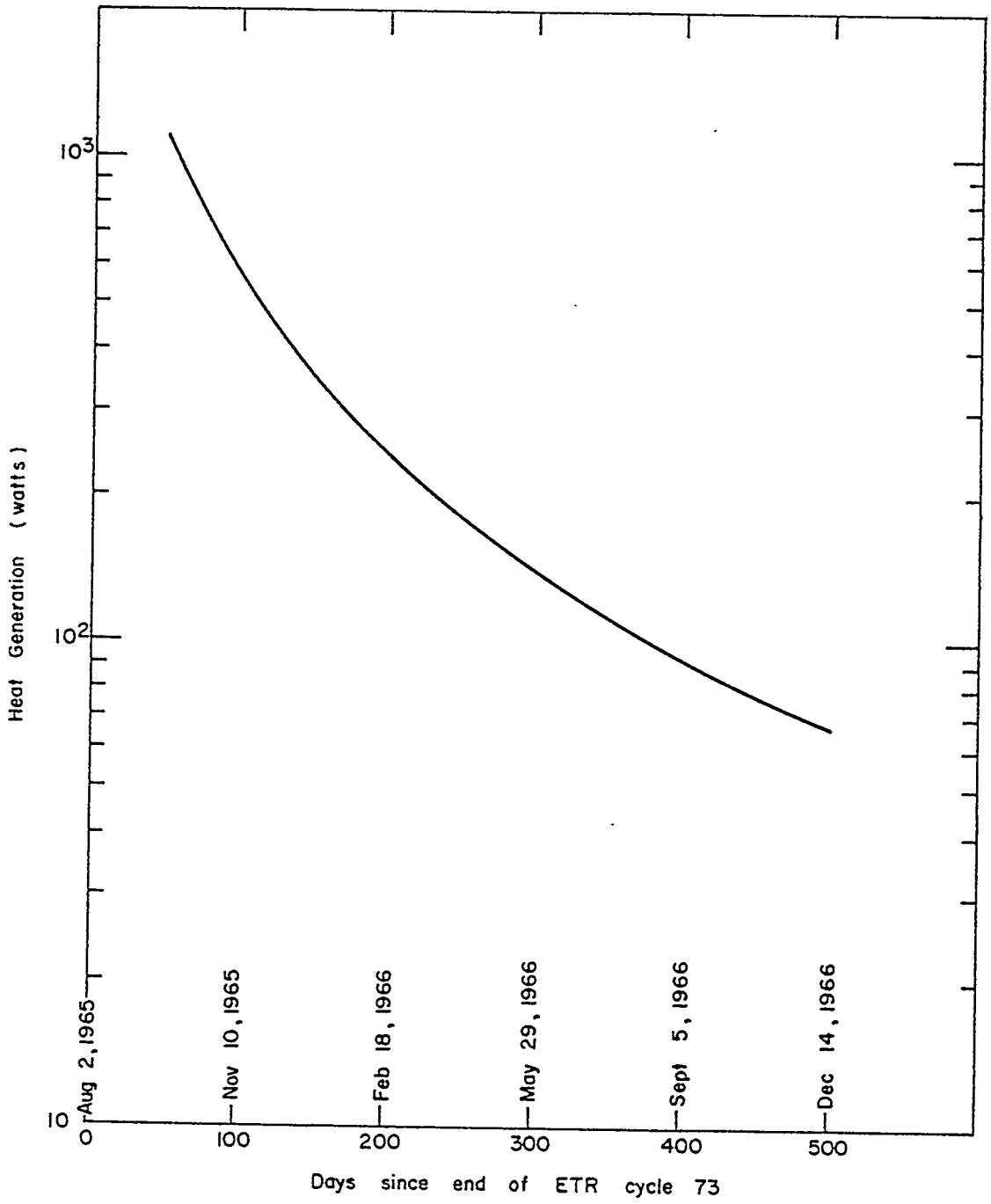


Fig. 6.2 Heat Generation Rate for All Canisters Except 2 and 4.

rod inserted through the cable port. No trouble was encountered in placing the can in the hole liner (tolerances are greater than in the carrier). A piece of tape was seen to be stuck to the top and side of the canister shield plug and may have caused the trouble.

The maximum radiation dosage received by any of those on the project during the entire loading period was 200 mr. Radiation levels immediately above the array holes (after installation of the scatter shields) are generally less than 10 mr/hr, and unlimited access is allowable everywhere except immediately over the holes.

6.2.3 Preliminary Results

Salt-Dose Measurements.--During the first week of operation, the dose rates in the air annulus between the hole liner and the salt and at various depths into the salt were measured with the specially developed chemical and glass-rod dosimeters. The results with the two types of dosimeter were in reasonable agreement with each other and with the theoretically calculated dose rates. The chief difference is that the peak dose rate appears to be at the surface of the salt, whereas the calculations showed the peak occurring at around 2 cm into the salt. The measured dose rate at the surface of the salt was about 5×10^4 rads/hr.

Temperature Rises.--Figure 6.3 shows the temperature-rise curves at the prime comparison point for the center and one peripheral hole. Data for both the electrical and radioactive arrays are shown, along with the theoretical curves calculated by using the 20°C thermal properties of salt. As may be seen from this figure, temperatures in both the electrical and radioactive arrays are satisfactorily close (both before and after placing of the canisters) to each other and to the theoretical calculations. As indicated in this figure, most temperatures, including the fuel element temperatures, are running somewhat lower than calculated. Fuel element temperatures range from about 225 to 265°C.

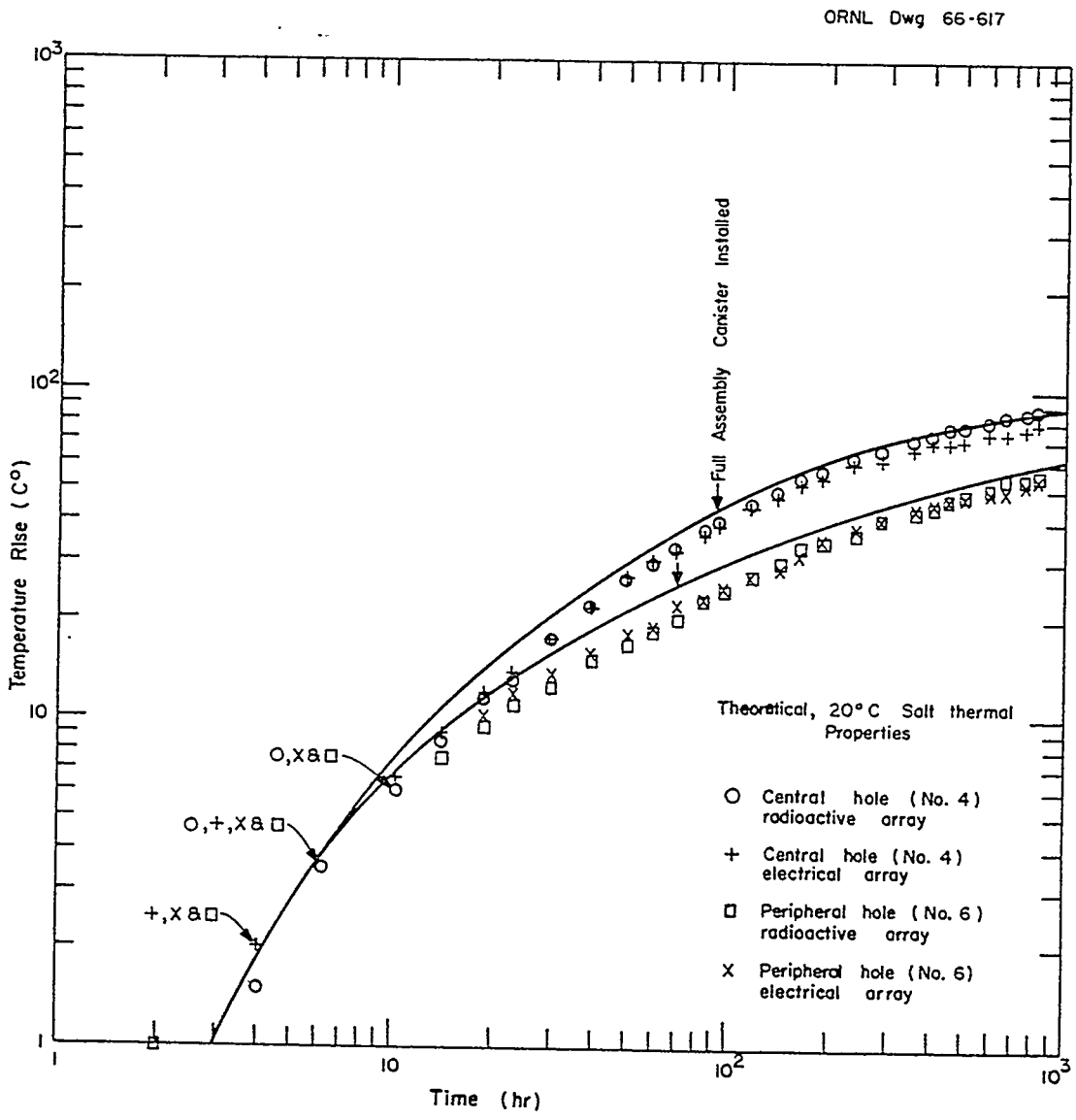


Fig. 6.3 Temperature Rises at 1-1/2 ft from Centers of Array Holes.

Rheological Measurements.--Figure 6.4 shows the floor-uplift profile along the north-south and east-west axes of room 1 (radioactive array) as of December 30, 1965, along with the time plot of the uplift in the center of the array. The results for room 4 are very nearly the same. As may be seen in Figure 6.4, the pillars (edges at 16-1/2 ft on the north-south plot) produce a restraining effect on the thermal expansion of the salt. As a consequence, the edges of the adjacent pillars are experiencing an increased stress (as if the overburden load had been increased), which has resulted in an increased transverse expansion rate in the pillars. In turn, this increased horizontal expansion has resulted in an increased thrust on the roof slab (about 2 ft thick), producing an accelerated rate of sag or separation from the formation above. The magnitudes of roof movement are small and do not constitute a hazard at the present time. As yet little or no temperature rise has occurred under (or in) the pillars themselves, and thus the increased pillar and roof movements are due only to transfer of thermal stress from the floor in the middle of the room.

To date, no significant differences in behavior between the two arrays have been observed, even though the peak salt dose had passed 10^7 rads by early December. In addition, no chlorine has been detected in the off-gas from the hole annulus.

6.3 Pillar-Model Studies

T. F. Lomenick

6.3.1 Effects of Shale Partings

Previous tests on scale-model specimens of rock-salt mine pillars have shown the effects of temperature, compressive loads, and time on cavity closure.[16] Lithologic changes in the salt column can also markedly affect the deformation of mine pillars. Even though some salt deposits, such as salt domes, are practically all salt, most bedded deposits contain lithologic discontinuities, or rock salt interbedded with layers of dolomite, shale, anhydrite, and other materials. For instance, the 300-ft-thick salt sequence at Lyons, Kansas, is only about

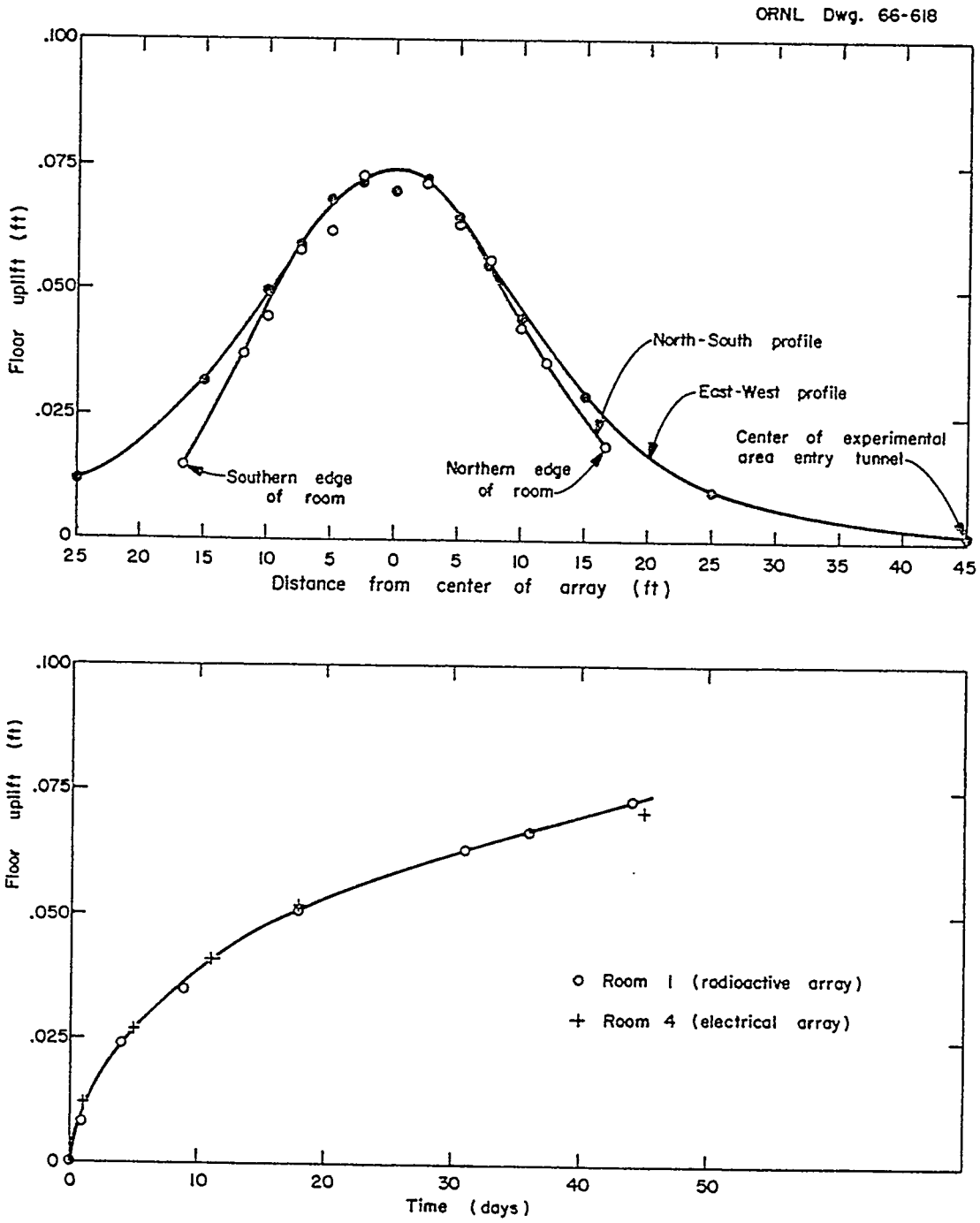


Fig. 6.4 Floor-Uplift Data.

60% NaCl with the other 40% being mostly shale and anhydrite.[17] In many cases these other materials may form a part of the roof, floor, or even the pillars in a mine and thus enter into the deformation of the openings. Shale layers (sometimes called "partings") are common in bedded salt deposits, and in many cases the salt is mined or falls to these layers since they form planes of weakness. The presence of these shale partings, even though they are quite thin, can have a significant effect on the rate of cavity deformation, depending on whether the shale is at the top and bottom of the pillar or in the center of it. This is shown in Fig. 6.5, where deformation curves are presented for model salt pillars that have been deformed (a) without any simulated shale partings, (b) with simulated shale partings at the top and bottom of a pillar, and (c) with a simulated shale parting in the center of the pillar. Thin sheets of Teflon lubricated with grease and graphite serve as friction reducers and thus simulate shale partings. (Analysis of data and observations from the Kansas mines indicates that the shale partings do have a lubricating effect, but it does not appear that they have so marked an effect as do the Teflon sheets. Therefore, the actual effects to be expected in a mine would lie somewhere between the two extremes shown in Fig. 6.5). For the model having no simulated shale partings, and for the model where the shale parting is in the center of the pillar, the deformational curves are almost identical, both showing about 0.03 in. or 3% deformation after 140 hr of testing. However, for the model with friction reducers at the top and bottom of the pillar, note that the deformation proceeds initially at a very fast rate before beginning to decrease with time. The model appears to then deform at a constant rate for a short time and then at an increasing rate that results in sudden failure after less than 130 hr. It is also of interest that for models with no simulated shale partings, sudden or catastrophic pillar failure could not be induced even under stresses as high as 14,000 psi.

The accelerated deformation rate of the models, when simulated shale partings occur at the top and bottom of the pillars, apparently results from the more or less independent deformation of the pillar from the roof and floor under these conditions. When there are no partings at

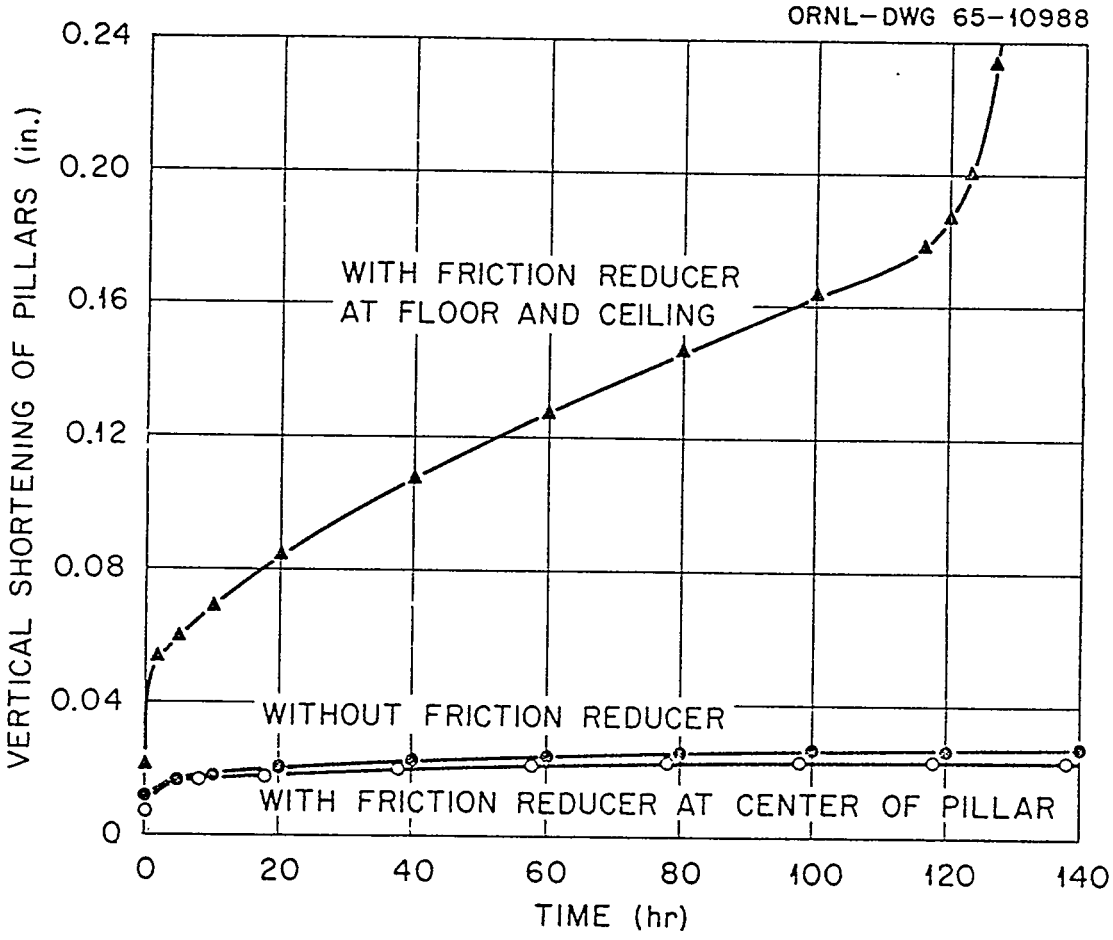


Fig. 6.5 Deformation of Model Rock-Salt Pillars at 4000 psi.

the top and bottom of the pillar, or even if the parting is in the center of the pillar, there is an interlocking effect of salt crystals from the pillar to the roof and floor which serves to allow the pillar, roof, and floor to deform more or less as a single unit. However, when partings exist between the pillar and the roof and floor, they serve as effective friction reducers, which consequently allow the pillar to deform more independently of the roof and floor, since horizontal confining pressures in the roof and floor are not transmitted into the pillar.

6.3.2 Deformational Behavior

Although the exact mechanisms of deformation within salt pillars are not fully understood at present, some generalizations as to movement have been formulated through observations of deformed specimens. Figure 6.6 shows cross-sectional views of two model pillars that have been cut vertically in half after deformation. Before deformation, the pillars were 4 in. in diameter and 1 in. high. In these specimens an attempt was made to define the principal movement through observing the relation of the pillar and the material above and below it after deformation. The dark horizontal lines seen in the salt specimens are 1/8-in.-diam holes that were bored horizontally through the top and bottom of the pillar and filled with colored salt before the specimens were deformed. In the model, deformed at 22.5°C, it is seen that the pillar is only slightly more than 4 in. in diameter. However, a considerable amount of loose salt from the outermost portion of the pillar had accumulated in the surrounding cavity opening but was subsequently removed. The cross-sectional view shows that the pillar did not deform independently of the roof and floor but that all three parts of the model entered into the closure of the cavity. Note especially how the roof and floor have flowed into the cavity opening. The most resistance to deformation in the models is believed to be found in the center portion of the pillar (due to confining pressure) and immediately above and below the pillar in the roof and floor. Thus, movement here is at a minimum. This is shown in the photograph by the greater distance between

PHOTO 81465

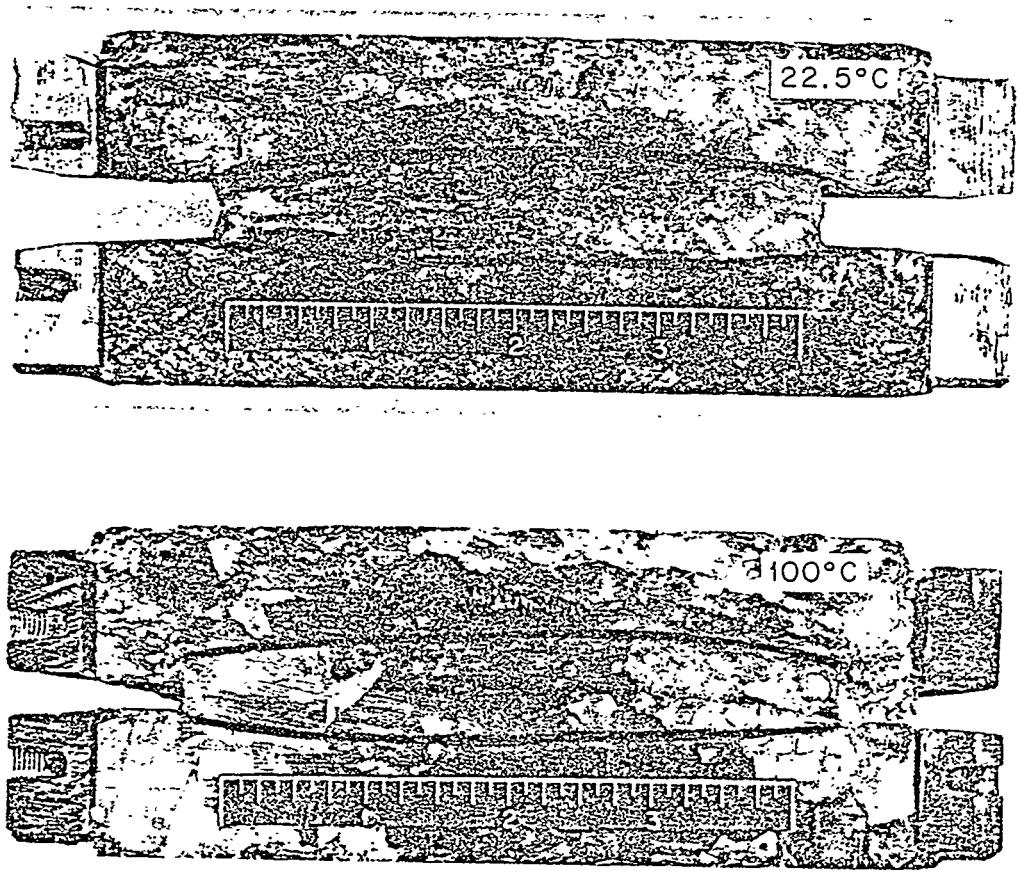


Fig. 6.6 Cross Sections of Model Pillars Deformed at 22.5 and 100°C.

the lines in the center portion of the pillar than at the edge of the pillar. Toward the outside of the pillar, there is less resistance to deformation; thus, salt from the pillars tends to move horizontally into the opening while material from above and below also moves in to fill the cavity.

In the model pillar, deformed at 100°C, the overall deformational pattern is similar to that for the sample tested at room temperature, but instead of the outermost portion of the pillar deforming through spalling, it stayed intact and deformed more plastically. The pillar diameter in this case increased from 4 in. to 4-1/2 in. as a result of the deformation.

In addition to these tests, model pillar tests have been performed on salt from mines at Hutchinson, Kansas; Retsof, New York; Detroit, Michigan; and Grand Saline, Texas. The Kansas salt is from a bedded deposit of Permian age, while the New York and Michigan salts are bedded and of Silurian age. The Grand Saline salt is a dome deposit. In general, there appear to be only slight differences in the deformational behavior of the salt from the mines at Lyons, Hutchinson, Detroit, and Grand Saline. For the Retsof salt, there is initially a much greater rate of deformation upon application of load at room temperature than for salt from the other places. However, after the initial deformation, the Retsof salt then deforms much slower. The reasons for these differences are not known at the present time.

7. SOIL STUDIES

7.1 Desorption of Cesium-137 from Clays and Soils

Tsuneo Tamura and O. H. Myers

The decrease with time in the amount of radiocesium leached when sodium acetate solution was used had been observed earlier with several reference clay minerals.[18] Since only NaOAc had been used and other possible factors had not been eliminated from consideration, it was decided to investigate this desorption more fully. The first factor

to be considered was the influence of anions other than acetate since it is known to cause expansion of the lattice of certain clay minerals.[19] Tests showed similar behavior of the radiocesium when NaCl solution was used, thus eliminating acetate as the cause. To test the influence of other cations, leaching was measured using the chloride salts of K, Ca, Mg, and Li. In these tests, only the A_p and B_2 horizons of the Captina soil were selected for study and for comparison with the reference clays. Figure 7.1 gives the results obtained for the A_p horizon. A decrease is noted with lithium, sodium, and possibly magnesium ions, but not with calcium or potassium ions.

When standard clay minerals were used in similar tests, NaCAc desorbed radiocesium continuously and more efficiently from the kaolinite and montmorillonite (Wyoming bentonite) samples. Muscovite, biotite, and illite behaved in general like the A_p and B_2 of the Captina. Figure 7.2 shows the response of illite obtained under the same conditions noted for the Captina A_p horizon, as shown in Fig. 7.1. Note the similarity in response; the maximum observed with NaCl in the A_p horizon was absent in the B_2, suggesting the influence of organic matter in the upper horizon. Compared with results of earlier tests, the maxima of desorption for these tests occurred at a shorter contact time for these two horizons.

The similarity in response between illite and the Captina samples shows that illite in soils plays an important role in the sorption of radiocesium. Even in the kaolinitic Fullerton soil, the response reported earlier suggests the presence of illite in the subsoil. X-ray diffraction diagrams confirm that illite (10.1 A) is indeed present in the Fullerton soil. The limited amount, however, reduces its influence in this soil. That illite in soil is an important mineral in cesium adsorption was noted early in Frederickson and his co-workers,[20] and also by Schulz *et al.*[21]

The data in Figs. 7.1 and 7.2 suggest that the order of desorption effectiveness is: K > Ca > Na > Li > Mg. Hence, if adsorption of radiocesium were to occur in the presence of these competitive ions,

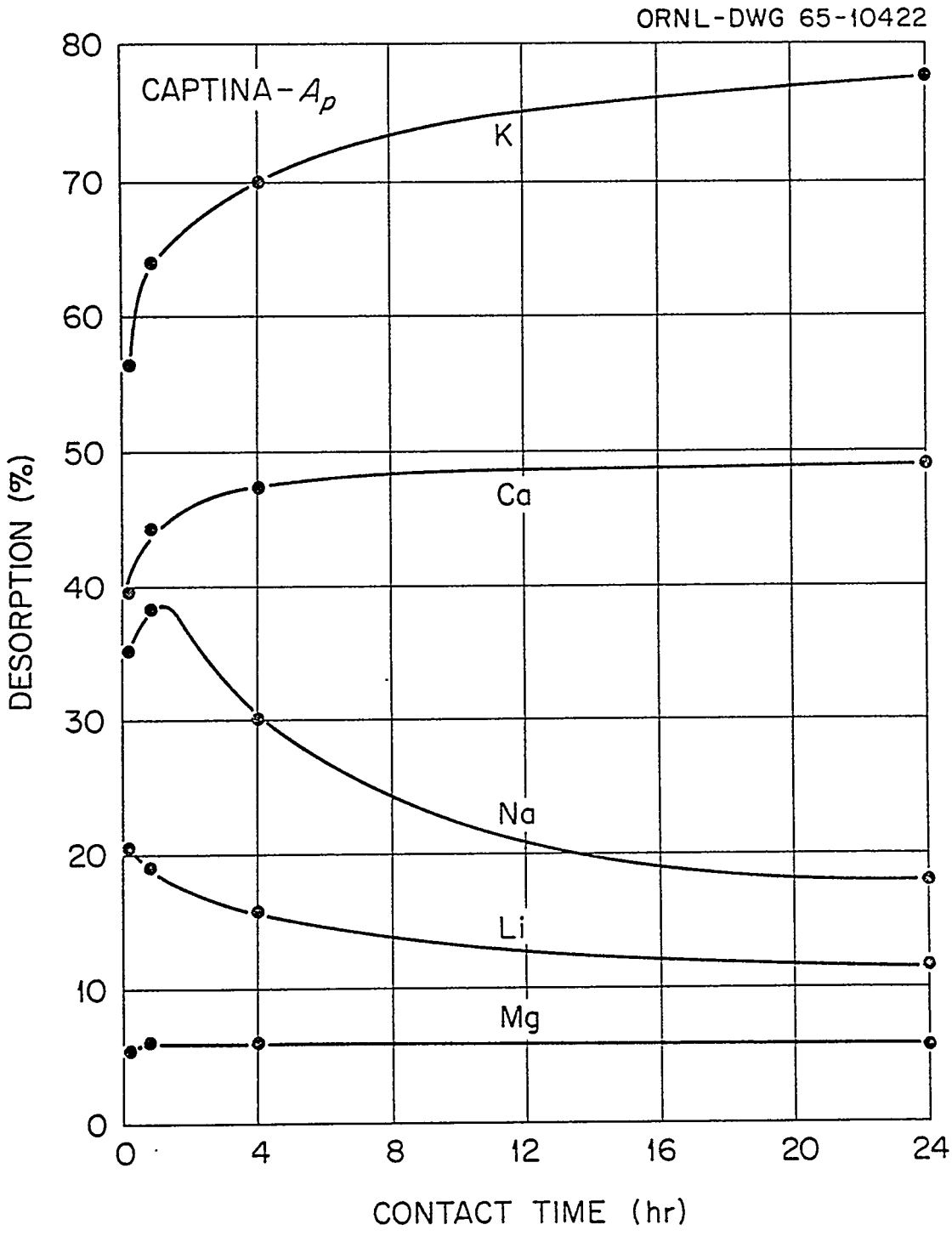


Fig. 7.1 Desorption of Carrier-Free Radiocesium from the A_p Horizon of the Captina Soil by Several Chloride Salts.

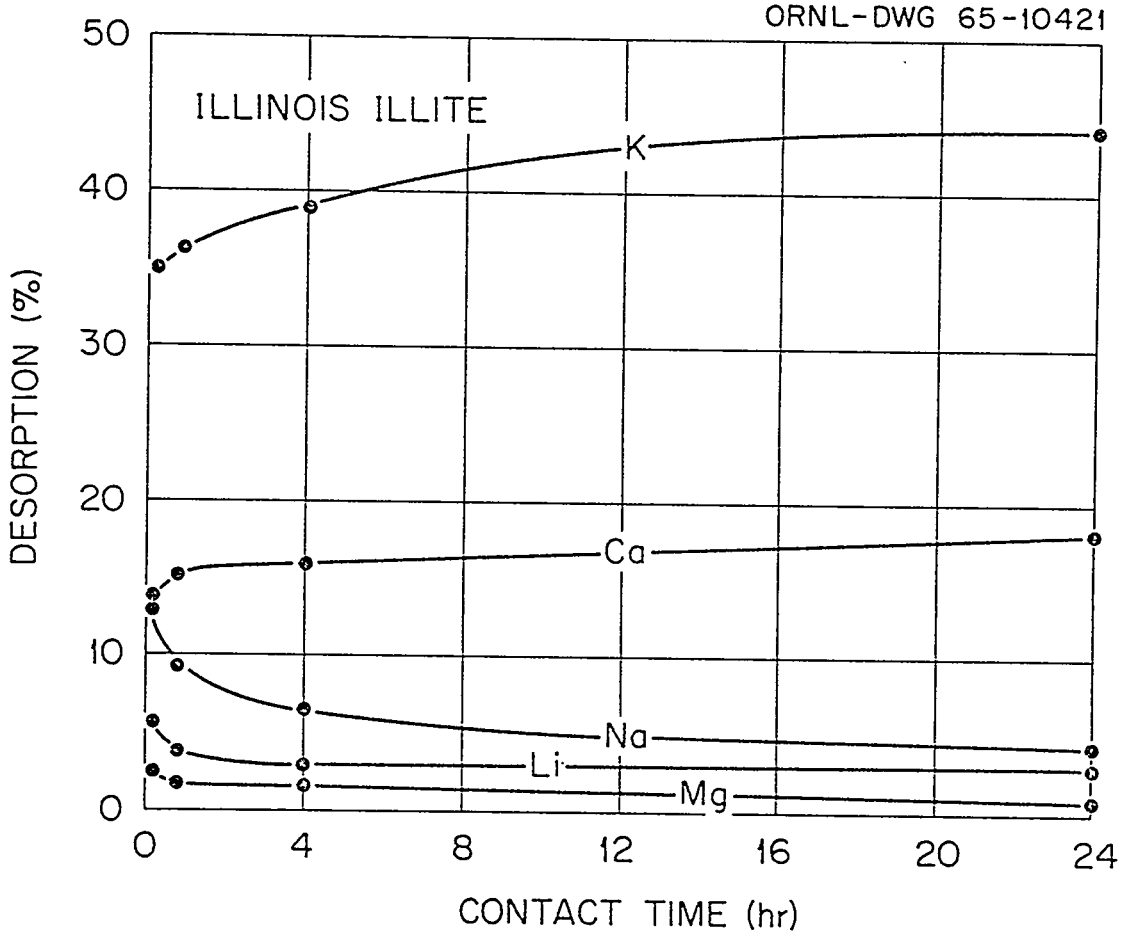


Fig. 7.2 Desorption of Carrier-Free Radiocesium from Illinois Illite by Several Chloride Salts.

more radiocesium, for example, should be adsorbed from a calcium solution than from an equivalent solution of potassium. Tests were made to corroborate this suggestion, and the results are shown in Table 13. The data show that the most effective competitor for radiocesium in tracer levels (2-6 x 10^{-5} mg per 0.1 g of clay) is potassium, followed by calcium, sodium, and magnesium. Hence, the same competitive order followed in desorption (Fig. 7.2) leads to the inference that the observed response is due to ion competition.

If the adsorption-desorption reactions are rapidly reversible, the data in Fig. 7.2 and Table 13 do not support each other. For potassium, one would have expected 96% of the radiocesium to be desorbed, according to the data in Table 13; instead 44% is desorbed (Fig. 7.2). Similarly, with calcium, 50% desorption is expected from the data in Table 13, but 18% is observed. This seeming anomaly may be explained by considering the nearly irreversible adsorption of radiocesium by minerals such as illite.

Table 13. Adsorption of Carrier-Free Radiocesium by Illinois Illite in 0.5 N Solutions of Selected Salts

Adsorption expressed in percent and as distribution coefficient, K_d; 50 cc of solution per 0.1 g of clay

Contact Time	KCl		$CaCl_2$		NaCl		$MgCl_2$	
	%	K_d	%	K_d	%	K_d	%	K_d
1	4.24	22	43.12	379	85.80	3020	98.17	26,820
24	3.40	18	49.11	482	91.12	5130	98.47	32,180
118	4.28	22	52.41	551	98.07	6720	98.78	40,480

The amount of radiocesium fixed irreversibly may be estimated from the response with potassium. From Fig. 7.2 it is seen that 44% is desorbed after 24 hr, leaving 56% on the clay. This 56% represents both irreversibly fixed cesium and cesium in equilibrium under 0.5 N KCl; the latter amounts to 1.5% based on the adsorption K_d for 24 hr, as

in Table 13; thus 54.5% of the cesium on the clay is fixed. Using this value as the amount of cesium not taking part in the desorption reaction with salts, one can calculate the expected desorption with the calcium, sodium, and magnesium salts. Thus, initially as much as 45.5% of the cesium could be desorbed (100% - 54.5% = 45.5%), of which nearly half (49%) would be resorbed in the 0.5 N calcium solution, as shown in Table 13. This should leave 23.2% in solution; the observed value is 18.5%. Similar calculations show that 4.5% and 0.7% of the cesium should remain in solution from the sodium and magnesium solutions after 24 hr, respectively. The observed values are 4.5% and 1.0%, as seen in Fig. 7.2 Hence, the difference in the observed desorption and adsorption of radiocesium is due to fixation in the mineral.

7.2 Movement of Cesium-137 by Runoff, Erosion, and Infiltration

A. S. Rogowski
E. R. Eastwood
Tsuneo Tamura
O. H. Myers

Rainfall for the 1964 to 1965 study period amounted to 53.1 in., and the annual erosion-index (EI) value was 329. The EI value is higher than the long-term average value for the area (210) and has the reoccurrence probability of about once every 15 to 20 years. On the basis of one year's data, the erodibility factor[a] for Captina soil was computed to be 0.40, and the appropriate cover factor[b] for the tall meadow plot was found to be 0.004. Other pertinent erosion parameters that were measured and obtained experimentally are given in Table 14. Large numbers of weeds with woody stems, along with heavy fertilization of plot 3, account for the large amount of plant material in 1965 on the vegetation-covered plots 2 and 3.

In Table 15 ^{137}Cs loss parameters are given. The distribution coefficient K_d for the A_p horizon of Captina soil was calculated to be 27,400 cc/g from field data and can be compared with the 30,000 cc/g value obtained in the laboratory. On the basis of ^{137}Cs concentration in the eroded solid and liquid runoff, the K_d values and the depth of penetration into the soil, the concentration in the soil, and the

[a] Erodibility factor = soil loss in tons per acre per unit of erosion index.

[b] Cover factor = (soil loss from vegetation-covered plot)/(soil loss from identical bare-soil plot).

Table 14. Erosion Parameters on Captina Soil for 1 Year of Experimentation

Parameter	Units	Plot 1, Bare Soil	Plot 2, Clipped Meadow	Plot 3, Tall Meadow
Slope	%	3.1	4.6	13.7
Slope length	m	2.2	2.0	2.0
Vegetation 1964	g/m^2	0	384	492
Vegetation 1965	g/m^2	0	2337	4611
Average runoff of water	%	53	39	19
Average infiltration	%	47	61	81
Soil loss[a]	g/m^2	2023	206	72

[a]To convert to tons per acre, multiply by 4.47×10^{-3}.

percentage contribution by the leach from vegetation and erosion were calculated. The fraction of ^{137}Cs fixed on the soil was taken as the difference between the percentage of radionuclide leached off the vegetation and estimated vegetation leach contribution to the runoff. Lower leach contribution and lower fixation on the soil of the clipped-meadow plot could be indicative of the physical impedance and retention of radiocesium by the overlying litter. The shallower estimated depth of penetration of the vegetation plots compared with a bare-soil plot could also reflect intermediate fixation in the litter material or in the topmost soil layer high in decaying organic matter.

In Table 16, the ^{137}Cs loss by erosion is given by season. It can be readily seen that highest loss occurred during the winter and spring months of 1964-65 on all plots, amounting to 77% for plot 1, 78% for plot 2, and very nearly 100% for plot 3. More than four-fifths and more than one-half of the cesium loss in the tall-meadow and clipped-meadow plots, respectively, were due to the five high-energy and -intensity rains that occurred during the winter and early spring seasons. The same five rains accounted for only one-third of ^{137}Cs loss on the bare soil plot. The equation, given previously, showing the relationship between soil loss and cesium loss was modified to read:

Table 15. Cesium-137 Loss Parameters on Captina Soil for 1 Year of Experimentation

Parameter	Units	Plot 1, Bare Soil	Plot 2, Clipped Meadow	Plot 3, Tall Meadow
Specific activity (eroded solids)	uc/g	0.14	0.86	0.86
Specific activity (runoff liquid)	$\mu c/cc \times 10^{-6}$	5.0	9.6	13.2
Depth of penetration[a]	cm	0.51	0.16	0.21
Concentration in soil	uc/g	0.12	0.39	0.29
Leach contribution to runoff[b]	%	--	55	66
Erosion contribution to runoff[c]	%	100	45	34
Fraction of leach fixed on soil[d]	%	--	89	95
Amount eroded	$\mu c/m^2$	277	177	62
Amount applied	$\mu c/m^2$	903	937	925
Percent eroded	%	30.7	18.9	6.7

[a]Estimated downward movement into the profile during the first year.

[b]Estimated percentage of ^{137}Cs carried away by runoff during the first year, that was leached from vegetation.

[c]Estimated percentage of ^{137}Cs lost that was actively eroded from the soil surface during the first year.

[d]Estimated percentage of ^{137}Cs leached from vegetation that was subsequently fixed on the soil during the first year of experimentation.

$$y = A(x/b)^m \qquad 0 < y < 100 \qquad x > 16 ,$$

where y is the cumulative percentage of cesium lost; x is the cumulative soil loss in g/m^2, and A has the values of 0.40, 0.69, and 0.37; and m has the values of 0.59, 0.62, and 0.68 for plots 1, 2, and 3, respectively. The correlation index, or R^2, values that are measures of fit of the equation were better than 90% for plot 1 and better than 98% for plots 2 and 3.

Table 16. Cesium-137 Loss by Erosion, Expressed as Percentage of that Applied for 1 Year of Experimentation[a]

Season	Plot 1, Bare Soil		Plot 2, Clipped Meadow		Plot 3, Tall Meadow	
	% of Applied	% of Eroded	% of Applied	% of Eroded	% of Applied	% of Eroded
Fall	4.0	13.1	4.1	21.6	0.01	0.1
Winter 1964-65	12.5	40.8	9.4	49.7	3.7	55.1
Spring 1965	11.1	36.3	5.4	28.5	3.0	44.7
Summer 1965	2.9	9.5	0.05	0.2	0.01	0.1
Fall 1965	0.1	0.3	0.00	0.0	0.00	0.0
Total loss	30.7	100	18.9	100	6.7	100

[a]Initially 903 $\mu c/m^2$ of ^{137}Cs was applied to plot 1, 937 $\mu c/m^2$ to plot 2, and 925 $\mu c/m^2$ to plot 3, on October 20, 1964.

In Table 17, loss of cesium by leaching of the vegetation is given. Following the spray application, all the ^{137}Cs was first found on the vegetation in the vegetation-covered plots. During the first month and after 6% of total rain, about 20% had leached off the vegetation; in 5 months and after 40% of total rain, about 75% had leached; and in 1 year, 95%. The slight increase noted in the litter of the clipped meadow after 153 days was probably due to sampling error. New 1965 vegetation contained less than 1×10^{-10} μc of radionuclide per gram, indicating that no significant uptake of cesium occurred during the 1965 growing season. Lack of uptake is probable due to the shallow penetration of the applied cesium into the profile, as shown in Table 15.

8. BEHAVIOR OF RADIONUCLIDES IN THE GROUND

D. G. Jacobs Y. E. Kim O. M. Sealand

8.1 Nonequilibrium Ion Exchange

A computer program was written to describe the transient behavior of radionuclides in the ground when the transporting solution is of a different concentration than the original ground water. The program

Table 17. Leaching Loss of ^{137}Cs from Vegetation for 1 Year of Experimentation

Time[a] (days)	Rain (in.)	Percentage Remaining on Vegetation[b]			
		Clipped Meadow		Tall Meadow	
		Plant	Litter	Plant	Litter
38	3.3	82.8	80.4	76.3	--[c]
71	7.8	30.1	25.3	46.7	--
153	20.2	23.9	28.4	25.8	--
356	53.1	0[d]	6.0[e]	0	5.3

[a]Time in days after October 20, 1964, date of application.

[b]Initially, all the applied ^{137}Cs was on the vegetation on the vegetation-covered plots. The concentration of ^{137}Cs was 2.95 μc/g of plant material on clipped-meadow plot, and 2.29 μc/g of plant material on tall-meadow plot.

[c]No litter present in 1964 vegetation.

[d]New 1965 vegetation contained less than 1×10^{-10} μc per gram of ^{137}Cs of plant material, indicating that no significant uptake of ^{137}Cs occurred during 1965 growing season.

[e]Values given for litter on both plots reflect the nonleached amounts of ^{137}Cs still on the 1964 vegetation.

is based on Gueckauf's model[22] for the passage of a wide band of solute through a chromatographic column, modified for changes in the adsorptive capacity due to changes in the total electrolyte concentration.

Figure 8.1 shows theoretical curves for a 1- x 1-1/2 x 12-in. core of Berea sandstone. The core is presaturated with 0.001 N $CaCL_2$ to represent ground water. Then radiostrontium is introduced in 0.05 N $CaCl_2$; the volume injected corresponds to 200%, 100%, etc. of the volume required to reach 50% breakthrough in a system containing only 0.05 N $CaCl_2$. Following the introduction of the tracer, leaching is done with 0.001 N $CaCl_2$ to correspond to the return of the original conditions.

Preliminary data show that the curves have the correct properties. The computer program is being modified to process the data and to fit the best curves, using K_d and the theoretical plate height as adjustable variables in the fitting process.

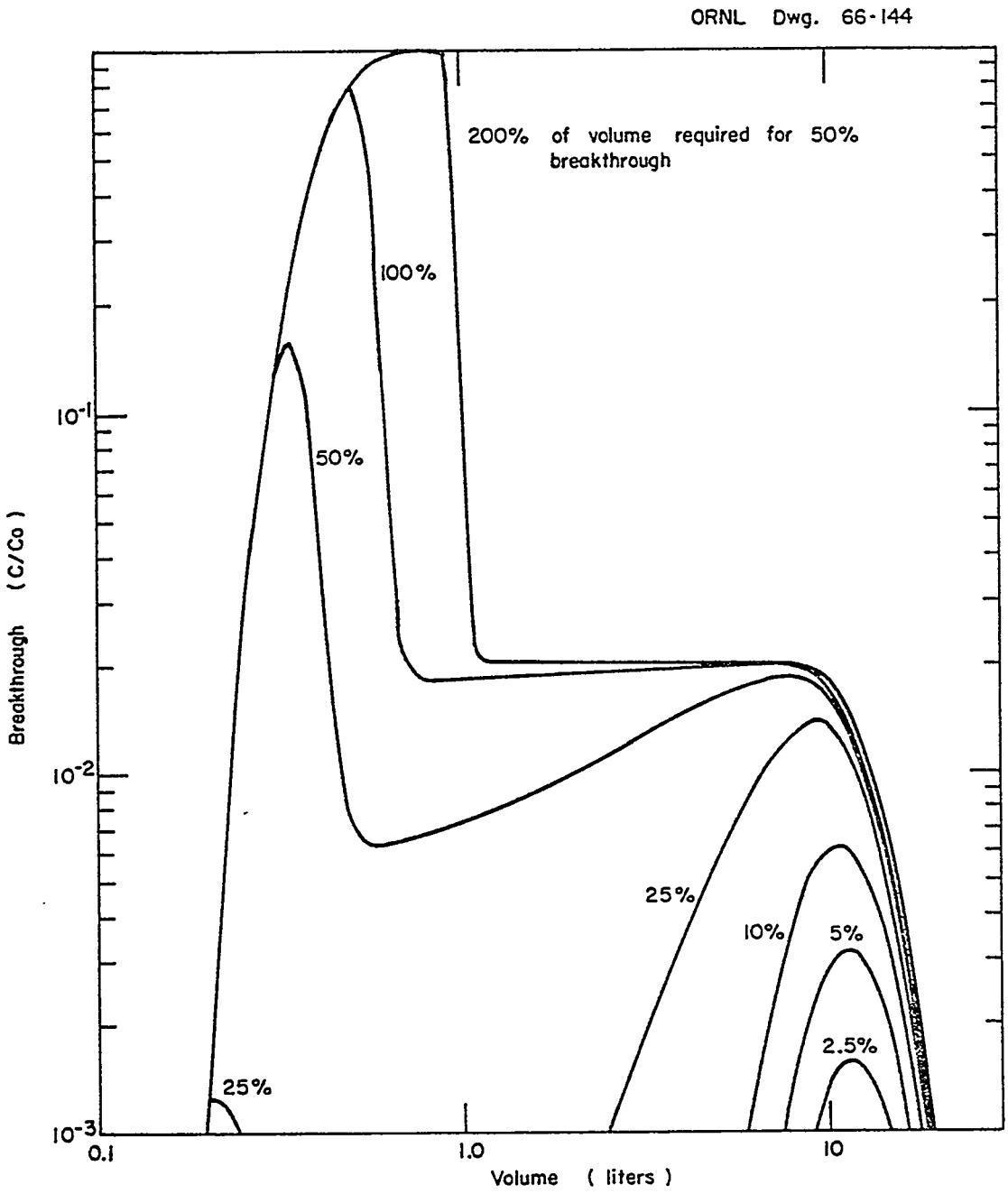


Fig. 8.1 Theoretical Curves for Passage of ^{85}Sr Through Berea Sandstone when Injected in 0.05 N $CaCl_2$ and Leached with 0.001 N $CaCl_2$.

8.2 Hydroxide Consumption by Conasauga Shale

In the vicinity of the intermediate waste trenches, small seeps have developed in which the pH of the seeping water has been gradually increasing. It was felt that the increase constituted a warning that only a small amount of the shale was being contacted by ground water moving from the trench to this seep and that a breakthrough of ^{90}Sr might be expected.

Samples of Conasauga shale were placed in solutions of different pH and allowed to stand overnight. The equilibrium pH was measured, and the consumption of hydroxyl ions was calculated. The results are shown in Fig. 8.2. The sorption of ^{85}Sr was also measured in each solution (Fig. 8.3). At pH 12 in 0.1 M Na, the K_d for ^{85}Sr is 143 ml/g and the K_d for hydroxyl ion is about 10 ml/g. This indicates that the strontium front leaving the waste trench would require about 14 times as long to reach the seep as did the hydroxyl-ion front. The severity of the problem will depend on the quantity of water carried through this seep.

9. DISPOSAL OF GASES INTO PERMEABLE FORMATIONS

D. G. Jacobs and O. M. Sealand

9.1 Estimation of the Behavior of Radionuclides Discharged to the Ground in a Gas

The fission product inventory was estimated for a reactor originally containing 5.82×10^{25} atoms of ^{235}U which had been operated for 1000 days at a neutron flux of 1.5×10^{13}. It was assumed that in an accident the fission products would be released as gases into a containment shell having a volume of 2.5×10^{6} ft^3 (7.1×10^{4} m^3). In the unrealistic case of complete fission product release as radioactive gases, the critical nuclide would be ^{90}Sr, and the critical organ would be bone. The initial concentration of radioactive contaminants in the containment shell would be about 2×10^{11} times the 40 hr/week occupational MPC_a (curve A, Fig. 9.1). Reduction in the level of hazard would correspond to decay of the ^{90}Sr.

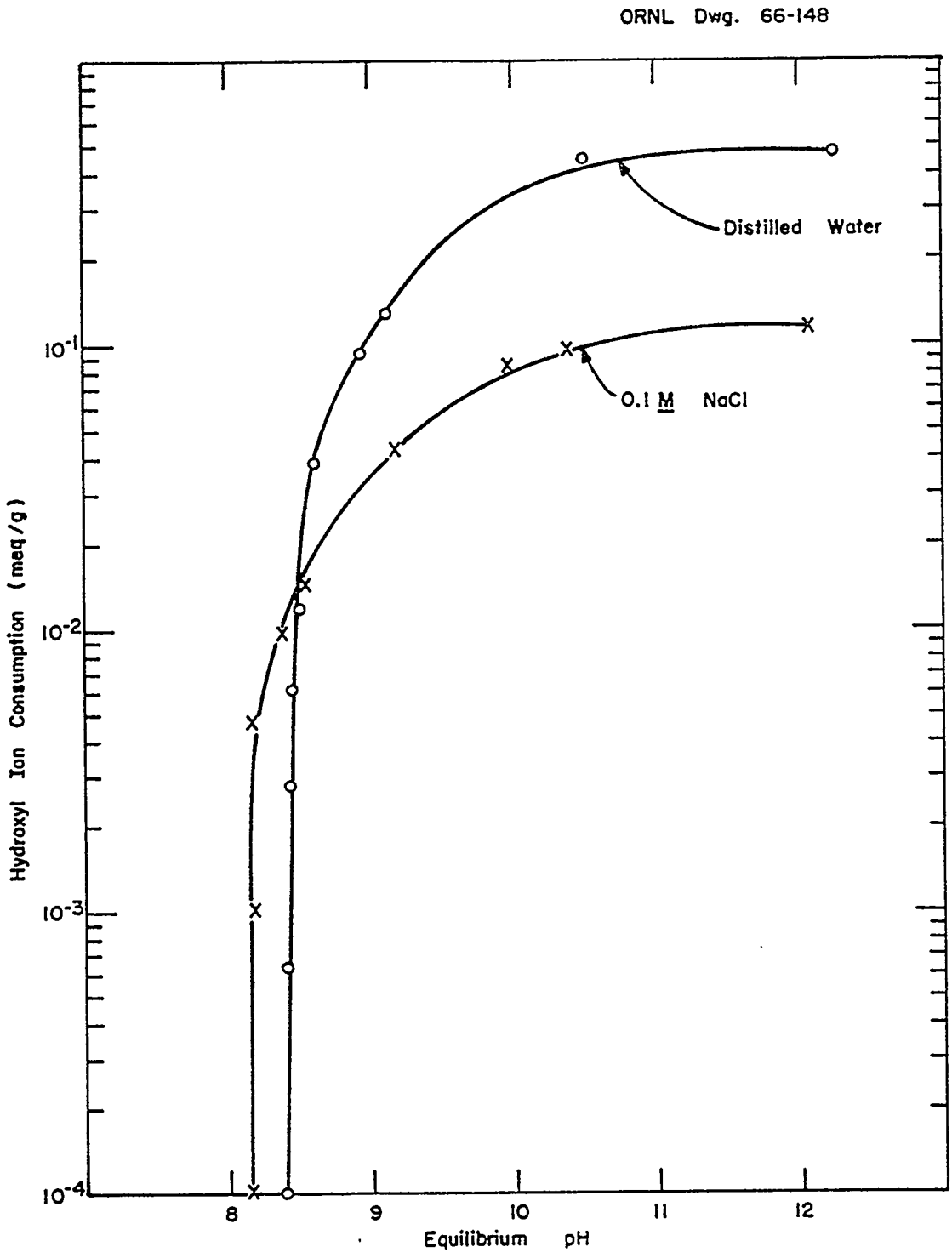


Fig. 8.2 Consumption of Hydroxyl Ions by Conasauga Shale.

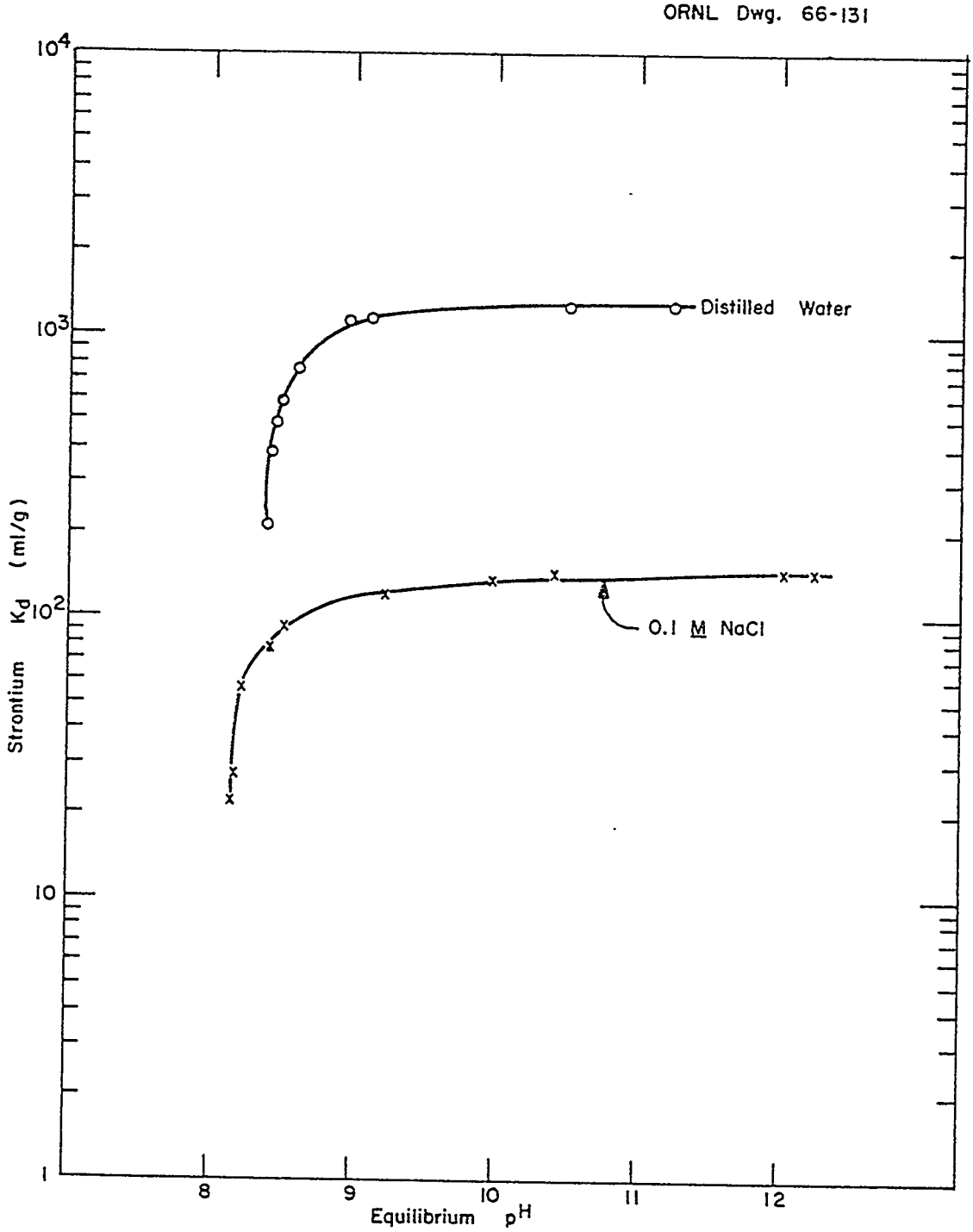


Fig. 8.3 Strontium Sorption by Conasauga Shale.

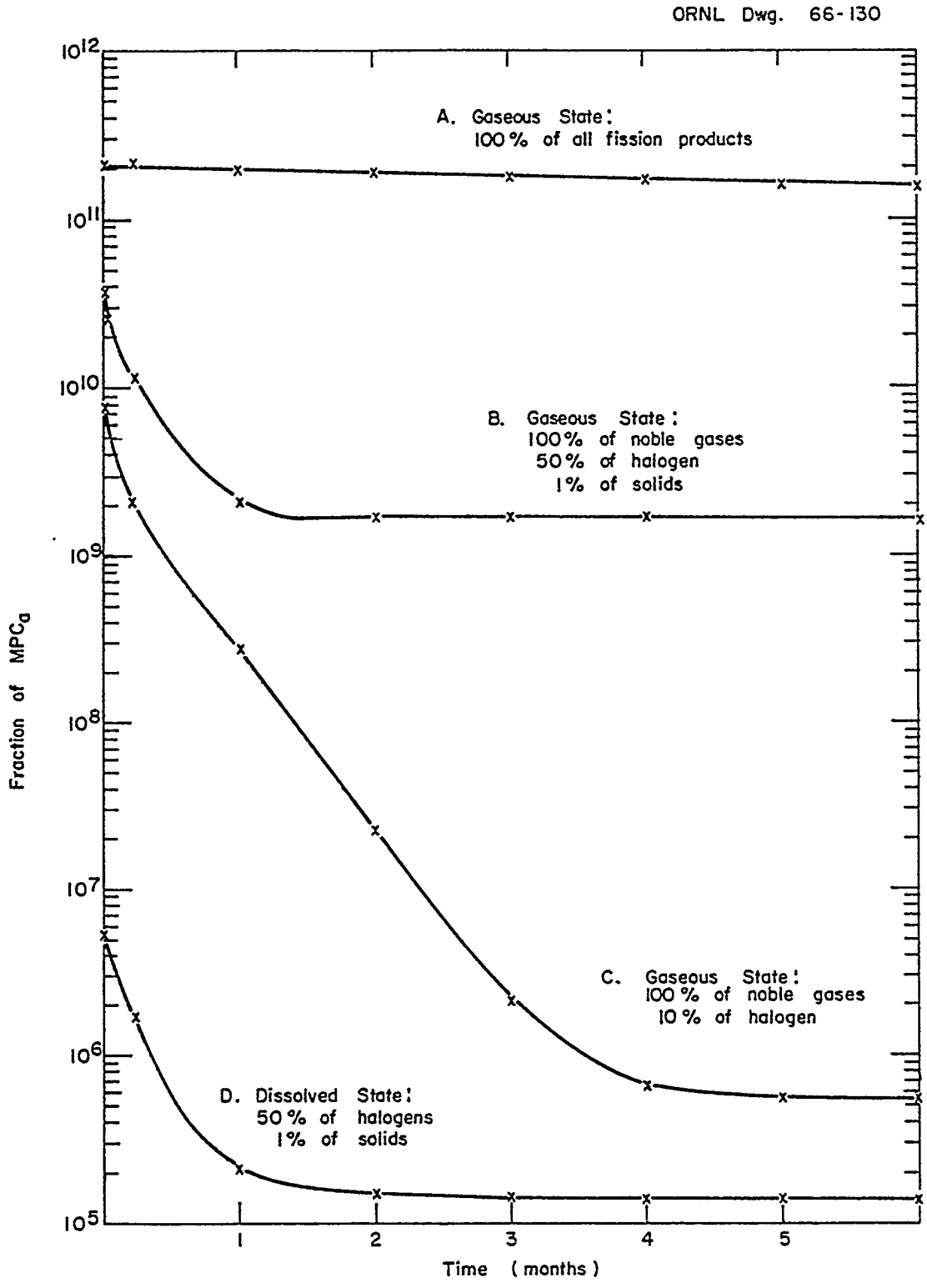


Fig. 9.1 Relative Hazard of Radionuclides Releases from a Reactor.

A more commonly accepted limit of release into the containment shell is: 100% of the noble gases, 50% of the halogens, 1% of the solids.[23] In this case, ^{131}I is the critical nuclide, and the thyroid is the critical organ for about the first month; thereafter ^{90}Sr is again the critical nuclide (curve B, Fig. 9.1). If the gases were pumped immediately from the containment shell into the ground, one would expect rather rapid condensation of the emitters that are normally solid. Part of the iodine would probably be in the form of methyl iodide and would remain gaseous. If we assume that 100% of the noble gases and 10% of the halogens remain in a gaseous state, ^{131}I is the critical element during the first four months. It decays leaving ^{85}Kr the limiting one thereafter (curve C, Fig. 9.1).

If a volume of ground water equal to the volume of the containment shell moves into the discharge zone and dissolves the released radionuclides, the hazard is even further reduced. This is due to two facts: A smaller volume of liquid is ingested than air is inhaled during a given time interval, and water is less mobile than air in a porous medium (by a factor of about 100). Most of the dissolved solid fission products could undergo ion exchange with the formation minerals and move at a much slower rate than the ground water.

For the purposes of calculations it was assumed that groundwater would flow at a rate of 1 ft/day and would be dispersed with a theoretical plate height of 50 ft. The delay factors due to ion exchange were assumed to be 100 ft strontium and most other elements, 200 for rare earths, 10,000 for cesium, and 10 for ruthenium. Table 18 lists the nuclides that would present the most serious contamination problems. The times given are the times required before radioactive decay plus dispersion and ion exchange in the formation reduces the concentration levels to permissible limits. The distance of migration is the maximum extent of longitudinal movement of a front at the permissible concentration before decay occurs. If the flow is radial, or if there is appreciable lateral dispersion, the extent of movement would be considerably reduced. Figure 9.2 shows the combined effects of ion exchange, dispersion, and radioactive decay on the lateral movement of ^{90}Sr by moving ground water.

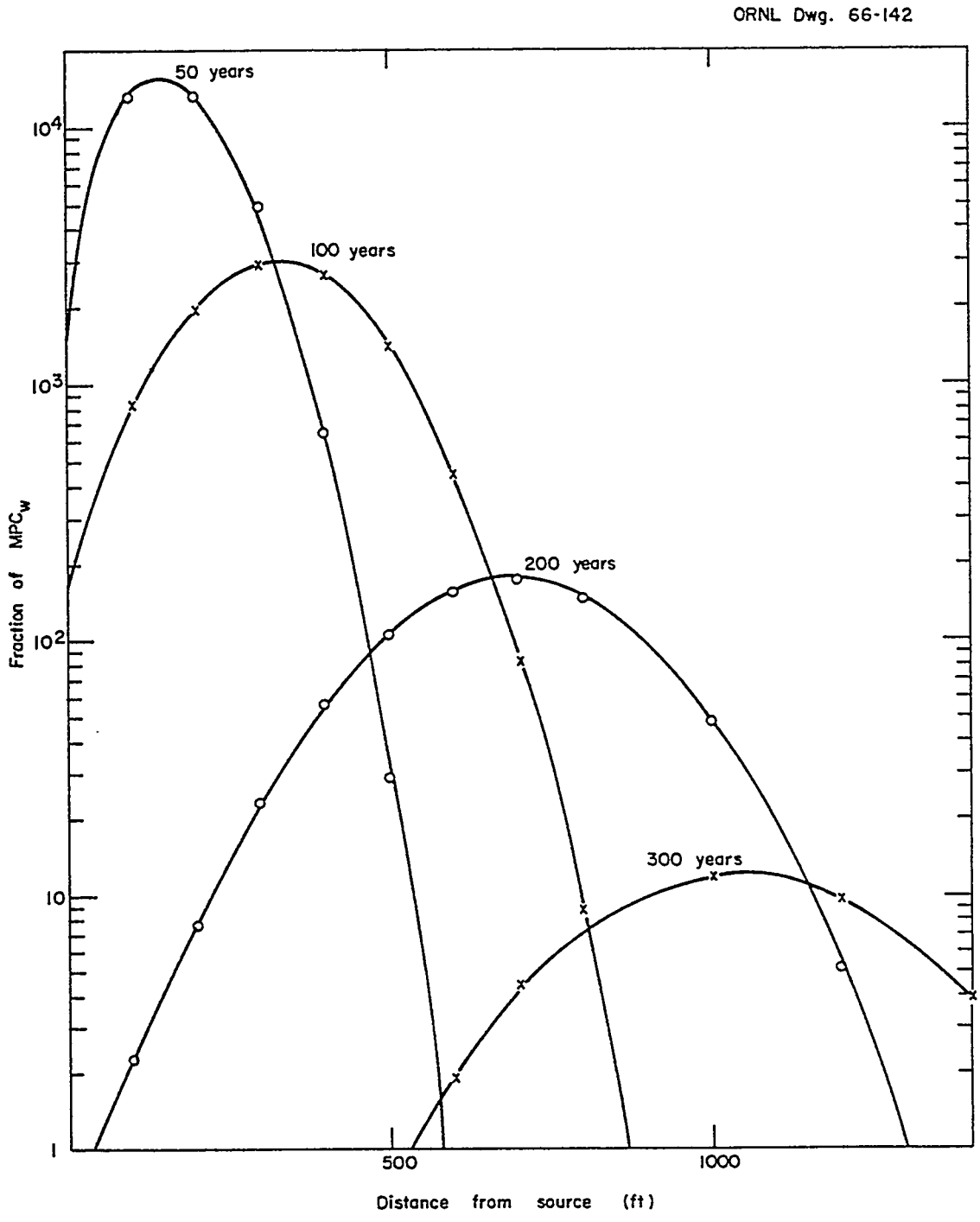


Fig. 9.2 The Lateral Movement of ^{90}Sr by Ground Water as Affected by Ion Exchange and Dispersion.

Table 18. Expected Extent of Movement of Fission Products in the Ground

Nuclide	Distance of Migration (ft)	Time Required for Decay and Dispersion to Permissible Levels (yr)
^{90}Sr	1600	380
^{90}Y	400	220
^{106}Ru	400	11
^{131}I	300	0.4
^{132}I	200	0.4

From the exercises we can conclude that the relative hazard due to release of airborne activity from a reactor incident could be markedly reduced by pumping the gases into the ground. The delay time afforded, especially for condensable radiation emitters, would greatly reduce the spread of contamination. Strontium would most likely present the most serious contamination of local ground water, if it were released to the extent of 1%, but its extent of movement would be about 1600 ft in an area where the groundwater moves at a mean velocity of 1 ft/day. The extent of vertical movement would be expected to be at least an order of magnitude lower, so no contamination of a second aquifer should occur.

9.2 Adsorption of Iodine by Minerals

A numerical error was found in the former calculations of the activation energy of desorption of iodine from Clinch River sediment. Subsequent calculations show that the corrected value for the activation energy for desorption ranges from 14.2 kcal/mole at a loading of 10^{-10} mole of I_2 per cm^2 to 54 kcal/mole at a loading of 10^{-11} mole of I_2 per cm^2. These values are consistent for a system containing condensed I_2 (energy of sublimation = 14.66 kcal/mole) plus some chemisorbed iodine on the mineral surfaces. Previously, it had been necessary

to postulate that some of the I_2 vapor had been converted to HI in order to account for the low values obtained for the activation energy.

A computer program is being written to determine the quantity of chemisorbed iodine and to refine the estimates of the energy required to desorb the two phases of iodine from the mineral surfaces.

It is difficult to compare the adsorption of iodine gas by different clays measured in individual nonflowing systems because the equilibrium concentration of iodine in the gas phase is likely to be different. An ordinary flow system also presents difficulties. Iodine was so readily adsorbed that nothing could be detected at the effluent end of a 1-1/2- x 12-in. core after several days of running. Therefore, an arrangement was devised whereby several clays could be tested in a single flow system. A 1-in.-thick glass column was used as the main reaction vessel (Fig. 9.3). The clay samples consisted of 1/8-in.-diam glass rods coated with a clay paste and then dried. Five samples could be placed on a rack that held the samples centered in the reaction vessel. At each end of the reaction vessel was placed a diffusion tube,[24] which consisted of 1 ft of silver-plated copper tubing, 1 ft of rubber hose, and 1 ft of charcoal-coated copper tubing. The diffusion tubes give a relative measure of the concentration of iodine at the two ends of the reaction vessel. The influent end was attached to a U-tube into which radioactive I_2 had been previously condensed. The effluent from the two diffusion tubes, the reaction vessel, and the U-tube could be regulated.

A run was made to test iodine sorption by Wyoming bentonite, illite, kaolinite, vermiculite, and Clinch River floodplain sediment at room temperature. The total input was 1140 μc. The recovery was 80% (Table 19). Based on the relative flow rates, one would have expected a total of 143 μc to have entered the first diffusion tube and 103 μc into the second. However, the concentration profile of iodine deposited in the diffusion tube indicated a loss of only about 2.5% of the amount entering each diffusion tube. The adsorption of iodine by the clays used in this run is seen to be closely related to their surface area (Table 20).

ORNL Dwg. 66-147

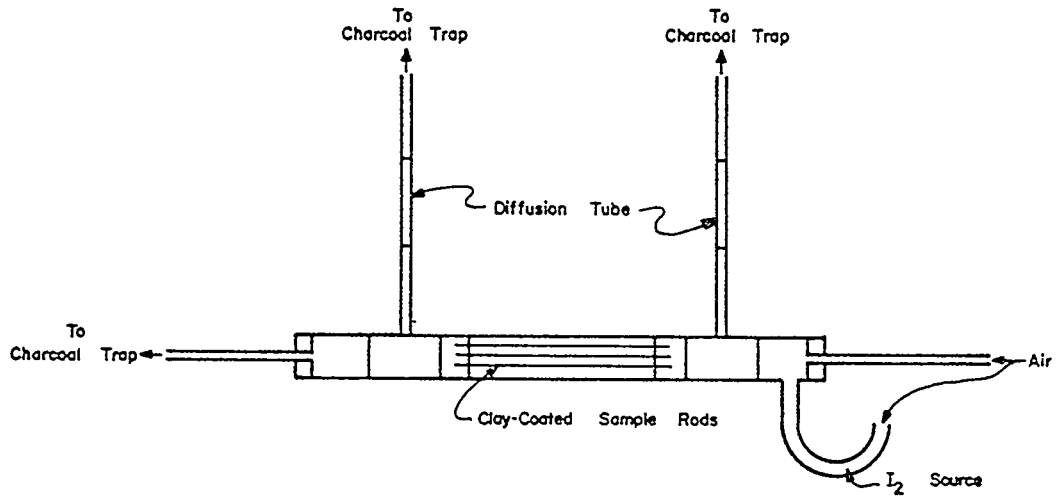


Fig. 9.3 Schematic of the System Used to Measure Iodine Sorption by Clays in a Flowing System.

Table 19. Mass Balance of Iodine in a Flowing Sorption Experiment

Total input	1140 μc
Amount in U-tube after the experiment	554
Total adsorbed by clays	150
Amount recovered in 1st diffusion tube	39
Amount recovered in 2nd diffusion tube	20
Total recovered	763 μc
Estimated Losses	
First diffusion tube	1 μc
Second diffusion tube	<1
Reaction vessel	150
Total accounted for	914 μc

Table 20. Sorption of Iodine by Clays in a Flow System

Clay	Iodine Adsorbed (μc/g)	Surface Area (m^2/g)	Iodine Adsorbed (μc/m^2)
Wyoming bentonite	34.4	64.2	0.54
Illite	31.9	58.4	0.55
Vermiculite	5.7	3.6	1.58
Kaolin	4.2	13.6	0.31
Clinch River flood-plain sediment	3.5	4.3	0.81

9.3 Nuclear Safety Pilot Plant Runs

A sorption pack containing two 115-g samples of Berea sandstone followed by three 18-g samples of charcoal was placed in the gaseous effluent line of Nuclear Safety Pilot Plant run 10. The activity levels of the released gas were too low to obtain satisfactory results, but the two samples of sandstone sorbed enough iodine to give 131 ± 31 and 88 ± 30 disintegrations of ^{131}I per minute, compared with 295 ± 44 for the first charcoal sample. No ^{85}Sr, ^{106}Ru, or ^{134}Cs was detected on any of the samples. On sandstone samples 1 and 2, 196 ± 90 and 102 ± 86 disintegrations of ^{144}Cs per minute were detected, but none was detected on the charcoal.

In run 11 the sorption pack contained, in order, Conasauga shale (62 g), Bo-4 Zonolite (28 g), exfoliated Zonolite (16 g), Berea sandstone (84 g), and two 18-g samples of charcoal. No ^{85}Sr, ^{134}Cs, or ^{106}Ru was detected on any of the samples. Iodine-131 and cerium-144 were sorbed as follows (Table 21):

Table 21. Sorption of Iodine and Cesium by Clays in NSPP Run 11

	^{131}I (dis/min) x 10^3	^{144}Ce (dis/min) x 10^3
Conasauga shale	540 ± 11	72 ± 9.8
BO-4 Zonolite	92 ± 2	12 ± 1.8
Exfoliated Zonolite	46 ± 1.1	4.1 ± 9.2
Berea sandstone	31 ± 0.7	4.4 ± 0.62
Charcoal	400 ± 5	34 ± 4.8
Charcoal	1.7 ± 0.15	0.32 ± 0.15

It has been suggested that the most important difference between run 10 and run 11 was a change in the furnace atmosphere from reducing conditions in run 10 to oxidizing conditions in run 11, causing HI release in run 10 and I_2 release in run 11.[25]

10. SAFETY EVALUATION

10.1 Clinch River Safety Studies

K. E. Cowser

Recent information on metabolic processes of children and adults permits a preliminary assessment of the importance of metabolic processes in estimating internal dose. In particular, Kulp and Rivera examined the effects of bone growth, rate of bone turnover, and the ratio of strontium to calcium in bone to that in diet on the retention of ^{90}Sr in the skeleton of man.[26,27] The difference equation for the model developed by Kulp (herein referred to as the age-dependent metabolic model) can be expressed as:

$$S_n = S_{n-1} - (f_n + \quad) S_{n-1} + K_n \frac{I_n C_n}{G_n} \left[f_n \, Ca_{n-1} + (Ca_n - Ca_{n-1}) \right],$$

where

S_n = pc ^{90}Sr skeleton burden at time n,

f_n = fractional bone turnover rate during the period from time n-1 to time n,

= ^{90}Sr radiological decay constant,

$K = \left(\frac{Sr}{Ca}\right)_{bone} \quad \left(\frac{Sr}{Ca}\right)_{diet}$,

I_n = fluid intake, liters/day,

C_n = ^{90}Sr concentration in water, pc/liter,

G_n = calcium intake, g/day,

Ca_n = calcium content of the skeleton, g.

The equation relates the loss and gain of ^{90}Sr during the period of interest, and is based on calcium metabolism. Calcium may enter and leave the skeleton each period. Bone turnover is defined as the quantity of calcium that enters and is excreted from the skeleton. The fractional

bone-turnover rate f is the bone-turnover rate divided by the quantity of calcium contained in the skeleton. Strontium-90 in the skeleton is lost as a result of bone turnover and radiological decay and is gained by bone remodeling and bone growth.

By recursive application of the difference equation, the skeleton burden can be determined. The dose rate is given by:

$$D_n = a \frac{S_n}{W_n} ,$$

where

D_n = dose rate, rems/yr,

W_n = mass of the skeleton at time n, kg,

a = a constant; for ^{90}Sr, 1.03×10^{-4} (rems/yr)/(pc/kg) .

These equations were coded for computer solution using intervals of one month during 0 to 2 years of age, three months during 2 to 24 years, and yearly intervals thereafter.[a]

Estimation of the dose received by the skeleton of males due to ingestion of Clinch River water were performed using the same values for fluid intake, and ^{90}Sr concentration in water and skeleton mass, that were previously employed with the adjusted ICRP model.[28] Values of daily calcium intake and calcium content of the body were taken from Albritton and Mitchell, respectively;[29,30] values of bone turnover rate and the observed ratio (K_n) were from Rivera.[2] Examples of the cumulative skeleton dose (1944 to 1963) to individuals of various ages are given in Table 22. For comparative purposes, the table also includes the skeleton dose calculated with the adjusted ICRP model. In all cases the age-dependent metabolic model yields a slightly larger estimate of total dose (an average of 15% for the individuals listed) than the adjusted ICRP model. Unquestionably, changes can be expected in the values of metabolic factors as new information becomes available.

---

[a]Calculations were performed by H. J. Fisher, U.S. Public Health Service, while working with the Internal Dose Estimation Section, Health Physics Division, ORNL.

Table 22. Dose (rems) Received by Skeleton of Males from Drinking Water

Cumulative dose from ingestion of Clinch River water for the period 1944 to 1963

Age at Start of Exposure	Age-Dependent Metabolic Model	Adjusted ICRP Model
0	2.2	1.7
5	2.4	2.3
9	3.1	2.6
14	3.3	2.9
19	3.3	2.8
25	2.9	2.6

11. REFERENCES

1. C. L. Fitzgerald, H. W. Godbee, M. H. Davis, and W. E. Clark, A Computer Code for Storing and Retrieving Data and Developing Improved Solids for Fixation of Highly Radioactive Wastes, ORNL-3824 (in press).

2. J. M. Holmes, R. E. Blanco, J. O. Blomeke, W. E. Clark, H. W. Godbee, C. W. Hancher, J. C. Suddath, and M. E. Whatley, Pot Calcination Process for Converting Highly Radioactive Wastes to Solids, "Symposium on Treatment and Storage of High-Level Radioactive Wastes," IAEA, Vienna, 1963, pp. 255-286.

3. H. W. Godbee and W. E. Clark, "Use of Phosphite and Hypophosphite to Fix Ruthenium from High-Activity Wastes in Solid Media," Ind. Eng. Chem. Product Research and Development 2, 157-62 (1963).

4. D. E. Ferguson, Chem. Technol. Div. Annl. Progr. Rept., May 31, 1965, ORNL-3830 (November 1965).

5. R. E. Blanco et al., Recent Developments in Treating Low and Intermediate-Level Radioactive Waste in the United States, TM-1289 (Dec. 1, 1965).

6. H. W. Godbee, E. J. Frederick, and N. S. S. Rajan, Incorporation of Intermediate-Level Radioactive Solutions and Slurries in Emulsified Asphalt, ORNL (in preparation).

7. J. H. Goode, Fixation of Intermediate Level Radioactive Waste in Asphalt: Hot-Cell Tests, TM-1343 (Nov. 18, 1965).

8. J. W. Gossett, Chemical Processing 28, 29 (October 1965).

9. D. E. Ferguson, Chem. Technol. Div. Annl. Progr. Rept., May 31, 1965, ORNL-3830 (November 1965).

10. R. E. Blanco et al., Recent Developments in Treating Low and Intermediate-Level Radioactive Waste in the United States, TM-1289 (Dec. 1, 1965).

11. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Semiannual Progress Report, July-December 1964, ORNL-TM-1081, pp. 104-12 (May 1965).

12. F. L. Parker and R. E. Blanco, Waste Treatment and Disposal Progress Report, May-October 1963, ORNL-TM-757, pp. 90-98 (April 1964).

13. M. G. D. Salamon, "Elastic Analysis of Displacements and Stresses Induced by the Mining of Sean or Reef Deposits," J. S. African Inst. Mining and Metallurgy 65 (4, 6, 10) (November 1963, Jan.-May 1964).

14. W. J. Boegly, Jr., Safety Analysis - Project Salt Vault, ORNL (in preparation).

15. P. N. Haubenreich, Review of Project Salt Vault - A Demonstration of the Disposal of High-Level Radioactive Solids in a Salt Mine, ORNL-CF 65-10-23 (Oct. 14, 1965).

16. F. L. Parker et al., Health Phys. Div. Annl. Progr. Rept. July 31, 1965, ORNL-3849, p. 16-18.

17. T. F. Lomenick, The Geology of a Portion of the Hutchinson Salt Member of the Wellington Formation in the Mine of the Carey Salt Company, Lyons, Kansas, ORNL-TM-597 (Sept. 3, 1963).

18. T. F. Lomenick and T. Tamura, Soil Sci. Soc. Amer. Proc. 29, 383-87 (1965).

19. K. Wada, Amer. Mineralogist 46, 79-85 (1961).

20. L. Frederickson et al., Proc. Second U.N. Intern. Cong. on Peaceful Uses of Atomic Energy 18, 449-70 (1958).

21. R. K. Schulz, R. Overstreet and I. Barshad, Soil Science 89, 16-27 (1960).

22. E. Gueckauf, Trans. Far. Society 60, 729 (1964).

23. J. J. Di Nunno, F. D. Anderson, R. E. Baker, and R. L. Waterfield, Calculation of Distance Factors for Power and Test Reactor Sites, TID-14844 (Mar. 23, 1962).

24. W. E. Browning, Jr., R. D. Ackley, and R. E. Adams, Nuclear Safety Program Semiannual Progress Report for Period Ending December 31, 1963, pp. 60-64, ORNL-3547 (1964).

25. Oak Ridge National Laboratory Status and Progress Report, October 1965, ORNL-3886, p. 18 (Nov. 4, 1965).

26. J. L. Kulp, "Radioactive Fallout from Nuclear Weapons Tests," Proc. of a Conf. held in Germantown, Md., November 15-17, 1961, TID-7632 p. 457 (1962).

27. J. Rivera and J. H. Harley, The HASL Bone Program 1961-1964, HASL-163, p. 7 (1965).

28. K. E. Cowser, "Clinch River Study: Hazards Analyses," in Waste Treatment and Disposal Progress Report for February-April 1963, ORNL-TM-603 (Dec. 16, 1963).

29. E. C. Albritton, Standard Values in Nutrition and Metabolism, W. B. Saunders Company, 1954.

30. H. H. Mitchel et al., "The Chemical Composition of the Adult Human Body and Its Bearing on the Biochemistry of Growth," J. Bio. Chem. 158, 625 (1945).

INTERNAL DISTRIBUTION

1. ORNL-Y-12 Technical Library Doc. Ref. Sec.
2-4. Central Research Library
5-14. Lab. Records
15. Lab. Records, ORNL-RC
16-17. R. E. Blanco
18. J. O. Blomeke
19. W. J. Boegly, Jr.
20. R. L. Bradshaw
21. J. C. Bresee
22. R. E. Brooksbank
23. F. N. Browder
24. K. B. Brown
25. P. H. Carrigan, Jr.
26. K. M. Chandra
27. W. E. Clark
28. K. E. Cowser
29. F. L. Culler
30. W. Davis, Jr.
31. W. de Laguna
32. F. M. Empson
33. D. E. Ferguson
34. E. J. Frederick
35. H. W. Godbee
36. H. E. Goeller
37. J. M. Googin
38. P. A. Haas
39. C. W. Hancher
40. C. E. Haynes
41. R. F. Hibbs
42. J. M. Holmes
43. D. G. Jacobs
44. W. H. Jordan
45. L. J. King
46. H. Kubota
47. T. F. Lomenick
48. H. G. MacPherson
49. W. C. McClain
50. K. Z. Morgan
51. R. J. Morton
52. E. L. Nicholson
53-54. F. L. Parker
55. J. J. Perona
56. R. M. Richardson
57. J. T. Roberts
58. M. J. Skinner
59-60. E. G. Struxness
61. J. C. Suddath
62. T. Tamura
63. J. W. Ullmann
64. M. E. Whatley

EXTERNAL DISTRIBUTION

65. E. L. Anderson, AEC, Wash.
66. W. G. Belter, AEC, Wash.
67. H. Bernard, AEC, Wash.
68. A. B. Joseph, AEC, Wash.
69. J. A. Lieberman, AEC, Wash.
70. W. H. Regan, AEC, Wash.
71. R. F. Reitemeier, AEC, Wash.
72. Vincent Schultz, AEC, Wash.
73. J. N. Wolfe, AEC, Wash.
74. H. M. Roth, AEC, ORO
75. C. S. Shoup, AEC, ORO
76. J. R. Horan, AEC, Idaho
77. K. K. Kennedy, AEC, Idaho
78. J. A. Buckham, PPC, Idaho Falls, Idaho
79. C. M. Slansky, PPC, Idaho Falls, Idaho
80. H. J. Carey, Jr., Carey Salt Co., Hutchinson, Kan.
81. C. W. Christenson, LASL
82. J. C. Frye, State Geological Sur. Div., Urbana, Ill.

83. W. B. Heroy, Sr., Geotechnical Corp., Dallas, Tex.
84. L. P. Hatch, BNL, Long Is., N.Y.
85. W. E. Winsche, BNL, Long Is., N.Y.
86. S. Lawroski, ANL
87. J. J. Weinstock, RAI, Long Is. City, N.Y.
88. E. W. Bloore, U.S. Army Nucl. Def. Lab., Edgewocd Arsenal, Md.
89. D. B. Lombard, LRL
90. S. J. Reno, State Health Dept. Topeka, Kan.
91. Wes Lewis, NFS, West Valley, N.Y.
92. C. R. Cooley, BNWL, Richland, Wash.
93. E. R. Irish, BNWL, Richland, Wash.
94. A. M. Platt, BNWL, Richland, Wash.
95. G. Rey, BNWL, Richland, Wash.
96. G. J. Alkire, BNWL, Richland, Wash.
97. B. W. Mercer, BNWL, Richland, Wash.
98. L. F. Coleman, BNWL, Richland, Wash.
99. J. R. Eliason, BNWL, Richland, Wash.
100. L. H. Meyer, du Pont, SRL
101. R. M. Girdler, du Pont, SRL
102. Harvey Groh, du Pont, SRL
103. C. H. Ice, du Pont, SRL
104. C. M. Patterson, du Pont, SRL
105. W. B. Scott, du Pont, SRL
106. E. B. Sheldon, du Pont, SRL
107. D. S. Webster, du Pont, SRL
108. V. R. Thayer, du Pont, Wilmington, Dela.
109. R. L. Nace, USGS, Wash. D.C.
110. P. H. Jones, USGS, Wash. D.C.
111. C. P. Straub, USPHS, Cincinnati, Chio
112. Dade Moeller, USPHS, Winchester, Mass.
113. W. J. Lacy, Of. of Civil Def., Wash. D.C.
114. J. E. Crawford, U.S. Bureau of Mines, Wash. D.C.
115. J. W. Watkins, U.S. Bureau of Mines, Wash. D.C.
116. H. Gladys Swope, U. of Wisc., Madison, Wisc.
117. P. A. Krenkel, Vanderbilt Univ., Nashville, Tenn.
118. E. F. Gloyna, Univ. of Texas, Austin, Texas
119. W. J. Kaufman, Univ. of Calif., Berkeley, Calif.
120. L. Silverman, Harvard Grad. Sch. of Public Health, Cambridge, Mass.
121. G. M. Fair, Harvard Univ., Cambridge, Mass.
122. H. A. Thomas, Jr., Harvard Univ., Cambridge, Mass.
123. John Geyer, Johns Hopkins Univ., Baltimore, Md.
124. W. A. Patrick, Johns Hopkins Univ., Baltimore, Md.
125. Abel Wolman, Johns Hopkins Univ., Baltimore, Md.
126. C. R. Naeser, George Washington Univ., Washington, D.C.
127. H. C. Thomas, U. of N.C., Chapel Hill, N.C.
128. H. H. Hess, Princeton Univ., Princeton, N.J.
129. W. H. Reas, GE, Vallecitos Lab., Calif.
130. Fred Herbert-Oettgen, Touramerica Div., The E. F. MacDonald Co., N.Y.
131. L. C. Watson, AECL, Chalk River, Can.
132. John Woolston, AECL, Chalk River, Can.
133. AECL, Chalk River, Can.; Attn: C. A. Mawson, I. L. Ophel

134. Librarian, AAEC, Res. Estb., Private Mail Bag, Sutherland, N.S.W., Australia; Attn: R. C. Cairns and L. Keher
135. AERE, Harwell, England; Attn: H. J. Dunster
136. AERE, Harwell, England; Attn: R. H. Burns, K. D. B. Johnson
137. AERE, Harwell, England; Attn: J. M. Fletcher
138. Peter Wace, AERE, Harwell, England.
139. Yehuda Feige, Min. of Def., AEC, Rehovoth, Israel
140. Jitender D. Sehgal, Bombay, India
141. Michio Ichikawa, Tokai-Refinery, At. Fuel Corp., Tokai-Mura, Ibraki-Ken, Japan
142. Atou Shimozato, Nucl. Reac. Des. Sect., Nucl. Power Plant Dept., Hitachi, Ltd., Hitachi Works, Hitachi-Shi, Ibaraki-Ken, Japan
143. Federico de Lora Soria, Grupo de Combustibles Irradiados, Junta de Energia Nucl., Div. de Mat., Ciudad Univ., Madrid-3, Spain
144. Baldomero Lopez Perez, Doctor en Quimica Ind., Centro de Energia Nucl., Juan Vigon, Ciudad Univ., Madrid-3, Spain
145. CEA, Saclay, France; Attn: A. Menoux, C. Gailledreau
146. CEA, Fontenay-aux-Roses, France; Attn: J. Sauteron
147. P. J. Regnaut, Centre d'Etudes Nucl., Fontenay-aux-Roses, France
148. C. J. Jouannaud, Plutonium Extraction Plant, Marcoule, France
149. Eurochemic, Mol, Belgium; Attn: R. Rometsch, T. J. Barendregt, F. Marcus
150-151. E. M. Shank, Eurochemic, Mol, Belgium
152. Centre d'Etude Nucleaire, Mol, Belgium; Attn: L. Baetsle
153. Centre d'Etude Nucleaire, Mol, Belgium; Attn: P. de Jonghe
154. Euratom, Casella Postale No. 1, Ispra, Italia; Attn: M. Lindner
155. F. Dumahel, Commissaire Boite Postale n° 149, Paris (15 eme), France
156. George Straimer, Rad. Protection Dept., Luisenstrasse 46, West Germany
157. Hubertus M. Holtzem, Rad. Protection Dept., 532 Bad Godesberg, W. Germany
158. Gerard M. K. Klinke, Const. Dept., Min. of Fed. Propert, Bad Godesberg, W. Germany
159. Helmut Krause, Decontamination Dept., Karlsruhe Nucl. Res. Center, 75 Karlsruhe, Siemensallee 83, W. Germany
160. Harold F. Ramdohr, Waste Storage Dept., Karlsruhe Nucl. Res. Center, Leopoldshafen/Bd. Max-Plandk-Str. 12, W. Germany
161. Hermann F. A. Borchert, Petrology, Mineralogy, and Economic Geology Dept., Mining Academy Clausthal, Siemensalle, W. Germany
162. Division of Research and Development, ORO
163-177. DTIE, AEC, OR