MASTER

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

ORNL-TM-482
15

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT

AUGUST-OCTOBER 1962

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.

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-482

CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL QUARTERLY PROGRESS REPORT AUGUST-OCTOBER 1962

R. E. Blanco F. L. Parker

DATE ISSUED
MAR 2 5 1963

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

FOR DAVE HAMRIN 3/22/95
Technical Information Officer Date
ORNL Site

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

ABSTRACT

High-Activity-Waste Calcination. A pot calcination run with simulated TBP-25 (aluminum nitrate) waste was made in the large-scale equipment to test the feasibility of feeding the continuous evaporator from a head tank by gravity flow rather than by a pump. Satisfactory control was achieved with a hydraulic head of about 10 ft. This information, along with operating information is needed to design the pot-calcination pilot plant to be installed at the Hanford Atomic Products Operation.

Design of the Pilot Plant. Liaison between ORNL and HAPO on design and component testing of the equipment for an integrated pot calciner--spray calciner at Hanford has been continued. Equipment installation for the mechanical test program at Georgia Nuclear Laboratories was completed and the positioning-test work started. Reproducible positioning results were obtained within the desired tolerances. Shielding calculations for calcined Purex wastes indicated a dose rate of 0.9 mr/hr for thirty-nine 10.2-cm-diam pots stored in the proposed Hanford Fuels Recycle Pilot Plant Mechanical Cell for a cooling time of 200 days.

Fixation of Waste in Glass. Melts containing 39 to 43% oxides from simulated high-sulfate Purex waste retained up to about 98% of the original sulfate when heated to 100°C above the softening temperature for 100 min. Ruthenium volatilized to the extent of about 24% from semiengineering-scale fixations of simulated TBP-25 waste in glass when either phosphate or hypophosphite was used as fluxing agents. About 77% of the mercury was volatilized.

Specimens of types 304L and 347 stainless steels corroded at rates of less than 0.1 mil/month in superheated vapor above refluxing simulated Purex waste solution vs 2.6 and 3.3 mils/month, respectively, for specimens in the condensing vapor. Type 304L stainless steel showed elongation of between 9.2×10^{-5} and 5.4×10^{-4} in./in. after being subjected to a Purex evaporation-fixation cycle followed by about 165 hr at 1050°C. Welded specimens of various stainless steels exposed for 31 days at about 575°C in the Carey Salt Mine, Hutchinson, Kansas, corroded at overall rates of 0.45 to 1.3 mils/month.

Low-Activity-Waste Treatment. The presence of 1, 2, or 3 ppm of phosphate added as ortho-, hexameta-, or polyphosphates in a synthetic waste solution increased the hardness of the effluent from a laboratory-scale clarifier to 8.5 to 43 ppm. Five parts per million of hexametaphosphate (4.6 ppm of phosphate) resulted in a residual hardness of 70 ppm. The addition of 0.01 M Na_2CO_3 reduced the hardness from 70 ppm to 24 ppm in 24 hours when 5 ppm of hexametaphosphate was present. Only 0.005 M Na_2CO_3 was required to reduce the hardness from about 43 ppm to less than 14 ppm in the presence of 1 to 3 ppm of phosphate. However, 0.005 M Na_2CO_3 doubled the total sodium concentration of the waste and reduced the cesium capacity of the resin by about 50%, from 1850 to 900 bed volumes.

Engineering, Economics, and Safety Evaluation. A conceptual design and cost estimate for the interim storage in water-filled canals of calcined Purex and Thorex wastes from a hypothetical 6-ton/day power reactor fuel reprocessing plant indicated costs ranging from 1.5×10^{-3} mills/kwhr$_e$ for 1-year storage of calcined 10-year-old Purex waste to 19×10^{-3} mills/kwhr$_e$ for 30-year storage of calcined, reacidified 120-day-old Thorex wastes. Costs of storage of the Purex and Thorex wastes together in the same facility ranged from 1.5×10^{-3} mills/kwhr$_e$ for 1-year storage to 4.8×10^{-3} for 30-year storage for the calcined acid wastes and from 1.8×10^{-3} to 6.3×10^{-3} mills/kwhr$_e$ for calcined reacidified wastes. The storage of acid wastes as calcined solids was cheaper by factors of 2 to 2.7 than storage of the same wastes as liquids; however, the storage of neutralized liquid wastes was slightly cheaper than the storage of reacidified Purex and Thorex solids.

An analysis is in progress to ascertain the radiation dose that man may receive as a result of discharge of radioactive liquids to the Clinch River. Of the many avenues of radiation exposure, those considered most important relate to the internal dose by contaminated drinking water, fish, and agricultural products and to the external dose by contaminated water, bottom sediments, and radionuclide concentration in water plants. The estimated exposure to the bone (by drinking contaminated water from Clinch River Mile (CRM) 14.5) was largest, attaining 0.51 of the MPC_w limit in 1954. A maximum immersion dose rate of 0.027 millirad per day of exposure (.016 of beta and .011 of gamma) is calculated at CRM 14.5 during 1960. Calculations of the likely dose received by the other pathways of exposure are continuing.

The evaluation of hazards associated with each step in the alternative methods of waste management, as a corollary of the engineering feasibility and economic studies previously reported, has started with a study of tank storage. The same assumptions used in the economic evaluation will serve as the bases for this study and the selected site will be that specified in Project Hope.

Disposal by Hydraulic Fracturing. Three waste-cement mixes meeting the prescribed requirements for use in the hydrofracturing experiments at ORNL have been developed under the Laboratory subcontract with Westco Research. Each formulation allows sufficient pumping time for disposal at the 1000-ft test schedule, shows a fluid loss of less than 20 cc/30 min and sets within seven days. The most promising mix utilizes CMHEC as a fluid loss additive; this formulation allows sufficient pumping time for use with ORNL intermediate level waste concentrated 10 times.

One of the Westco mixes (No. 12) requiring some modification to obtain satisfactory setting time, was laboratory tested and pump tested by the Halliburton Company for pumpability, fluid loss, fluid friction, and compressive strength. The tests showed that desirable slurry properties can be controlled and that pumping operations are easily managed.

A contract with the Halliburton Company for engineering assistance in the design and operation of the Fracturing Disposal Pilot Plant is being negotiated. Meanwhile,

some assistance in the preliminary design of the injection well and the plant has been provided by Halliburton under an interim purchase order.

Disposal in Natural Salt Formation. Calipering of the floor- and wall-heater holes showed an apparent decrease in the diameter of the hole - about 1 in. at a depth of 6 ft. Maximum expansion of the column and of the floor around the wall and floor heaters occurred at 2 ft from the heater. The expansion was 0.5 in. and 0.8 in. for the wall and floor, respectively.

Clinch River Study. Coring of Clinch River bottom sediments was completed, and gamma spectroscopy has begun with the use of an especially designed core scanner. Criteria of acceptability of analytical results of the water-sampling program were established, based on a comparison of the radioactive concentrations at four stations on the Clinch River. The dispersion effects of the power wave caused by the release from Melton Hill Dam were found in preliminary evaluations of flume tests to be similar to those caused by steady-flow conditions.

Fundamental Studies of Minerals. Continued collapse of vermiculite lattices, accompanied by interlayer fixation of cesium, occurs when the sodium nitrate influent solution to a vermiculite-filled column contains potassium. The absence of collapse-inducing cations in the influent solution results in the expansion of previously collapsed lattices, and this then results in an increase in exchange capacity but a reduction in the cesium loading. The rates of these reactions are increased by rises in the temperature of the system.

White Oak Creek Basin Study. A series of samples taken in White Oak Creek during a rise and subsequent fall of the creek due to a light rainfall reveals that (1) the largest quantities of cesium and strontium transported downstream occur prior to the maximum stream flow when the suspended solid concentration is high, and (2) the amount of cesium associated with suspended solids increases considerably with a rise in the creek while the amount of strontium associated with the water, itself shows a pronounced increase. A time-of-travel study in White Oak Creek at low base flow using fluorescein dye showed an average velocity of 0.4 fps.

Foam Separation. The effect of column diameter, sludge height, and flow rates in the precipitation of calcium and magnesium from ORNL low-activity waste was studied. Column diameters varied from 2 to 9 in. and flow rates from 7.4 to 60 gal ft^{-2} hr^{-1}. Within this range the hardness of the waste water was reduced from about 100 to 2 to 4 ppm (as $CaCO_3$) when precipitation was induced by making the water 0.005 M each in NaOH and Na_2CO_3. An apparatus was tested for the removal by foaming of the surface active agent sodium dodecylbenzene sulfonate; 90% was separated from a solution containing the above listed chemicals plus 50 ppm of the surfactant.

Engineering studies were continued in 6-in.-ID columns, using dodecylbenzene-sulfonate (DBS) as the surfactant. One liquid feed distributor gave HTU_x values of less than 2 cm for flows of 120 gal ft^{-2} hr^{-1} or less; the HTU_x values were 2 to 20 cm

for other distributors or higher flow rates. The difference in HTU_x values for the spinnerette gas spargers with 50- and 80-μ diam holes was small, variable, and probably not significant. Recovery of DBS by simple foaming could be applied to give effluents of about 5 ppm of surfactant for 0.02 N Na^+, and about 20 ppm for 0.001 N Na^+. Process water was used to simulate low-activity waste. The calcium and magnesium were precipitated, and the slurries were used as feed for the foam separation column. Decontamination factors of 81 to 162 for strontium obtained with $CaCO_3$-$Mg(OH)_2$ slurry feed were reduced to less than 3 when 10 ppm of FAB household detergent was added to simulate the effect of such detergents in low-activity wastes.

CONTENTS

	Page
1. Introduction	6
2. High-Level-Waste Calcination	7
2.1 Engineering Development	7
2.2 Design of the Pilot Plant	12
2.3 Fixation of Waste in Glass	14
2.4 Corrosion Studies	18
3. Low-Level-Waste Treatment	20
3.1 Pilot-Plant Test	20
3.2 Laboratory Development	20
4. Engineering, Economics, and Safety Evaluation	22
4.1 Interim Solids Storage	22
4.2 Analysis of the Safety of Routine Operating Discharges from White Oak Creek to the Clinch River	27
4.3 Safety of Tank Storage of High-Activity Liquid Wastes	35
5. Disposal in Deep Wells	37
5.1 Disposal by Hydraulic Fracturing	37
5.2 Design of the Fracturing Disposal Pilot Plant	49
6. Disposal in Natural Salt Formations	55
6.1 High-Temperature Experiments	55
6.2 Mine Observations on Salt Flowage at Ambient Temperature	57
7. Clinch River Study	57
7.1 Bottom Sediments	57
7.2 Water Sampling	58
7.3 Power-Wave Dispersion	59
8. Fundamental Studies of Minerals	72
9. White Oak Creek Basin Study	73
9.1 Movement of Radionuclides in White Oak Creek	73
9.2 Sources of Contamination	76
9.3 Geology and Hydrology of White Oak Creek Basin	79
10. Foam Separation	81
10.1 Pretreatment of Low-Activity Waste	81
10.2 Recovery of Foaming Agent	85
10.3 Engineering Development	85
11. References	89

1. INTRODUCTION

This report is the ninth* 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 the 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.

Principal current emphasis is on the 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 would be discharged to the environment. The retained waste solids or slurries would be combined with the high-activity wastes. Alternatively, the retained solids or the untreated waste could be discharged to the environment in deep geologic formations. The high-activity wastes would be stored at their sites of origin for economic periods to allow for radioactive decay and artificial cooling.

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

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

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

---

*ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, ORNL-TM-169, ORNL-TM-252 and ORNL-TM-396.

2. 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 the construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes. The first phase of the program is concerned with direct calcination processes where melting does not occur and little or no additives are combined with the wastes. In the second phase, enough additives are used to induce melting to form a glass-like material in which the fission products are fixed.

2.1 Engineering Development

J. C. Suddath C. W. Hancher

The purpose of pot-calcination test R-68 was to determine the feasibility of feeding a waste calciner pot by gravity from a head tank. This design information along with operating experience is needed to design the pot-calcination pilot plant to be installed at the Hanford Atomic Products Operation (HAPO).

Feed for the test was synthetic TBP-25 waste (Table 2.1). The calciner was fed from the hold tank by gravity, with about 10 ft of hydraulic head. The continuous evaporator was filled with water at the start of the test, and the calciner condensate was returned to the continuous evaporator, allowing mercury compounds and nitrates to build up. The evaporator was held at a constant liquid level by controlling the evaporator steam rate, and water was added to the evaporator to control the evaporator nitrate composition.

Process control was very successful. The calciner liquid was brought up to the operating level on manual control, and the calciner liquid-level controller was then matched to the manual feed rate and set on automatic, resulting in a very smooth operation.

2.1.1 Operating Conditions and Results

The head tank was hydraulically 10 ft above the calciner feed flange. For feed rates up to 50 liters/ hr the system operated satisfactorily. The feed to the calciner at the startup was set at 40 liters/hr. When the liquid level reached the sensing thermocouple, control was switched to automatic at the same rate. A feed rate of 40 to 30 liters/hr was maintained for the next 10 hr before it began to decrease. However, at the 13th hour of operation the off-gas line suddenly plugged, and the secondary off-gas line vented the system to the atmosphere. The system was allowed to cool for 8 hr, and then the off-gas line was removed and cleaned. A plug of partially calcined aluminum nitrate-oxide mixture was found about 1 ft above the feed flange. The cause of the plug was not determined; however, it is felt that if the off-gas line had not been heated in excess of 250°C, the material might have run back into the calciner. Therefore, the procedure will be changed so that the off-gas line will not be heated until the

calcination period begins. Also, the diameter of the off-gas line will be increased from 1 in. to 2 in., which may help to lessen the plugging.

The average feed rate for the run was about 26 liters/hr, and Table 2.2 shows a number of hourly system variables and parameters. The resulting calcined solids had a bulk density of 0.54 g/cc (Table 2.1). The nitrate composition of the solid was 180 ppm. (This was lower than usual. However, the solid had been calcined for 6 hr in excess of 860°C.) The mercury concentration in the solid was also very low, 0.34 wt %.

Table 2.1. Compositions of Synthetic TBP-25 Feed and Resultant Calcined Solid for Test R-68

Bulk density = 0.54 g/cc
Average gravity feed rate to calciner = 26.4 liters/hr

	NO_3^-	Fe^{3+}	Al^{3+}	Hg^{2+}	
Feed	439	0.34	47.5	4.4	g/liter
Solid	180 ppm	1.04	50.0	0.34	wt %

The material balance for test R-68 was satisfactory, varying from 108% for the nitrate to 74% for the mercury (Table 2.3). The high iron balance of 210% was due to the large amount of corrosion products from the stainless steel equipment.

A mercury trap was used in this test, and it retained 42% of the mercury (Table 2.4). The off-gas line leading to the trap was heated to a terminal temperature of 435°C, and it contained only 2% of the mercury fed to the system. The calciner condensate from the time that the calcination period started returned about 10% of the mercury in the system to the evaporator. This condensate had an approximate volume of 20 liters, in contrast to the 320 liters of calciner condensate during the feeding period, in which also 10% of the mercury in the system was returned to the evaporator.

2.1.2 System Control

Since gravity feed was used in this test, the control of the evaporator was somewhat different from the usual. The evaporator was filled with water to the operating liquid level at the beginning of the test, and the calciner condensate was continuously returned to the evaporator throughout the test. The liquid level in the evaporator was used to control the boil-up rate, thus maintaining a constant level. The evaporator density was not controlled. The conductivity of the evaporator vapor controlled the water addition for the reduction of the nitrate in the evaporator liquid. The operating set points, proportional bands, and reset rates are given in Table 2.5.

Table 2.2. HOURLY SYSTEM VARIABLES AND PARAMETERS - PART A

TEST NO R-68 FEED TYPE - TBP-25 OPERATION MODE - CONTINUOUS

RUN TIME	FEED	WATER	CALCINER ADDITIVE	EVAP. COND.	CALCINER FURNACE	CALCINER COND.	EVAP. COND.	SYSTEM OFF-GAS	EVAP. DENSITY
HOURS	LITERS	LITERS	LITERS	LITERS	(HUNDRED-THOUSANDS OF BTUS)			CU FT	GM/CC
1	41.	26.	0.	67.	0.	2.03	0.79	29.	1.00
2	71.	27.	0.	98.	1.26	4.07	1.78	58.	1.05
3	112.	55.	0.	167.	2.90	6.30	2.60	86.	1.11
4	146.	111.	0.	257.	4.58	8.52	5.23	114.	1.18
5	181.	195.	0.	376.	5.91	10.59	8.84	143.	1.12
6	220.	307.	0.	527.	7.51	12.55	11.86	172.	1.16
7	250.	418.	0.	668.	11.99	15.03	14.46	201.	1.16
8	271.	472.	0.	743.	10.24	16.48	15.43	231.	1.16
9	286.	549.	0.	835.	11.03	18.02	16.25	259.	1.16
10	293.	584.	0.	877.	11.88	19.26	16.83	288.	1.16
11	307.	638.	0.	945.	12.60	20.48	17.68	316.	1.17
12	323.	670.	0.	993.	13.18	21.57	17.88	344.	1.12
13	343.	698.	0.	1041.	13.69	29.85	18.96	372.	1.12
14	0.	698.	0.	1041.	14.31	32.20	18.96	400.	1.15
15	0.	698.	0.	1041.	14.48	32.41	19.07	429.	1.15
16	0.	728.	0.	1071.	15.13	32.85	19.52	458.	1.14
17	0.	728.	0.	1071.	15.95	33.39	19.85	487.	1.17
18	0.	754.	0.	1097.	16.39	34.04	20.03	516.	1.15
19	0.	754.	0.	1097.	16.90	34.69	20.56	545.	1.16
20	0.	780.	0.	1123.	17.11	35.24	20.75	574.	1.17
21	0.	780.	0.	1123.	17.45	35.79	20.75	603.	1.16
22	0.	780.	0.	1123.	17.72	36.27	21.91	632.	1.13
23	0.	806.	0.	1149.	17.96	36.73	22.23	661.	1.13
24	0.	832.	0.	1175.	18.10	37.04	22.23	690.	1.13
25	0.	832.	0.	1175.	18.34	37.47	22.23	719.	1.10
26	0.	832.	0.	1175.	18.61	37.82	22.23	748.	1.08
27	0.	858.	0.	1201.	18.82	38.15	22.63	777.	1.12
28	0.	858.	0.	1201.	19.02	38.66	22.63	806.	1.13
29	0.	858.	0.	1201.	19.33	39.00	22.63	834.	1.05
30	0.	888.	0.	1231.	19.50	39.41	22.63	863.	1.09
31	0.	888.	0.	1231.	19.74	39.85	22.63	891.	1.08
32	0.	888.	0.	1231.	19.98	40.40	22.63	919.	1.09
33	0.	888.	0.	1231.	20.18	40.77	22.63	919.	1.08

Table 2.2. HOURLY SYSTEM VARIABLES AND PARAMETERS - PART B

TEST NO R-68 FEED TYPE - TBP-25 OPERATION MODE - CONTINUOUS

RUN TIME	EVAP. LIQUID NITRATE	EVAP.MAJOR CATION FE OR AL	CALCINER COND. NITRATE	EVAP COND. H+	EVAP.COND. MAJOR ION FE OR AL	EVAP. COND. RU	EVAP. LIQUID TEMP.	EVAP. VAPOR TEMP.	CALCINER FEED TEMP.	CALCINER OFF-GAS TEMP.
HOURS	MOLAR	GM/LITER	MOLAR	MOLAR	GM/LITER	GM/LITER	DEG.C	DEG.C	DEG.C	DEG.C
1	0.41	0.0	1.03	0.03	0.	0.	97.	98.	108.	286.
2	3.46	0.1	3.29	0.13	0.	0.	100.	101.	113.	282.
3	8.10	0.1	4.65	1.71	0.	0.	107.	109.	119.	327.
4	8.70	0.2	5.37	2.41	0.	0.	108.	111.	123.	320.
5	8.11	0.3	1.95	1.59	0.	0.	108.	110.	123.	290.
6	7.37	0.3	5.94	1.41	0.	0.	106.	109.	123.	283.
7	7.52	0.3	6.24	1.51	0.	0.	106.	108.	120.	258.
8	7.76	0.3	7.16	1.73	0.	0.	107.	109.	120.	275.
9	7.37	0.3	6.30	1.38	0.	0.	106.	108.	115.	270.
10	7.56	0.3	5.41	1.46	0.	0.	108.	109.	117.	240.
11	8.02	0.3	5.05	1.60	0.	0.	106.	108.	117.	260.
12	7.90	0.3	4.76	1.59	0.	0.	108.	109.	117.	239.
13	7.79	0.3	13.52	1.75	0.	0.	110.	109.	119.	210.
14	6.90	0.3	14.13	0.56	0.	0.	92.	102.	112.	50.
15	6.83	0.3	12.60	1.59	0.	0.	106.	106.	116.	295.
16	6.73	0.2	11.29	1.03	0.	0.	107.	109.	116.	430.
17	7.86	0.2	12.05	1.43	0.	0.	108.	109.	117.	430.
18	6.51	0.2	11.29	1.81	0.	0.	106.	107.	114.	430.
19	7.14	0.2	10.71	0.89	0.	0.	107.	108.	115.	435.
20	7.32	0.3	10.00	1.38	0.	0.	107.	108.	114.	435.
21	6.22	0.2	8.57	1.14	0.	0.	93.	81.	109.	435.
22	4.73	0.2	7.44	0.49	0.	0.	104.	106.	116.	435.
23	5.87	0.2	6.30	0.73	0.	0.	105.	105.	113.	425.
24	5.14	0.2	5.52	0.95	0.	0.	100.	90.	109.	435.
25	4.25	0.2	0.	0.10	0.	0.	100.	83.	109.	425.
26	3.84	0.2	0.	0.38	0.	0.	102.	100.	110.	425.
27	5.59	0.2	0.	0.32	0.	0.	105.	105.	112.	425.
28	5.54	0.2	0.	0.27	0.	0.	104.	102.	112.	435.
29	4.73	0.2	0.	0.05	0.	0.	104.	102.	111.	445.
30	4.06	0.2	0.	0.05	0.	0.	104.	102.	111.	440.
31	3.89	0.2	0.	0.05	0.	0.	102.	100.	110.	420.
32	4.10	0.2	0.	0.06	0.	0.	102.	101.	109.	430.
33	3.94	0.2	0.	0.14	0.	0.	102.	100.	109.	435.

Table 2.3. Material Balance for Test R-68

	NO_3^-	Fe^{3+}	Al^{3+}	Hg^{2+}
Material in, g	150,577	166	16,293	1,520
Material out, g				
Solid	6	335[a]	16,100	103
Evaporator	6,200	14	600	312
Condensate	156,877	--	15	27
Mercury trap	--	--	--	650
Off-gas	--	--	--	27
Total, g	163,083	349	16,715	1,119
Balance, %	108	210[a]	103	74

[a]The excess iron may be due to the corrosion of the stainless steel equipment.

Table 2.4. Distribution of the Mercury at the End of Run R-68

Input, 1,520 g

Location of the Mercury	Weight of Mercury (g)	Percentage of the Original Mercury
Calcined solid	103	6.8 (0.34% of the solid)
Evaporator	312	20.5
Condensate	27	1.7
Mercury trap	650	42.7
Off-gas	27	1.7
Total percentage		73.4%

Table 2.5. System Control Data for Run R-68

	Set Point (%)	Proportional Band (%)	Reset Rate (min)	Stream Controlled
Calciner liquid level	60	200	240	Feed
Evaporator liquid level	50	200	100	Steam
Evaporator vapor conductivity	60	100	10	Water
Evaporator vapor pressure	40	25	1	Noncondensables

2.1.3 Design of the Calciner Pot

A calciner pot designed for the HAPO waste pilot plant was used in this test (Figure 2.1). The top of the pot is designed to match the automatic feeding station now being tested by Georgia Nuclear Laboratory, operated by Lockheed on a subcontract basis. The top can have a plug inserted which later can be welded. This pot design has the internal thermocouples entering at the top of the pot and encased in 3/4-in.-diam tubes, each holding six thermocouples. One thermocouple bundle is on the center line of the pot, and the other bundle is 1-1/2 in. from the wall.

2.2 Design of the Pilot Plant

J. O. Blomeke J. M. Holmes E. J. Frederick
H. Pfohl E. D. Arnold

2.2.1 Flowsheets for Waste Pilot Plant

Liaison between ORNL and HAPO on the design of the High-Level-Waste Pot-Calciner Pilot Plant to be installed at Hanford is continuing. Initial efforts were directed toward integrating the ORNL Pot Process and the Hanford Spray Process in order to minimize the duplication of equipment. A preliminary process flowsheet was prepared by Hanford and submitted to ORNL for review.

Discussions were held at Brookhaven National Laboratory about the status of the rotary ball calciner process and their scheduled 1000-hr continuous run. Process data was requested from the run for evaluation and the writing of a material-balance flowsheet preparatory to the design of a process for use in the Hanford Waste Pilot Plant.

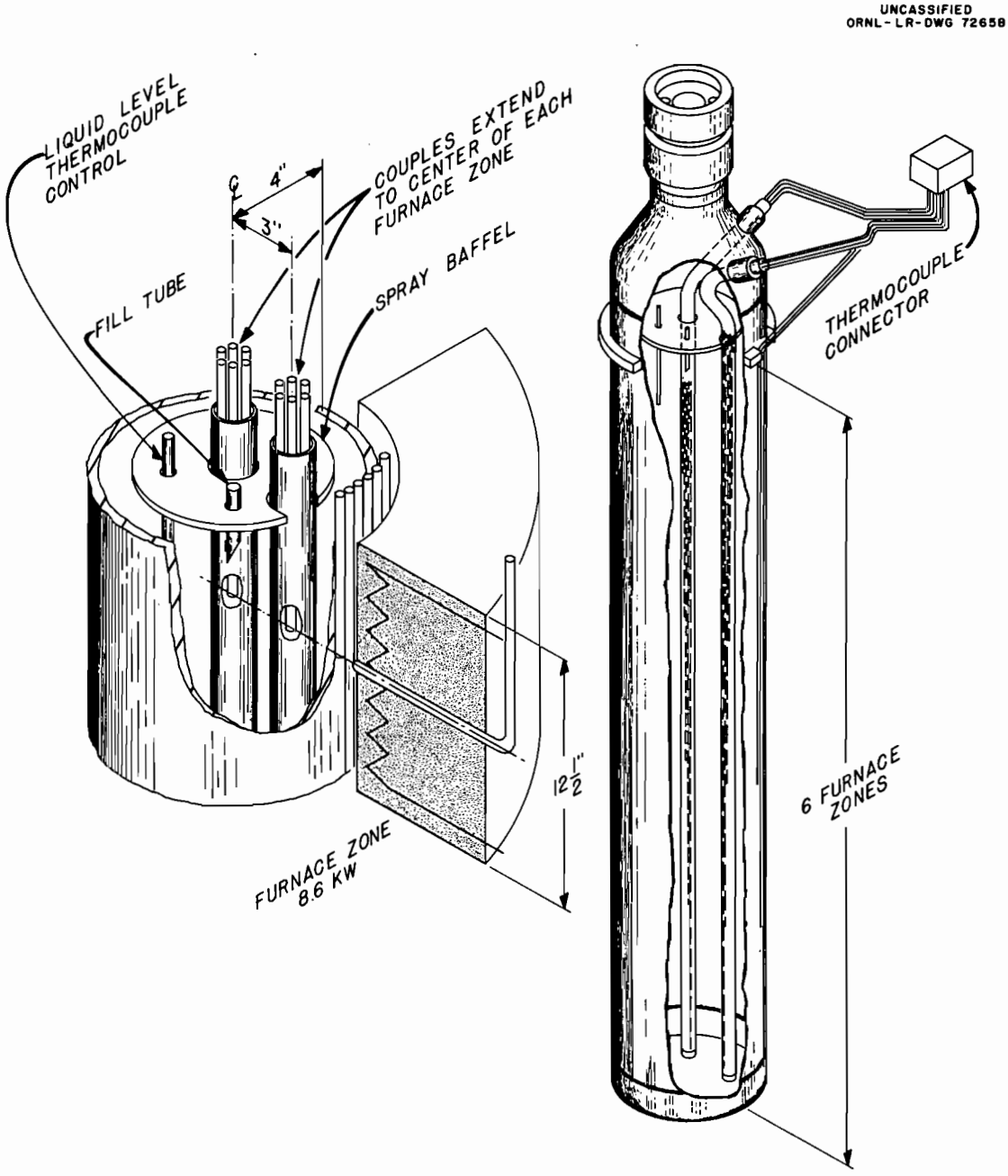

Fig. 2.1. ORNL Designed Waste Calciner Pot for Hanford Waste Pilot Plant.

2.2.2 Mechanical Test Program

Equipment installation was completed at Georgia Nuclear Laboratories, and all systems were given preliminary tests. Phase I testing was started. It includes determining the accuracy of positioning the dolly beneath the filling station and raising the pot into the filling position. Preliminary results indicate that dolly positioning is reproducible within about 0.025 in., with transverse and longitudinal deflections of the filling station of about 0.10 in. and about 0.08 in., respectively, when the pot is raised into the filling position. Approximately 30 min are required to load the pot into furnace, position the dolly at the filling station, raise the pot and lower it, and return the dolly. (This does not include heating or cooling the pot, nor leak testing. A time cycle for the complete operation will be determined upon completion of the connect-disconnect test.)

Tests were completed on the evaluation of the Grayloc seal. With the seal subjected to 100-psi internal pressure and 300°C, the leak rate was 72 cc/year.

2.2.3 Shielding Calculations

Shielding calculations were made with an IBM-7090 code to determine the gamma dose rate from an array of 39 calcination pots stored in the mechanical cell planned for the Hanford Fuels Recycle Pilot Plant. The results for three different waste types are shown on Fig. 2.2 as gamma dose rate in millirems per hour vs cooling time. Two pot diameters for Purex waste are also shown. The pot diameter for the Consolidated-Edison and APPR wastes was 8 in. and the active pot length was 72 in.

Conditions for the calculation were as follows: Thirty-nine calcination pots having a 6- or 8-in. diam, stored on 18-in. centers in three rows spaced 24 in. apart, were considered. The concrete shield was 4 ft thick, with a density of 200 lb/ft^3. The center line of the closest pot row was 24 in. from the shield wall. The shielding effect of the pots stored in front of the second and third rows was not included in the calculation. The waste types considered were: (1) Consolidated-Edison fuel irradiated to a burnup of 23,100 Mwd per metric ton of thorium and treated by the Darex process. The solid waste volume was 422 liters per metric ton of thorium; (2) Purex waste having a solid waste volume of 19.0 liters per metric ton of uranium. (3) APPR fuel of average burnup of 42% of the U^{235} and treated by the Darex process. The solid waste volume was about 9.7 liters per kilogram of U^{235}, based on the U^{235} content before burnup.

2.3 Fixation of Waste in Glass

W. E. Clark
F. R. Clayton
H. W. Godbee
J. F. Easterly

The study of the thermal stability of the solid products from the fixation of simulated high-sulfate Purex waste in phosphate and borophosphate melts was continued.

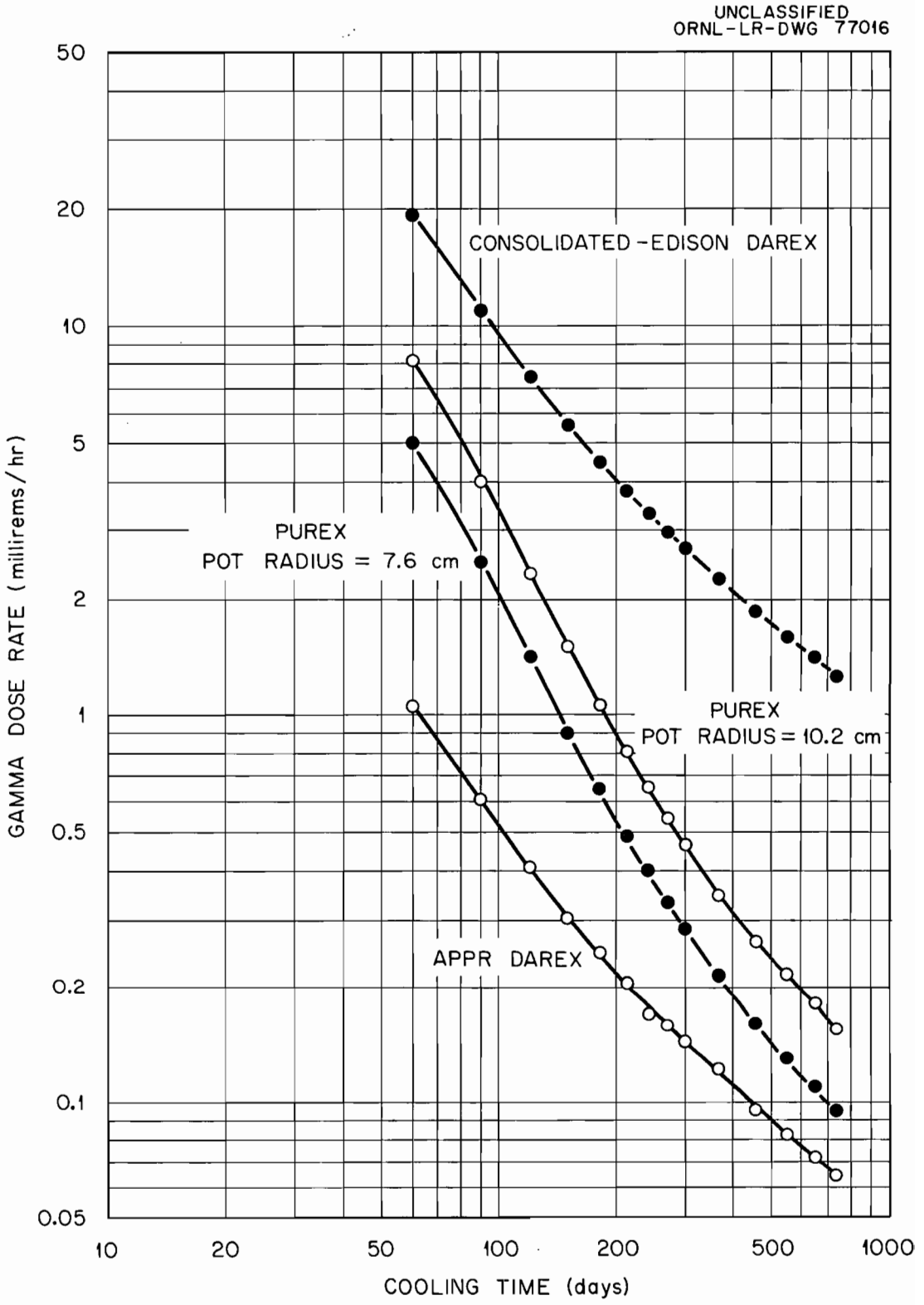

Fig. 2.2. Comparison of the Gamma Dose Rates from the Different Wastes (Mechanical Cell).

In addition, two semiengineering-scale glass-fixation experiments were run with simulated TBP-25 waste, and corrosion studies were continued on candidate materials of construction under conditions expected in the waste evaporator and fixation pot and in salt-mine storage.

2.3.1 Batch Formation of Glass

Thermogravimetric analysis of glass melts containing about 38.8 to 42.7 wt % of simulated Purex waste oxides indicated that it will probably be possible to retain at least 85 to 95% of the sulfate in the solid product. Apparent sulfate losses varied from 2.1 to 22% (Table 2.6).

Initial experiments consisted in calcining the solid residues (from the evaporation step) to 650°C, transferring the material to the thermobalance, and recording the weight loss while the temperature was raised to 1100°C at the rate of 6°C/min. Approximate softening temperatures were obtained by visual observation during melting in a muffle furnace. Calcined solids from the more promising mixtures were analyzed thermogravimetrically at 100°C above the approximate softening temperatures. At these temperatures all the products investigated were sufficiently fluid to pour easily. This temperature difference should, therefore, be considered the operational maximum for a practical fixation process.

For the melts investigated, such "operational temperatures" varied between 850 and 950°C (Table 2.6), well within the range of usefulness of stainless steel as a container material. No true glasses were among the products investigated. In general, sulfate retention was more complete for those products that had an excess of the cations Na^+, Ca^{2+}, and Mg^{2+} over the nonvolatile anions. In the absence of adequate phase data this can be taken only as an approximate, empirical rule.

Sufficient information appears to be available to allow the selection of a satisfactory range of compositions for the fixation of this particular high-sulfate waste with a minimum of sulfate loss. Future experiments will be designed to define a similar range of compositions for more nearly contemporary wastes.

2.3.2 Formation of Glass Semicontinuously

Two semicontinuous experiments were run in which simulated TBP-25 waste was evaporated, calcined, and melted to a glass in a stainless steel pot, 24 in. high and 4 in. in diameter. Operation was with a slowly rising liquid level [1] in both cases. Objectives were to (1) determine the effect of phosphite vs phosphate on ruthenium volatility under these conditions and (2) to develop more experience in the operation of the glass-fixation equipment.

In one case, additives included 2.0 moles of NaH_2PO_4 per liter and 0.25 mole of PbO per liter; in the other, NaH_2PO_2 replaced the phosphate, and sufficient Ru^{106} was added to yield a concentration of 0.1 μc/ml. The condensate was continuously

Table 2.6. Sulfate Volatility from Experimental Melts Incorporating 39% to 43% Simulated Purex Waste Oxides

Purex Waste Composition, M: 6.1 NO_3^-, 5.6 H^+, 1.0 SO_4^{2-}, 0.5 Fe^{3+}, 0.1 Al^{3+}, 0.01 Cr^{3+}, 0.01 Ni^{2+}, 0.02 Ru

	Melt Number							
	1	2	3	4	5a	6a	7a	8a
Additives (g-moles/liter waste)								
NaH_2PO_2	1.26	1.26	1.26	1.26	1.46	1.56	1.46	1.26
H_3PO_3	--	--	--	0.50	--	--	--	0.51
NaOH	1.36	0.61	0.76	0.86	0.42	0.98	1.08	--
$Ca(OH)_2$	0.41	0.41	0.41	0.41	0.92	0.40	0.53	0.92
MgO	--	--	0.30	--	--	--	--	--
$Na_2B_4O_7$	--	0.125	--	--	--	--	--	--
Composition of melt (Wt % theoretical oxides)								
Fe_2O_3	11.8	11.5	11.7	10.9	11.1	11.2	11.2	11.0
Al_2O_3	1.5	1.5	1.5	1.4	1.5	1.5	1.5	1.5
Na_2O	29.4	24.2	23.9	23.0	21.7	27.6	27.5	16.0
Cr_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
NiO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
RuO_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SO_3	23.6	22.9	23.5	21.8	21.0	21.2	21.1	20.9
P_2O_5	26.2	25.8	26.4	34.2	29.5	31.7	29.6	35.5
CaO	6.9	8.8	9.0	8.4	14.8	6.3	8.5	14.7
MgO	--	--	3.6	--	--	--	--	--
B_2O_3	--	5.0	--	--	--	--	--	--
Totals	99.9	100.2	100.1	100.2	100.1	100.0	99.9	100.1
Weight % waste oxides	42.7	41.6	42.6	39.5	39.1	39.4	39.4	38.8
Excess cation equivalents	0.79	--	0.79	--	0.86	0.38	0.74	--
Excess anion equivalents	--	0.21	--	0.21	--	--	--	0.07
Ratio $\left(\frac{\text{g eqs Na + Ca + Mg}}{\text{g eqs } SO_4^{2-}+PO_3^-+BO_3^-}\right)$	1.24	0.944	1.24	0.944	1.25	1.11	1.21	0.982
Approximate softening temp.(°C)	850	850	880	800	875	800	850	950
Wt % SO_3 lost during 100 min at 100°C above softening temp	5.3	22.0	2.1	Excessive.	19.0	12.5	9.5	14.3
Appearance	Gray-white, crystalline; strong only if quenched	Light-tan, weak; glassy	Dark brown, strong; crystalline, some voids	Gray, crystalline; weak	Light green, crystalline	Light gray, crystalline	Light greenish gray, crystalline	Shiny, gray, metallic

[a]Listed in Table 2 of the bimonthly report for June-July, 1962, as Nos. 3,5,6, and 8, respectively.

monitored in order to obtain a record of the ruthenium volatilized. In both cases the equipment was thoroughly flushed with NO to remove oxygen prior to startup. Also in both cases the operation covered parts of four working days. Instead of operating on a "straight-through" basis, which requires about 16 hr with only one startup and one final calcination melting period, four start-up and shut-down cycles were employed in each case. Operation was quite smooth in both experiments.

About 24% of the ruthenium was volatilized regardless of whether phosphite or phosphate was added as fluxing agent (Table 2.7). Prior results obtained during calcination with operation at a fixed liquid level and no fluxing additive showed that 17.6 to 19.5% of the ruthenium volatilized.[2] About 77% of the mercury added volatilized (Table 2.7).

2.4 Corrosion Studies

W. E. Clark

Work done by L. Rice, D. N. Hess, and P. D. Neumann, Reactor Chemistry Division

Specimens of types 347 and 304L stainless steels corroded at overall rates ≤ 0.1 mil/month during 1008 hr of exposure in the superheated vapor (150 to 305°C) over refluxing simulated Purex waste solution (Table 2.8). In the solution and in the condensing vapor regions overall rates were 1.9 and 2.8 mils/month for type 304L, and 2.6 and 3.3 for type 347, respectively. It appears that a stainless steel head assembly for the fixation pot will have excellent durability if it can be kept at or above 150°C.

Current plans call for the fixation container pot to hang from its top flange while in the furnace. The limiting factor in the durability of the pot is expected to be its high-temperature strength under these combined conditions -- high temperature, tensile stress, and corrosivity. Small type 304L stainless steel pots were filled with simulated Purex waste plus fluxing additives and then subjected to a tensile stress of 150 lbs/in. while undergoing the evaporation-fixation cycle (about 3 hr), followed by a period of about 165 hr at 1050°C. One specimen showed elongations of 9.2×10^{-5} and 5.4×10^{-4} in./in. on opposite sides of the pot, while a second warped at the flange weld, making exact elongation measurements impossible. Four corrosion specimens of type 304 stainless steel exposed in the pots during this regimen showed overall corrosion rates of 19, 22, 43, and 47 mils/month. These tests will be repeated under conditions of higher stress to determine the probable limit of usefulness of type 304L stainless steel.

Welded specimens of various stainless steels exposed on the side of a disposal pot sunk in the floor of the Carey Salt Mine, Hutchinson, Kansas, and held at about 575°C for 31 days underwent severe localized corrosion involving cracking, knife-line attack, pitting, and intergranular attack, though the overall rates varied only from about 0.45 to 1.3 mils/month. These test conditions are far more aggressive than are foreseen for the ultimate storage or disposal of actual wastes in salt. In the actual case the age and dilution of the waste and the diameter of the container will be selected so that the

Table 2.7. Volatility of Ruthenium and Mercury During the Semicontinuous Formation of Phosphate Glass from TBP-25 Waste at About 1050°C

	Percent Volatilized			
	Ruthenium		Mercury	
	Glass Additive		Glass Additive	
Stream	PO_4^{3-} [(a)]	$H_2PO_2^-$ [(b)]	PO_4^{3-}	$H_2PO_2^-$ [(c)]
Condensate	24.05	22.65	73.86	
Secondary off-gas	8.4×10^{-6}	0.86	0.22	
Jet pot liquid	2.6×10^{-6}	0.29[d]	0.06[d]	
Recycle liquid	0.06	1.68[d]	2.64	
Shut-down water	0.11	--[c]	0.14[d]	
Totals	24.22	23.51 (minimum)	76.72 (minimum)	

[a]Stable ruthenium determined by activation analysis.

[b]Determined by spiking with Ru^{106} and counting.

[c]No determination made.

[d]Figures represent limits of detection. Not included in totals.

Table 2.8. Corrosion Rates of Types 304L and 347 Stainless Steel in Refluxing Purex Waste Solutions[a]

Test Period (hr)	Alloy	Heated Specimen Temp. (°C)	Corrosion Rate (mils/month)		
			Vapor (heated)	Vapor	Solution
168	304L	305	<0.1	1.0	1.5
	347	305	<0.1	2.5	1.8
672	304L	305[b]	<0.1	2.4	1.7
	347	305[b]	<0.1	3.5	2.3
840	304L	150	<0.1	2.5	1.8
	347	150	<0.1	3.2	2.5
1008	304L	150	<0.1	2.8	1.9
	347	150	<0.1	3.3	2.6

[a]Solution contained H^+, 5.6 M; Na^+, 0.57 M; Fe^{3+}, 0.47 M; Cr^{3+}, 0.01 M; Ni, 0.01 M; Al^{3+}, 0.11 M; Ru^{3+}, 0.001 M; SO_4^{2-}, 0.99 M; NO_3^-, 6.04 M.

[b]After 672 hr of exposure at 305°C the temperature was lowered to 150°C. Boiling point of the solution was about 111°C.

maximum temperature reached by the exterior of the pot will be about 300°C. Tests under these more realistic conditions are planned.

3. LOW-LEVEL-WASTE TREATMENT

A scavenging -- ion exchange process is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations, with ORNL low-activity waste being used for the study. The process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; the cesium-from-sodium separation factor is 160 for phenolic groups and 1.5 for sulfonic groups. Other cations, for example, strontium and the rare earths, are also sorbed efficiently. Inorganic ion exchangers, such as vermiculite and clinoptilolite, are being studied as alternatives. The waste solution must be clarified prior to ion exchange because the resins do not remove colloids efficiently. Water clarification methods are being developed both for the ion exchange processes and for the ORNL lime-soda process waste water treatment plant, both in development and pilot-plant programs.

3.1 Pilot-Plant Test

An ORNL topical report is being prepared in order to describe the successful pilot-plant program that has been reported in previous bimonthly reports.

3.2 Laboratory Development

W. E. Clark R. R. Holcomb

In the scavenging—ion exchange[3] process developed for decontaminating the large volumes of slightly radioactive water produced in nuclear installations, the water is made 0.01 M in NaOH and 5 ppm in ferrous iron, the so-called "standard, caustic-copperas" treatment. This treatment removes those radionuclides that are not effectively sorbed on the phenolic ion-exchange resin, removes hardness ions that compete for resin exchange sites from solution, and provides the high pH (about 11.7) necessary for ionization of the phenolic groups of the resin. However, when the treatment was applied to ORNL process waste, difficulty was encountered in reducing the hardness prior to ion exchange. This hardness supersaturation was attributed to the presence of hexametaphosphate,[4] a constituent of some commercial detergents and decontaminating solutions. The laboratory studies of this treatment have been continued, utilizing the laboratory-model clarification equipment (Fig. 3.1).

The clarifier unit was operated on tap water to determine the effect of different amounts of sodium hexametaphosphate and the amount of sodium carbonate required to overcome the effect. This was studied in the following way: A steady-state hardness of 3 to 4 ppm (as $CaCO_3$) was established in the clarifier effluent with the standard

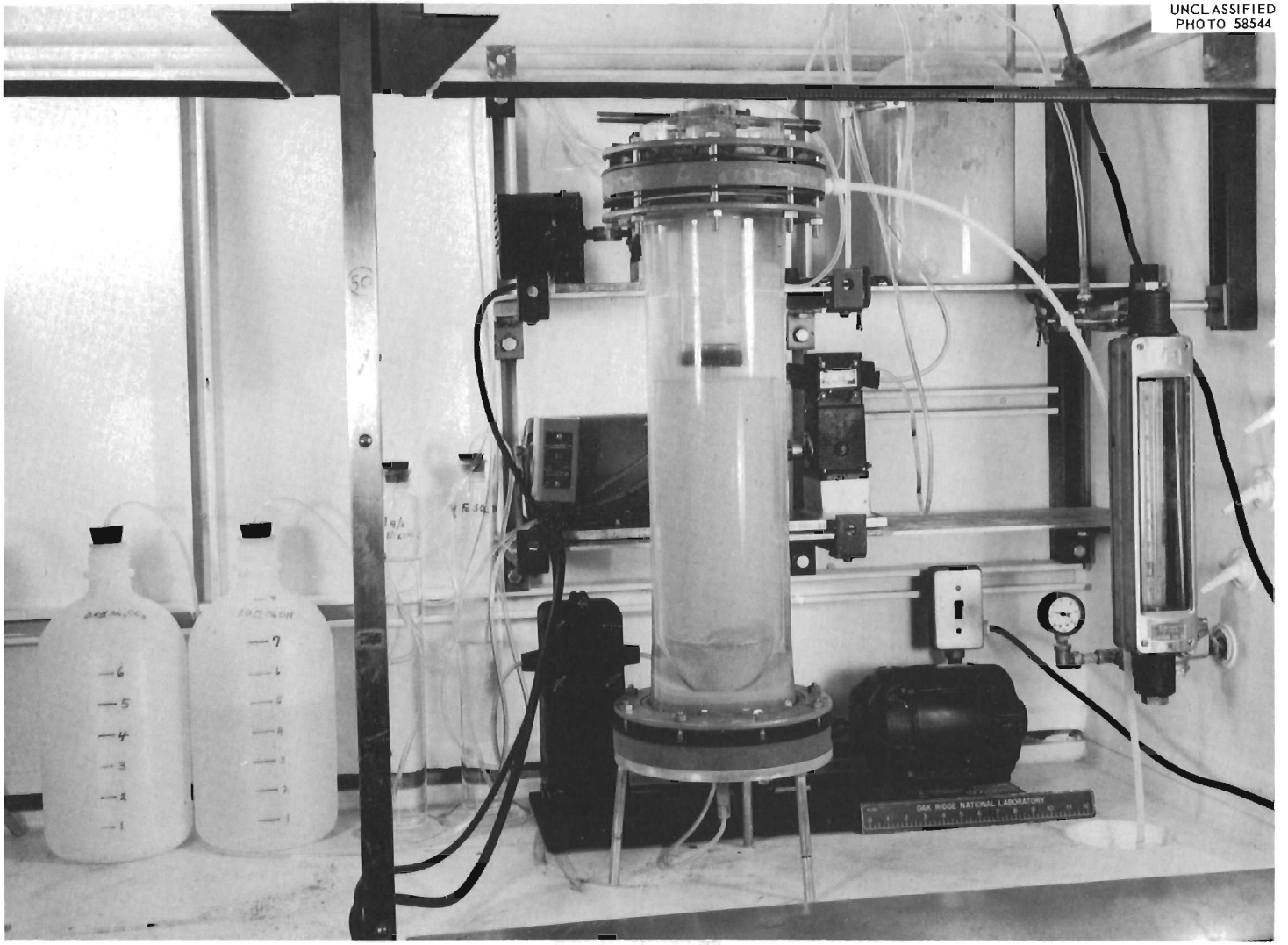

Fig. 3.1. Laboratory-scale Continuous Clarification Equipment.

caustic-copperas treatment. The feed water was then made 1 ppm in sodium hexametaphosphate, resulting in a steady-state hardness of 6 ppm. An increase to 2 ppm of the complexing agent caused an increase to about 20 ppm of hardness in 24 hr and a gradual increase to a steady-state hardness of 42 ppm in 3 days. Hexametaphosphate concentrations of 3 and 5 ppm resulted in steady-state hardnesses of 60 and 70 ppm (as $CaCO_3$), respectively. At the 5-ppm concentration, making the water 0.005 M in Na_2CO_3 had no effect on the 70-ppm residual hardness, but when the water was made 0.01 M in Na_2CO_3 the hardness fell to 24 ppm in 24 hr.

The above experiment was repeated with trisodium (ortho) phosphate as the complexing agent. When the tap water was made 12 ppm in trisodium phosphate, the effluent hardness increased from 2 ppm (as $CaCO_3$) to 51 ppm in 24 hr. This increase is comparable to that obtained previously with the same concentration of phosphate as sodium hexametaphosphate. Similar results were obtained with varying amounts of a household detergent (FAB) that contains polyphosphates. The results indicate that phosphate ion will create hardness supersaturation problems regardless of its ionic species.

The sodium carbonate was added in order to overcome the phosphate effect. So long as the phosphate concentration remained below 3 ppm (as phosphate), 0.005 M Na_2CO_3 was sufficient to reduce residual hardness to less than 14 ppm as $CaCO_3$. However, this addition doubles the concentration of sodium ion and consequently reduces the cesium capacity of the ion-exchange resin by 50% at the 0.1% breakthrough level. The volumetric distribution coefficients were 3387 and 3158 at 0.01 and 0.02 N sodium, respectively.

If high-hardness effluent water is allowed to reach the ion-exchange resin, the capacity for cesium and strontium are reduced as a result of the increased competition for resin sites. Therefore, the effect of different amounts of hardness on the cesium capacity was studied, and the quantitative effect on strontium remains to be determined. For example, increasing the calcium concentration of the ion-exchange influent from 0 to 8.5 and to 43 ppm (as $CaCO_3$) reduced the cesium 0.1%-breakthrough capacity from 1850 to 1350 and 520 bed volumes, respectively.

4. ENGINEERING, ECONOMICS, AND SAFETY EVALUATION

4.1 Interim Solids Storage

J. O. Blomeke J. J. Perona
H. O. Weeren R. L. Bradshaw

As part of the continuing study of the economics of high-activity waste management, a conceptual design and cost estimate was prepared for interim storage of calcined wastes prior to their shipment to a final disposal site. The details of the study, summarized below, are presented in ORNL-3355, now in press.

4.1.1 Description of Solids-Storage Facility

The interim storage facility was designed to handle cylinders of calcined waste produced by the pot-calcination plant described in ORNL-3192. In this 6-ton/day plant, Purex waste from the recovery of 1500 tons per year of uranium converter fuel, irradiated to 10,000 Mwd/ton, and Thorex waste from recovery of 270 tons per year of thorium converter fuel, irradiated to 20,000 Mwd/ton, was converted to solids and calcined in cylinders 6, 12, and 24 in. in diameter by 11 ft high. Calcination after storage of the wastes as both acid and neutralized solutions was considered, as was the production of a glass from acid Thorex waste. The number of cylinders of calcined solids produced annually is given in Table 4.1.

Table 4.1. Numbers of Calcination Vessels per year Required for Wastes from 6-ton/day Processing Plant

Waste Type	Number of Calcination Vessels		
	6-in.-diam	12-in.-diam	24-in.-diam
Acid Purex	925	231	58
Reacidified Purex	2320	580	145
Acid Thorex	1390	348	87
Reacidified Thorex	4110	1028	257
Thorex glass	1800	-	-

Interim solids storage periods of 1, 3, 10, and 30 years in water-filled canals was considered for cylinders with contents aged 120 days, 1 year, 3 years, and 10 years by interim liquid storage. Although the wide range of conditions resulted in facilities of different sizes and configurations, they consisted, in essence, of a central-facility canal for the receiving and removal of cylinders, canals for the storage of the cylinders, and a service area containing the equipment for cooling and purifying the water, a personnel office, and a change room.

The central-facility canal was designed for receiving cylinders of solid waste from the calcination plant, for storing them briefly to permit the detection of defective containers, and for routing them to the proper canal for interim storage. It also served for the underwater loading of the cylinders into casks prior to shipping off-site. This canal was 30 ft wide, 40 ft deep, and varied in length from 24 to 146 ft, depending on the number and size of the storage canals (Fig. 4.1). It was equipped with an overhead 100-ton bridge crane for lifting the shipping casks and capable of traversing 20 ft of canal length and, with a 5-ton bridge crane for manipulating the individual cylinders under water, operable over the remaining area of the central-facility canal.

UNCLASSIFIED
ORNL-LR-DWG 77017

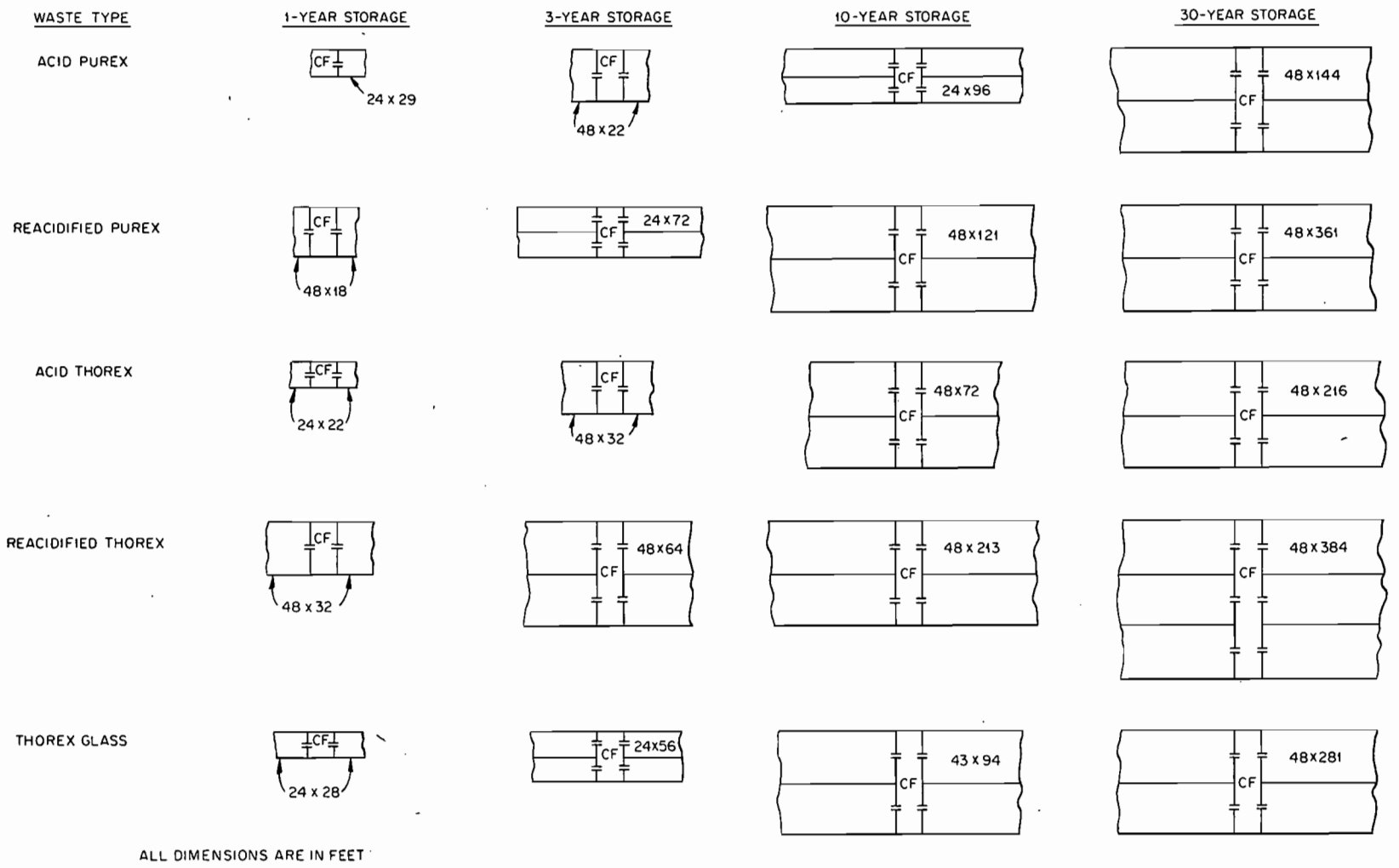

Fig. 4.1. Layouts of Central Facility and Storage Canals for Various Waste Types and Interim Storage Times.

The cylinders of solidified waste were assumed to be stored upright in canals adjoining the central facility. It was assumed that they were arranged in parallel rows, each row consisting of two cylinders staggered back-to-back, with a space between rows for moving them in and out. With this arrangement, each cylinder was allowed a space 1.5 times its diameter along the row and twice its diameter across the row, permitting in the case of a 48-ft-wide canal, 24 rows of 6-in.-diam cylinders, 12 rows of 12-in.-diam cylinders, or 6 rows of 24-in.-diam cylinders. It can be shown that the length of canal required for the storage of these wastes in this array is a function only of interim storage time and is independent of cylinder diameter. The lengths of 48-ft-wide canal required for the various waste types for different storage times (Table 4.2) were broken into more economically and practically sized segments (Fig. 4.1). To provide for drainage and maintenance, 25% excess storage capacity was added to the facility, and each segment was sized to handle no more than 25% of the total cylinders, except in those cases where the central facility was larger than a segment. The canals were assumed to be made of 1-ft-thick reinforced concrete around the sides and on the bottom, with interior walls 2-ft thick separating them from the central facility and from each other. The concrete was assumed to be painted with an epoxy-base paint, and each canal segment was equipped with a 5-ton bridge crane for underwater manipulation of the cylinders.

The depth of the canals was a function of the depth of water required to attenuate the radiation dosage to 0.25 mr/hr at the surface. The depth of the water required for shielding varied from 15.4 ft for 120-day-old acid Purex waste to 10 ft for 10-year-old reacidified Thorex waste, which, together with an additional fixed depth of 13 ft for cylinder height and freeboard, determined the total depth.

As an aid in locating defective cylinders during storage, the canals were provided with aluminum partitions 12 ft apart along their length in order to channel the water for monitoring.

The canal water was recycled for demineralization and cooling. Filters and demineralizers were provided to process the water at a turnover rate of once a week. The cooling system consisted of primary and secondary loops, with pumps, intermediate heat exchangers, and a cooling tower, and was designed to handle the maximum heat generation rates computed for Purex and Thorex wastes of different ages and for various storage times (Table 4.3).

It was assumed that a masonry building would enclose the central facility, service area, offices, and change rooms and that the storage canals would be housed in a frame building of lighter construction.

4.1.2 Costs and Amortization

Capital costs expressed on an annual basis were computed as the sum of the costs of the various components, allowing 4% interest. They were amortized as follows:

Component	Amortization Time (yr)
Excavation and concrete	50
Aluminum partitions	25
Epoxy lining	10
Cranes	25
Cooling system	20
Demineralizer system	10
Radiation monitors	10
Buildings	50

To these costs, 40% was added for construction overhead, 15% for engineering, and 20% for contingencies. In the case of 30 years of interim storage, the present-worth values were used. The total capital costs ranged from about $20,000/year for 1-year-interim storage of 10-year-old acid Purex waste to $634,000/year for 30-year-interim storage of 120-day-old reacidified Thorex waste.

Table 4.2 Lengths, in Feet, of 48-ft-Wide Canal Required for Interim Storage of the Calcined Solids from Different Types of Wastes

Type of Waste	Length Required for an Interim Storage Time of:			
	1 yr	3 yr	10 yr	30 yr
Acid Purex	14.5	43.3	145	433
Reacidified Purex	36.2	108	362	1085
Acid Thorex	21.7	65.0	217	650
Reacidified Thorex	64.1	192	640	1920
Thorex glass	28.1	84.5	281	845

Labor costs were assumed to be $113,000/year for all cases considered. This allowed for 9 man-years (4 shift operators, 1 supervisor, 1 health physicist, and 3 maintenance craftsmen).

Total costs, expressed in terms of mills per electrical kilowatt-hour, were computed for handling each waste type separately and for the combinations of acid Purex--acid Thorex and reacidified Purex--reacidified Thorex wastes. Highest costs were for the storage of 120-day-old wastes and ranged from 19×10^{-3} mills/kwhr$_e$ for 30-year

storage of reacidified Thorex waste to 1.8×10^{-3} for 1-year storage of acid Purex (Fig. 4.2). Lowest costs were for storage of 10-year-old wastes, which ranged from 18×10^{-3} mills/kwhr$_e$ for 30-year storage of reacidified Thorex to 1.5×10^{-3} for 1-year storage of acid Purex (Fig. 4.3). The costs of storage of Purex and Thorex wastes together in the same facility ranged from 1.5×10^{-3} mills/kwhr$_e$ for 1 year of storage to 4.8×10^{-3} for 30 years of storage for the calcined acid wastes, and from 1.8×10^{-3} to 6.3×10^{-3} mills/kwhr$_e$ for the calcined reacidified wastes (Fig. 4.4). The storage of acid wastes as solids was cheaper by factors of from 2 to 2.7 than the storage of the same wastes as liquids, reported in ORNL-3128. However, for most storage times, the storage of neutralized liquid wastes was slightly cheaper than that of reacidified Purex and Thorex calcined solids.

Table 4.3. Maximum Heat Generation Rates (Btu/hr x 10^6) of Calcined Wastes During Interim Storage

Age at Time of Calcination (yr)	Interim Storage Time (yr)			
	1	3	10	30
		Calcined Purex Waste		
1/3	23.0	35.0	47.0	68.0
1	10.5	18.9	30.9	52.6
3	3.87	8.37	18.5	38.6
10	1.77	3.97	11.8	28.2
		Calcined Thorex Waste		
1/3	8.30	12.6	16.9	24.5
1	3.78	6.81	11.1	18.9
3	1.39	3.01	6.69	13.9
10	0.49	1.43	4.26	10.2

4.2 Analysis of the Safety of Routine Operating Discharges from White Oak Creek to the Clinch River

K. E. Cowser

When radioactive material is relaesed to the environment, it can reach man via a number of routes. The pathways taken are complex, and in many cases data is lacking to assess the dose that may be received. Virtually all the radioactivity emanating from the Laboratory and reaching the Clinch River comes through White Oak Creek. Thus, an analysis was begun in order to ascertain the safety of routine operating discharges from White Oak Dam to the Clinch River.

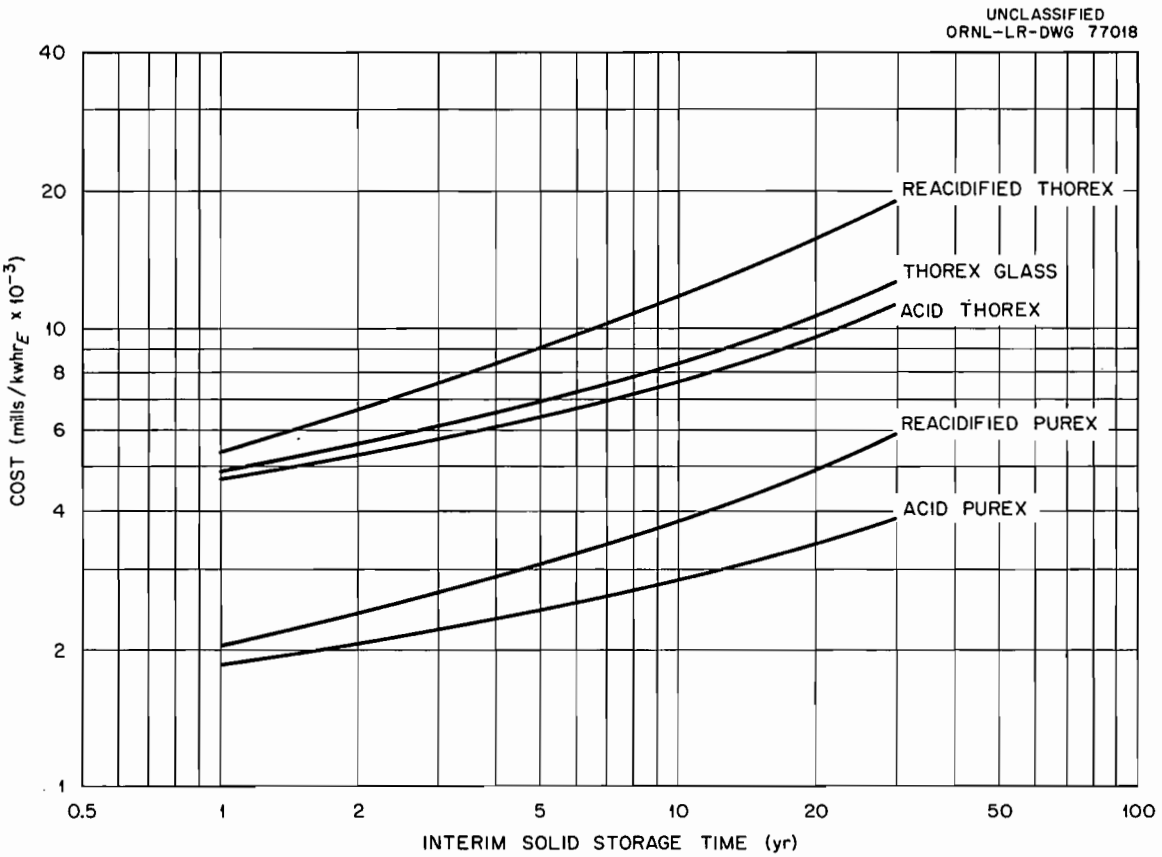

Fig. 4.2. Costs of Interim Storage of Calcined Wastes. Age of wastes: 0.38 year.

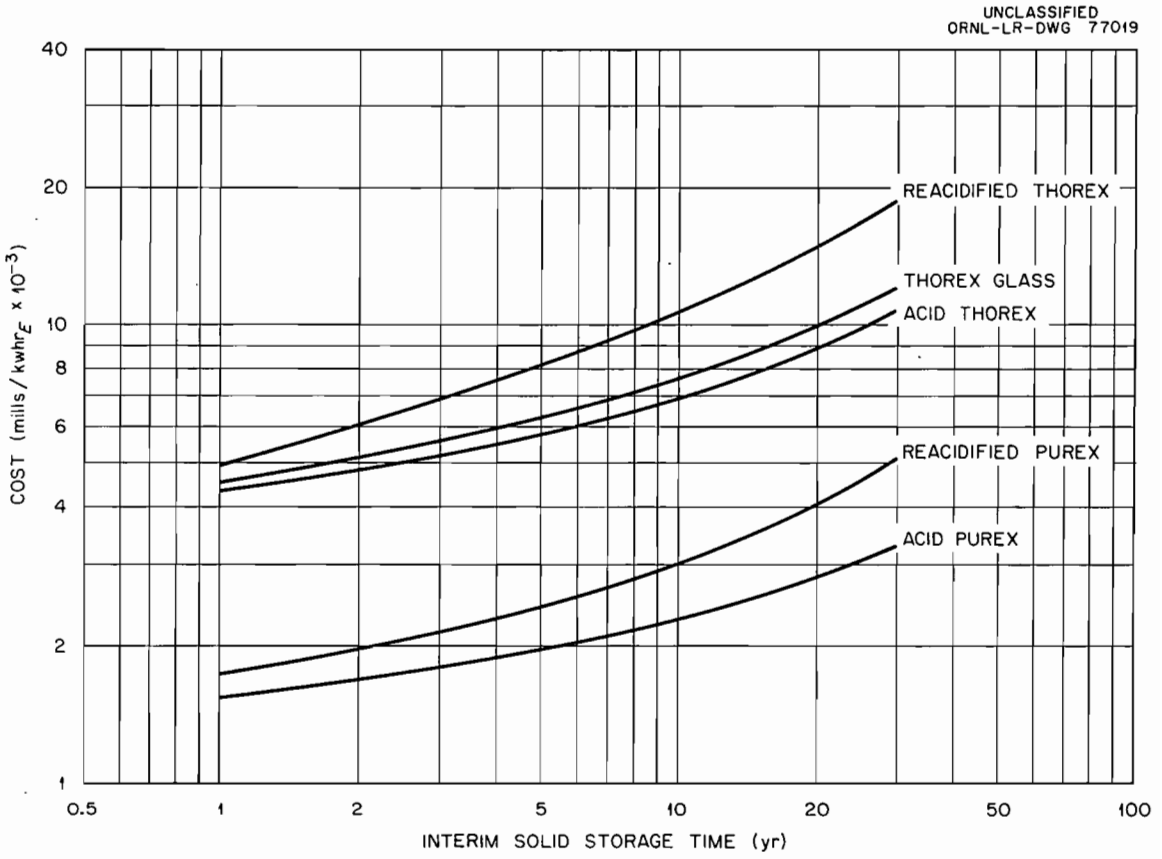

Fig. 4.3. Costs of Interim Storage of Calcined Wastes. Age of wastes: 10 years.

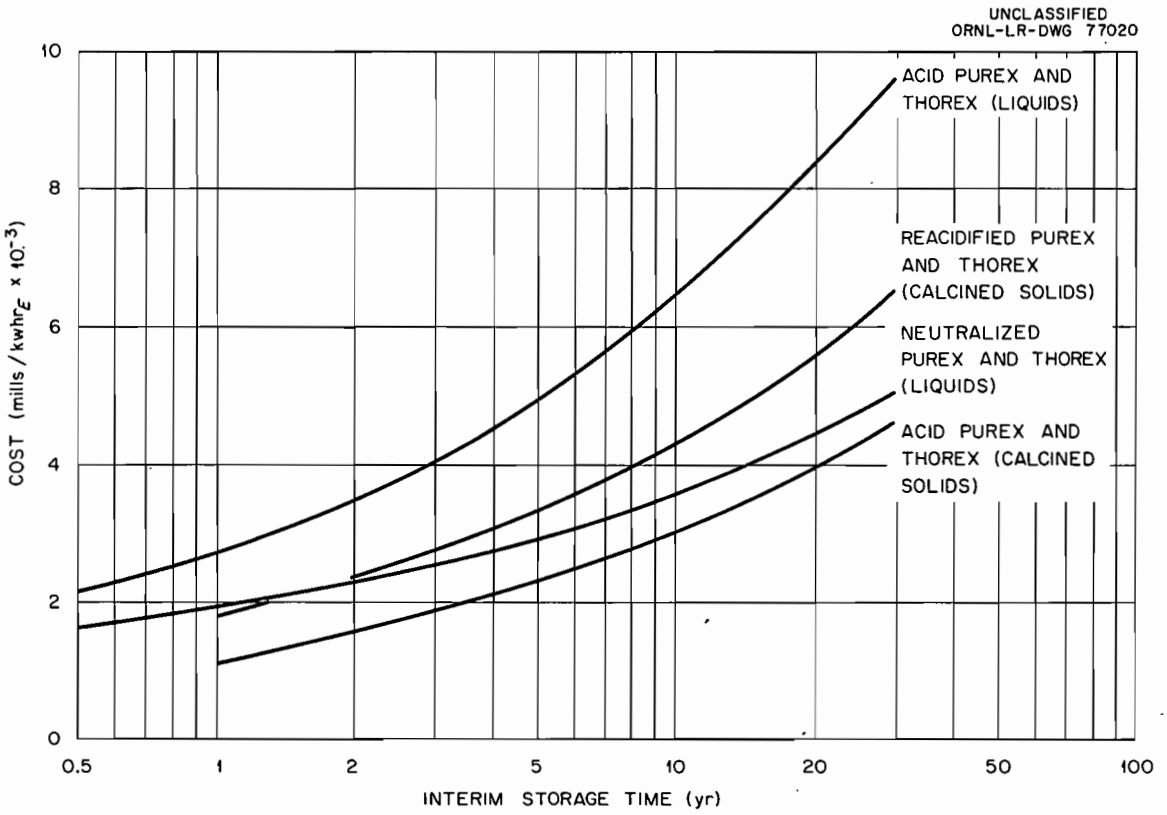

Fig. 4.4. Comparative Costs of Interim Storage of Liquid and Calcined Wastes.

According to flow measurements and analyses of samples collected at White Oak Dam, the curies per year of each radionuclide released was calculated (Table 4.4). The increase in 1955 of the quantity of Cs^{137} released is attributed to the draining of White Oak Lake. The subsequent reduction in release of this nuclide is associated with the treatment of process waste and reimpounding of the lake. The increase in Ru^{106} released is associated with operation of the waste pits, while the decrease in Sr^{90} released can again be related to the operation of the Process Waste Water Treatment Plant. Calculations are in progress to estimate the gross activity released during the period 1943-47. The concentration of radionuclides in the river waters is calculated from average flow conditions and is based on the assumption of complete and uniform mixing.

Although the avenues of human exposure are many and complex, experience indicates that certain ones will be of greater significance. Those considered in this analysis include: (1) consumption of contaminated water and fish, (2) consumption of agricultural produce irrigated with river water, (3) external dose due to contaminated water and bottom sediments during recreational and industrial use of the water, and (4) build-up of radionuclides in water systems that use river water.

A most direct means of evaluating exposures due to the ingestion of contaminated water or foods would be to measure the body burdens in members of the exposed population. However, for the present, exposures will be assessed on the measured or anticipated amount of radioactive material in the various environmental media and assumption of that reaching the exposed population. Dose limits recommended by the ICRP (1959) are chosen as a basis of comparison prior to 1961, and subsequent events use the basic guides of the FRC.

The fraction of maximum permissible levels for water (MPC_W) received from drinking Clinch River water and Tennessee River water is based on the consumption of river water. This approach is conservative and provides a higher estimate of dose received because some of the radionuclides would be removed by water treatment and some would be associated with bottom sediments. The fraction of the MPC_W attained by drinking water at Clinch River Mile (CRM) 14.5 and (TRM) 465.5 is shown graphically in Figs. 4.5 and 4.6. Bone, gastro-intestinal tract, total body, and thyroid were chosen for analyses after consideration of the type and concentration of radionuclides released, MPC_W limits, avenues of exposure, and the types of individuals. For the particular mixture of radionuclides in the river water, estimated exposure to the bone constitutes a greater fraction of the maximum permissible limit than the calculated exposure to the other body organs. This is attributable to the Sr^{90} that is released. The largest fraction of the MPC_W bone dose attained was 0.51 in 1954. Applying the most restrictive FRC limit of the thyroid dose (for the average child of the population at large, this is 1/600 of the continuous occupational exposure), the fraction of the MPC_W that would be attained at CRM 14.5 is less than 0.04. The increase in internal dose to the G. I. tract in 1960 and 1961 is due to the increased release of Ru^{106}.

Table 4.4. Yearly Discharges of Curies of Radionuclides to Clinch River[a]

Year	Gross Beta	Cs^{137}	Ru^{106}	Sr^{90}	TRE(-Ce)	Ce^{144}	Zr^{95}	Nb^{95}	I^{131}	Co^{60}
1948	496									
1949	718	77	110	150	77	18	180	22	77	---
1950	191	19	23	38	30	---	15	42	19	---
1951	101	20	18	29	11	---	4.5	2.2	18	---
1952	214	9.9	15	72	26	23	19	18	20	---
1953	304	6.4	26	130	110	6.7	7.6	3.6	2.1	---
1954	384	22	11	140	160	24	14	9.2	3.5	---
1955	437	63	31	93	150	85	5.2	5.7	7.0	6.6
1956	582	170	29	100	140	59	12	15	3.5	46
1957	397	89	60	83	110	13	23	7.1	1.2	4.8
1958	544	55	42	150	240	30	6.0	6.0	8.2	8.7
1959	937	76	520	60	94	48	27	30	0.5	77
1960	2190	31	1900	28	48	27	38	45	5.3	72
1961	2230	15	2000	22	24	4.2	20	70	3.7	31

[a]Data furnished by Applied Health Physics Section.

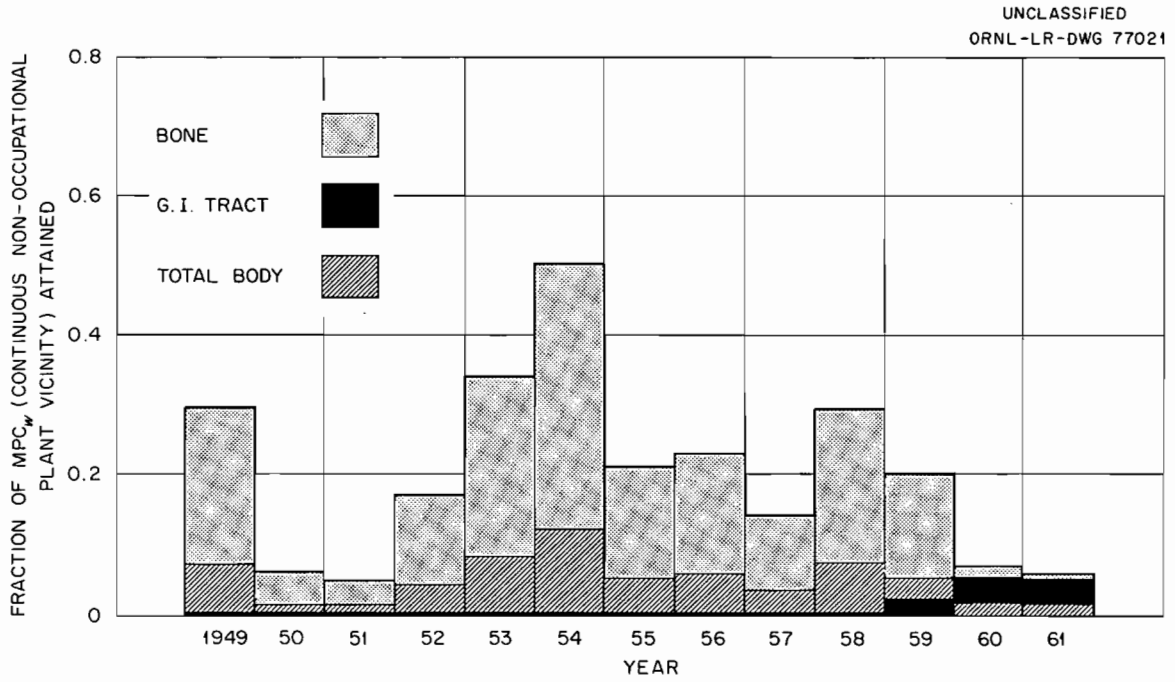

Fig. 4.5. Fraction of MPC_W Attained at Clinch River Mile 14.5.

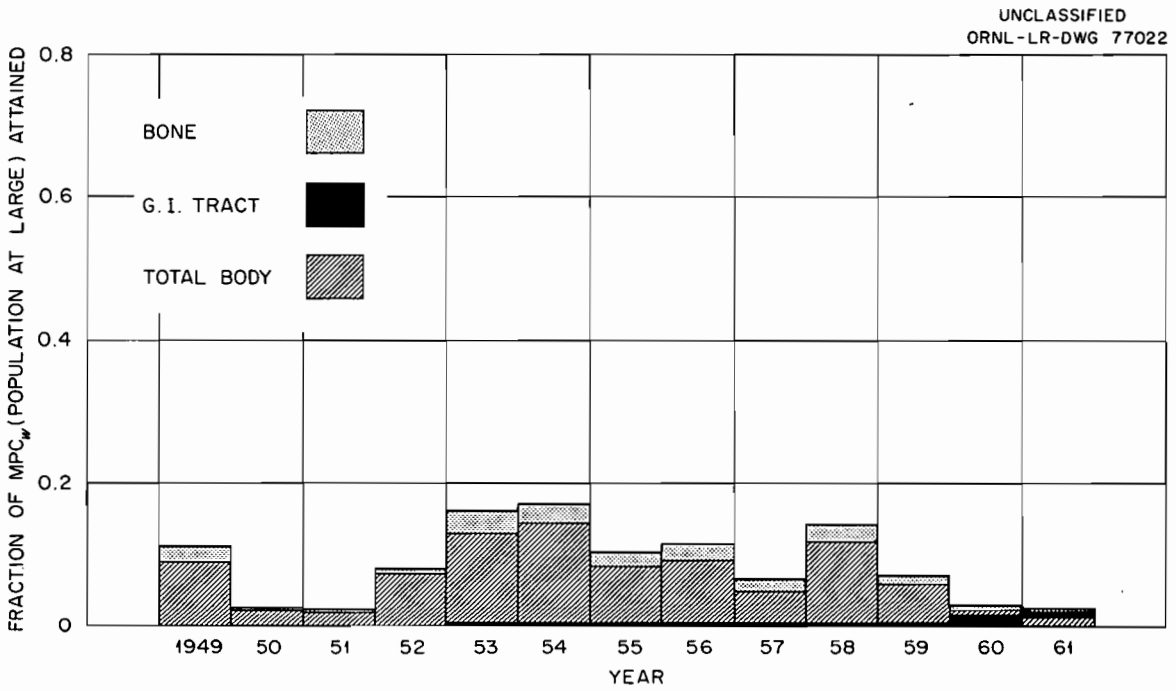

Fig. 4.6. Fraction of MPC_W Attained at Tennessee River Mile 465.5.

Due to the presence of radionuclides, the river will act as a source of radiation to persons swimming, boating, fishing, and water skiing. Without direct measurements, it is necessary to calculate the dose rate associated with each radionuclide. The total dose rate is simply the sum of the individual dose rates. The immersion dose rate due to beta and gamma radiation at CRM 14.5 and TRM 465.5 is shown graphically in Fig. 4.7. A maximum dose rate of 0.027 millirad per day of exposure (0.016 of beta and 0.011 of gamma) is calculated at CRM 14.5 during 1960. The dose rate is a function of nuclide type and concentration. Until 1958, the largest dose was generally due to Cs^{137}-Ba^{137}. Since then, Ru^{106}-Rh^{106} has accounted for about 75% of the immersion dose.

Calculations will continue and estimates will be made of other exposure doses. Finally, an estimate will be available of the aggregate dose likely to be received by the occupational worker, by the population in the vicinity of ORNL, and by the average individual of the population at large.

4.3 Safety of Tank Storage of High-Activity Liquid Wastes

L. C. Emerson

To be most meaningful, studies of waste management must be based on considerations of safety as well as economics. It is intended, therefore, that each of the operations which are being investigated from the standpoint of economics be evaluated as to their safety. The objective is to assign an indemnity cost that can be used with the estimated capital and operating costs to optimize the over-all complex.

As the first of these safety evaluations, a study of the tank storage of high-activity wastes was started, and it is intended to serve as a corollary of the economic evaluation of interim liquid storage reported earlier.[5] The same basis as used in the economic evaluation is assumed: a hypothetical 6-ton/day processing plant, processing 1500 tons/year of uranium converter fuel at a burnup of 10,000 Mwd/ton, and 270 tons/yr of thorium converter fuel at a burnup of 20,000 Mwd/ton. It is expected that this study will be extended to include permanent as well as interim storage of the wastes produced by this plant.

The investigation of the hazards of tank storage started several years ago under a somewhat modified set of postulates.[6,7] The basic difference between the present study and the incomplete earlier study is that of the assumed location of the tank farm site. The site for the earlier investigation was dictated by the economic study and was specified to lie within the Ohio River valley between Cincinnati and Louisville. During the course of the study it developed that the meager knowledge of the underlying geologic formations was a severe deterrent to the study of the underground movement of waste streams. The site for the present study has been specified to be that selected by the project Hope Study Committee.[8] In addition to having the advantage of site specificity location at ORNL permits a more thorough investigation of the atmospheric and hydrospheric contamination problems by virtue of the detailed

Fig. 4.7. Immersion Dose at Clinch River Mile 14.5 and at Tennessee River Mile 465.5.

knowledge of the local environment developed over years of extensive study. Other than its relative inaccessibility the ORNL location presents no obvious characteristic that would eliminate its selection for such a facility; conversely, because of its favorable soil structure, ORNL would be rather well suited for a tank farm site.

The study is to be carried out within four general areas of investigation. The first is to be concerned with the possible mechanisms of tank failure. The history of failure of underground storage tanks will be reviewed, and some consideration will be given to the possible cause and the extent of tank failure. The next two parts of the study will be concerned with environmental contamination. Contamination patterns and resulting population exposures resulting from activity releases will be obtained under a variety of possible meteorological conditions. In this phase of the study use will be made of the extensive knowledge of local atmospheric conditions. Underground activity releases will also be treated on the basis of known directions and rates of flow of water within the local ground-water reservoir. Interactions of the waste with local soils and possible outcropping into surface streams will be considered. The last part of the study will be an attempt to evaluate the cost associated with the degree of hazard inherent in operation of the tank farm over an indefinite time. Other than the liability associated with a catastrophic accident it is believed that the principal cost will be determined by the need and extent to which alternative drinking water supplies will have to be provided in the event of sizeable releases of radioactive chemicals.

5. DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing

5.1.1 Studies of Waste Mixes (T. Tamura)

Mix Development for Normal ORNL Intermediate Level Waste. — Studies conducted thus far have shown that ORNL waste solution, Portland cement, and additives normally used in hydrofracturing operations are compatible. The slurry properties, including viscosity and pumping time, can be changed as well as controlled. Three formulations using presently available ORNL waste have been made, and they meet the requirements for use in hydrofracturing at Oak Ridge. One of these formulations meets the desired slurry characteristics even with ORNL waste containing ten times the dissolved ion content.

Over 100 formulations have been tested since subcontract work was initiated with Westco Research of Dallas, Texas. One of the most difficult requirements to establish was an acceptable limit of fluid loss of the slurry. Without reliable information on the permeability of the shale and on the nature and extent of hair-line fractures created during pumping operations, fluid-loss limits cannot be established with confidence. Hence, the emphasis has been on developing mixes that exhibit minimum fluid loss. Three formulations that show very low loss and meet the requirements of thickening time (pumping time) and setting time, are given in Table 5.1.

Table 5.1. Waste Mix Formulations

Mix Number	Volume of waste/pound of cement (cc)	Bentonite (%)	Calcium Ligno-sulfonate (%)	Fluid Loss Additive Material	(%)
1	250	6	1.0	ET 181-6	1.3
2	332	6	0.7	Cemad	2.0
3	265	6	0.8	CMHEC	1.0

The principle difference in the formulations is in the additive selected to reduce fluid loss. (These additives are proprietary materials whose performance in the oil well industry have proved reliable.) Calcium lignosulfonate (CLS) is an effective dispersant for the cement; it also reduces fluid loss properties of the slurry but is less efficient than materials selected expressly for this purpose. Bentonite is used to reduce the cost of the mix, as a substitute for some of the cement, and to permit a larger volume of waste to be used. In addition, bentonite aids in the retention of radiocesium and reduces its loss from the slurry when fluid loss occurs.

Data on thickening time, fluid loss, and compressive strengths for these mixes are shown in Table 5.2. The lowest pumping time, 6 hr 35 min, was obtained with Mix 2 for a test schedule of 3000 ft. This pumping time is below the minimum requirement of 8 hr; however, by increasing the CLS concentration to 1.0%, the thickening time was increased to 15 hr. Each mix showed a fluid loss of less than 20 cc/30 min at 100 psi. By way of comparison, a simple cement slurry showed a fluid loss of 550 cc when mixed with ORNL waste; with 6% bentonite and 0.8% CLS added to the cement slurry, the loss was reduced to 160 cc/30 min.

Compressive-strength tests were made after curing at various temperatures and various time intervals. Compressive-strength tests are made primarily to establish whether the slurry will produce a set after a reasonable period. For ORNL's purposes, the initiation of set within seven days is considered reasonable, though this period in the petroleum industry is considered to be extremely long. Set of the slurry is necessary in order to ensure immobility of the grout, and compressive strength is considered to be of secondary importance. All the mixes set after seven days.

From the data in Table 5.2 it is seen that longer curing times, at least up to seven days, increase the compressive strength of the grout. Additionally, higher temperatures tend to reduce the compressive strength when ET 181-6 or Cemad are used. These data were obtained with specimens cured under atmospheric conditions. Other tests, of a preliminary nature, showed that compressive strength increases when the slurry is allowed to set under pressure.

Table 5.2. Thickening Time, Fluid Loss, and Compressive Strength of Three Selected Mixes

Mix Number	Thickening Time (hr:min) 1000 ft	Thickening Time (hr:min) 3000 ft	Fluid Loss (cc/30 min)	Compressive Strength Temperature (°F)	Compressive Strength Curing Time (days)	Compressive Strength Strength (psi)
1	24:30	19:26	19.5	80	1	i.s.[a]
				110	1	i.s.[a]
				80	5	2590
				110	5	2075
2	10:25	6:35	13	80	1	75
				110	5	50
				110	7	470
				140	4	n.s.[b]
				140	7	25
3	--	30:22	15	80	6	10
				110	6	1435
				140	6	1580

[a] i.s. = initial set.

[b] n.s. = no set.

Mix Development for ORNL Waste Concentrated Ten Times. — Waste solutions used in preparing these three mixes consisted of those stable ions that approximate present ORNL intermediate-level wastes. Since plans are underway to concentrate the waste by evaporation, the three formulations discussed below were tested with solutions whose concentrations of dissolved ions were 10 times higher. Thus, the test solution was 3 M in $NaNO_3$ and 2.0 M in NaOH, with appropriate increases in the minor constituents of the waste.

Mix 1, which contains ET 181-6, did not meet ORNL requirements for hydrofracturing when the ten-fold concentrated waste solution (10X) was used. The slurry developed a high initial gel strength and showed a high fluid loss.

Mix 2, containing Cemad, was pumpable, but the thickening time was reduced to 1 hr 40 min, and the fluid loss increased from 19.5 cc/30 min to 33 cc/30 min. The reduced thickening time was probably caused by the lower water content in the concentrated waste solution. On increasing the waste volume from 332 cc to 420 cc, the viscosity was reduced to 13 poises, and thickening time was increased to 2 hr 48 min. Lower viscosity and a longer thickening time was obtained by adding 0.1% CFR-1 (a proprietary additive supplied by the Halliburton Co.); however, the fluid loss increased to 111 cc/30 min. These tests demonstrate that certain slurry properties can be controlled by the use of selected additives.

Mix 3, which contains CMHEC, showed the greatest promise for use with ORNL waste. The thickening time, fluid loss, and compressive strength of this mix, prepared with three different waste compositions, are shown in Table 5.3. Note that thickening time exceeds the minimum requirements, even with the waste concentrated 10 times and under a 5,000-ft test schedule. Set was observed in all mixes within six days. Tests with 0.5% CMHEC showed that the fluid loss was increased to 53 cc from 21 cc when ten-fold concentrated waste was used. Also, when the slurry was mixed for 15 min, instead of 1 or 2 min, and then subjected to the fluid loss test, loss was reduced from 53 cc to 16 cc with the 0.5% CMHEC mix.

It is highly desirable to have a mix formulation that will perform satisfactorily over a wide range of waste compositions because it would not be necessary to analyze each waste batch or to establish the need for particular additives before each injection operation begins. Studies with Mix 3 are now in progress to establish the formulation that will perform over the full ten-fold concentration range.

Halliburton's Evaluation of Westco Mix 2. — Under a purchase order issued to the Halliburton Company (Duncan, Oklahoma) by the Laboratory, testing was performed on Westco Mix 2. Some modification was required to obtain satisfactory setting time with this slurry, and, in addition, further development work of a limited nature was done to ascertain what improvements might be possible.

1. Laboratory Tests. The mixing fluid was a solution that had the approximate analysis of intermediate-level waste at ORNL, as shown below:

Table 5.3. Slurry Properties of Mix Number 3 with ORNL Waste Containing Different Concentrations of Dissolved Ions

Concentration of the Simulated ORNL Waste	Thickening Time (hr:min)		Fluid Loss (cc/30 min)	Compressive Strength		
	3000 ft	5000 ft		Strength (psi)	Curing Temp. (°F)	Curing Time (days)
Usual concentration	30:22	23:34	15	10	80	6
				1435	110	6
				1580	140	6
concentrated fivefold	20:13	15:25	21	275	80	3
				695	110	3
				425	140	3
concentrated tenfold	18:21	11:18	21	755	80	3
				285	110	2
				565	140	2

Chemical	Molarity
Sodium hydroxide	0.220
Sodium nitrate	0.315
Sodium sulfate	0.037
Sodium chloride	0.006
Aluminum nitrate	0.022
Ammonium nitrate	0.025

Specific Gravity... 1.0325

In view of the probability that an evaporator will be employed in the intermediate-level waste stream, most tests were conducted with a waste concentration ten times that shown above and having a specific gravity of 1.2905. Slurries were also tested to determine the effect of this high concentration of the individual chemicals (except sodium hydroxide and aluminum nitrate) on certain properties of the cement, such as setting time and viscosity. The slurries tested are shown in Table 5.4.

(a) Pumpability (Thickening Time). These tests were made with a Pan-American high-pressure thickening-time tester, wherein both pressure and temperature can be applied to the slurry in simulation of pumping it into a well. Two basic test schedules were used for selected slurries; that is, some tests were made at 91°F and 1,540 psi, while others were made at 89°F and 3,300 psi. For future testing, these two characteristics can be varied to fit any specific set of well conditions, but, in order to ensure pumpability, it would be desirable to know the temperature in the injection well.

The tests indicate that the two major accelerating factors influencing the set of the slurry are (1) the concentration of the waste solution and (2) the increase in pressure applied to the slurry. The latter effect would be expected, based on the knowledge that pressures up to 3000 psi do cause cement slurries to set faster and that beyond this pressure there is no significant effect, at least on the more conventional slurries.

The effect of concentration of the waste solution in causing faster setting appears to be due principally to the influence of sodium hydroxide, an acknowledged cement accelerator. Decreasing the quantity of caustic while maintaining the other chemicals at ten-fold concentrations did create delayed setting, as shown in Table 5.5, approaching the setting time of a similar slurry mixed with fresh water. With concentration of the waste, the sodium sulfate, the sodium chloride and ammonium nitrate, and the minor constituents appear to be present in a quantity sufficient to cause slight to moderate acceleration of setting, while the sodium nitrate would be present in such quantity as to create severe retardation. The net influence of these four chemicals apparently is to more or less counteract each other and thereby neutralize their separate effects on setting time, although the sodium nitrate concentration may be partially responsible for substantially reducing the compressive strength.

Table 5.4. Halliburton Test Slurries

Slurry No.	CEMAD-1 (%)	Bentonite (%)	Calcium Ligno-Sulfonate (%)	Calcium Chloride (%)	Ratio of Waste/Cement (cc/lb)	Slurry Properties Density (lb/gal)	Volume (gal/sk)	Viscosity (poises)
				Normal Waste				
1	2.0	6.0	0.7	0.5	332	14.1	12.10	9
2	0.5 HALAD-9	6.0	0.7	0.5	332	14.1	12.10	9
				Concentrated (tenfold waste)				
3	2.0	6.0	0.7	0.5	332	15.6	12.10	25
4	2.0	6.0	0.7(0.1 CFR-1)	0.5	332	15.6	12.10	5
5	2.0	6.0	0.7(0.2 CFR-1)	0.5	332	15.6	12.10	4
6	2.0	6.0	0.7	0.5	420	14.8	14.29	13
7	2.0	6.0	0.7(0.1 CFR-1)	0.5	420	14.8	14.29	2
8	2.0	6.0	0.7 (0.2 CFR-1)	0.5	420	14.8	14.29	3
9	0.5(2% HL X-5)	6.0	0.7	0.5	420	14.8	14.29	4
10	2% HL X-5	6.0	0.7	0.5	420	14.8	14.29	2
11	2% HL X-4	6.0	0.7	0.5	420	14.8	14.29	15
12	0	12.0	0	0	585	14.0	18.63	13
13	0	12.0	1.0	0	585	14.0	18.63	3
14	1.0	12.0	1.0	0	585	14.0	18.63	--
15	0	12.0	0.2% CFR-1	0	585	14.0	18.63	1
16	0	12.0	0.2% CFR-1	0	264	16.5	10.70	3
17	0.5	12.0	0.2% CFR-1	0	264	16.5	10.70	4
18	0	16.0	0.3% CFR-1	0	264	16.6	10.85	5
19	0	20.0	0.2% CFR-1	0	264	16.6	11.00	7
20	0	20.0	0.3% CFR-1	0	264	16.6	11.00	4

Table 5.5. Slurry Properties

Slurry No.	Thickening Time (hr:min) (1)[a]	Thickening Time (hr:min) (2)[b]	Free Water (cc)	Fluid Loss (cc/30 min) 100 psi	Fluid Loss (cc/30 min) 1000 psi	Compressive Strength (psi) 1 day	Compressive Strength (psi) 3 days	Compressive Strength (psi) 7 days
1	10:39	6:48	0	19.1(12.4)[f]	11.8(8.8)	70	1240	1975
2	--	--	0	115(89)	--	--	--	--
3	1:41	--	0	32.9(30.3)	--	--	--	--
4	--	8:00+(13.2)[e]	0	(59.0)	--	--	--	--
5	--	8:00+(11.0)	0[c]	(68.0)	--	--	--	--
6	2:48	--	0	55.6(49.4)	(68)	95	200	330
7	8:00+ (53.8)	--	-	111 (88)	(172)	70	--	--
8	12:00+(5.2)	--	6.8	(96)	(181)	NS[d]	325	455
9	--	--	-	99 (81.4)	--	--	--	--
10	--	--	-	126 (122)	--	--	--	--
11	--	--	-	137 (57.6)	--	--	--	--
12	--	--	0	(183)	--	--	--	--
13	--	--	0	210 (262)	--	--	--	--
14	--	--	0	95	--	--	--	--
15	--	--	4.2	(437)	--	--	--	--
16	--	--	0[c]	(130)	--	1035	--	--
17	--	--	0[c]	(53.4)	(141)	--	--	--
18	--	--	0[c]	(75)	(190)	--	--	--
19	10:37	9:01	0	(107)	(251)	1435	--	--
20	12:00+ (28.4)	13:00+(25.0)	0	(70)	(164)	1380	--	--

[a]Test conditions: temperature, 91°F; pressure, 1540 psi.

[b]Test conditions: temperature, 89°F; pressure, 3300 psi.

[c]Trace of free water before setting; disappeared upon setting of cement.

[d]48-hr strength was 200 psi.

[e]Figures in parentheses on thickening time represent the viscosity in poises at end of indicated time.

[f]Figures in parentheses for fluid loss represent the loss measured after stirring the slurry 20 min at 90°F. Other data were obtained immediately after mixing the slurry.

Aluminum nitrate apparently causes high slurry viscosity when the caustic concentration is reduced, as well as being another possible contributor to lower strength. The viscosity could actually become economically helpful by permitting the use of larger quantities of waste per pound of cement.

None of the effects noted above should present a problem with respect to designing a slurry for disposal. Acceleration can be accommodated by the use of small quantities of a retarder such as CFR-1, which was used in obtaining the longer thickening times. CFR-1 also controls viscosity very effectively.

(b) Fluid Loss. The data for loss of fluid is shown in Table 5.5. Two types of tests were made in attempting to ascertain this property of a slurry. The first of these was simply a matter of pouring a slurry specimen into a container that could be sealed and then observing whether phase separation occurred; specifically of interest was the matter of water separation, which would indicate the need for a lower ratio of waste to cement. The second test was that commonly known as a fluid-loss test whereby a pressure is applied to the slurry, which is supported by a permeable filter medium (325-mesh screen), and the loss of fluid by filtration is measured over a 30-min interval. Both tests are relative tests for the comparison of slurries, and it is generally agreed that they are not an absolute measurement of fluid retention under the conditions contemplated for waste disposal. In view of this, it appears that modifications must be made to more nearly fit the expected conditions.

Fluid retention, as indicated by either of the two tests, can be attained in a number of ways, and a relatively wide latitude exists for controlling fluid loss by filtration. In view of what can be accomplished in obtaining sufficient thickening time and suitable setting and strength development, fluid retention and radionuclide retention appear to be the major properties requiring more study.

(c) Fluid Friction. The data are given in Table 5.4. The viscosity of each slurry was measured by use of the Halliburton Consistometer. However, the non-Newtonian nature of cement slurries makes this property of little value in calculated frictional pressure. A variable-speed viscometer (Fann V-G meter, model 35) will have to be used to obtain shear-stress -- shear-rate data for the slurries, and this data will then be used to obtain the rheological parameters: flow behavior index and consistency index. These parameters can then be used to calculate the frictional pressure to be anticipated from pumping at various rates through pipe of appropriate diameters.

(d) Compressive Strength. The data are shown in Fig. 5.1. The time-strength relationship was obtained by using standard 2-in. cube specimens on which strength was measured by crushing the specimen to failure. These data were obtained on the Westco slurry and the modified slurry containing sufficient retarder to obtain satisfactory pumpability. The time-strength measurements on the normal-waste slurry substantiate those made by Westco, and, as shown in Fig. 5.1, the effect of concentrating the waste is clearly evident.

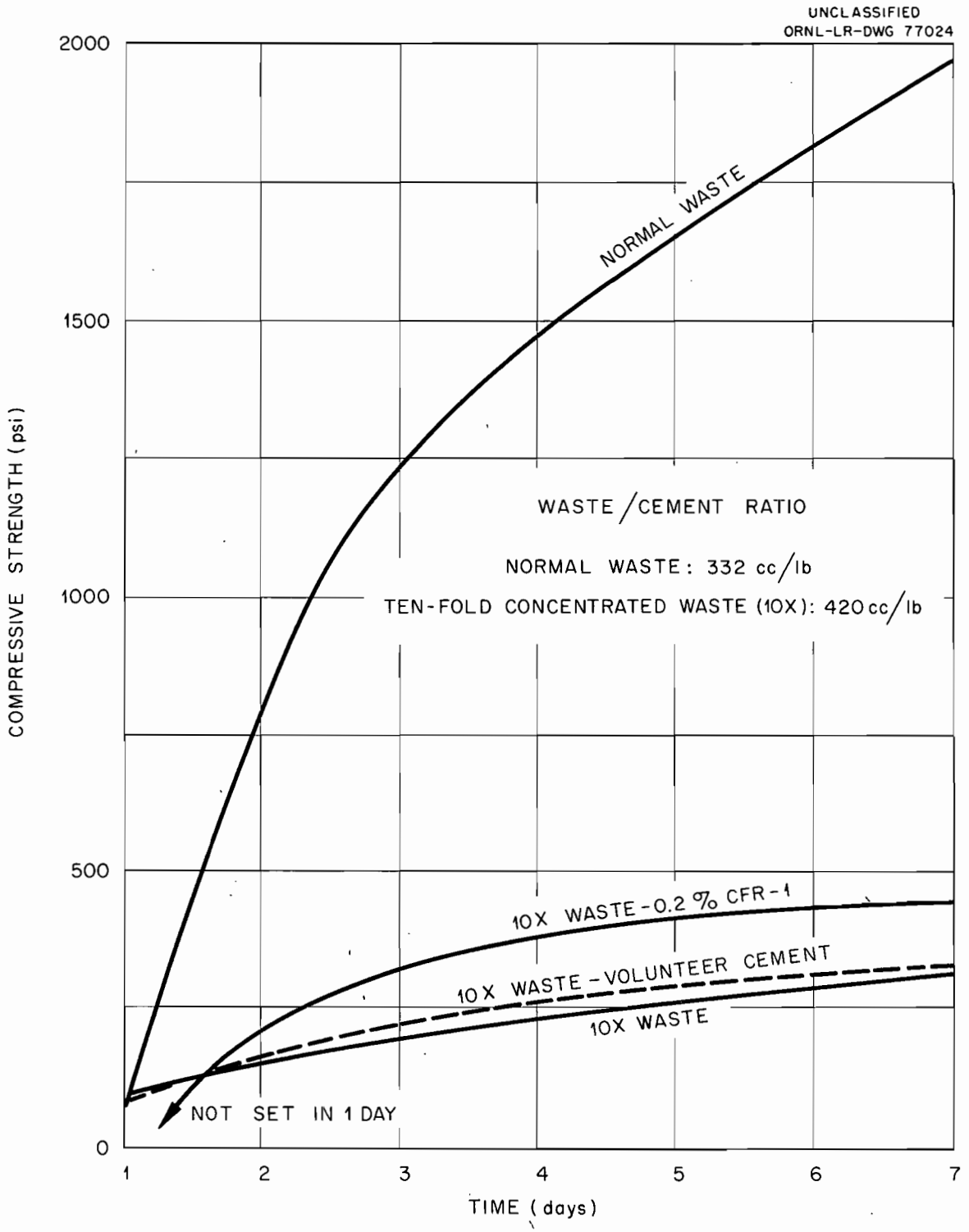

Fig. 5.1. Halliburton Tests of Mix 2 and a Modified Slurry: Time vs Compressive Strength.

Slurry-Pumping Test. — A large-scale test was also conducted to determine the mixing and pumping characteristics of the modified slurry. This involved preparing about 25 bbl of slurry and circulating it through a closed loop of 2-in. tubing for 8 hr. During this pumping test, the slurry was sampled each hour and tested for viscosity and compressive strength.

One of the main considerations in planning the test was a method of maintaining a relatively constant temperature of the cement slurry. It was anticipated that about 220 hp or 9300 Btu/min would be added to the cement slurry. It was desired to hold the temperature of the slurry below 110°F. The Halliburton Test Well No. 5 was selected as being the best available heat exchanger of this size.

Figure 5.2 shows a schematic diagram of the pumping equipment and flow manifold used in the test. Two strings of 2-in. tubing were connected on the lower end with a 180° tube turn. Each slurry tubing string consisted of 1580 ft of 2-in. tubing plus 60 ft of 2-1/2-in. tubing, giving a surface area in the well as provided by 3280 ft of tubing. On the surface, this 2-in. tubing was connected to an HT-400 pump powered by a 400-hp engine. A slurry sump tank was provided to maintain a circulating volume of fluid on the surface. Two visual pressure gages and one recording pressure gage were located between the pump and the wellhead. Visual-type temperature gages were installed at the wellhead to measure the slurry temperature into the well and returning from the well. A series of plug valves were used in the return line to serve as chokes to maintain the circulating pressure at about 3,000 psi.

To provide for additional cooling, a string of 2-1/2-in. tubing with an open end was also lowered into the well beside the slurry-circulating tubing in order to circulate cooling water past the slurry tubing. This 2-1/2-in. tubing was connected to a large cooling tower, and a T-10 pump driven by a 335-hp engine was used to circulate the cooling water in the well bore.

Before pumping the slurry, the system was tested in order to ascertain that the temperature of the mud could be maintained within the desired limits. The test was run for 3 hr and proved that the heat exchanger was satisfactory.

Standard equipment was used for mixing the slurry. The water and chemicals were premixed according to specifications. The cement and bentonite blend was taken to the mixing site in a Halliburton Rotovoy transport. A Halliburton LP mixer and tub with a standard LP mixing pump was used for making the slurry, and an auxiliary centrifugal pump transferred the slurry from the mixing tub to the HT-400 sump tank. A Halliburton Densometer was used during mixing in order to check and control the slurry at the proper weight.

Immediately after the cement slurry was prepared, the pumping test was begun by circulating the slurry through the tubing in the well. At the start of the test, slurry temperature and pressure readings were recorded at 5-min intervals. Later, this interval

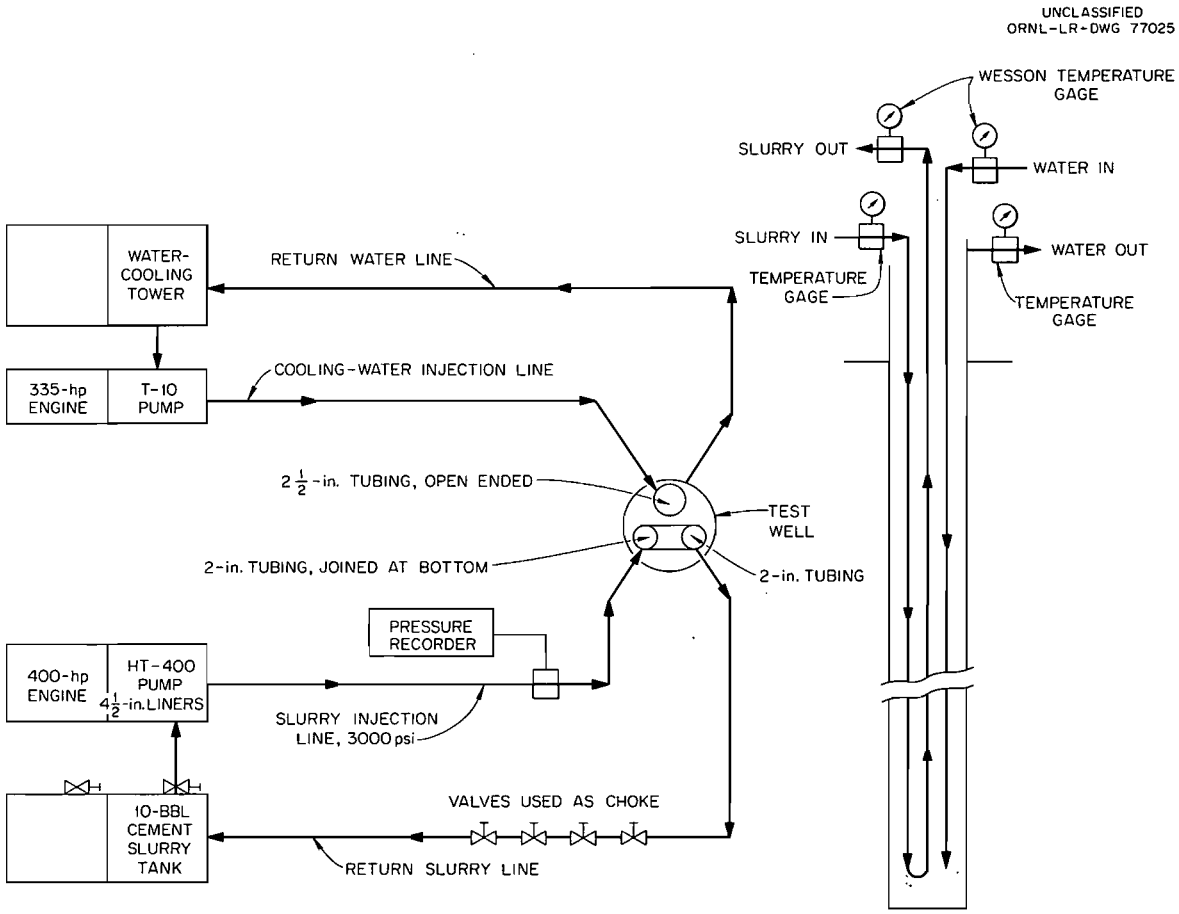

Fig. 5.2. Schematic of Pumping Equipment and Flow Manifold Used in the Slurry Pump Test.

was changed to 15 min because of the relatively constant temperature of the slurry. Figure 5.3 shows a plot of the temperature and pressure recorded during the 8 hr 35 min test. (The pressure fluctuations were due mainly to erosion in the plug valves used as chokes in the system.) During the first 5-1/2 hr of the test, no additional cooling other than the well heat sump was required. Cooling water was circulated during the last 3 hr of the test to keep the slurry temperature below 110°F. Friction pressure drop was determined during the pumping operation and remained relatively constant during the 3-hr period between determinations. This pressure drop was measured as being 1800 psi at a rate of 3.17 bbl/min through the 3280 ft of 2-in. tubing plus the surface manifolding.

After the pumping test was completed, pump valves and inserts were inspected and were in satisfactory condition. The pump packing was not disturbed due to the possibility of future endurance tests on this packing.

This pumping test indicates that Mix-2 slurry, with modification to ensure sufficient thickening time, can be mixed and handled for a long time without trouble. Over dilution of the chemical solution occurred prior to mixing the cement slurry; consequently, about a 6.5-fold concentration of waste was actually used. The increased shearing action applied to the slurry during recirculation resulted in better water retention characteristics than were obtained on laboratory prepared samples. Free water was zero on samples taken each hour during the pumping, and fluid loss by filtration was substantially reduced. Delayed setting was also noticed on these samples, the majority of which were not set at three days, and was probably attributable to the lower concentration of chemicals in the synthetic waste.

The slurry was pumped continuously for 8 hr 35 min at about 2.5 bbl/min at an average pressure of 3200 psi. The pump packing did not leak, and no tightening adjustments were made in the packing. There was no maintenance of any type made on any of the pumping equipment, and the valve inserts were in satisfactory condition at the end of the test. Additional inspections are being made on valve inserts to determine whether there is any deterioration due to ageing.

5.2 Design of the Fracturing Disposal Pilot Plant

E. G. Struxness W. de Laguna H. O. Weeren

5.2.1 Preliminary Design of Injection Well

Under a purchase order issued to the Halliburton Company by the Laboratory, a preliminary design of the injection well was obtained for use by the Engineering and Mechanical Division in preparing final drawings and supervising the construction. The essential features are shown in Figs. 5.4 and 5.5. A 9-5/8-in.-diam surface casing is inserted into a 12-1/4-in. hole (drilled to a depth of about 105 ft) and cemented in. Then an 8-3/4-in. hole is air-drilled to a depth of 1050 ft and a 5-1/2-in. Hy-dril triple seal casing run in, with centralizers appropriately spaced. The long string is then cemented in, using a conventional two-plug system.

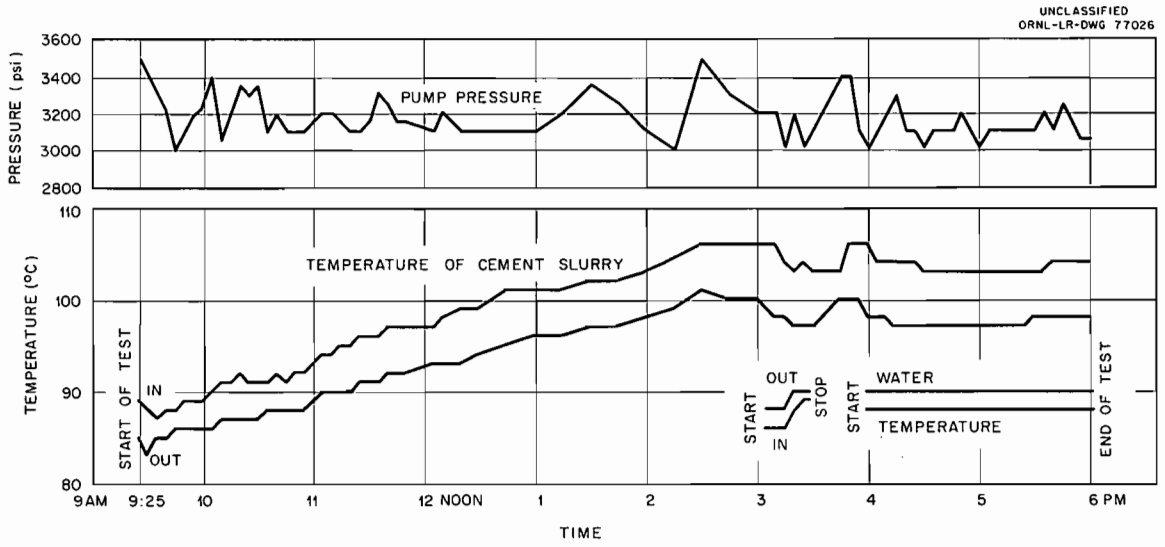

Fig. 5.3. Data for the Pumping of the Cement Slurry. HT-400 pump, 4-1/2-in. plungers, August 8, 1962.

UNCLASSIFIED
ORNL-LR-DWG 77027

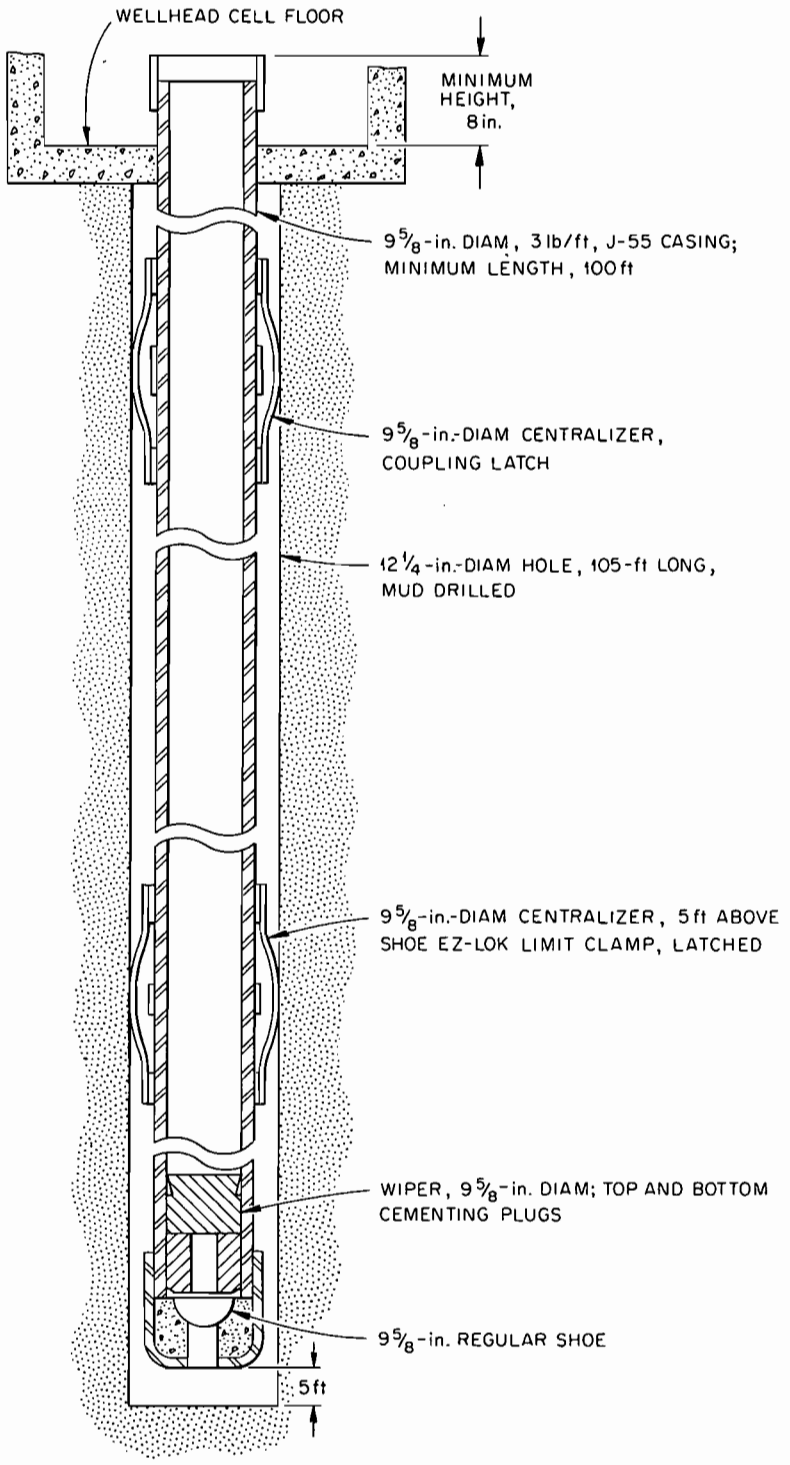

Fig. 5.4. Surface String of the Oak Ridge Waste Disposal Well.

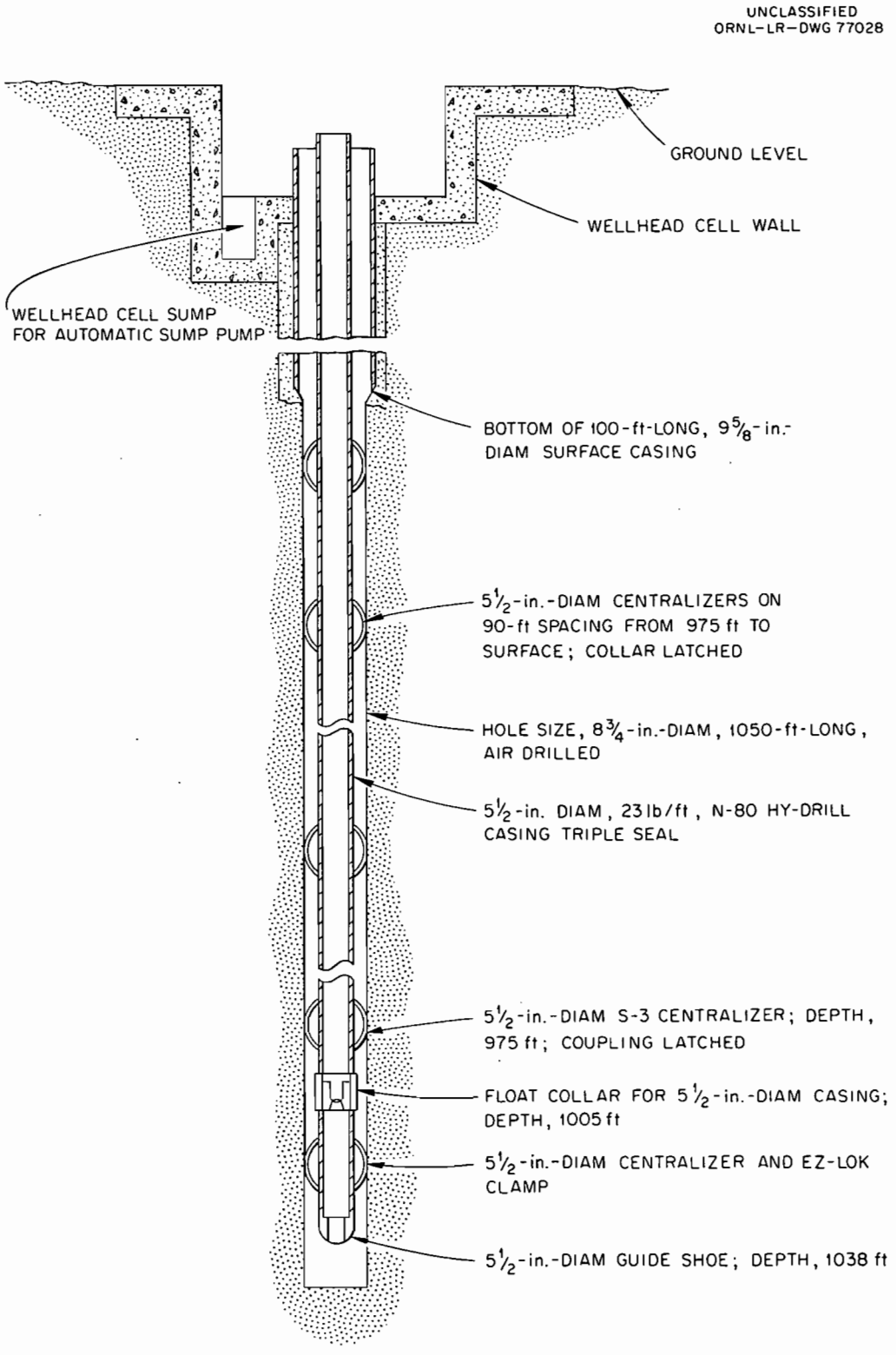

Fig. 5.5. Long String of the Oak Ridge Waste Disposal Well.

Well Drilling. — A contract is being negotiated for the drilling of the 1050-ft injection well and one observation well. These wells will probably be drilled consecutively rather than simultaneously because the wells will be more likely to have similar slants if they are drilled by the same crew and the same rig. The observation well will be a 6-in.-diam well with 2-7/8-in. casing cemented in. The purpose of the observation well is to determine whether a gamma log of the observation well subsequent to an injection of radioactive material in the injection well will indicate the depth of the fracture zone and, hence, serve as a useful indication of horizontal fractures. The observation well will be located 150 feet up-dip of the injection well -- the direction in which a fracture is deemed most likely to propagate.

5.2.2 Preliminary Design of Pilot Plant (H. O. Weeren)

Present plans call for three injection experiments to be made prior to the injection of radioactive waste. The first experiment will be an injection of about 5,000 gal of water into the injection well to determine the fluid-retention properties of the fracture. The second will be an injection of about 50,000 gal of water into the same fracture to determine the effect of injection volume on the fluid-retention properties. The third experiment will be an injection of about 50,000 gal of water and fluid-loss additive into a new fracture to determine the effect of the additive. These experiments will be followed by the injection of the mixtures of radioactive waste and cement.

Waste tanks, waste handling equipment, and equipment cells will be installed by ORNL; the high-pressure pump, the solids handling equipment, and some stand-by pumping equipment will be supplied by Halliburton. Most of their equipment will be brought in just before the injection and moved away when the injection has been completed.

The radioactive-waste injection experiment will consist of the following steps: (1) initial slotting of the casing, (2) fracture of the shale formation, (3) injection of the waste and mix, (4) sealing the injected waste with a cement plug, and (5) evaluation of results. A flowsheet for the experiment as presently conceived is shown in Fig. 5.6.

The initial slotting of the casing will be done by a sand erosion process. A slurry of about one pound of sand per gallon of water will be pumped down a tubing string through a number of hydraulic jets at the bottom of the string and directed against the casing at high velocity. The erosive action of the sand will cut the casing, the surrounding cement, and the shale formation to a depth of a foot or so. The sand-water mixture will be withdrawn to the surface through the annulus between the tubing string and the casing and recycled. The tubing string can be rotated during operation to cut a complete circle; it is believed that a horizontal fracture is more likely to occur if it is initiated from a cut of this nature. The flow rate of the sand-water slurry will be about 170 gpm at a 3000-psi surface pressure (3500-psi jet pressure).

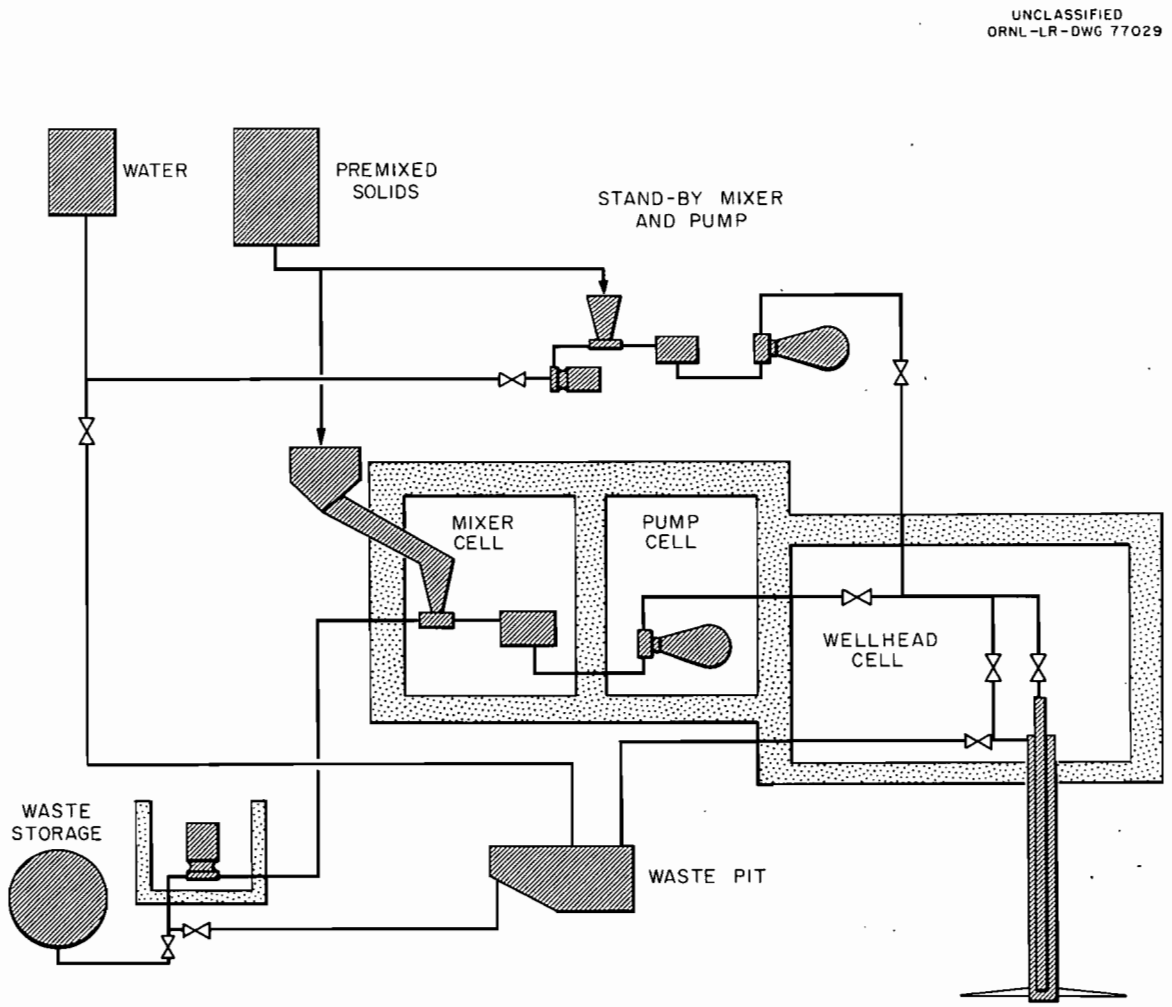

Fig. 5.6. Flow Diagram of Fracturing Disposal Pilot Plant.

At the end of the slotting operation the sand will be washed from the well with clear water, and the high-pressure injection pump will be used to apply pressure to the well until the formation fractures.

The waste solution will be stored on site in two 30,000-gal underground tanks. It will be pumped from the tanks to the mixer and mixed with the premixed solid constituents of the mix. The resulting mix will be pumped down the well by the high-pressure injection pump. The probable flow rate will be about 180 gpm at an estimated surface pressure of 1,400 psi; 160 hydraulic horsepower will be required. A standard HT-400 Halliburton cementing pump will be used. These pumps will produce over 4,000 hydraulic horsepower and will therefore have ample excess capacity for this job. In the event of pump or blender trouble during a run, a stand-by mixing unit and high-pressure pump will be available to pump uncontaminated mix so that failure of the primary equipment will not force the termination of a run with the well full of cement.

At the end of a run several hundred gallons of uncontaminated mix will be pumped down the well to serve as a plug. This will be followed by a rubber cementing plug (to clean the cement from the tubing walls and to keep separate the cement and the water that follows it); the cementing plug will be forced down the tubing with water. The well will then be held under pressure until the cement has had time to set.

A contract has been negotiated with the Halliburton Company for design and development assistance on the hydrofracture experiment. Under this contract Halliburton is to develop and recommend to ORNL three cement mixes for the injection experiment. Halliburton is also to provide engineering assistance as requested for the design of the injection experiment. Further contracts will be negotiated as the need arises for the use of their equipment and services for the injection experiment proper.

6. DISPOSAL IN NATURAL SALT FORMATIONS

6.1 High-Temperature Experiments

R. L. Bradshaw F. M. Empson W. J. Boegly, Jr.

The floor- and wall-cylinder tests were terminated after 792 hr of operation, and the salt temperatures were allowed to decrease to ambient temperature prior to heater removal. The floor heater was removed without difficulty; however, the wall heater was encased in the salt shattered from the sides of the hole where the temperatures were greater than 280°C.[9] Consequently, removal was difficult. Calipering of the holes for the floor and wall heaters showed an apparent decrease in diameter of about 1 in. at a depth of 6 ft. Below this depth it was not possible to measure the diameter; however, a new gage is being fabricated in order to obtain this information. The extent of the shattered zone has not been determined, but in cleaning out loose and recrystallized salt from the wall hole, 59 lb or about 0.4 ft^3 was removed. If the shattering is assumed to be uniform around the sides of the 4-ft-long heater, this would amount to about a 0.9 in. increase in diameter.

Column expansion around the wall heater is shown in Fig. 6.1. The maximum expansion was about 0.5 in. and occurred 2 ft from the center of the heater. The expansion 2 ft out from the hole was greater than that at 1 ft out (See Fig. 6.1.), possibly because the salt near the hole was able to flow plastically into it, thereby reducing expansion in the other direction. As the temperatures in the salt decreased upon completion of the experiment, only a small fraction of the expansion was recovered, indicating that the expansion was inelastic. Similar observations were made around the floor heater; however, the expansions were greater -- 2 ft from the heater the expansion was 0.8 in.

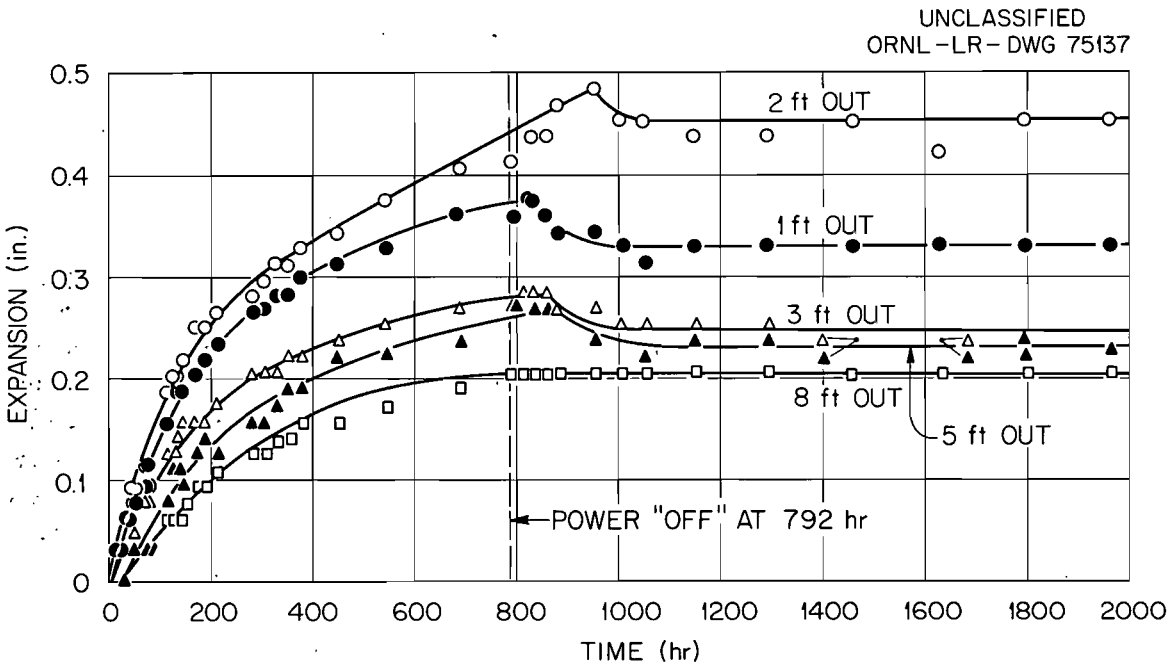

Fig. 6.1. Expansion of Column at Various Distances on Horizontal Line from Center of Heater Hole. Wall-cylinder test.

Calculation of the thermal expansion around the wall-heater hole, using the salt-temperature profile at 620 hr and assuming unrestrained expansion in the axial direction, indicates that a thermal expansion of 1.14 in. could have been produced. This value is higher than that observed and was expected to be so, since the salt was restrained and some movement had occurred radially into the hole.

The array experiment was reduced to a single heat source by failure of the six peripheral heaters.[9] The single heater was operated at a power level (3.7 kw) that did not produce shattering temperatures in the salt adjacent to the heater holes. Floor expansions followed the same general trend as in the floor- and wall-cylinder tests, but the magnitude was smaller.

Water evaporated from shale partings or released by disintegration of the salt was condensed at mine temperature in air-cooled condensers. About 15.5 liters was recovered from the floor heater hole, 250 ml from the wall heater, and 8.75 liters from the array central heater. One-gallon samples of the water from the floor holes, together with a reference sample of known recent water, were submitted to the laboratory of the U.S. Geological Survey for tritium dating.

6.2 Mine Observations on Salt Flowage at Ambient Temperature

W. J. Boegly, Jr. T. W. Hodge

Curves to predict the necessary combinations of the percentage of salt extraction and depth for various stability conditions were developed.[10] These curves are based on mine observation and do not provide information on the time at which the stability condition will be achieved or the rate at which the salt will flow in any condition of structural stability.

Eleven extensometer stations were located in the Hutchinson mine (depth 650 ft) and four stations in the Lyons mine (depth 1000 ft) to obtain measurements on the flow rate at different depths and the percentage extraction. Although the stations have been installed for less than a year, and the data is not complete, some trends are apparent. First, for openings of the same depth and percentage extraction, the rate of movement is least in the oldest openings. For openings of about the same age and depth, the movement is greater in an opening of 80% extraction than it is in one of 75% extraction. The measurements to date also indicate that in the first years after the opening is created the rate of salt movement near the columns is less than that in the center of the room, whereas, in older openings, the rate in the center of the room is about equal to that near the column. During this latter phase, it appears that the changes are mainly due to the columns squeezing, with the roof moving downward as a continuous structural member.

7. CLINCH RIVER STUDY

7.1 Bottom Sediments

R. J. Pickering*

Coring of Clinch River bottom sediments by Sprague and Henwood, Inc., with the Swedish Foil Sampler was completed on August 28. Measurement of the variation in gross radioactivity with depth in each core with a special core scanner began in November 1962. The core scanner 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 x 2 in. collimator slit, and a hoist which automatically moves the core vertically past the collimator in 2-in. increments. By putting the phototube output through various associated instruments, either the gross gamma activity or a gamma ray spectrum of the core segment can be obtained. The slit height of the collimator and the incremental movement of the hoist are adjustable.

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

7.2 Water Sampling

R. J. Pickering

Of the many determinations of the concentrations of the major radionuclides in samples of Clinch River water collected at the Oak Ridge Water Treatment Plant and at Centers Ferry, a few results appear unreasonable. However, anomalous results are to be expected in a program involving a very large number of analytical determinations. Nevertheless, criteria for correcting or excluding such data must be established when the results are used in calculating cumulative radionuclide loads at a sampling station.

During 1961, an auxiliary sampling station was operated at the water intake of the Water Treatment Plant at the Oak Ridge Gaseous Diffusion Plant (K-25). Although sampling was not carried out in precisely the same manner at the auxiliary sampling station as it was at the Oak Ridge Water Treatment Plant and Centers Ferry sampling stations, the concentrations of the various nuclides at the K-25 water intake could be expected to be approximately the same as those that would have resulted had comparable sampling procedures been used.

Adjustments of analytical data were made in the following manner:

1. The concentration of the radionuclide in the Clinch River at Mile 20.8 was estimated by calculating the dilution of the nuclide concentration in the White Oak Dam sample on the basis of White Oak Creek and Clinch River discharges during that period, and adding that diluted concentration to the concentration of the nuclide at the Oak Ridge Water Plant sampling station.

2. The estimated concentration in the Clinch River at Mile 20.8 was compared with the concentrations at the K-25 water intake and at Centers Ferry.

3. If two of the three values were in approximate agreement, and if the third differed from them by an appreciable amount, the anomalous concentration was adjusted to be in more reasonable agreement with the other two values. (When sufficient analytical data have been accumulated such anomalous values can probably be omitted, rather than adjusted).

An example of an anomalous concentration value can be observed by inspection of data presented in Progress Report No. 2, submitted by the Subcommittee on Water Sampling and Analysis to the Clinch River Steering Committee on October 27, 1961, which indicate an anomalously high Ru^{106} activity in Clinch River water at the Oak Ridge Water Plant "background station" during the ninth calendar week of 1961 (February 26 through March 4). The weekly composite of daily water samples taken at the water plant contained a ruthenium concentration more than five times higher than the highest weekly values during the preceding 15 weeks. It was supposed that radioactive fallout might be responsible for the high concentrations.

Tables 7.1 and 7.2 present the data on the gross radioactivity in air and rain water, the amount of rainfall, and the Ru^{106} content of river water for the first quarter of 1961. It can be seen that there were no periods of unusually high radioactivity in the air or rain preceding the ninth calendar week of 1961. Assuming that ruthenium accounted for 20% of the fallout, 11 curies of Ru^{106} accumulated in the drainage area above the Oak Ridge water plant (3290 square miles) during the first 9 weeks of 1961 (ending February 27), whereas 145 curies of Ru^{106} passed the sampling station during the ninth week of 1961. It is possible that unusually heavy rainfall (in excess of 5 in. throughout much of the drainage basin) during the ninth week of 1961 washed off and flushed out fallout that had accumulated on plants and in the soil during the preceding several months, thus contributing to the high ruthenium content of river water passing the sampling station that week.

If Clinch River water actually had a high "background" ruthenium content during the ninth week of 1961, that content should have been only slightly diluted when the water reached the unofficial sampling station at K-25 or the official sampling station at Centers Ferry. The last three columns in Table 7.2 list computed concentrations of Ru^{106} in Clinch River water at Mile 20.8 and the concentrations at the K-25 and Centers Ferry sampling stations. The ruthenium concentration at Clinch River Mile (CRM) 20.8 appears unreasonably high when compared with the concentrations at the two downstream stations. Since the ruthenium content of the water sample taken at Oak Ridge water plant accounts for most of the high concentration at CRM 20.8, the comparison suggests that Clinch River water passing Oak Ridge water plant during the ninth week of 1961 did not have the high ruthenium content indicated by the analysis. The high Ru^{106} content of the sample is thus considered to be the result of contamination at some stage between the taking of the sample and its analysis.

Eight analytical values in all were adjusted. Three of these values were from the sample of the ninth week, which is assumed to have been contaminated after it was collected.

Unadjusted and adjusted radionuclide loads passing the Clinch River water sampling stations during a 44-week period (32-week period for Sr^{90}) are shown in Tables 7.3 and 7.4 and in Figs. 7.1 to 7.4. The computed loads indicate that any transfer of the radionuclides from the water to the bottom sediments involves only a small percentage of the total radionuclide load transported by the river between the upstream and downstream sampling points. Apparent gains in certain radionuclides in the water phase between the mouth of White Oak Creek and Centers Ferry are indicative of the magnitude of errors inherent in the sampling and analytical methods.

7.3 Power-Wave Dispersion

P. H. Carrigan F. L. Parker

As a result of hydroelectric power operations at Melton Hill Dam, the flow duration in the Clinch River at White Oak Creek may vary from 0 hr to 24 hr in each day,

Table 7.1. Radioactive Fallout Data[a]

H. P. Week No. 1961	Month 1960-1961	Inclusive Dates	Rainfall (in.)	Rainwater Radioactivity (10^{-7} x μc/cc)	Air Radioactivity: Particle Fallout (10^{-4} x μc/ft^2)	Air Radioactivity: Air Filter (10^{-13} x μc/cc)
1	Dec.-Jan.	28-3	1.85	0.14	1.30	0.08
2	Jan.	4-9	0	--	0.23	0.43
3		10-16	1.01	0.05	0.19	0.40
4		17-23	0.71	0.39	0.47	0.26
5		24-30	0.42	0.08	0.34	0.98
6	Jan.-Feb.	31-6	0.42	0.17	0.41	0.89
7	Feb.	7-13	1.14	0.05	0.36	0.76
8		14-20	0.96	0.08	0.14	0.80
9		21-27	5.00	0	0.43	0.86
10	Feb.-Mar.	28-6	0.81	0.13	0.32	0.60
11		7-13	3.00	0.09	0.51	0.31
12		14-20	1.21	0.43	0.51	0.59
13		21-27	0.30	0.17	0.41	0.45

[a]Data from Area Monitoring Group, Health Physics Division, Oak Ridge National Laboratory.

Table 7.2. Clinch River Water Sampling Data, Ru^{106}

Calendar Week No. 1961	Month 1960-1961	Inclusive Dates	Oak Ridge Water Plant: Ru^{106} Conc (μμc/liter)	Oak Ridge Water Plant: Clinch River Discharge (cfs)	Oak Ridge Water Plant: Ru^{106} Load (curies)	ORWP Plus White Oak Creek (diluted) Ru^{106} (μμc/liter)	K-25 Ru^{106} Conc (μμc/liter)	Centers Ferry Ru^{106} Conc (μμc/liter)
	Dec. (1960)	25-31	210	5,170	18.8	1,231	1,070	840
1	Jan. (1961)	1-7	5	1,450	0.1	2,408	1,410	1,500
2		8-14	<5	4,100	<0.4	282	297	130
3		15-21	<5	4,150	<0.4	876	315	390
4		22-28	<5	5,930	<0.5	275	189	365
5	Jan.-Feb.	29-4	10	5,180	0.9	318	383	180
6	Feb.	5-11	<5	2,840	<0.3	1,090	2,130	2,400
7		12-18	5	545	0.1	3,352	2,090	2,300
8		19-25	5	4,210	0.4	2,880	2,337	5(?)
9	Feb.-Mar.	26-4	1,200	8,420	174.8	1,513 (?)	271	350
10	Mar.	5-11	10	13,370	2.3	440	324	350
11		12-18	<5	15,990	<1.4	204	293	280
12		19-25	<5	5,200	<0.5	340	333	310

Table 7.3. Radionuclide Loads in Curies, Clinch River Water, Analytical Values not Adjusted

Sampling Station	Ru^{106} [a]	Cs^{137} [a]	Co^{60} [a]	Sr^{90} [b]
Oak Ridge Water Plant	282.1	3.8	4.1	3.4
White Oak Creek	1555.6	16.1	24.1	21.4
Oak Ridge Water Plant, plus White Oak Creek	1837.7	19.9	28.2	24.8
Centers Ferry	1585.0	33.6	22.0	20.3
White Oak Creek to Centers Ferry, % gain or loss	-13.8	+68.8	- 22.0	- 18.1

[a]Data are for period, Nov. 13, 1960, to Sept. 16, 1961.

[b]Data are for period, Nov. 13, 1960 to June 24, 1961.

Table 7.4. Radionuclide Loads in Curies, Clinch River Water, Analytical Values Adjusted

Sampling Station	Ru^{106} [a]	Cs^{137} [a]	Co^{60} [a]	Sr^{90} [b]
Oak Ridge Water Plant	108.8	3.8	0.7	1.7
White Oak Creek	1555.6	16.1	24.1	21.4
Oak Ridge Water Plant Plus White Oak Creek	1664.4	19.9	24.8	23.1
Centers Ferry	1773.7	22.0	22.0	21.9
White Oak Creek to Centers Ferry, % gain or loss	+6.6	+10.6	- 11.3	-5.2

[a]Data are for period, Nov. 13, 1960 to Sept. 16, 1961.

[b]Data are for period Nov. 13, 1960 to June 24, 1961.

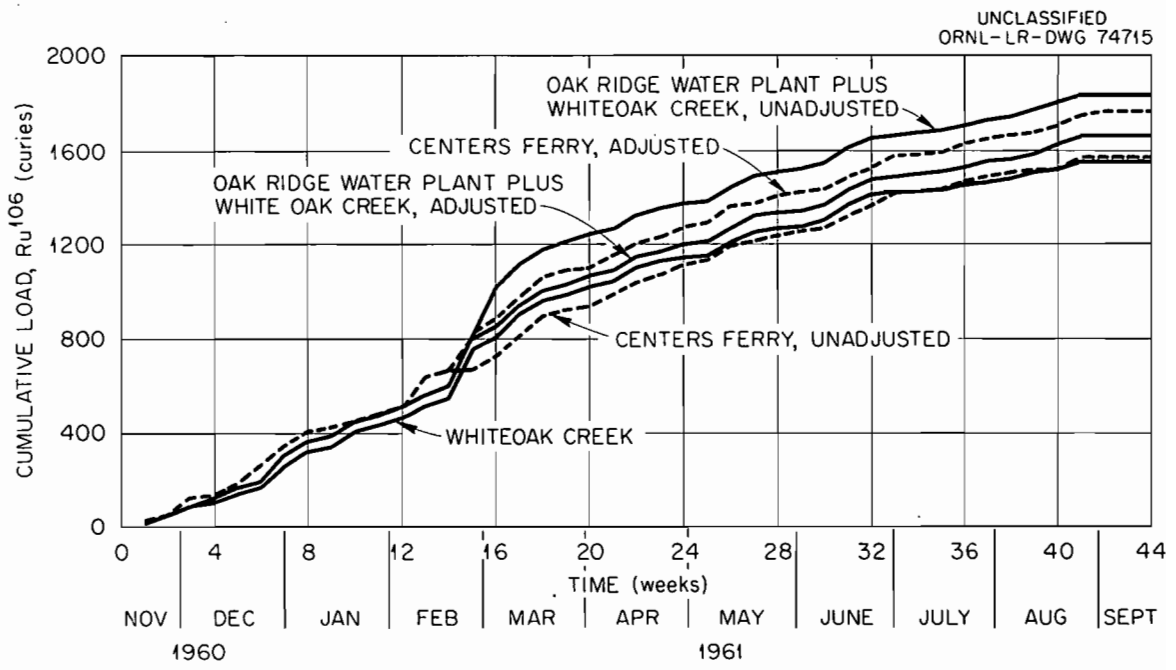

Fig. 7.1. Cumulative Load of Ru^{106} in the Clinch River System.

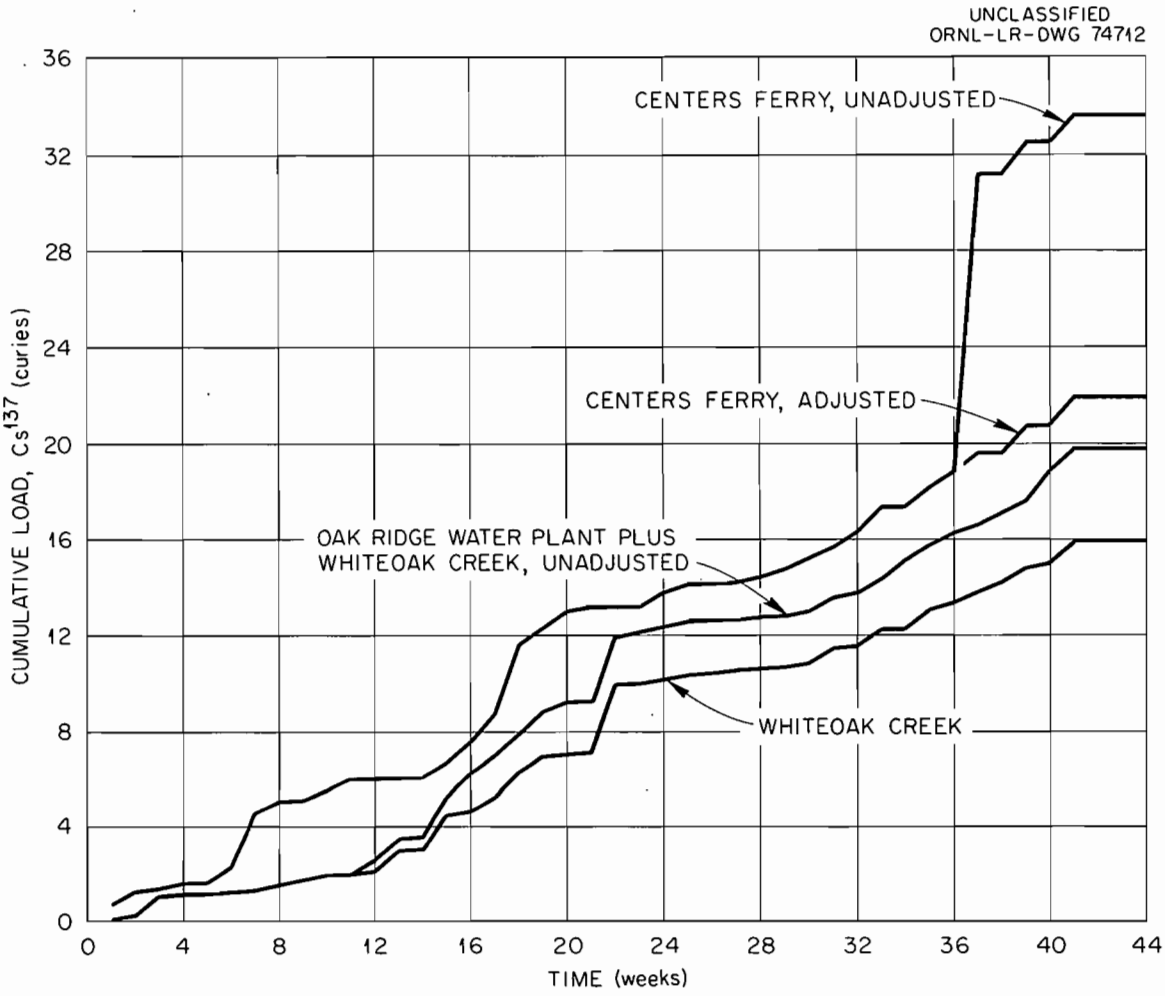

Fig. 7.2. Cumulative Load of Cs^{137} in the Clinch River System.

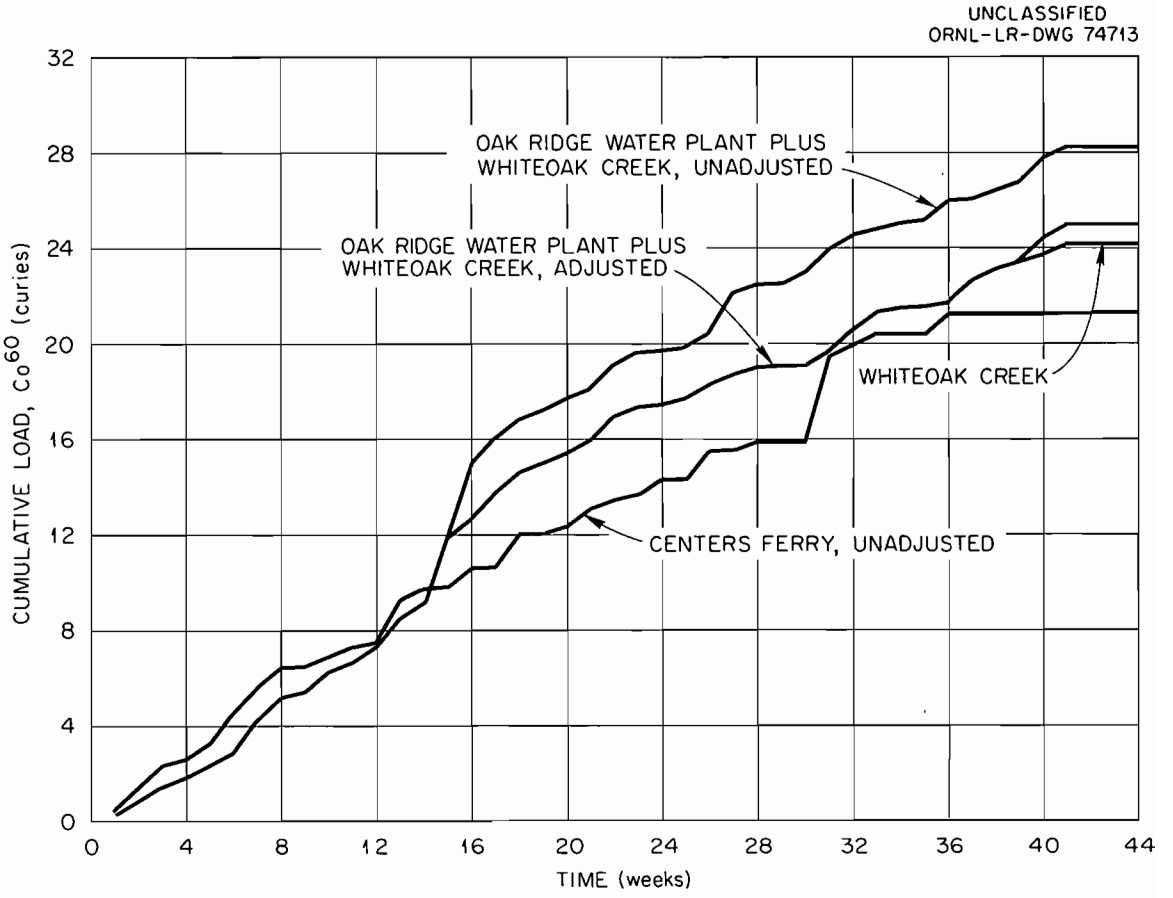

Fig. 7.3. Cumulative Load of Co^{60} in the Clinch River System.

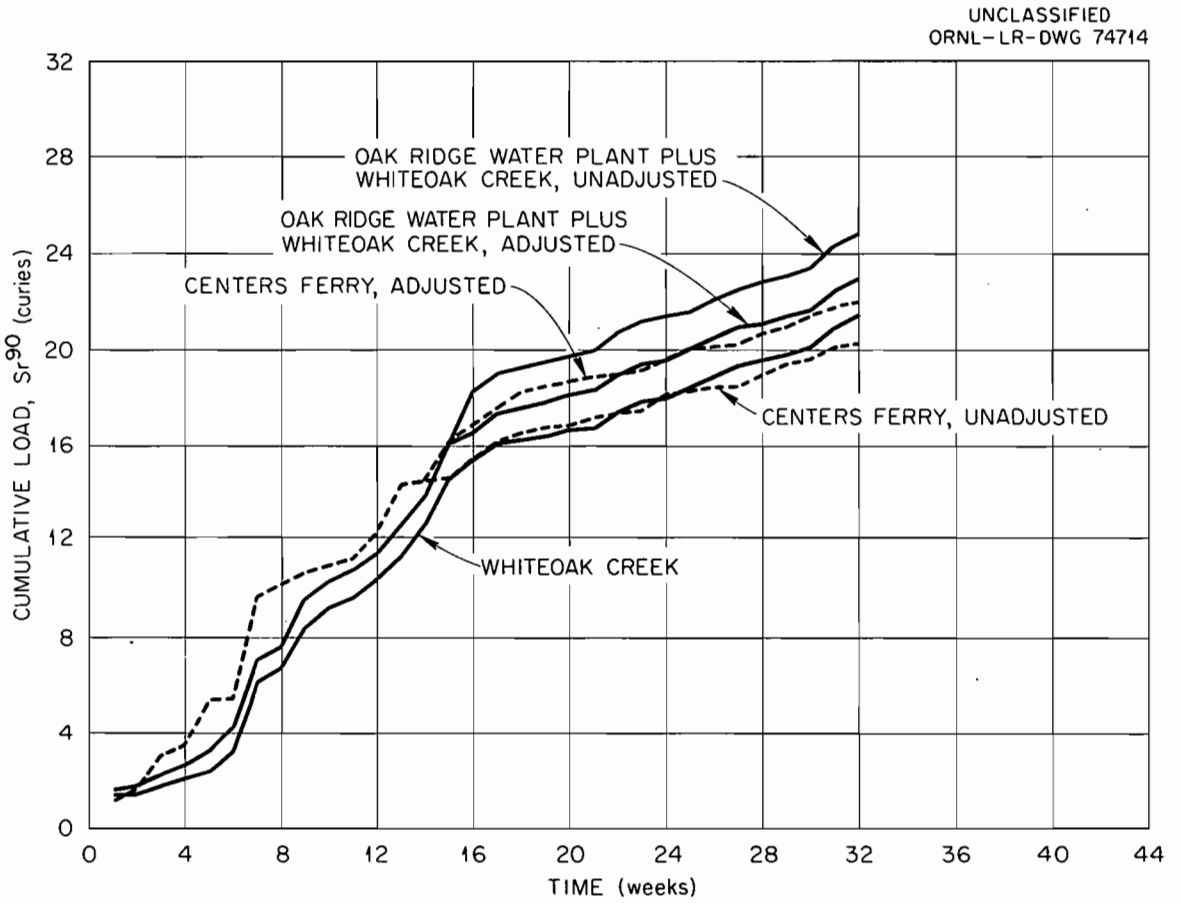

Fig. 7.4. Cumulative Load of Sr^{90} in the Clinch River System.

depending on the quantity of water available and the power demands of the TVA system. Beginning in mid-1963, flows in the lower Clinch River will almost instantaneously change from zero to several thousand cubic feet per second.[1]

Assuming that the present methods of releasing radioactive materials from White Oak Lake are continued, radioactivity will accumulate in Clinch River waters in the vicinity of White Oak Creek during no-flow periods. During periods of power releases from Melton Hill Reservoir, this accumulated radioactivity will be swept downstream in a "cloud." The concentration of radioactivity in the cloud will be appreciably higher than levels presently experienced.

A laboratory study of the dispersion of the radioactive cloud due to power waves in the lower Clinch River is being made, and a series of distorted-model dispersion tests were made in a flume operated by the U. S. Geological Survey at the Hydraulics Laboratory, National Bureau of Standards, Washington, D. C. The tests were undertaken to acquire immediate qualitative information on the effects of power waves on the dispersion of radionuclides and to develop numerical methods of describing the diffusion process.

A photograph of the test facilities is shown in Fig. 7.5. The flume is 150 ft long, 3.5 ft wide, and 1.5 ft deep. It was divided into a 1.5-ft-wide test channel and a 2.0-ft-wide by-pass channel and may be tilted to any desired gradient. Discharges in the flume were obtained from a 300,000-gal recirculating system. Depths in the flume are controlled by a tail gate. A double-notch weir plate was installed in the forebay so that flow could be instantaneously diverted from the by-pass channel to the test channel by operation of simple slide gates at the weir.

The discharge, bed slope of the flume, water depth for no-flow conditions, and bed roughness were adjusted to conform, at distorted scales to anticipated conditions in the Clinch River. Horizontal distortions were about 250:1, and vertical distortions were about 20:1. In open-channel flow problems, where gravity is predominant, dynamic similarity is approximated if the ratio of the inertial forces to the gravitational forces (the Froude number) is the same in the model and the prototype. Generally, consideration of the influence of viscosity, surface tension, and elastic forces may be safely ignored for open-channel flow.

The Froude number F is expressed as

$$F = \frac{V}{\sqrt{gy}} ,$$

in which

V = velocity, ft/sec,
g = gravitational acceleration, ft/sec^2, and
y = depth of flow, ft.

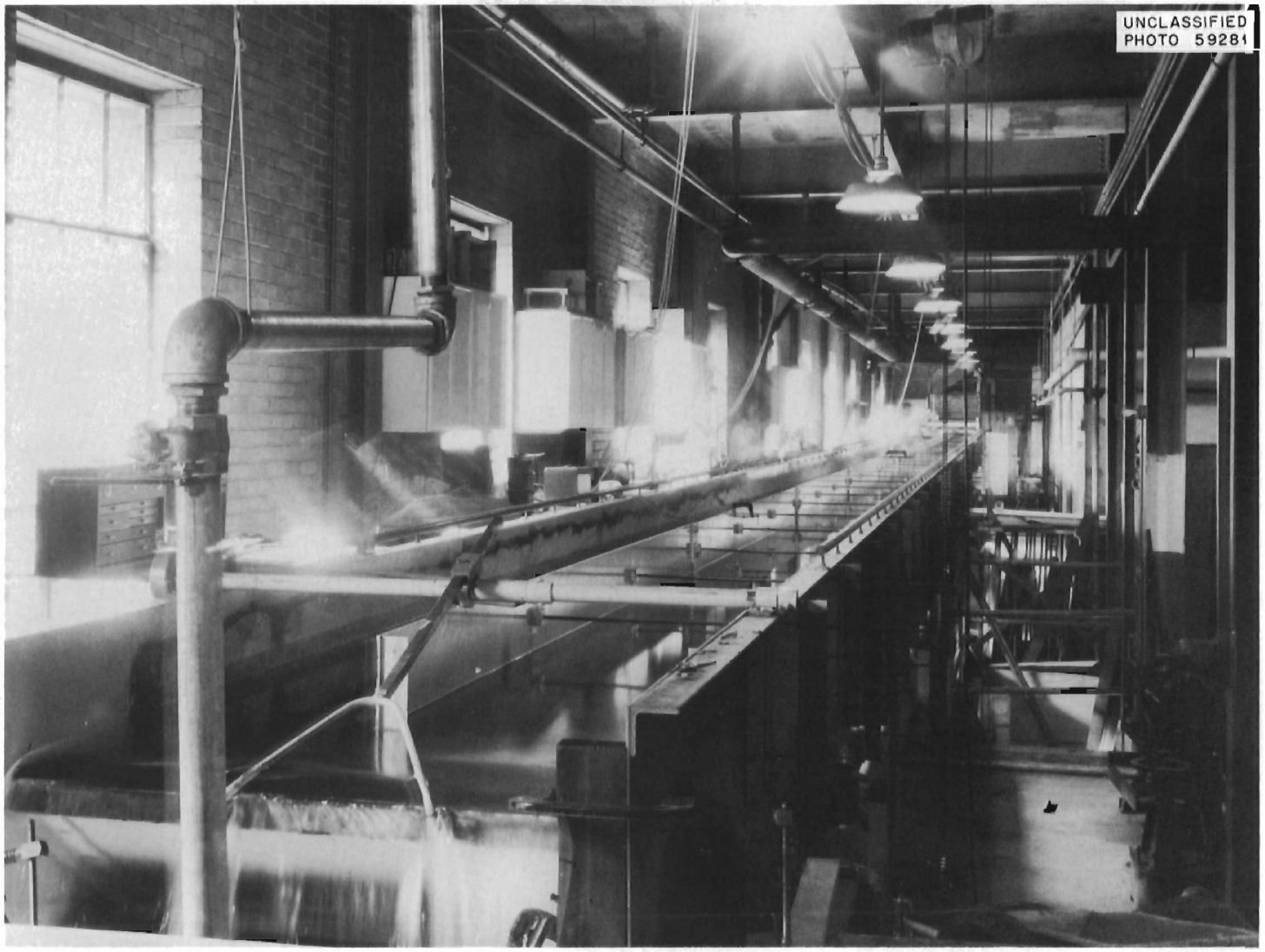

Fig. 7.5. Flume for Power-wave-Dispersion Tests.

If the horizontal scale ratio is α (1:250) and the vertical scale ratio is β (1:20), then the velocity V, discharge Q, time t, and bed slope s, scale ratios are

$$V: \beta^{1/2} = 1:4.45,$$

$$Q: \alpha \beta^{3/2} = 1:22{,}500,$$

$$t: \frac{\alpha}{\beta^{1/2}} = 1:56.2,$$

$$s: \frac{\beta}{\alpha} = 1:0.08.$$

The procedure consisted in establishing the desired flume slope and water depth for no-flow conditions in the test channel and the desired discharge in the by-pass channel. The power wave was created by diverting suddenly the established discharge from the bypass to the test channel. At the instant the wave was created, a tracer was released. In most tests the tracer was composed of potassium chloride, water, and ethyl alcohol. The density of the solution was the same as that of the laboratory water. The variation of salt concentration with time was measured continuously at several points in the flume, using recording conductivity bridges. At the completion of a wave test, a steady-flow test was run. The discharge, slope, tracer, and water depth were the same as for the wave test.

The variation of concentration with time for one complete test is shown in Fig. 7.6. The results indicate that the dispersion process due to power releases is not greatly different from that for steady flow, especially at sections sufficiently removed from the tracer injection section. At equivalent CRM 15.9, about 1.5 miles upstream from the water plant intake for the Oak Ridge Gaseous Diffusion Plant, the peak concentrations and the durations of the tracer cloud for the wave and steady-flow conditions are about the same (Fig. 7.6).

Some work on dispersion in steady flows was done in the Clinch River.[1] As a check on model similitude, the wave height and travel time for the model were compared with height and times predicted by TVA for the Clinch River. For flow conditions shown in Fig. 7.6, the equivalent wave height was 7.72 ft, compared with the predicted height in the river of 7.70 ft. The equivalent travel time for the scale ratios indicated in Fig. 7.6 was about 3% greater than the time interpolated from information furnished by TVA.

A computer program to determine time-concentration curves and diffusion coefficients is being developed by the U.S. Geological Survey in Washington, D.C. Further study of the experimental data will be implemented through use of the computer program.

In this further work, the general diffusion equation,

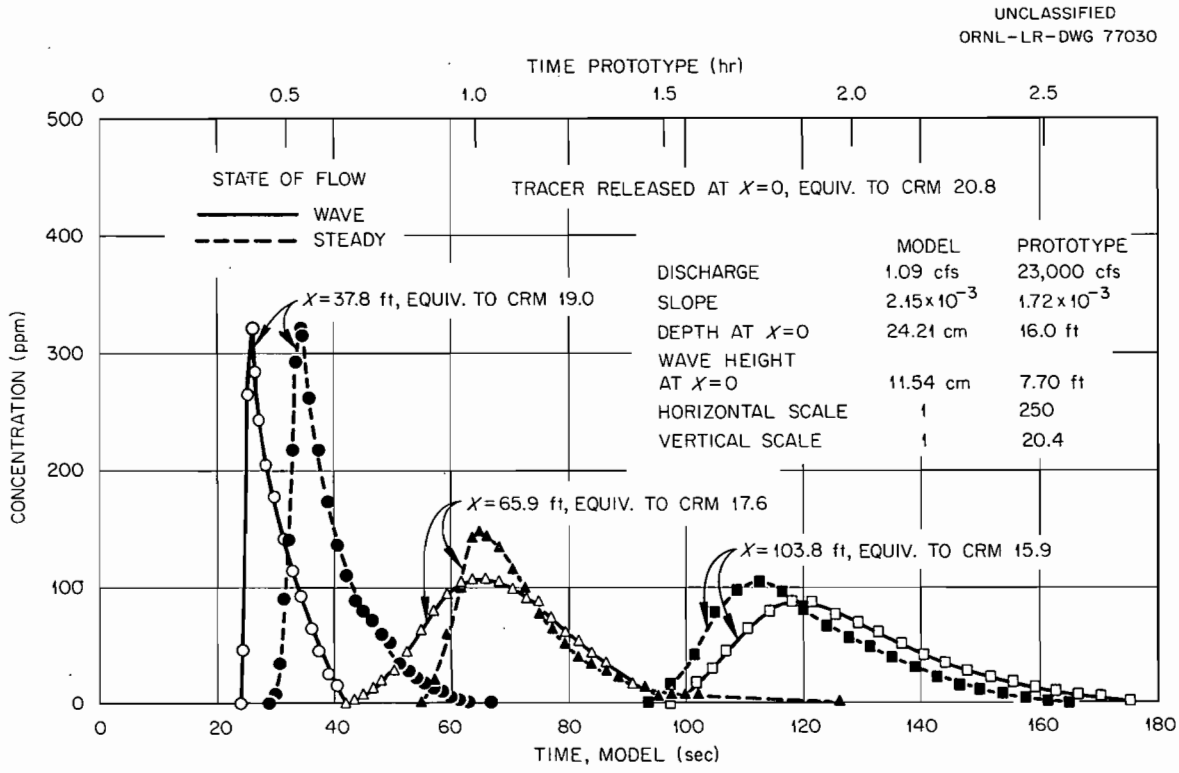

Fig. 7.6. Variation of Tracer Concentration with Time and Distance.

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AK_x\frac{\partial C}{\partial x}\right), \tag{1}$$

in which

C = concentration of contaminant, curies/liter,
t = time, sec,
u = mean velocity in x-direction, ft/sec,
x = longitudinal distance, ft,
A = cross-sectional area, ft^2, and
K_x = longitudinal turbulent diffusion coefficient, ft^2/sec,

will be solved with numerical techniques. Analytical solutions of the diffusion equation are available if u, A, and K_x are constant. However, for the case of power waves in Clinch River, u and A are not constant, and K_x possibly varies with discharge (steady-flow condition) and distance.

If the variation of K_x with discharge and distance is defined for steady flow, the variation of contaminant concentration, with time and in space, during periods of power releases may be numerically described by the following expression:

$$C_{x+\Delta x,t} = C_{x,t}\left[1 - \frac{E\Delta x}{D} - \frac{\Delta x}{D\Delta t}\right] + C_{x,t+\Delta t}\left[\frac{\Delta x}{D\Delta t}\right], \tag{2}$$

in which

C = concentration at time, t, or $t+\Delta t$, and at distance, x, or $x+\Delta x$, curies/liter,

x = distance, ft,
Δx = incremental distance, ft, $= \frac{2K_x}{D}$
t = time, sec,
Δt = incremental time, sec,

$$D = \frac{1}{A}\left[-Q + K_x\left(\frac{A_{x+\Delta x} - A_{x-\Delta x}}{2\Delta x}\right) + A\left(\frac{K_{x+\Delta x} - K_{x-\Delta x}}{2\Delta x}\right)\right],$$

ft/sec,

$$E = -\frac{1}{A}\left[\frac{Q_{x+\Delta x} - Q_{x-\Delta x}}{2\Delta x}\right], \ sec^{-1},$$

Q = discharge, ft^3/sec,
A = cross-sectional area, ft^2, and
K_x = diffusion coefficient, x-direction in ft^2/sec.

The general applicability of Eq. (2), and its associated corollary assumptions, will be tested with the experimental data. This equation will then be applied to power-wave dispersion problems in the Clinch River.

8. FUNDAMENTAL STUDIES OF MINERALS

D. G. Jacobs

The addition of collapse-inducing cations (NH_4^+, K^+, Rb^+, or Cs^+) to a 0.5 M $NaNO_3$ influent causes a reduction of the (001) spacing of the vermiculite lattice and results in the physical entrapment of trace quantities of cesium sorbed at basal exchange sites. This increases the cesium loading of vermiculite columns and reduces the amount of cesium that can be exchanged from the column.

The addition of barium salts to a 0.5 M $NaNO_3$ influent did not yield a net beneficial effect on the sorption of trace quantities of cesium by vermiculite (Table 8.1). There was no loss in exchange capacity with increasing influent barium concentrations up to 0.05 M, although the desorption of cesium during the determination of exchange capacity appears to have been reduced. Partial collapse of the vermiculite lattice by barium treatment does not appear to be sufficiently drastic for the "interlayer fixation" of cesium.

Increased temperatures resulted in faster rates of exchange by vermiculite-biotite systems, but the effect on sorption of trace quantities of cesium was influenced primarily by the effects on the sodium-potassium exchange in the system. When 0.5 M $NaNO_3$ tagged with Cs^{137} was passed through columns of sodium- or potassium-treated vermiculite, a more rapid release of potassium from the collapsed vermiculite or biotite layers was favored at higher temperatures and resulted in a greater degree of lattice expansion. This resulted in a higher exchange capacity but a lower cesium loading due to the decreased number of cesium fixation sites (Table 8.2).

When the 0.5 M $NaNO_3$ influent solution was brought to 0.04 M with respect to potassium nitrate, the reverse reaction was favored. As a result, more complete lattice collapse and a reduced exchange capacity were favored by higher temperatures. However, at 81°C the potassium of the influent provided too much competition for cesium and resulted in lower cesium sorption than at room temperature. Either the lattices were collapsed to 10 A before the cesium could arrive at the exchange sites within the basal spacing or the elevated temperature reduced the hydration of the potassium ion, resulting in a higher relative affinity of the vermiculite surface for potassium. In the cold system (0°C), collapse of the vermiculite was not sufficiently complete to obtain optimum cesium removal. This was evident from the high final exchange capacity.

Several 4-g columns of vermiculite were run at a constant flow rate of 0.80 ml cm^{-2} min^{-1} at room temperature. The runs were terminated after various lengths of

time had elapsed. The columns were quartered for determination of the exchange capacity and the cesium loading of each segment. The results show that when the influent solution is deficient in collapse-inducing cations, the exchange capacity increases slowly with continued leaching (Table 8.3). The increase in exchange capacity was directly proportional to the square root of time, suggesting that the release of potassium from collapsed lattices is a diffusion-controlled process.

When the influent solution was potassium rich, the exchange capacity decreased with time, indicating continued conversion of vermiculite to biotite (collapsed lattice). Continued lattice collapse was accompanied by increased interlayer fixation of cesium. In the columns filled with sodium-treated vermiculite the cesium loading increased slowly with time, presumably due to slow penetration of the collapsed biotite layers by the cesium ions. As time passed, more of the cesium migrated to the interlayer fixation sites of the closed lattices and was, therefore, less subject to leaching than when it occupied fixation sites near the edges of the basal spacing.

In the case where columns filled with potassium-treated vermiculite were saturated with a potassium-deficient solution of 0.5 M $NaNO_3$, the advantage of increased time was counterbalanced by re-expansion of the closed lattices after 24 hr, and after 48 hr there was a slight decrease in the net cesium loading.

Table 8.1. Influence of Barium on the Sorption of Trace Quantities of Cesium from 0.5 M $NaNO_3$ by Vermiculite Columns

Barium Concentration (M)	Cesium K_d (ml/g)	Exchange Capacity (meq/100 g)	Cesium Leached (%)
0.00000	113	80.3	14.8
0.00005	109	80.7	14.6
0.0005	108	79.2	14.7
0.005	106	81.0	11.4
0.05	111	83.7	8.5

9. WHITE OAK CREEK BASIN STUDY*

9.1 Movement of Radionuclides in White Oak Creek

T. F. Lomenick

During periods of high stream flow and/or suspended solid load in White Oak Creek, substantial increases occur in the quantities of cesium and strontium transported

*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).

Table 8.2. Influence of Temperature on the Sorption of Cesium by Vermiculite

Material	Temperature (°C)	Solution	Cesium K_d (ml/g)	CEC (meq/100 g)	Cesium Leached (%)
Na-Vermiculite	81	6 liters of 0.5 M $NaNO_3$	95	84.7	22.0
	25		109	67.3	23.0
	0		115	63.4	22.4
Na-Vermiculite	81	8 liters of (0.5 M $NaNO_3$ + 0.04 M KNO_3)	140	8.0	3.42
	25		610	14.9	5.82
	0		379	28.0	7.06
K-Vermiculite	81	8 liters of 0.5 M $NaNO_3$	106	74.8	15.6
	25		218	62.9	13.7
	0		301	52.2	9.8

Table 8.3. Influence of Time on the Sorption of Cesium by Vermiculite

Time (hr)	0.5 M $NaNO_3$, 0.04 M KNO_3			0.5 M $NaNO_3$			0.5 M $NaNO_3$		
	Na-treated Vermiculite			Na-treated Vermiculite			K-treated Vermiculite		
	Cs K_d (ml/g)	CEC (meq/100 g)	Cs Leached (%)	Cs K_d (ml/g)	CEC (meq/100 g)	Cs Leached (%)	Cs K_d (ml/g)	CEC (meq/100 g)	Cs Leached (%)
1	54	62.0	3.75	39	75.4	48.2	59	18.0	29.2
2	93	56.7	2.74	52	75.3	42.0	80	20.4	27.9
4	183	49.6	2.23	66	76.9	40.6	149	24.8	21.7
8	334	43.7	1.92	82	76.5	35.6	205	31.0	18.8
24	513	34.4	1.17	116	80.0	36.9	247	48.3	11.7
48	857	29.0	1.04	134	80.2	35.5	249	59.8	13.0
72	903	26.5	0.83	141	79.9	29.8	243	62.9	23.0
96	1240	23.8	0.78	145	81.1	27.4	225	68.4	24.1
120	1290	22.6	0.79	--	--	--	--	--	--
144	--	--	--	160	83.4	33.6	226	73.8	17.6
168	1360	20.7	0.77	166	83.3	30.4	218	74.6	18.3
240	1540	20.1	0.78	--	--	--	--	--	--
336	--	--	--	162	83.3	29.6	221	82.1	20.9
435	--	--	--	166	85.3	28.2	--	--	--

downstream.[10,11] To define further the transport of activity in the creek with high discharge and sediment load, a series of samples was taken during the rise and subsequent fall of the creek due to a light rainfall. Stream discharge, suspended-solid concentration, and strontium and cesium transport during the cycle are shown in Fig. 9.1. Note that the sediment load in the stream does not vary directly with stream discharge. The suspended-solid concentration rises quite abruptly to a peak concentration well before the stream-flow crest is reached. From the figure it is also seen that the quantity of cesium and strontium transported downstream is greatest when the sediment load is highest, which is prior to the peak stream discharge. Finally, it is observed that there is little variation in the quantity of cesium transported downstream that is associated with the liquid phase of creek water, but the amount associated with suspended solids increases considerably with an increase in stream flow and/or suspended-solid concentration. For strontium, however, there is little variation in the quantity sorbed on sediments, while significant increases occur in the quantity of that associated with the water, itself.

The exact source of the additional cesium and strontium that accompany a rise in stream flow and/or suspended solid concentration is not known. It is likely that much of the increase is due to scouring of the stream bed. However, some may be due to surface- and ground-water leaching.

9.2 Sources of Contamination

There are 23 known sources of contamination in the White Oak Drainage Basin (Fig. 9.2). The creek receives directly the discharges of partially treated process waste water, laundry, sanitary sewage, and reactor retention-pond effluents and, eventually, seepage from the intermediate-level waste seepage pits and five solid waste burial grounds. Runoff from land surfaces that are subjected to local fallout from four tall stacks and to general fallout also contributes some activity to the creek. In addition, some radionuclides enter the creek from the beds of former White Oak Lake and Intermediate Pond.

Permanent water-sampling stations now exist along White Oak Creek at White Oak Dam and at White Oak Creek Mile (WOCM) 1.8, on each of the two streams that drain the intermediate-level waste seepage pit 4 area, on Melton Branch just upstream from its confluence with White Oak Creek, and on the effluents from the Process Waste Water Treatment (PWWTP), as shown on Fig. 9.2. These stations, which employ proportional sampling devices, provide information primarily on the amount and type of activity that is discharged to the Clinch River and that which leaves the major contamination sources at ORNL. Temporary water-sampling stations were established at WOCM 2.6 and 3.9 and on the tributary stream that drains the northwest portion of the area (Fig. 9.2). These stations helped to determine the amount and type of activity contributed to the system from fallout, burial grounds, and other sources in Bethel Valley that could not be monitored directly.

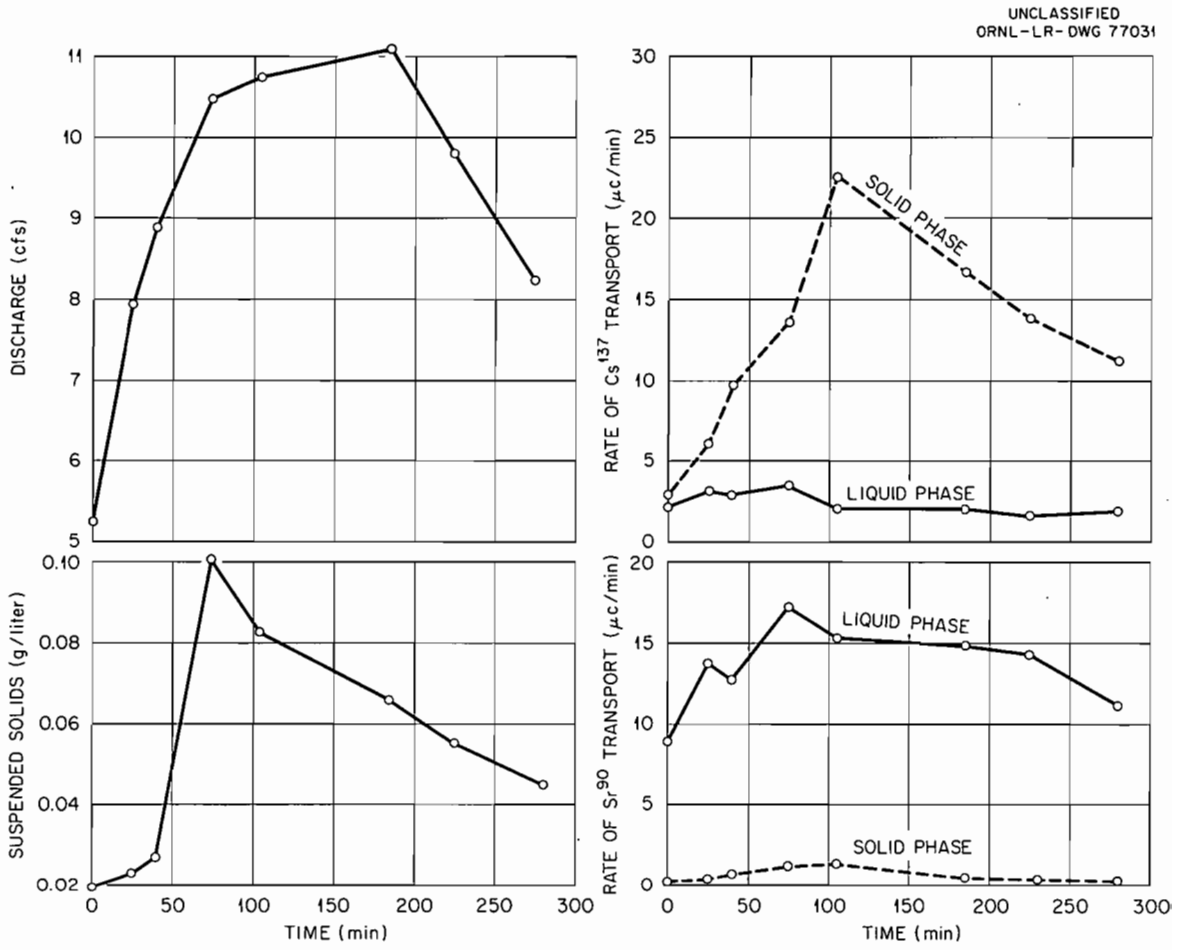

Fig. 9.1. Stream Flow, Concentration of Suspended Solids, and Sr^{90} and Cs^{137} Transport in White Oak Creek Resulting from Light Rainfall.

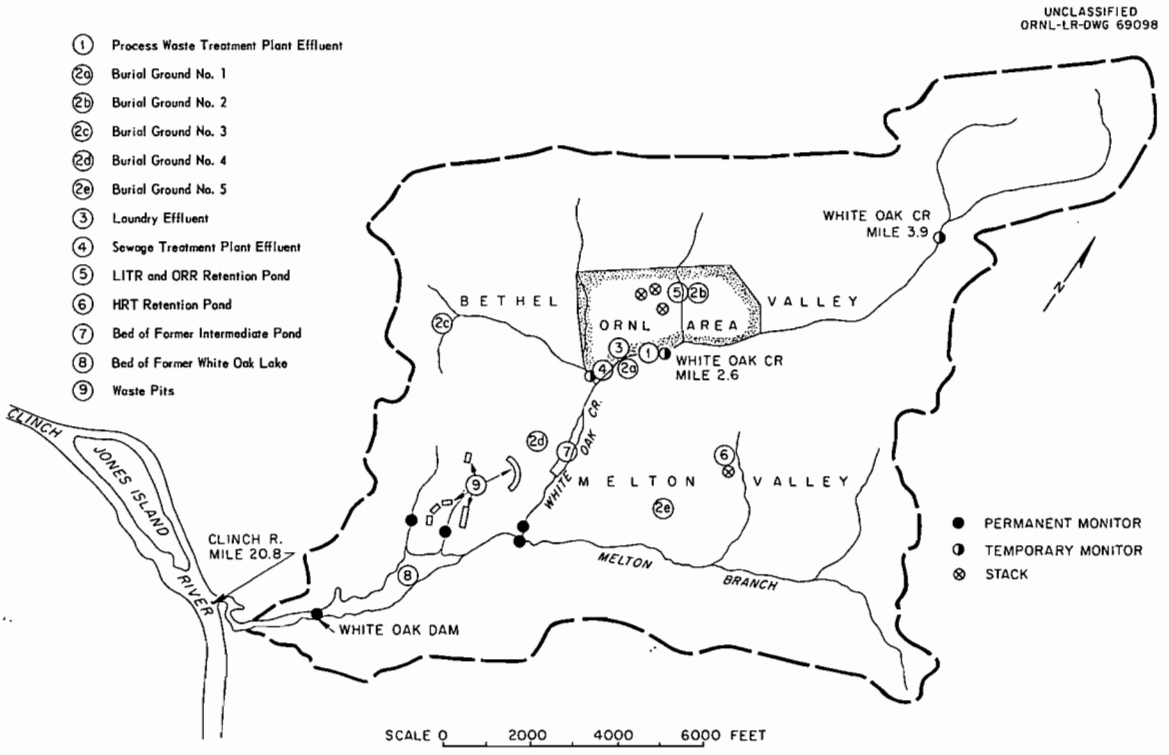

Fig. 9.2. Map of White Oak Creek Basin, Showing Sources of Radioactive Contamination and Stream-Monitoring Stations.

Representative samples of the effluent from the laundry and the sewage-treatment plant were also taken, and a contaminated storm sewer that discharges into White Oak Creek downstream from the station at WOCM 2.6 in Bethel Valley was monitored. Because of the relatively high degree of contamination in White Oak Creek below the PWWTP, it is extremely difficult to detect small quantities of waste that may seep directly into the creek from Burial Ground 4 and the beds of former White Oak Lake and Intermediate Pond. A previous study of Burial Ground 4 showed that radionuclides are leached from the buried waste and transported by ground water through the soil to points of discharge in or near surface streams.[12] However, the amount of activity that reaches White Oak Creek from this source is so small in comparison with that already in the creek that it is undetectable. Detailed geologic and hydrologic studies in the beds of former White Oak Lake and Intermediate Pond are incomplete, but preliminary data indicate little movement of the radionuclides that are associated with sediments at these sources. The sampling instruments at the creek stations have been described previously.[11]

A summary of activity released to the creek from the various sources of contamination for the period, May through December 1961, is shown in Table 9.1. It may be noted that the PWWTP is the largest single contributor of Sr^{90} and Cs^{137} to the creek, but seepage from the waste pits accounts for practically all the Co^{60} and Ru^{106} in the system.

9.3 Geology and Hydrology of White Oak Creek Basin

W. M. McMasters* R. M. Richardson*

On October 31, 1962, a time-of-travel study was made in White Oak Creek under conditions of low-base flow, using fluorescein dye as a tracer. About 3/4 lb of dye in solution was injected into the stream near the southeastern end of Building 4500, at the rate of 180 ml/min, for a 7-min period. Discharge at the gaging station White Oak Creek below ORNL during the study was 4.5 cfs; discharge at White Oak Dam was 6.0 cfs.

Six sampling stations were established downstream at: the gaging station at White Oak Creek (WOCM 2.6) at ORNL,the new bridge at the water gap in Haw Ridge, the old intermediate pond dam, the gaging station at White Oak Creek (WOCM 1.8) below ORNL, the old boat dock bridge, and at White Oak Dam. Samples were collected at 5-min intervals (beginning at each station at a time based on two previous studies made in May 1962). Sampling continued for at least 3 hr at each station.

Samples collected at the new bridge and the earth dam showed no fluorescence above background when read on the fluorometer, even though samples collected at two stations downstream from these gave good results. No explanation can be offered at this time.

The station at White Oak Dam, equipped with a recording fluorometer through which White Oak Lake water was pumped, also did not show the passage of the dye.

---

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

Table 9.1. Radionuclides Released to White Oak Creek above White Oak Dam

May - December 1961

	Sr^{90}		Cs^{137}		Co^{60}		Ru^{106}	
	(mc)	(%)	(mc)	(%)	(mc)	(%)	(mc)	(%)
Process Waste Water Treatment Plant (PWWTP)[c]	4,200	63.93	1,120	50.82	443	0.67	416	<0.01
Sanitary sewage	197	3.00	37	1.68	7	0.01	7	< 0.01
Laundry	11	0.17	22	1.00	8	0.01	3	< 0.01
Watershed above northwest tributary station	61	0.93	31	1.41	1	< 0.01	11	< 0.01
Watershed above WOCM 2.6 station	170	2.59	187	8.48	94	0.14	43	< 0.01
Storm sewer below PWWTP Equilization Pond in Bethel Valley[a,c]	1,135	17.27	127	5.76	208	0.31	68	< 0.01
Watershed above Melton Branch Station	782	11.90	205	9.30	289	0.43	5,207	0.07
Waste pits[b]	14	0.21	475	21.55	65,000	98.42	6,838,000	99.92
Totals	6,570	100.00	2,204	100.00	66,050	100.00	6,843,755	100.00

[a]Values based on quantities detected April - October 1962.

[b]Values represent quantities released from pits.

[c]Values obtained from Operations Division.

The failure at this station was probably due to density gradients caused by temperature differences between lake water and stream water. Dye injected at the boat dock bridge on the following day, November 1, under practically identical conditions, was not detected at the dam.

The results obtained from samples collected at the gaging stations, White Oak Creek at ORNL, and White Oak Creek below ORNL, and at the old boat dock bridge are shown in Fig. 9.3. The average maximum velocity for the length of channel studied, based on the arrival of detectable dye, was 0.54 fps; the average velocity (velocity of the center of mass) was 0.43 fps; and the average velocity of peak concentration was 0.45 fps. The value of 0.35 fps for the average minimum velocity was obtained by extrapolation of the receding limb of the curve obtained for the station at the boat dock bridge, where the background reading did not return to the value that existed before passage of the dye.

The time of travel required for the mass of colored water to reach the boat dock bridge, which is near the head of White Oak Lake, was 5 hr 15 min; the time required for peak concentration to reach the bridge was 6 hr 15 min. The time of travel measured during this study is probably close to that generally to be expected during the period when low base-flow conditions prevail in White Oak Creek, that is, from August to mid-November. Beginning in mid-November, in general, runoff increases, and high stages are more frequent; accordingly, the time required for water to pass downstream varies. Future time-of-travel studies are planned to characterize the range of flow conditions in the stream. Also, future studies will be made by using Rhodamine B, which is superior to fluorescein because of its light fastness and its stability over a wide range of pH values.

10. FOAM SEPARATION

10.1 Pretreatment of Low-Activity Waste

W. Davis, Jr. E. Schonfeld*

Previous work showed that it is desirable to decrease the hardness of low-activity waste in an initial step in order to increase the efficiency of foam separation as a decontamination method. Experiments were conducted to measure the effects of the sludge-height-to-column-diameter ratio and feed flow rates on the head-end precipitation of calcium and magnesium from ORNL low-activity waste. The experiments were performed in 3-, 4-, and 9-in.-diam columns (Fig. 10.1) as a continuation of the previous work with 2-in.-diam columns. The apparatus consists of a single-chamber agitated-bed contactor that does not require a separate flocculator, premixing chamber, or baffles as are used in some commercial or laboratory units. Precipitation occurs by making the water 0.005 M in both NaOH and Na_2CO_3. Ferric ion is added (2 to 5 ppm) as a coagulant and to combine with interferring phosphates. The results, including previous work,[13] are summarized in Table 10.1.

*Radiation Applications, Inc.

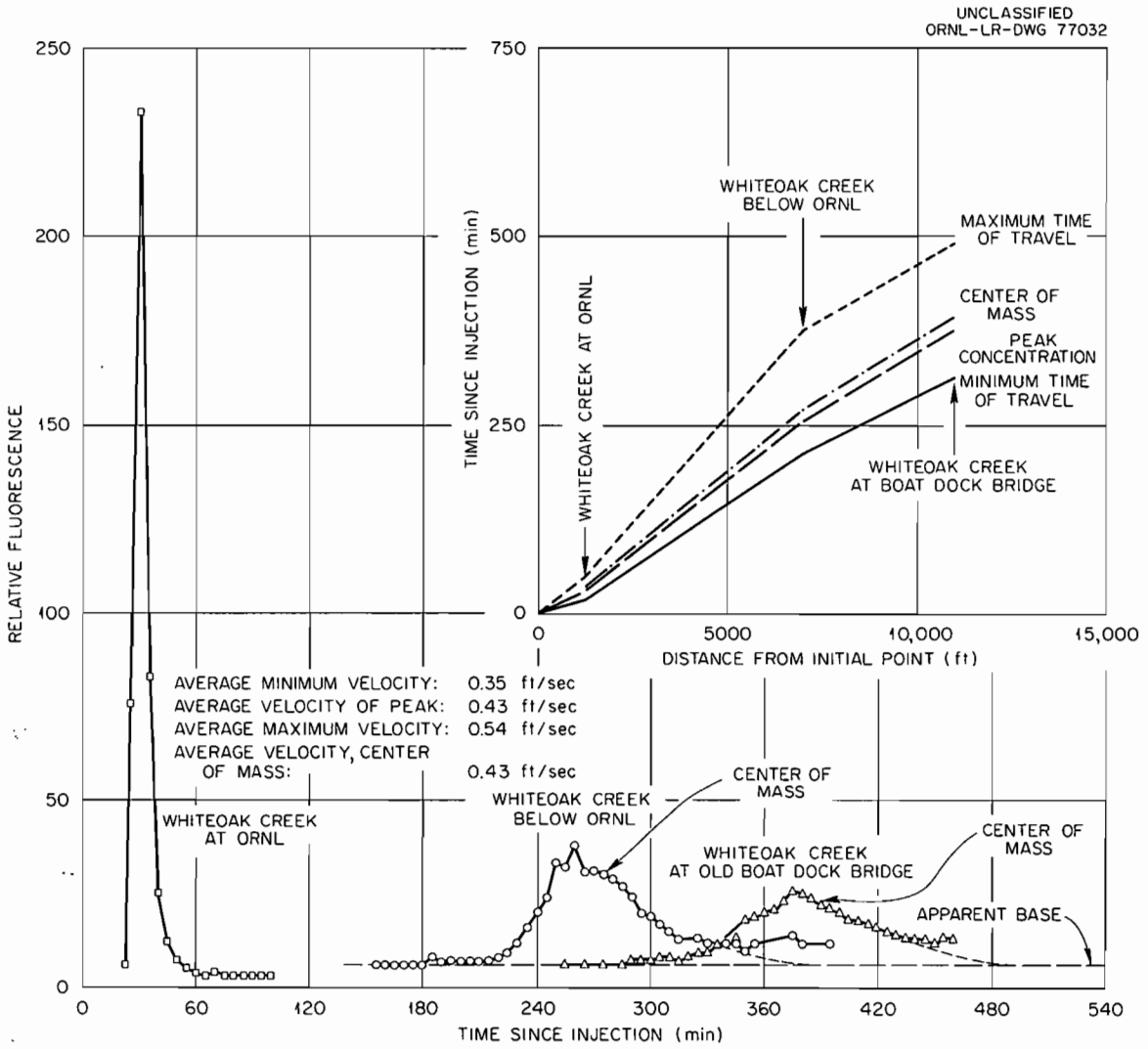

Fig. 9.3. Time-of-Travel Study, White Oak Creek, October 31, 1962.

UNCLASSIFIED
PHOTO 58793

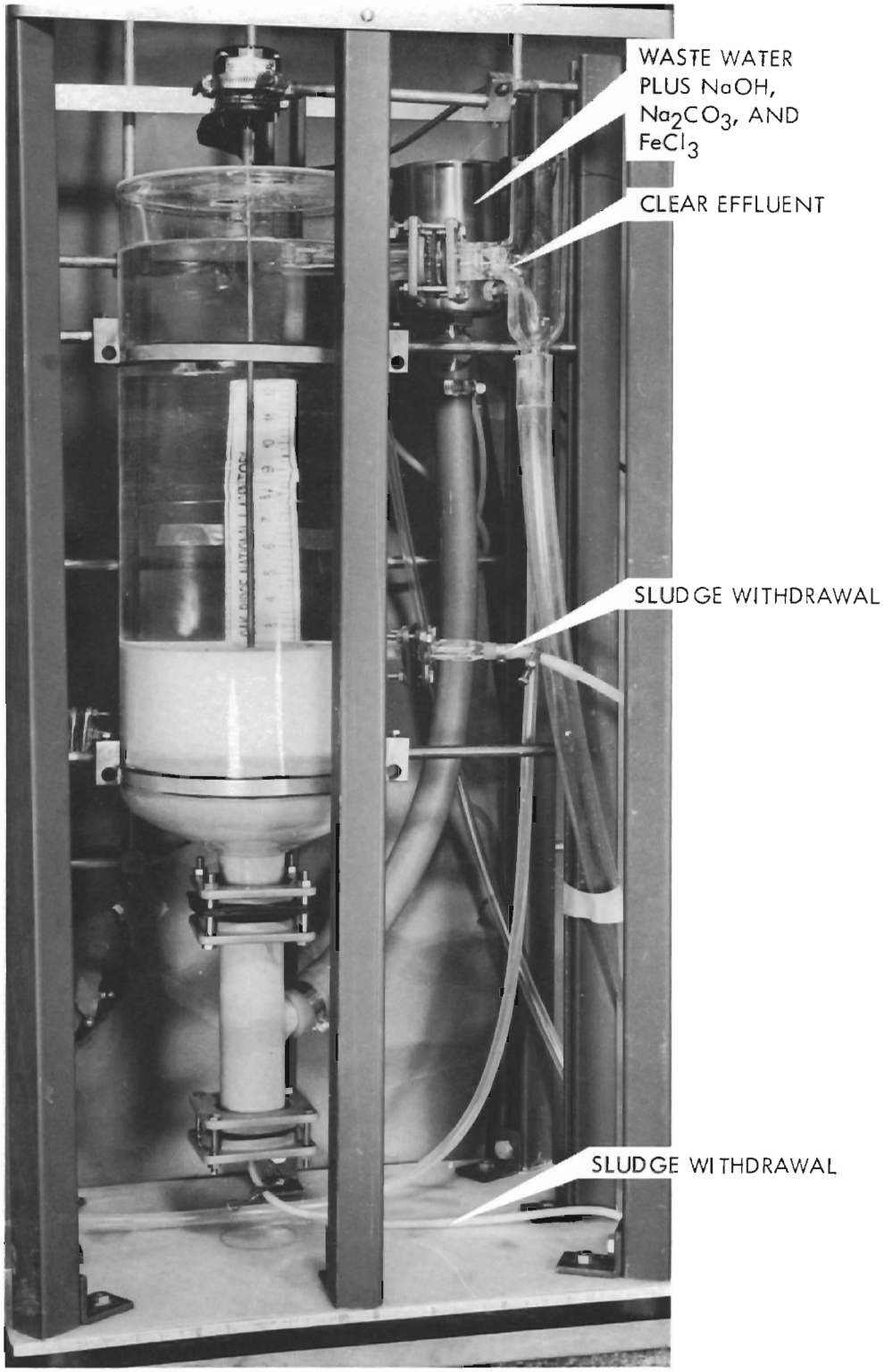

Fig. 10.1. Sludge Column-Clarifier for Softening Waste Water.

Table 10.1. Results with the Single-Chamber Agitated-Bed Precipitator

Column Diam (in.)	Type of Water Treated[a]	Feed Flow Rate (Gal ft^{-2} hr^{-1})	Reten. Time in Sludge (min)	Paddle Speed (rpm)	Effluent Turbidity (ppm)	Ratio: Bed Height to Diam	Effluent Total Hardness (ppm as $CaCO_3$)	Total P in the Feed (ppm as PO_4^{3-})
2	ORNL tap	8.4	--	30-60	--	3.4	2.2	--
2	ORNL tap	26.0	--	60	--	4	2.5	--
2	ORNL LAW[b]	8.4	--	30-60	--	4	4.5	2.6-3.4
3	ORNL tap	7.4	31	5	--	2	2.8	--
3	ORNL tap	12.3	19	25	--	2	2.5	--
3	ORNL tap	21.2	11	25	--	2	2.1	--
3	ORNL tap	27.5	8	25	--	2	3.5	--
4	ORNL tap	11.0	14	9	0	1	2.5	--
9	ORNL tap	10.0	22	2	--	0.5	2.5	--
9	ORNL tap	15.0	15	7	--	0.5	2.5	--
9	ORNL tap	20.0	16	5-10	--	1	2.3	--
9	ORNL LAW	10.0	33	6-10	1-1.5	1	2.0-3.5	1.6-2.3
9	ORNL LAW	15.0	23	10	0.5-1.5	1	2.0-4.0	1.7-2.0
9	ORNL LAW	20.0	17	7	0-3.5	1	2.0-4.0	0.9-1.6
9	ORNL LAW	26.0	13	10	0.5-1.5	1	2.0-2.5	1.0
9	ORNL LAW	40.0	8	10	1.0-2.0	1	2.0-4.0	1.4-3.0
9	ORNL LAW	60.0	5.6	10	1.5-6	1	2.5-4.5	1.9-2.1

[a]Composition: about 65 ppm Ca and 35 ppm Mg as $CaCO_3$; pH ~7 - 8.5.

[b]Low-activity waste.

Columns of diameters 2 to 9 in. are very similar in operation and physical behavior for equal linear flow rates. Thus, there appear to be no unusual problems in the scaleup of this process. The ratio of height of the sludge bed to the diameter of the column is not critical in the region 4 to 0.5, suggesting that it may be reduced still further. Sludge was removed from the column once or twice a day from a point about half a column diameter above the bottom. It was collected in a container and allowed to settle for about an hour, and the supernatant liquid was returned to the aqueous feed stream. An overall volume reduction of 1200 was obtained with the 9-in.-diam column with ORNL low-activity waste at 10 gal ft^{-2} hr^{-1} during four days of continuous operation. The other observation was that the hardness 1 in. above the bed and at the top of the column were the same, indicating that no further precipitation had occurred in the visually clear water.

One important factor is the presence of phosphates in the waste and the occlusion of $CaCO_3$ particles by the magnesium and ferric hydroxides and organic matter in the waste.[13,14] Both tend to decrease the rate of hardness removal. Phosphate inhibition can be overcome by pH control and the addition of carbonate and ferric hydroxide. The occlusion problem can be minimized by gentle agitation that liberates the heavier $CaCO_3$ particles from the light magnesium and ferric hydroxide precipitates and the organic matter.

10.2 Recovery of Foaming Agent

A sodium dodecylbenzene sulfonate recovery of 90% was achieved in a multistage countercurrent foam column at a flow rate of 7.5 gal ft^{-2} hr^{-1}. The feed solution initially contained 0.005 M each of NaOH and Na_2CO_3 and 50 ppm of NaDBS at pH 11.5.

10.3 Engineering Development

P. A. Haas

10.3.1 HTU_x Determinations

Engineering problems for the design and application of foam separation columns were studied in 6-in.-ID columns, using dodecylbenzenesulfonate as the surfactant and Sr^{89} tracer. One liquid-feed distributor gave the most uniform distribution of feed across the column cross-section and the lowest HTU_x values (0.5 to 2.3 cm) for liquid flows below 120 gal ft^{-2} hr^{-1}. This distributor and three others gave HTU_x values of 2 to 4 cm for flows of 140 to 160 gal ft^{-2} hr^{-1}. Use of a single tube on the column center line as a liquid-feed distributor gave large HTU_x's of 13 to 20 cm for 23- to 27-cm columns and very variable HTU_x values for longer columns.

The difference in HTU_x values for the spinnerette gas spargers with 50- and 80-μ diam holes were small, variable, and probably not significant, but both gave lower HTU_x values than the extra-coarse fritted-glass gas spargers. The bubble sizes are most uniform for the spinnerette with 80-μ diam holes, slightly less uniform for the other spinnerette, and much less uniform for the fritted glass. Use of the chi-square

statistical test with a 95% significance resulted in the acceptance of normal diameter size distributions for foam from spinnerette gas spargers and resulted in the rejection of the normal distributions for fritted-glass or porous-metal gas spargers.

10.3.2 Surfactant Recovery

The recovery of surfactant from the foam column effluent liquid was briefly investigated. This recovery would represent a significant economic saving, and besides, high surfactant concentrations in low-activity waste to be discharged would be objectionable. Low-activity waste treated with sodium hydroxide and other reagents to precipitate calcium and magnesium could probably be stripped to a residual concentration of about 5 ppm of dodecylbenzenesulfonate (DBS). Concentrations were determined by ultraviolet absorption for Trepolate F-95 (about 90% NaDBS or 85% DBS) and sodium hydroxide or sodium bicarbonate in demineralized water (Table 10.2). The minimum final concentrations decreased from 21 to 24 ppm at 0.001 M Na^+ to 4.3 ppm at 0.02 M Na^+. Foam separation columns should be operated with concentrations above those listed for the appearance of voids, but the recovery system could probably discharge liquid near the concentrations listed for sporadic foam discharge. Other impurities would probably affect the stability of the foam; therefore, the exact minimum concentrations possible for any particular system would have to be determined by experiments.

Table 10.2. Trapolate F-95 Recovery Tests

Conditions: 10-13 liters of solution charged to a 6-in.-ID column and foamed at 4 liters/min until the discharge of foam to the foam breaker became negligible. About 1 ft of 6-in.-diam drainage section above liquid surface.

Added Chemical		Trepolate F-95 Concentrations (ppm)			
Formula	Concentration (M)	Starting	Appearance of Voids	Sporadic Foam Discharge	Final Conc
$NaHCO_3$	0.001	100	35	27	24
$NaHCO_3$	0.001	40	--	--	21
NaOH*	0.01	21	21	--	12
NaOH	0.01	45	--	8	7
NaOH	0.02	40	12	5	4.3

*NaOH added to solution from previous test.

10.3.3 Decontamination of Synthetic Low-Activity Waste

The ORNL low-activity waste has concentrations of about 30 ppm for Ca^{++}, 7 ppm for Mg^{++}, 100 ppm for HCO_3^-, and smaller concentrations for other solutes, including Sr^{90} and Cs^{137}. Since the removal of all the calcium, magnesium and strontium by foam separation requires an excessive amount of surfactant and surface per volume of liquid, and since the preferential removal of the strontium does not appear possible, reduction of the calcium and magnesium concentrations prior to foam separation appears necessary. Conditions for removal by precipitation have been studied in the laboratory. Five runs were made to determine decontamination factors with process water plus Sr^{89} (to simulate low-activity waste) in the 6-in.-diam foam column.

By making process water (plus Sr^{89}) 5×10^{-3} M in NaOH and 5×10^{-3} M in Na_2CO_3, calcium carbonate and magnesium hydroxide were precipitated. Then, when this slurry was used as foam column feed for run 38, strontium decontamination factors were 81 to 162 (Table 10.3). This result shows that it is possible to remove a precipitated solid by the foam concurrently with the separation of a surface active complex. These smaller decontamination factors (DF's) compared with results for runs with a demineralized water feed, would be expected because the presence of soluble calcium and magnesium reduces the distribution factor for strontium. A somewhat similar result is shown for a precipitation with NaOH, Na_3PO_4, and $FeCl_3$ in runs 51B and 51C. This precipitate formed large, wet flocs and seem to cause increased channeling in the column.

The remaining runs were made with 10 ppm of FAB added to process water in order to simulate the detergent and total phosphorus content of ORNL low-activity waste. ("FAB" is widely used at ORNL.) While visible precipitation occurred within 1 min after the addition of the NaOH and Na_2CO_3 to the process water for run-38 feed, the addition of the same reagents to process water plus 10 ppm of FAB did not give any visible precipitation within 30 min. Decontamination factors in the foam column for the slurry feed that contained FAB were less than 3 (run 38, Table 10.3). The precipitation and loss of soluble Sr^{89} from solution continued in the samples of the column effluent. The same low DF's and the continued precipitation after leaving the column occurred when 50 ppm of PO_4^{3-} plus 4×10^{-3} N NaOH (run 40) or 5×10^{-3} N NaOH, 5×10^{-3} M Na_2CO_3 and 5×10^{-3} M precipitated $CaCO_3$ as a seed slurry (run 41) were used to precipitate the calcium and magnesium. Laboratory results indicated that the precipitation with PO_4^{3-} and Fe^{3+} as used for runs 51B and 51C is much less sensitive to the presence of "FAB." An experiment was made at run-51 conditions with sufficient "FAB" added to produce a 10-ppm concentration. A flocculated precipitate formed immediately, and the column effluent did not show continued precipitation. Analytical results are not complete.

From these results, it appears that the foam column could handle precipitated $CaCO_3$ and $Mg(OH)_2$ concurrently with the foam separation of strontium. However, the precipitation of the calcium and magnesium by simple mixing of the low-activity waste with NaOH and Na_2CO_3 solutions was too slow to permit practical hold-up

Table 10.3. Decontamination of Simulated Low-Activity Waste in the 6-in.-ID Foam Column

Surfactant: DBS added to liquid pot as Trepolate F-95.

Feed: Process water with following sequence of additions with mixing: "FAB" (when used); Sr^{89} tracer; precipitating reagents except $FeCl_3$ as one concentrated, mixed solution, $FeCl_3$ solution.

Column conditions: Extra-coarse sintered-glass gas spargers, coarse or fine liquid feed distributors, 10.5-in.-ID drainage section.

Item Measured	Symbol	Units	Run Numbers									
			38A	38B	38C	39A	39B	40A	40B	41B	51B	51C
"FAB" added to feed	--	ppm	0	0	0	10	10	10	10	10	0	0
NaOH added to feed	--	10^{-3} M	5	5	5	5	5	4	4	5	4	4
Na_2CO_3 added to feed	--	10^{-3} M	5	5	5	5	5	0	0	5	0	0
PO_4^{3-} as Na_3PO_4	--	ppm	0	0	0	0	0	50	50	0	50	50
Precipitated $CaCO_3$ as slurry	--	10^{-3} M	0	0	0	0	0	0	0	5	0	0
Fe as $FeCl_3$	--	ppm	0	0	0	0	0	0	0	0	10	10
Time from reagent addition to run	--	hr	24	25	26	3	4	3	4	4	2	3
Liquid rate in	$L + E_p$	cc/min	750	1100	1800	750	1800	750	1100	1100	1100	600
Gas rate	V/a	cc/min	4100	4100	4100	4100	4100	4100	4100	4100	4100	4100
Condensed foam rate	E_p	cc/min	16	17	19	18	19	16	15	13	40	20
Net liquid rate	L	cc/min	730	1080	1780	730	1780	730	1085	1090	1060	580
Surfactant (Trepolate) concentration out (calculated)	--	ppm	270	270	270	270	270	270	270	270	270	350
Countercurrent length	Z	cm	50	50	50	50	50	86	86	86	86	86
Surface area rate	V	10^5 cm^2/min	4.4	4.6	4.8	5.2	5.2	4.9	5.3	5.1	4.8	4.8
Surface/liquid ratio	V/L	sq cm/cc	600	430	270	710	290	670	480	470	440	820
Gross β in liquid feed	x_2	cpm/cc	9200	9200	9200	9200	9200	8200	8200	8800	9400	9400
Gross β in liquid out	x_b(also x_1)	cpm/cc	57	89	114	4960	4600	4100	4600	7500	290	390
Gross β in condensed foam	$y_2V + x_i E_p$	10^3 cpm/min	6760	10,150	15,400	1700	4200	2670	2800	1000	--	--
Gross β material balance	--	%	98	101	95	78	77	93	87	95	--	--
Decontamination factor	$DF = x_2/x_b$	dimensionless	162	103	81	1.9	2	2	1.8	1.2	32	24
Volume reduction	L/E_p	dimensionless	47	59	95	42	95	47	73	85	28	30

times for a full-scale waste-treatment plant. This verifies the advantage of using a clarifier to increase the rates of precipitation, as investigated in laboratory studies, although the one-step removal of precipitated calcium and magnesium and complexed strontium may be possible when they are precipitated by $NaOH-Na_3PO_4-FeCl_3$.

11. REFERENCES

1. 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).

2. Chem. Technol. Div. Ann. Prog. Rept. May 31, 1961, ORNL-3153 (Sept. 14, 1961).

3. 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).

4. Personal communication, W. Davis, Jr. and E. Schonfeld, May 1962.

5. Evaluation of Ultimate Disposal Methods for Liquid and Solid Radioactive Wastes, Part I. Interim Liquid Storage, ORNL-3128 (Aug. 7, 1961).

6. Health Physics Division Annual Progress Report for Period Ending July 31, 1959, ORNL-2806 (Oct. 23, 1959).

7. Health Physics Division Annual Progress Report for Period Ending July 31, 1961 ORNL-3189 (Oct. 24, 1961).

8. Project Hope, A Chemical Reprocessing Plant for a Nuclear Power Economy, ORNL-1638 (Jan. 21, 1954).

9. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for June and July 1961, ORNL-TM-15 (Oct. 24, 1961).

10. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for February and March 1962, ORNL-TM-252 (Sept. 10, 1962).

11. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for October and November 1961, ORNL-TM-133 (Mar. 13, 1962).

12. T. F. Lomenick and K. E. Cowser, Status Report on Evaluation of Solid Waste Disposal at ORNL: II, ORNL-3182 (Dec. 29, 1961).

13. R. E. Blanco and E. G. Struxness, Waste Treatment and Disposal Progress Report for April-May 1962, ORNL-TM-376 (Nov. 5, 1962).

14. R. E. Blanco, Chem. Technol. Div., Chem. Dev. Sec B, Summary Progress Report, Jan. 1-July 1, 1962, ORNL-TM-377 (Oct. 31, 1962).

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-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
26. W. E. Clark
27. K. E. Cowser
28. F. L. Culler
29. W. Davis, Jr.
30. W. de Laguna
31. F. M. Empson
32. D. E. Ferguson
33. E. J. Frederick
34. H. W. Godbee
35. H. E. Goeller
36. J. M. Googin
37. P. A. Haas
38. C. W. Hancher
39. C. E. Haynes
40. R. F. Hibbs
41. R. R. Holcomb
42. J. M. Holmes
43. D. G. Jacobs
44. W. H. Jordan
45. H. Kubota
46. T. F. Lomenick
47. K. Z. Morgan
48. R. J. Morton
49. E. L. Nicholson
50. F. L. Parker
51. J. J. Perona
52. R. M. Richardson
53. J. T. Roberts, IAEA, Vienna
54-55. E. G. Struxness
56. J. C. Suddath
57. J. A. Swartout
58. T. Tamura
59. J. W. Ullmann
60. M. E. Whatley

EXTERNAL DISTRIBUTION

61. E. L. Anderson, AEC, Washington
62. W. G. Belter, AEC, Washington
63. H. Bernard, AEC, Washington
64. J. A. Lieberman, AEC, Washington
65. W. H. Regan, AEC, Washington
66. H. M. Roth, AEC, ORO
67. C. S. Shoup, AEC, ORO
68. J. R. Horan, AEC, Idaho
69. K. K. Kennedy, AEC, Idaho
70. J. A. Buckham, Phillips Petroleum Company
71. J. A. McBride, Phillips Petroleum Company
72. C. M. Slansky, Phillips Petroleum Company
73. H. J. Carey, Jr., Carey Salt Company, Hutchinson, Kansas
74. C. W. Christenson, Los Alamos Scientific Laboratory
75. J. C. Frye, State Geological Survey, Div., Urbana, Ill.
76. W. B. Heroy, Sr., Geotechnical Corp., Dallas, Texas
77. E. F. Gloyna, University of Texas, Austin
78. W. J. Kaufman, University of California, Berkeley
79. L. Silverman, Harvard Graduate School of Public Health
80. G. M. Fair, Harvard University, Pierce Hall

81. H. A. Thomas, Jr., Harvard University, Pierce Hall
82. John Geyer, Johns Hopkins University
83. C. R. Naeser, George Washington University
84. W. A. Patrick, Johns Hopkins University
85. H. C. Thomas, University of North Carolina
86. L. P. Hatch, Brookhaven National Laboratory
87. H. H. Hess, Princeton University
88. Abel Wolman, Johns Hopkins University
89. O. F. Hill, Hanford
90. C. R. Cooley, Hanford
91. E. R. Irish, Hanford
92. A. M. Platt, Hanford
93. W. H. Reas, Hanford
94. G. Rey, Hanford
95. R. L. Moore, Hanford
96. W. H. Swift, Hanford
97. J. H. Horton, Savannah River
98. R. M. Girdler, Savannah River
99. Harvey Groh, Savannah River
100. C. H. Ice, Savannah River
101. J. W. Morris, du Pont, Savannah River
102. C. M. Patterson, du Pont, Savannah River
103. W. B. Scott, Savannah River
104. E. B. Sheldon, Savannah River
105. D. S. Webster, Savannah River
106. V. R. Thayer, du Pont, Wilmington
107. A. A. Jonke, Argonne National Laboratory
108. S. Lawroski, Argonne National Laboratory
109. W. A. Rodgers, W. R. Grace and Company, Naperville, Ill.
110. J. J. Weinstock, RAI
111. J. F. Honstead, IAEA, Vienna
112. D. W. Pearce, IAEA, Vienna
113. R. L. Nace, USGS
114. P. H. Jones, USGS
115. C. P. Straub, U. S. Public Health Service
116. Dade Moeller, U. S. Public Health Service, Winchester, Mass.
117. W. J. Lacy, Office of Civil Defense, Washington, D. C.
118. J. E. Crawford, U. S. Bureau of Mines, Washington, D. C.
119. J. W. Watkins, U. S. Bureau of Mines, Washington, D. C.
120. AECL, Chalk River, Attn: C. A. Mawson, I. L. Ophel, L. C. Watson.
121. AEC, Sidney, Australia, Attn: R. C. Cairns, L. Keher
122. AERE-Harwell, Attn: H. J. Dunster
123. AERE-Harwell, Attn: R. H. Burns, R. D. B. Johnson
124. CEA, Grenoble, Attn: G. Wormser
125. CEA, Saclay, Attn: M. Duhamel, M. Menou, M. Gailledreau

126. CEA, Fontenay-aux-Roses, Attn: P. Regnaut, P. Faugeras, M. Bourgeois
127. Centre d'Etude Nucleaire, Mol, Belgium, Attn: L. Baetsle
128. Centre d'Etude Nucleaire, Mol, Belgium, Attn: P. de Jonghe
129. Euratom (ISPRA), Casella Postale No. 1, Attn: M. Lindner
130. Eurochemic, Mol, Belgium, Attn: E. Luscher, H. Moeken, R. Rometsch
131. Jitender D. Sehgal, Bombay, India
132-146. DTIE