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WASTE TREATMENT AND DISPOSAL PROGRESS REPORT

FOR JUNE AND JULY 1962

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CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT FOR JUNE AND JULY 1962

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DATE ISSUED

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

ABSTRACT

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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1. INTRODUCTION

This report is the eighth 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 of concern include those of high, intermediate, and low levels of radioactivity in liquid, solid, or gaseous states.

Principal current emphasis is on high- and low-activity liquid wastes. Under the integrated plan, low-activity wastes, consisting of very dilute salt solutions such as cooling water and canal water, would be treated by scavenging and ion exchange processes to remove radioactive constituents, and the water would then 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 liquids to solids by high-temperature "pot" calcination or fixation in the final storage container (pot) itself and storage in a permanently dry environment such as a salt mine. This is undoubtedly the safest method since complete control of radioactivity can be ensured within present technology during treatment, shipping, and storage. Another approach is disposal of the liquid directly into sealed or vented salt cavities. Research and development work is planned to determine the relative feasibility, safety, and economics of these methods, although the major effort will be placed on conversion to and final storage as solids.

Tank storage or high-temperature calcination of intermediate-activity wastes may be unattractive because of their large volumes, and other disposal methods will be studied. One method, 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 feasible.

Environmental research on the Clinch River, motivated by the need for safe and realistic permissible limits of waste releases, is included in this program. The objective is to obtain

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*ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, ORNL-TM-169, ORNL-TM-252, and ORNL-TM-376.

a detailed characterization of fission product distribution, transport, and accumulation in the physical, chemical, and biological segments of the environment.

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. A general flowsheet was shown previously.[1] In the second phase, enough additives are used to induce melting to form a glasslike material in which the fission products are fixed.

2.1 Evaporation-Calcination

J. C. Suddath C. W. Hancher

Process and equipment development for the ORNL Pot Calcination Process is continuing, with the principal objective during this period being to provide experimental data necessary for the design of a pilot plant facility.

A test (R-67) using TBP-25 simulated feed was made to (1) test the design of a mercury trap, (2) evaluate gravity feeding to the calciner, and (3) determine the effect of prolonged heating on the calcined cake.

2.1.1 Performance of the Mercury Trap

The mercury trap retained only 5.5% of the mercury contained in the feed to the system. A poor material balance for mercury indicated that only 56.3% of the mercury had been accounted for, with 72% of the recovered mercury in the evaporator. During the filling period, the calciner was overfilled, resulting in a large quantity of the calciner feed being caught in the mercury trap, which could explain its poor performance. Tests to date indicate that even under good conditions, a large fraction of the mercury passes through the trap and is retained by the evaporator.

2.1.2 Gravity-Feed Results

The static head for the test was 7 to 9 ft from the head tank level to the calciner head flange. During this test, the

evaporator was used to concentrate and acid strip the calciner condensate, but the evaporator product was not recycled. Maximum feed rate to the calciner was 30 liters/hr, due to pressure drop in the feed line and valve. It required 9 hr to bring the calciner up to the operating level at the low feed rate.

The calciner overfilled during the 15th hour of operation, probably due to inadequate freeboard in the top of the calciner, resulting in a large carry-over of concentrated waste solution to the mercury trap and back to the evaporator. The average feed rate for the 23 hr of filling was 17 liters/hr, but only 80% of the feed was retained in the pot and calcined.

2.1.3 Postcalcination Pressure Test

The cake was thoroughly calcined for 24 hr after the feeding period while connected to the normal off-gas system. A simulated storage test was made in which the calciner vessel was sealed with a cap and then reheated to 900°C. During the reheat period the pressure rose to 4 psig (due to the thermal expansion of the gas in the cavity) and then decreased slowly to atmospheric pressure over the next 4 hr. The calciner was held at 900°C for an additional 96 hr with no detectable pressure change.

2.1.4 Results and Conclusions

The feed for test R-67 was standard TBP-25 feed, 45 g/liter aluminum, 6.5 M nitrate (Table 1). The purpose was to test the operation of a gravity feed head tank using feed that had not been previously evaporated. The hydraulic head from the feed tank to the calciner flange was 7 to 9 ft. The mode of operation for this test was as follows: The feed was fed by gravity from the feed hold tank to the calciner, which operated on liquid-level control. The calciner condensate was condensed and then routed to the evaporator. The evaporator was charged with 25 liters of water at the start of the test, and the steam was set at a very low boilup rate to keep the evaporator condensate warm. The steam was controlled by an evaporator liquid level maintaining a constant inventory. The water addition for acid stripping was controlled by the electrical conductivity of the evaporator condensate. The evaporator was operated at a 1-psig vacuum.

The flow through the feed valve to the calciner was not large enough, only a 15 to 30 liters/hr. It took 9 hr to fill the pot to the operating liquid level of 60 liters. During this time, serious foaming occurred, and it may have been caused by operating at a low level and high heat flux. During the 15th hour of operation, a large amount of foaming occurred, resulting in the mercury trap being partially filled with foam and calciner feed.

Table 1. Feed and Solid Composition for Test R-67

	H^+ (M)	Al^{3+}	NO_3^-	Fe^{3+}	Hg^{2+}
Feed	1.61	45.1	420	0.355	5.73
Solid % wt					
Top		47.7	0.010	0.88	0.94
Middle		47.7	0.006	1.85	0.74
Bottom		49.5	0.006	1.33	0.49
Average		47.9	0.007	1.35	0.73
Total wt	30 kg				
Bulk density	0.50 g/cc				

The calciner condensate sample contained a large amount of aluminum. The feed period continued for 23 hr. A total of 391 liters of feed was used, with an average feed rate of 17 liters/hr. The calcining period was 24 hr.

The resulting solids were satisfactorily calcined. The average nitrate content of the calcined solids was 70 ppm, however, the residual mercury in the solids was 0.7%; 0.9% at the top to 0.5% at the bottom of the calcined solids (Table 1). The bulk density was 0.50 g/cc. The thermal conductivity, averaged over 42 hr of filling time, was 0.99 Btu hr^{-1} ft^{-1} $^{o}F^{-1}$ from the skin to the first thermocouple at 1 in. and 1.06 Btu hr^{-1} ft^{-1} $^{o}F^{-1}$ from the skin to the center line. The material balances for test R-67 were satisfactory except for mercury and iron. The nitrate material balance was 94.3% (Table 2). The aluminum material balance was 83.3%. The iron balance was high, up to 250%, principally in the solid, probably contributed by corrosion of the system. The mercury material balance was 50%. There was a large discrepancy in the calciner condensate mercury samples and the evaporator samples. The 50% material balance was calculated from the evaporator samples. However, if the calciner condensate samples were used, a 90% balance could be obtained. Water-to-feed ratio was 2.9. This was lower than usual because the evaporator was used as a calciner condensate receiver only.

The mercury trap only retained 5% of the mercury fed to the system. The reason the mercury trap operated so poorly may be that it was partially filled with calciner feed. The off-gas line to the mercury trap was kept at about 500°C. The top of the calciner was kept at about 300 to 400°C. A large fraction of the mercury passed through the mercury trap and was caught in the evaporator, from 40 to 80%, depending on the method of calculating the

Table 2. Material Balance for Waste Calciner Test R-67

	NO_3^-		Al^{3+}		Fe^{3+}		Hg^{2+}	
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
IN								
Feed, g	164,000		17,986		158		2,346	
OUT								
Evap.	7,700	4.7	673	3.8	27	17	953.8a	40.7
Cond.	147,173	89.6	1.9	0.01	1.5	1.0	18.4	0.8
Solid	2.0		14,300	79.5	405	252	218	9.3
	70 ppm							
Total		94.3		83.3		270		50.8

Other Results

System feed rate, liters/hr	17.0
Total feed, liter	391
Water-feed ratio	2.92
Feed time, hr	23
Calcine time, hr	24
Bulk density, g/cc	0.50
Off-gas, ft^3	Down

[a]825 g, 35.2% in evaporator.
129 g, 5.5% in mercury trap.

material balances. Removing the mercury trap would allow all the mercury to accumulate in the evaporator, and draining the evaporator between tests may prove to be the best method of operation.

2.2 Pilot Plant Design and Mechanical Test Program

J. M. Holmes E. J. Frederick J. O. Blomeke

A pilot plant to demonstrate the pot, spray, and possibly the rotary-ball calciners will be located at Hanford and installed in the new Fuels Recycle Pilot Plant Building. This facility is now in Title 2 design. Process design of the pot and spray calciners and associated off-gas cleanup equipment has been started. The cell available for the equipment will have a 23 by 25 ft floor and a height of 27 ft to the bottom of the crane hook. Four feet of high density (200 lb/ft^3) concrete shielding will be provided on one wall, and

the remaining walls will have at least 5.33 ft of normal-density concrete. Shielding calculations indicate that an 8-in.-diam by 6-ft-long calcination pot filled with 180-day-old Purex waste will give a dose rate of about 0.6 mr/hr through the shield when placed 3 ft from the inside wall. It is presently planned to place the vessels in four units that can be removed from the cell remotely by disconnecting the piping and moving each unit with the cell crane into the air lock, where it can be decontaminated. Waste feed will be brought in by transfer cask from the Purex or Redox plants.

A preliminary process meeting was held with Hanford personnel to discuss the program. ORNL will continue work on the nonradioactive pot-calcination process, with emphasis on the development of a mercury trap, gravity feeding to the calciner, a conductivity cell for the evaporator over-head acidity, and a pump capable of feeding Purex solutions containing solids to the calciner. An engineering program to develop a glass-making process for the pot calciner will also be started. The mechanical program at Lockheed Nuclear Products will be continued to its completion except that the development of a welding machine will be transferred to Hanford for inclusion in their remote welding closure program for fission product containers. ORNL will undertake a flowsheet study of the rotary calciner.

2.2.1 Welding Program

The test welds made by the automatic method developed at Lockheed have been sectioned and photomicrographed. A report is in preparation on the results.

2.2.2 Grayloc Seal Leak Test

Mechanical problems in the mass spectrometer system prevented this test from being completed. The test and evaluation will be continued as soon as the necessary adjustments are made to the apparatus.

2.2.3 In-Cell Testing

The furnace, dolly, and respective control system were installed, and operational checks have begun.

Fabrication of the filling station, clamp, and two calciner pots (welded closure and Grayloc closure) were completed at ORNL and sent to Lockheed Nuclear for installation in the test cell. The testing procedure to be used for evaluating the mechanical equipment performance was prepared and transmitted to Lockheed.

2.2.4 Calciner-Pot Irradiation Experiment

To assess the effects of internal fission product heat on the calcined cake during long-term storage, it was proposed to perform an experiment in which a pot of calcined solids would be exposed to the gamma flux of an operating reactor.

Calculations indicate that during 1-yr storage of 180-day cooled calcined Purex waste the integrated internal dose that the cake would receive will be about 10^{11} rads. In order to reduce the reactor residence time for such an experiment, it was suggested that a U^{235} spike be added to the cake and that the internal fission heat generated be utilized. However, the quantity of U^{235} and the neutron flux to which the pot could be exposed are limited by the low thermal conductivity of the cake itself. Further work on planning of the experiment has been curtailed because of smaller in-cell experiments being planned both at ORNL and HAPO with full-activity-level waste.

2.3 Laboratory-Scale Development

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

2.3.1 Fixation in Glass

Studies were started in order to investigate the possibility of retaining all the sulfate in high-sulfate Purex waste solutions (Table 3) in the solid product when the latter is a glass. Past experience with this waste solution indicated that glasses can be formed after driving out part or all of the sulfate or by quenching small batches of melt. Slow cooling of large batches that lost little sulfate invariably resulted in the formation of crystalline materials. (Glasses are preferred to crystalline products because of their smaller micro-surface areas, greater tendency toward homogeneity, and property of softening gradually with increasing temperature. A crystalline solid may, however, be satisfactory, depending upon its solubility, homogeneity, and melting characteristics. In general, thermal conductivity is somewhat greater for crystalline solids than for glasses.) The problem should be much less acute for the Purex wastes that contain lower amounts of sulfate. If the problem can be solved for the most intractible type (i.e., the variation containing the most SO_4, fixation of the other types will be relatively simple. Existing and expected Purex wastes vary rather widely in composition (Table 3).

Ten melts were prepared by adding varying amounts of Ca^{2+}, Na^{+}, $H_2PO_2^{-}$ and Al^{3+} to Purex waste solution (Table 4), evaporating, and then calcining to 650°C. Compositions were chosen so as to produce melts containing a theoretical waste-oxide content of 39%. Weight losses below 650°C were assumed to be due to denitration and dehydration. Samples of the calcines were then placed on a

Table 3. Various Compositions of Purex Waste Solutions (Exclusive of Fission Products)

Constituent	Types of Waste									
	High Sulfate[a]	Formaldehyde[b] Killed, High Sulfate	Van Tuyl[c]			1965[d] FTW	Nonsulfate[e]		SRP[f,g] Gelatin Flowsheet	SRP, $KMnO_4$ Flowsheet No Primary Recovery
			Maximum	Best Estimate	Minimum		Maximum	Minimum		
H^+	5.6	0.3	9.0	7	5.0	0.5	h	h	6.0	4.0
Na^+	0.6	1.2	2	0.8	0.2	0.30	0.60	0.05	0.59	2.0 (est)
K^+									0.0008	0.5 (est)
Al^{3+}	0.1	0.2	0.3	0.1	0.03	0.05	0.20	0.01	0.39	0.2
Fe^{3+}	0.5	1.0	0.3	0.2	0.15	0.10	0.05	0.005	0.05	0.02
Cr^{3+}	0.01	0.02	0.02	0.01	0.005	0.02	0.006	0.006	h	h
Ni^{2+}	0.01	0.02	0.02	0.01	0.002	0.01	0.006	0.006	h	h
Hg^{2+}	h	h	h	h	h	0-0.0035	0.02	0.02	h	h
Mn^{2+}	h	h	h	h	h	h	h	h	h	0.02
U	h	h	0.02	0.01	0.002	h	h	h	h	h
SO_4^{2-}	1.0	2.0	1	0.3	0.15	0.15	0	0	0.1	h
PO_4^{3-}	h	h	h	h	0.01	0.005	0.02	0.02		0.02
SiO_3^{2-}	h	h	h,i	h,i	h,i	0.01	h	h	0.0008	h
F^-	h	h	h	h	h	0.02	h	h	0.001	h
NO_3^-	bal	bal	bal	bal	bal	bal	bal	bal	bal	7.5
Gallon/ton U	40	20	h	h	h	82	h	h	h	h

[a]H. W. Godbee and J. T. Roberts, ORNL-2986, p 13.

[b]From low temperature denitration and concentration to 1/2 vol of high-sulfate waste.

[c]J. J. Shefcik, private communication to J. M. Holmes, Aug. 11, 1961.

[d]A. M. Platt, private communication to W. E. Clark, May 22, 1962.

[e]Assembled from data of G. B. Barton, Report of 2nd Working Meeting on Fixation of Radioactivity in Stable Solid Media, Idaho Falls, Sept. 27-29 (1960), book 2, p 463 (TID-7613).

[f]W. Jacober, private communication to A. F. Rupp, Nov. 3, 1961.

[g]Waste also contains 0.09 M hydrazine. Total % nonvolatile = 12.7

[h]Not specified.

[i]These wastes contained 4 to 5% solids, predominately zirconium phosphate, silica, and metal silicates.

Table 4. Theoretical Compositions of Melts Containing 39% Simulated Purex Waste Oxides

	Melt No.									
	1	2	3	4	5	6	7	8	9	10
Additives (moles/liter)										
$NaH_2PO_2.H_2O$	1.67	1.56	1.46	1.67	1.56	1.46	1.26	1.26	1.26	1.26
NaOH	0.22	0.33	0.42	0.88	0.98	1.08				
$Ca(OH)_2$	0.66	0.79	0.92	0.22	0.40	0.53	1.06	0.92	0.78	0.92
H_3PO_3							0.41	0.51	0.61	0.20
$Al(NO_3)_3.9H_2O$										0.43
Theoretical oxides (wt %)										
Fe_2O_3	11.1	11.1	11.1	11.2	11.2	11.2	11.0	11.0	11.0	11.0
Cr_2O_3	0.2	0.2	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	0.2	0.2
Al_2O_3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	7.7
Na_2O	21.7	21.7	21.7	27.8	27.6	27.5	16.0	16.0	16.1	16.0
SO_3	21.0	21.0	21.0	21.2	21.2	21.1	20.8	20.9	20.9	20.9
P_2O_5	33.7	31.5	29.5	34.1	31.7	29.6	33.4	35.5	37.6	29.3
CaO	10.5	12.6	14.8	3.6	6.3	8.5	16.8	14.7	12.4	14.7
RuO_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	100.0	99.9	100.1	99.9	100.0	99.9	100.0	100.1	100.0	100.1
Wt % of original SO_3 lost after prolonged heating at 1100°C	89.3	83.4	73.1	86.8	75.6	58.0	68.8	44.0		63.2
Na equivalents	2.49	2.49	2.48	3.15	3.14	3.14	1.86	1.86	1.86	1.86
Ca equivalents	1.32	1.58	1.84	0.44	0.80	1.06	2.12	1.84	1.56	1.84
Al equivalents										1.29
Total cation equivalents[a]	3.81	4.07	4.32	3.59	3.94	4.20	3.98	3.70	3.42	3.70[a]
PO_3^- equivalents	1.67	1.56	1.46	1.67	1.56	1.46	1.67	1.77	1.87	1.46
SO_4^-	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Total anion equivalents	3.67	3.56	3.46	3.67	3.56	3.46	3.67	3.77	3.87	3.46
Excess cation equivalents[a]	0.14	0.51	0.86	-0.08	0.38	0.74	0.31	-0.07	-0.45	0.24
gm eqs (Na + Ca)/ gm eqs (SO_4^{2-} + PO_3^-)	1.04	1.14	1.25	0.975	1.11	1.21	1.08	0.982	0.884	1.07
Softening point (°C)	825	850	875	800	800	850	1000	950	875	1000
Description of melt	light green, micro-crystal-line	light green, crystal-line	light green, crystal-line	light gray-green, micro-crystal	light gray, crystal-line	light green-gray, crystal	Shiny gray, metal-lic-type	Shiny gray, metal-lic	green, glassy & crys-talline portions	brown-gray, crystal-line

[a]Only Na and Ca are included in these totals.

recording thermobalance and the temperature raised to 1100°C at a rate of 6°C/min. Upon reaching 1100°C the sample was kept at this temperature and the weight-loss-vs-time-curve recorded. Other portions of each calcined product were heated in a muffle furnace with occasional observation in order to determine approximate softening temperatures.

Three series of three melts each were prepared. In each series the gram equivalents of sodium were held constant at 2.49, 3.14, and 1.86, respectively, per liter of solution. The gram equivalents of calcium and of phosphorous (as metaphosphate, PO_3^-) were varied so as to give products in which the ratio

$$\frac{\text{gm equivalents (Na + Ca)}}{\text{gm equivalents } (SO_4^{2-} + PO_3^-)}$$

varied from 1.04 to 1.25, from 0.98 to 1.21, and from 1.08 to 0.88, respectively. (In calcination-nonmelting-experiments sulfate can be completely retained in the solid if the above ratios are > 1. The presence of the network formers, P_2O_5, B_2O_3, and SiO_2, and the formation of a melt, introduces complications because equilibrium conditions exist more readily in a melt. It has not been proved that sulfate volatility can be completely prevented in glass formation. A low ratio is desirable for the formation of glass; glasses in which the ratio is > 1 has never been observed in these studies.) A tenth melt was prepared to which aluminum was added, the PO_3^- being decreased correspondingly. Sulfate was lost from all melts at temperatures of 50 to 100°C or more above the softening point (Fig. 1a-c). In each series studied, the rate of sulfate loss at a given temperature was, as expected, less for the melt with the greatest excess of cation equivalents (Table 4) (Fig.1a-c). This correlation was not valid for comparison of melts in the different series. For example, melt 8, in which anion and cation equivalents were almost exactly balanced, lost about 41% of its sulfate on heating at 1100°C for 100 min, compared with about a 72.5% loss for melt 3 in which the cation/anion ratio was 1.25 (Fig. 2). From a practical standpoint a comparison would need to be made at a temperature a given number of degrees above the softening points since these varied from about 800 to 1000°C. On this basis either melts 5 or 6 might be expected to retain the greatest percentage of sulfate because their losses at about 100°C above the softening points were only 4 to 5% (Fig. 1b). For a valid comparison, however, these need to be kept at constant temperature for a long time. Softening points increased with increase in CaO content (Fig. 3). Operational temperatures can be expected to be as much as 100°C above the softening temperature, but should be as low as practicable. Eleven hundred degrees centigrade probably approaches the extreme maximum temperature allowable if a stainless steel calcination pot is to be used.

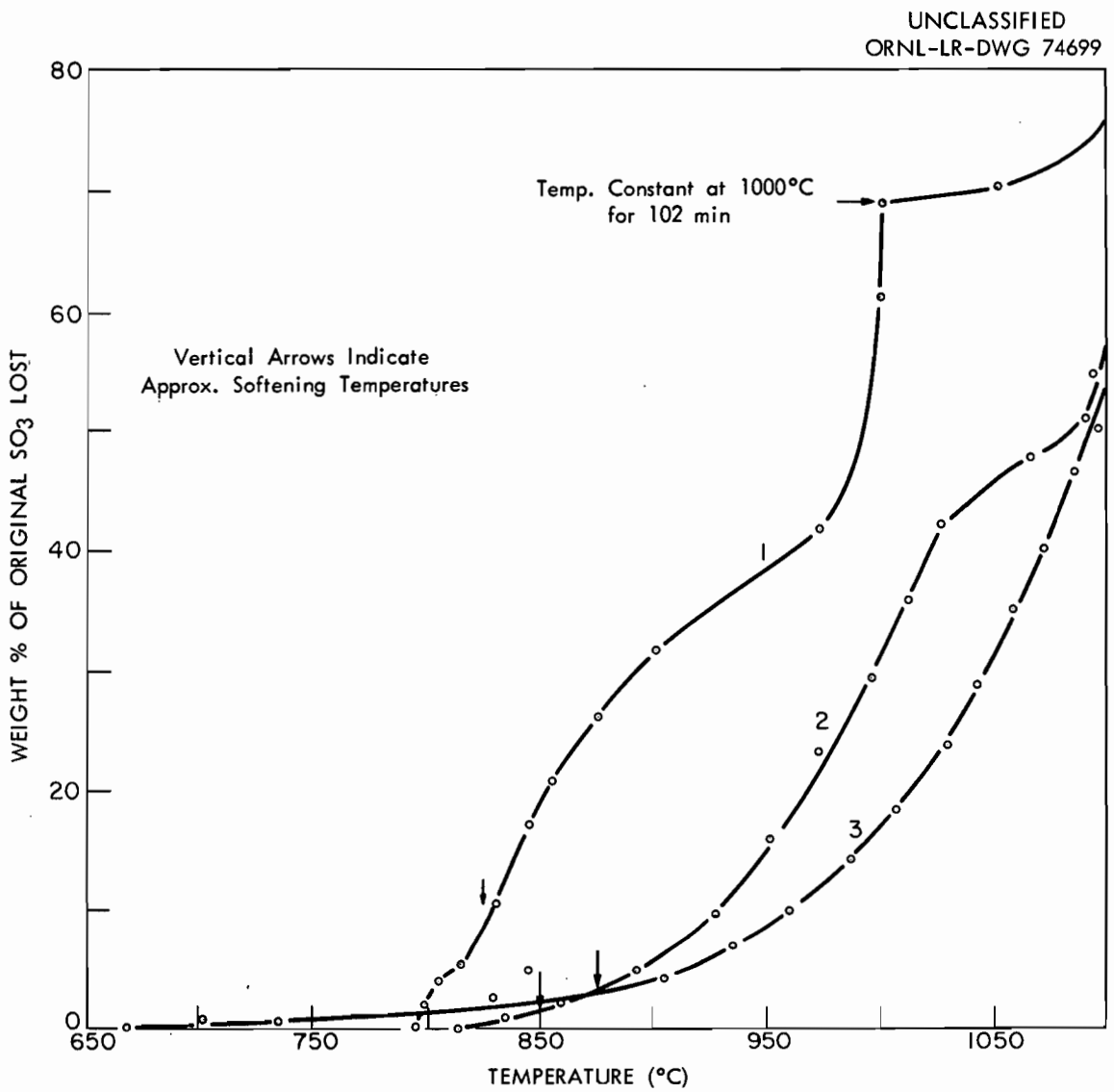

Fig. 1a. Sulfate Loss from Purex Melts. Na_2O constant at 22 wt %; temperature rise = 6°C/min.

Curve 1: CaO, 10.5%, P_2O_5, 33.7%; excess of cations over anions, 0.14 N.

Curve 2: CaO, 12.6%; P_2O_5, 31.5%; cation excess, 0.51 N.

Curve 3: CaO, 14.8%; P_2O_5, 29.5%; cation excess, 0.86 N.

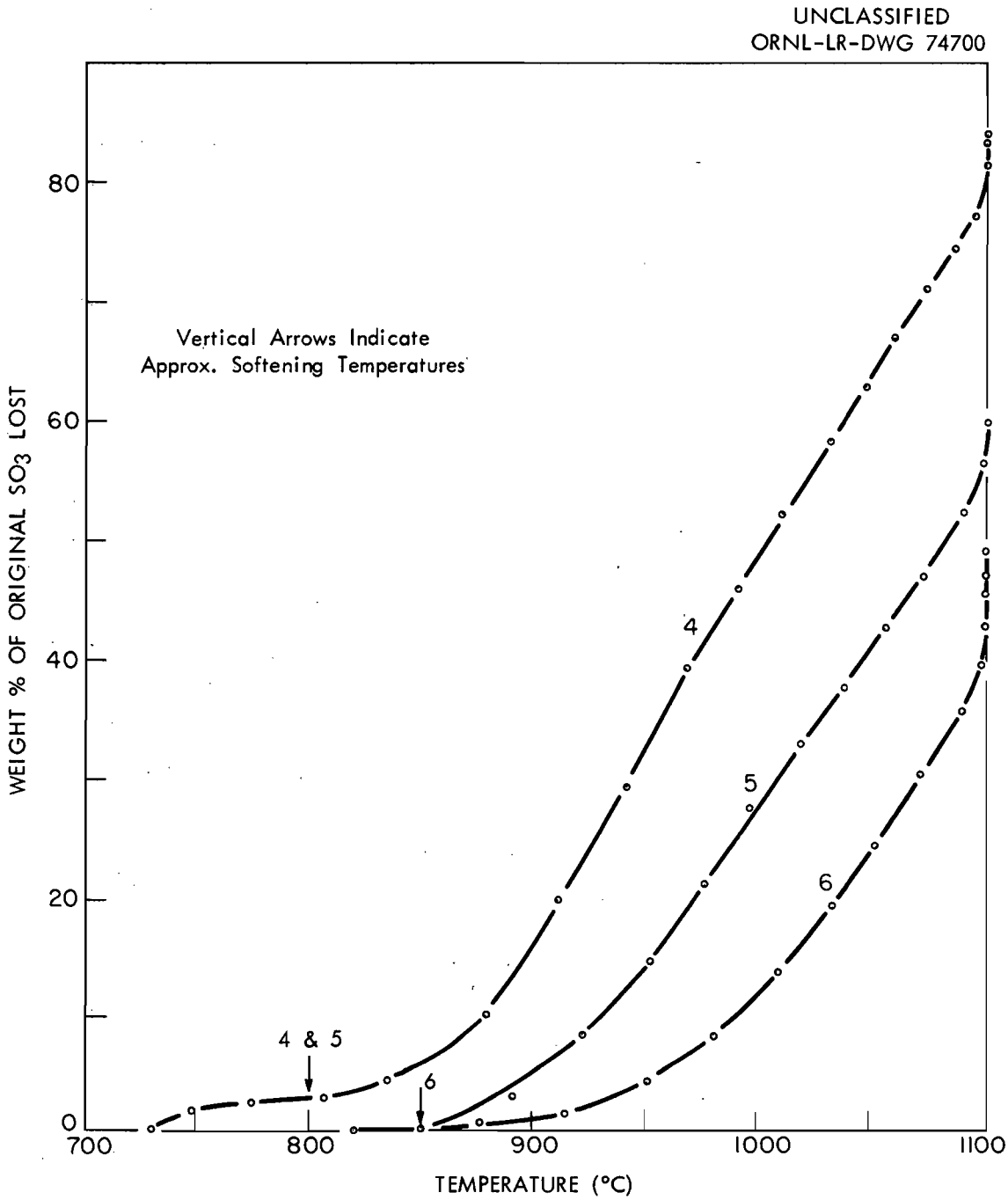

Fig. 1b. Sulfate Loss from Purex Melts. Na_2O constant at 28 wt %; temperature rise = 6°C/min.

Curve 4: CaO, 3.6%; P_2O_5, 34.1%; anion excess, 0.04 N.

Curve 5: CaO, 6.3%; P_2O_5, 31.7%; cation excess, 0.38 N.

Curve 6: CaO, 8.5%; P_2O_5, 29.6%; cation excess, 0.78 N.

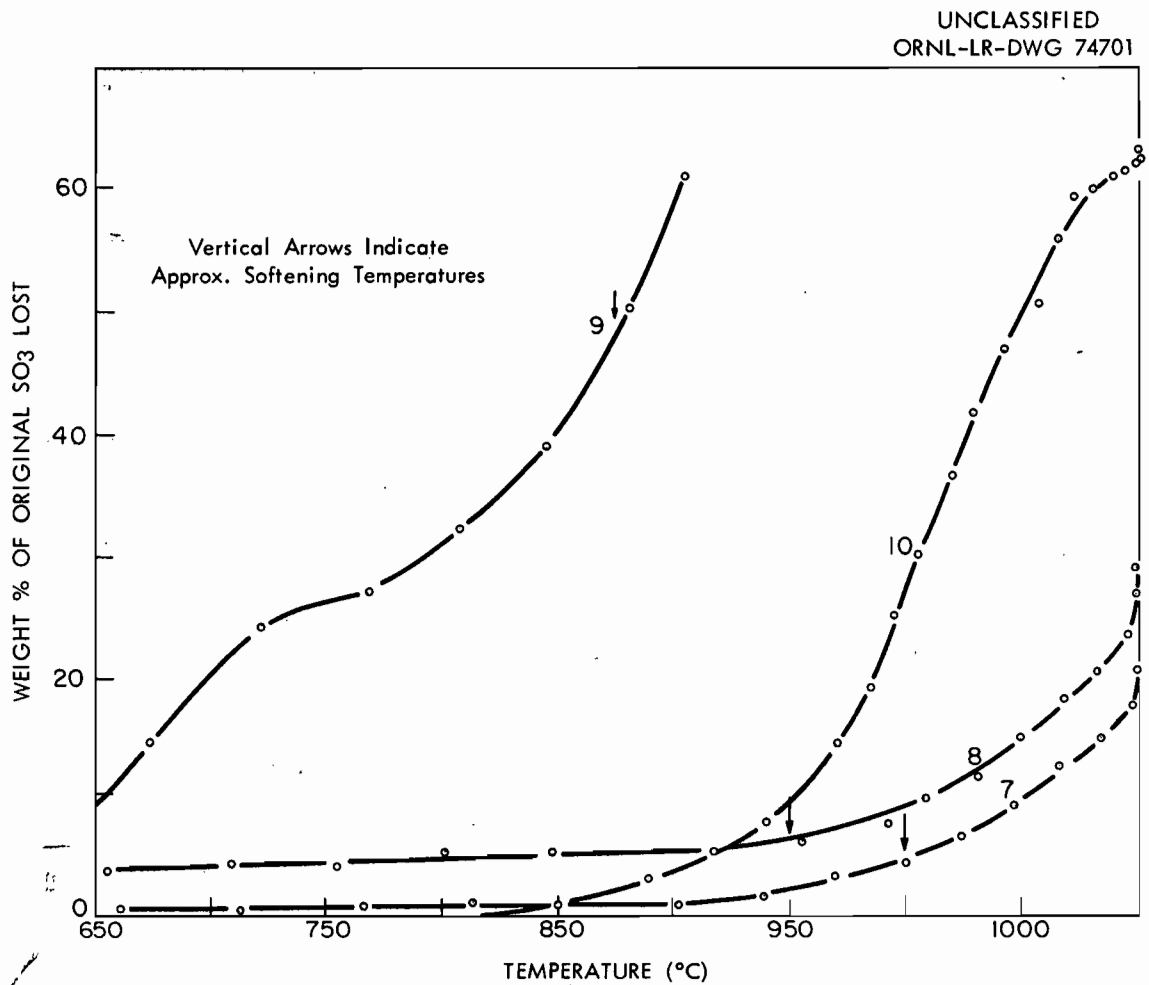

Fig. 1c. Sulfate Loss from Purex Melts. Na_2O constant at 16 wt %; temperature rise = 6°C/min.

Curve 7: CaO, 16.8%; P_2O_5, 33.4%; cation excess, 0.31 N.

Curve 8: CaO, 14.8%; P_2O_5, 35.5%; anion excess, 0.07 N.

Curve 9: CaO, 12.4%; P_2O_5, 37.6%; anion excess, 0.45 N.

Curve 10: CaO, 14.7%; Al_2O_3, 7.7%; P_2O_5, 29.3%; cation excess, 0.24 N (neglecting Al^{3+}).

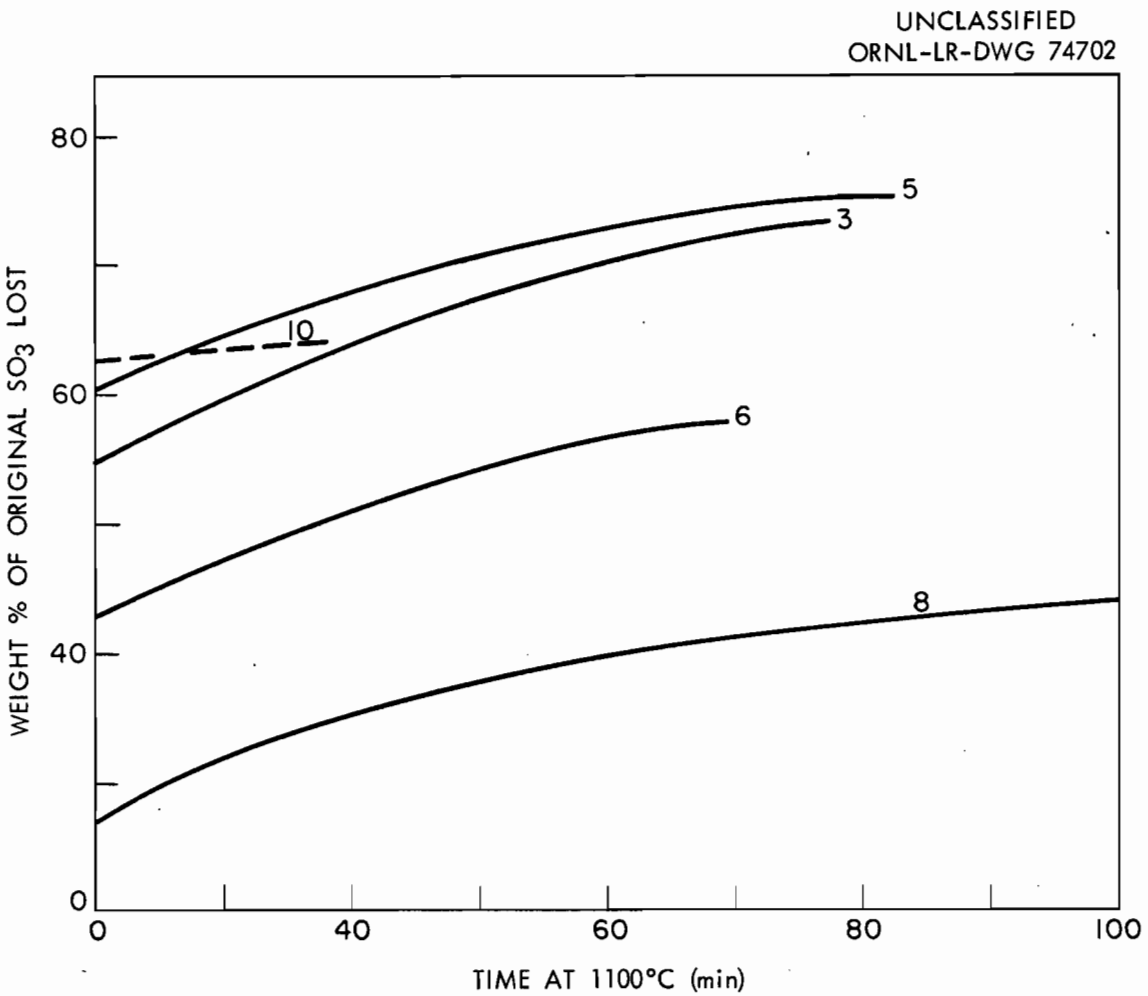

Fig. 2. Weight Loss of Sulfate from Purex Melts at 1100°C. Excess of cations over anions: melt 3, 0.86 N; melt 5, 0.38 N; melt 6, 0.74 N; melt 8, 0.07 N; melt 10, 0.24 N (plus 1.29 N Al^{3+}). Approximate softening temperatures (°C): melt 3, 875; melt 5, 800; melt 6, 850; melt 8, 950; and melt 10, 1000.

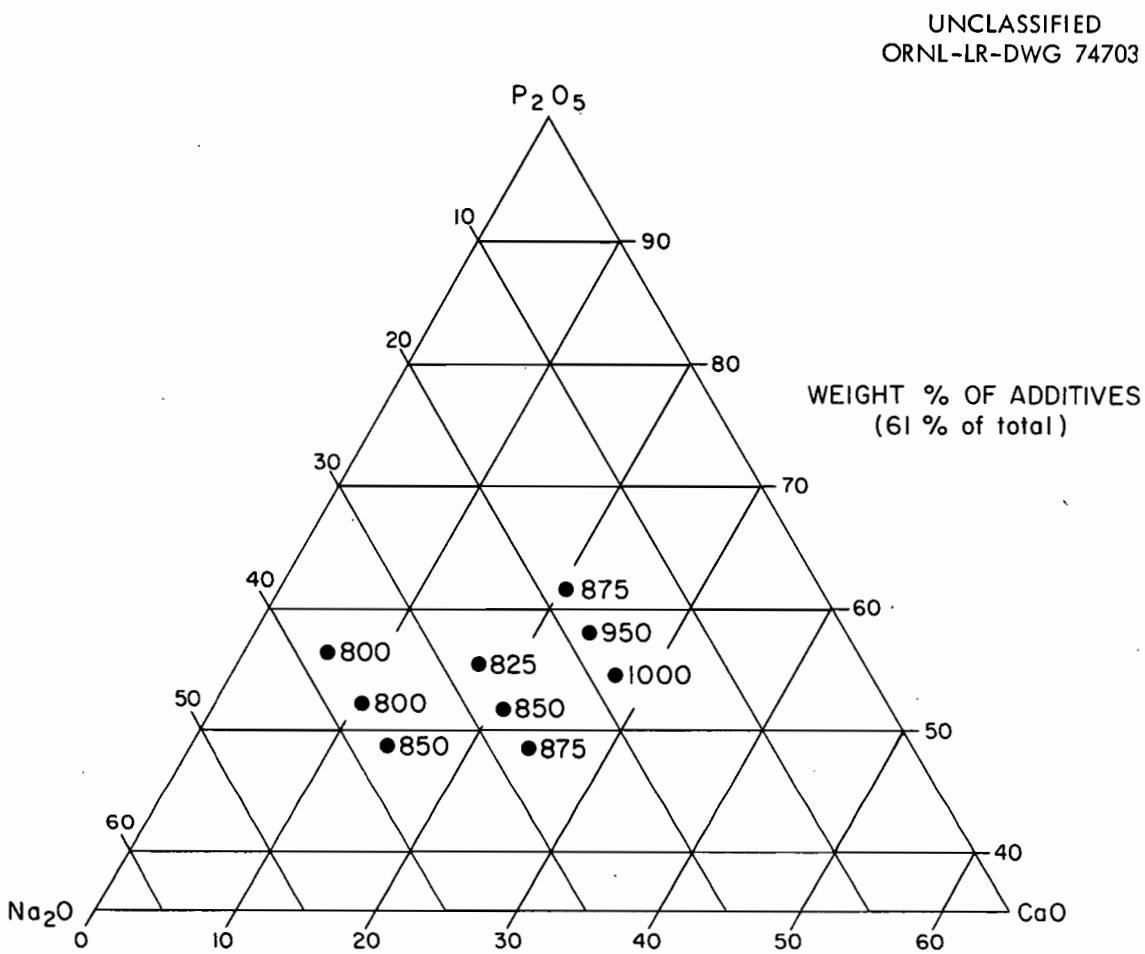

Fig. 3. Approximate Softening Points (^{o}C) of Solid Products Incorporating 39 wt % Purex Waste Oxides, with Na_2O, CaO, and P_2O_5 as Additives.

The only melt that showed marked signs of glass formation on cooling was No. 9 which lost roughly 50% of its sulfate below the softening point (Fig. 1c). Additional experiments are planned to determine if systems with higher cation-to-anion ratios will retain sulfate quantitatively in the fluid state during protracted periods.

A series of scouting tests in which borate, Al, Ba, Ca, and Pb were added to Purex-phosphite solutions in various combinations failed to produce a homogeneous glass (Table 5).

2.3.2 Vapor-Liquid Equilibrium Studies on Simulated Waste Solutions of Low Acid Content

Vapor-liquid equilibria for simulated Darex waste solutions were determined for solutions containing initially 1.2, 0.6, and 1.8 M Fe^{3+} with corresponding amounts of Cr^{3+} and Ni^{2+} at acid concentrations between 0.5 and 1.5 M. Data obtained are listed in Table 6 and plotted, together with previously obtained Darex data[2] (Fig. 4).

3. LOW-LEVEL WASTE TREATMENT

A scavenging--ion exchange process[3,4] is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations, with ORNL low-activity-waste as a medium for study. The process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; the Cs/Na separation factor is 160 for phenolic groups and 1.5 for sulfonic groups. Other cations, for example, strontium and 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 since these media do not remove colloidal materials efficiently. Water clarification techniques are being developed for both the ion exchange processes and for the ORNL lime-soda process waste water treatment plant, in both development and pilot plant programs.

3.1 Pilot Plant

R. E. Brooksbank

The current series of demonstration runs was completed, and the preparation of the terminal report for the Pilot Plant study was initiated. In all, 16 runs were completed during the program; twelve of these have been reported previously.

Table 5. Melts Prepared from Simulated Purex Waste Solution with Miscellaneous Additives

	Melt No.							
	11	12	13	14	15	16	17	18
Additives (moles/liter								
Purex waste								
$NaH_2PO_2.H_2O$	2.8	2.8	3.0	3.0	3.0	4.0	2.0	2.0
B_2O_3	0.25	0.25						
$Ba(NO_3)_2$	1.0	1.0						
$Al(NO_3)_3.9H_2O$	2.0	3.0	2.4	3.0	4.0	2.5		
H_3BO_3			0.8	0.8	0.8	0.8		
$Ca(NO_3)_2.4H_2O$			0.8	0.8	0.8	0.8		
$Pb(NO_3)_2$							0	1.0
$Na_2B_4O_7.10H_2O$								0.1
Theoretical oxides (wt %)								
Fe_2O_3	5.7	5.3	6.2	5.9	5.5	5.3	7.0	6.7
Cr_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NiO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na_2O	15.0	14.0	17.3	16.5	15.3	18.9	14.1	14.6
SO_3	11.4	10.6	12.4	11.8	11.0	10.6	14.0	13.5
Al_2O_3	15.2	20.9	19.7	23.3	28.7	17.6	0.9	0.9
B_2O_3	2.5	2.3	4.3	4.1	3.8	3.7		2.3
BaO	21.8	20.3						
P_2O_5	28.2	26.3	32.9	31.5	29.3	37.7	24.8	24.0
CaO			6.9	6.6	6.2	6.0		
PbO							39.0	37.7
RuO_2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	100.03	99.93	99.93	99.93	100.03	100.03	100.03	99.93
Wt % waste oxides	20.7	19.3	22.5	21.5	20.0	19.3	25.4	24.5
Softening point (°C)	900	900	950	1000	1050	950	800	750
Appearance	crystalline with some glass, brown	crystalline segregated, dark brown	glassy inhomogeneous, brown-black	crystalline, orange	crystalline, red-orange	glassy inhomogeneous, brown	crystalline light green	crystalline light green

Table 6. Vapor-Liquid Equilibrium in Simulated Darex Waste Solutions at 747 to 749 mm Hg

Solution	H+ Analyzed (M)	Equilibrium Boiling Point (°C)	Absolute Pressure (mm Hg)
D-1aa (1.2 M Fe^{3+})	0.79		
pot	0.86		
distillate	0.29	107	747.0
D-2aa (0.6 M Fe^{3+})	0.63		
pot	0.72		
distillate	0.025	102.0	747.0
D-4aa (1.8 M Fe^{3+})	0.98		
pot	1.24		
distillate	1.04	104.5	748.5
D-1bb (1.2 M Fe^{3+})	1.26		
pot	1.35		
distillate	0.46	108.5	747.0
D-2bb (0.6 M Fe^{3+})	1.04		747.0
pot	1.18		
distillate	0.073	103.0	
D-4bb (1.8 M Fe^{3+})	1.31		
pot	1.14		
distillate	1.70	105.0	748.5

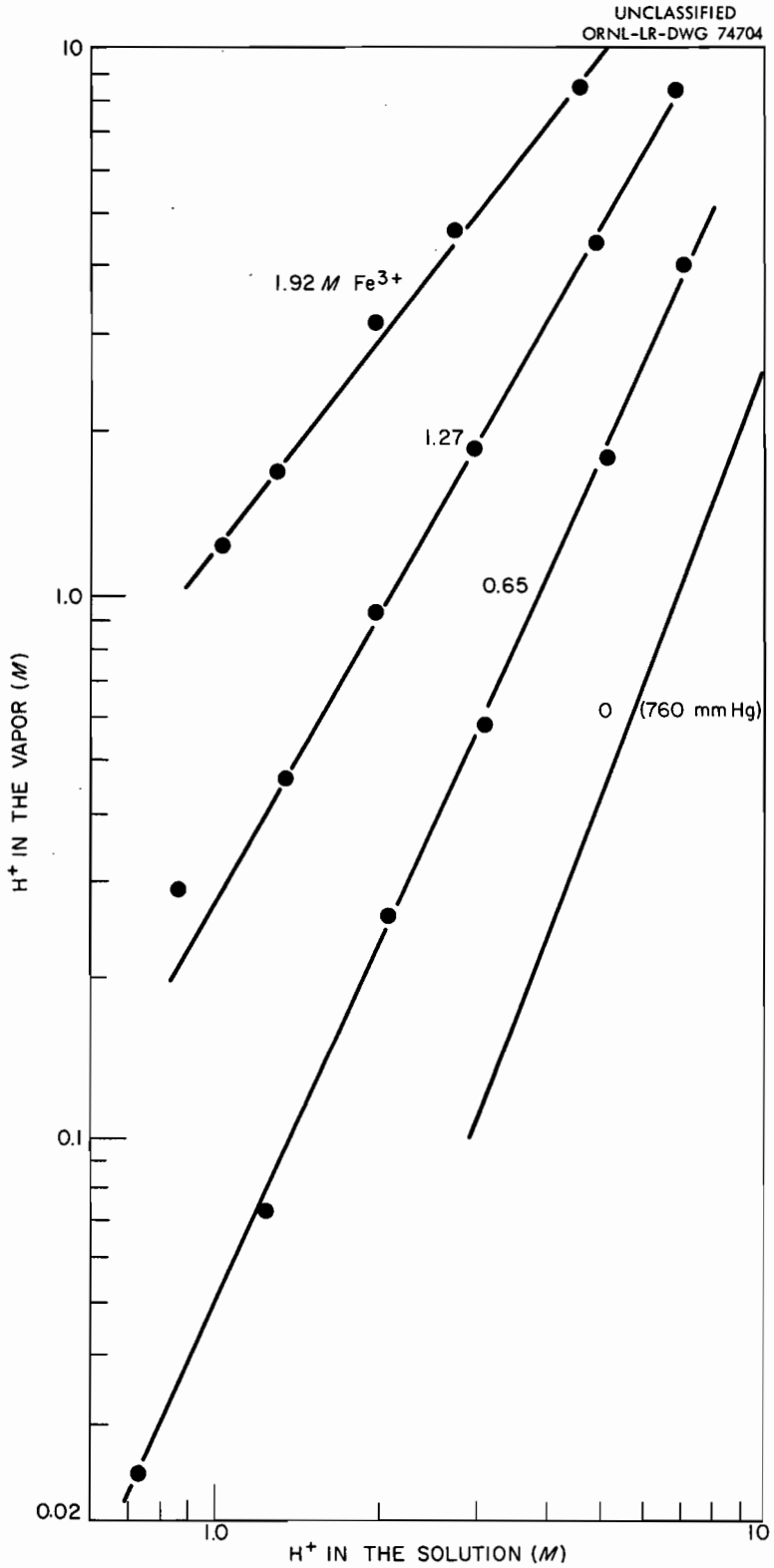

Fig. 4. Vapor-Liquid Equilibrium in Simulated Darex Waste Solutions at 746 to 751 mm Hg.

The use of Na_2CO_3 as a process additive has been proposed to decrease the postprecitation of calcium and magnesium hardness in the clarifier. The presence of excessive amounts (up to 3 ppm) of phosphate in process wastes decreases the rate of hardness precipitation. The presence of Turco 4324 a decontamination agent which contains hexametaphosphate, has been shown[5,6] to reduce the precipitation of $CaCO_3$ from water. For this reason, the last four runs (HR-13, 14, 15, 16) were made to ascertain the effect of 0.005 M Na_2CO_3 in reducing the residual hardness of the clarifier effluent. Run HR-13 was conducted using only the flocculation-precipitation equipment and was terminated after 577 hr of continuous processing; the remainder of the runs used both the precipitation and ion exchange equipment.

3.1.1 Effect of Na_2CO_3 on Hardness Reduction

The use of carbonate as an additive was successful in reducing the residual hardness of the clarifier effluent by a factor of three less than that observed in previous runs (Table 7). The reduction of the hardness in this stream reduces the burden on the polishing filters and increases the quantity of solids removed by the sludge blanket.

Table 7. Beneficial Effect of Na_2CO_3 on the Retention of the Effluent from the Clarifier

Run No.	Avg. Hardness of Process Streams (ppm as $CaCO_3$			
	Feed	Clarifier Effluent	Polishing Filter Effluent	Resin Column Effluent
HR-1 through HR-12	117	60	12	< 1.0
HR-13 through HR-16[a]	100	20	14	< 1.0

[a] Na_2CO_3 addition.

3.1.2 Effect of Na_2CO_3 on Fission Product Removal

The removal of Sr^{90} from ORNL process wastes was not affected by the addition of 0.005 M Na_2CO_3. In run HR-14, a premature Sr^{90} breakthrough occurred, at the 1% level, after 729 column volumes of waste had been treated. This breakthrough was caused by an excessively high sludge-withdrawal rate from the clarifier, which caused channeling in the sludge blanket with subsequent polishing filter breakthrough. Greater than 99.96% of the Sr^{90} was removed

after 1650 bed volumes during runs HR-15 and HR-16, when 0.005 M Na_2CO_3 was utilized.

The use of carbonate has a pronounced effect on the removal of Cs^{137}. The removal during runs HR-15 and HR-16 was 92.5 and 39.5% for the same operating periods. The differences between the Cs^{137} removal efficiencies of these runs may be explained by an additional quantity of NaOH used during HR-16. The flowsheet used for HR-13, -14, and -15 used a terminal feed concentration of 0.005 M NaOH and 0.005 M Na_2CO_3; the flowsheet used for HR-16 consisted of 0.01 M NaOH and 0.005 M Na_2CO_3. The flowsheet alteration was deemed necessary to study the effect of increased pH during Na_2CO_3 addition. Holcomb has subsequently shown[7] in laboratory studies that the presence of excess sodium will decrease the sorption of Cs^{137} on Duolite CS-100 resin.

3.2 Process Development

R. R. Holcomb W. E. Clark

Laboratory studies for improving the headend or precipitation portion of the scavenging--ion exchange process were continued, utilizing the laboratory-model clarification equipment and methods described previously.[7,8] The minor difficulties encountered with hardness supersaturation in these studies and in the operation of the 15,000-gal/day pilot-plant were attributed to a combination of three conditions: (1) the presence of complexing agents such as phosphates in the waste stream; (2) improper flash-mixing--flocculation equipment and procedures; and (3) the presence of other materials such as algae and detergents, which produce a physically different floc from that obtained with tap water. These problems were studied on an individual basis, using both tap water and actual waste as feed. The results can be seen in Table 8, along with some corresponding results of pilot-plant runs.

The detrimental effect of complexing agents such as hexametaphosphate was demonstrated by the 40-ppm hardness, (all hardness readings are reported in ppm, as $CaCO_3$) obtained with tap water and 3.2 ppm of Turco (line 4, Table 8), and the failure of the pilot-plant polishing filter to remove soluble hardness (line 7) from actual waste. In the latter case, saturation of the ion exchange resin with hardness ions and premature breakthrough resulted. The addition of 0.005 M Na_2CO_3 (lines 5 and 8) overcame the phosphate effect in both of the above cases. The 30 to 40-ppm hardness obtained in the laboratory clarifier unit with actual waste (line 8) was a result of the third problem mentioned above, a light, large-particle floc that permitted channeling in the blanket and prevented the seeding effect necessary to break hardness supersaturation. This problem was overcome (line 9) by seeding the blanket with finely divided $CaCO_3$ particles, which circulated between the clarifier and flash mixer. The high pilot-plant clarifier-hardness readings in the

Table 8. A Comparison of Laboratory and Pilot Plant Results in the Head-End Treatment of Low-Activity Waste by the Scavenging--Ion Exchange Process

Feed	Line No.	Coagulants: NaOH (M)	Coagulants: Na_2CO_3 (M)	Coagulants: Fe (ppm)	Resulting pH	Average Steady-State Residual Hardness in Effluent (ppm as $CaCO_3$): Lab-Model Clarifier	Pilot Plant: Clarifier	Pilot Plant: Polishing Filter
Tap water	1	0.01	0	5	11.8	< 5	11-12	11-12
Tap H_2O, plus:								
1.7 ppm Turco	2	0.01	0	5	11.8	< 5		
2.4 ppm Turco	3	0.01	0	5	11.8	< 5		
3.2 ppm Turco	4	0.01	0	5	11.8	40		
	5	0.01	0.005	5	11.9	< 5		
Waste water (early runs)	6	0.01	0	5	11.8		60-70	8-10
Waste water with high PO_4^{3-}	7	0.01	0	5	11.8	40-50	60-70	50-60
	8	0.01	0.005	5	11.9	30-40	10	8-10
	9	(seeded with $CaCO_3$ due to light floc)				5- 6		
	10	0.005	0.005	5	11.3	< 8	8-10	8-10
	11	0.005	0.01	5	11.4	3		
	12	0.0075	0.0075	5	11.5	3		
	13	0.0075	0.0025	5	11.5	30		

early runs on the waste stream were reduced by passage through the polishing filter (line 6). Operation of the laboratory-model unit with a 30-min holdup in the flash mixer, no flocculation, and recycle of 5 to 10% of the sludge from the clarifier to the flash mixer, showed that this supersaturation can be broken prior to exiting the clarifier, thus removing the burden from the polishing filter. If hardness is broken in the flash mixer, the clarifier serves only to remove turbidity, thus eliminating fluctuations in soluble hardness resulting from minor variations in the sludge blanket. During the laboratory-model-clarifier demonstrations on actual waste, the presence of phosphate was verified periodically by stopping the Na_2CO_3 addition. The presence of phosphate then caused a rapid increase of effluent hardness to about 40 ppm, which again decreased to low values when the carbonate addition was resumed.

The treatment of ORNL tap water containing 6 ppm of a commercial detergent (Fab) showed 20 and 14 ppm of residual hardness in the flash mixer effluent and clarifier overflow as compared with 12 and 2.4 ppm for tap water only (Fig. 5). An increase to 10 ppm of detergent produced 42 and 32 ppm of hardness. While the detergent caused high residual hardness, it also produced a larger floc, which caused better fines removal in the sludge blanket, resulting in a less turbid effluent. The addition of 0.005 M Na_2CO_3 reduced the 32-ppm clarifier hardness to 14.

4. ENGINEERING, ECONOMICS, AND HAZARDS EVALUATION

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

4.1 Effects of Fission Product Removal

As a basis for this study, a conceptual flowsheet for fission product recovery was examined. It had been prepared at Hanford for use in the development of a waste management program at that site.[9] In the Hanford flowsheet, formaldehyde-treated Purex waste (30 gal per ton of uranium processed) was first treated with a phosphotungstate precipitation for removal of more than 98% of the cesium, following which more than 98% of the strontium and more than 97% of the rare earths were separated by solvent extraction using D2EHPA and TBP. An effluent stream of 50 gal per ton uranium processed, containing Na^+, NO_3^-, SO_4^{2-}, CO_3^{2-}, and the remaining fission products was postulated. Although this flowsheet was speculative and may represent future technology, it appears to offer reasonable justification for the following assumptions made for the purposes of the present study:

1. Acid Purex waste is treated for 90 or 99% removal of <u>all</u> fission products.

2. The cost of these separations and for all subsequent handling of the separated fission product concentrates is borne by their eventual sale.

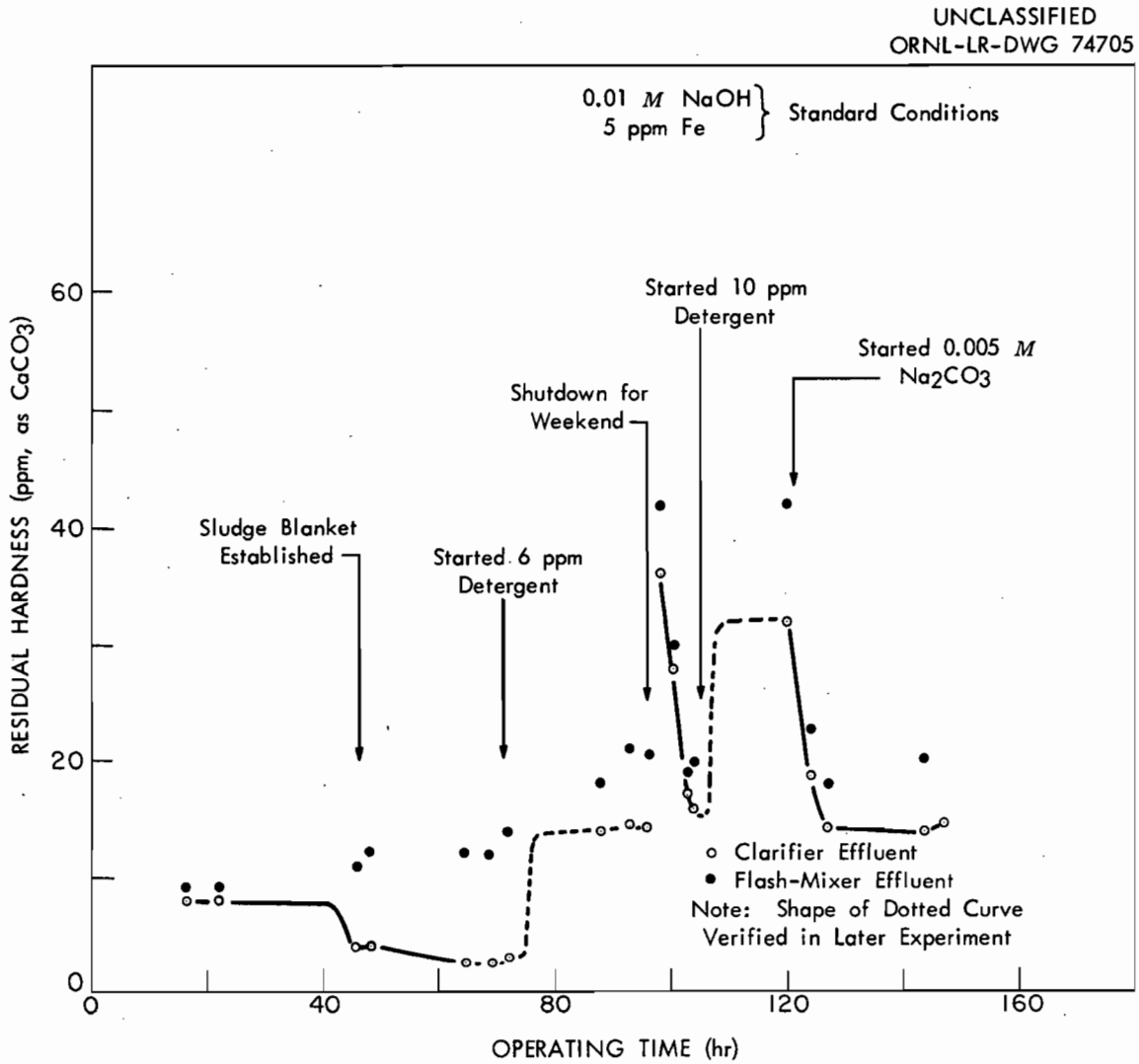

Fig. 5. Effect of a Commercial Detergent (FAB) on the Treatment of ORNL Tap Water by the Standard Caustic-Copperas Process in the Laboratory-Model Clarifier Equipment.

3. The compositions and volumes of the waste from the fission product separation plant (in liquid and solid forms) are identical to the neutralized Purex waste previously treated in this study;[10,11] that is to say, the processes for the removal of the fission products did not greatly increase the volume or solids content of the waste produced per ton or uranium processed. With these assumptions, adjustments in the costs of waste management are attributable to the reduced heat removal and shielding requirements caused by fission product removal.

Costs of interim liquid storage were decreased about 30% by the reduction in tank-cooling coils, heat exchangers, and cooling towers (Fig. 6). Pot calcination costs were the same for fission product removal wastes as for reacidified Purex (Fig. 7); however, calcined fission product waste could be processed immediately in 24-in.-diam vessels, while reacidified Purex waste must be aged for at least 1.8 years.

Fission-product-removal wastes could be shipped immediately upon discharge from the calcination plant in shipping casks containing four 24-in.-diam cylinders. These are the largest casks considered feasible to handle. Minimum ages of 3 and 11 years are required before shipping reacidified Purex and acidic Purex in this manner. Shipping costs were about 25 and 50% less than for reacidified Purex for 90% and 99% fission-product-removal wastes for a 1000-mile distance to the disposal site (Fig. 8). Lower costs for the fission-product-removal wastes were due to the thinner shielding required, which resulted in lower capital costs for casks and lower transportation charges.

Minimum total costs for interim liquid storage, pot calcination, and shipping were about 0.0141 mills/kwh for 99% fission-product-removal waste, 0.0147 for 90% fission-product-removal waste, and 0.0147 for Purex waste left in its acid form and from which fission products have not been extracted (Fig. 9). Discontinuities in the curves for acid Purex waste are due to major reduction in shipping costs at certain ages when more economically sized casks can be used. Although final disposal costs have yet to be calculated and added in, it does not appear that fission product removal, even based on future technology, will significantly decrease waste management costs.

5. DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing

W. de Laguna

The rocks in the general area of ORNL belong to four principal categories: the Rome formation, the Conasauga group,

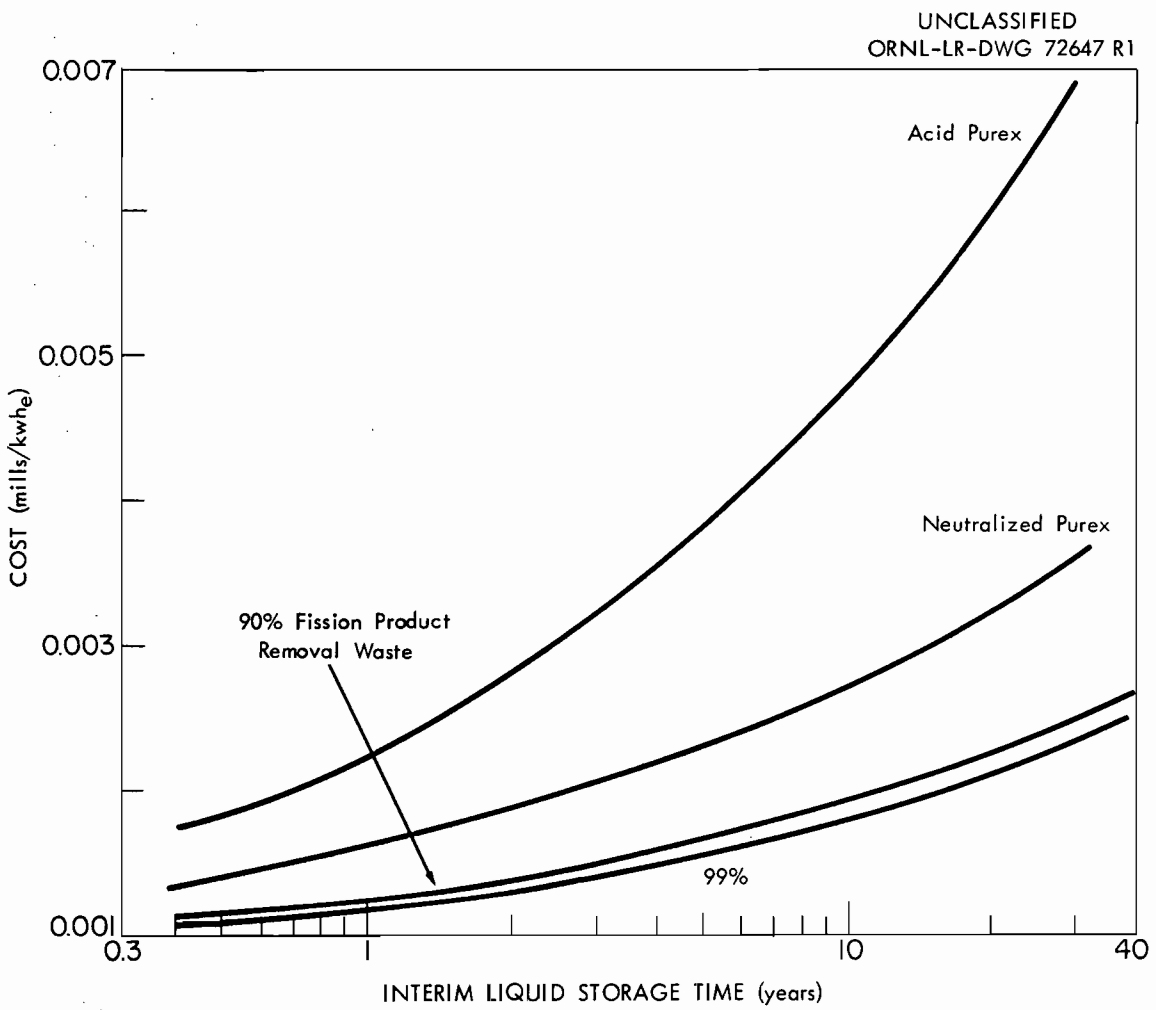

Fig. 6. Costs for Interim Liquid Storage.

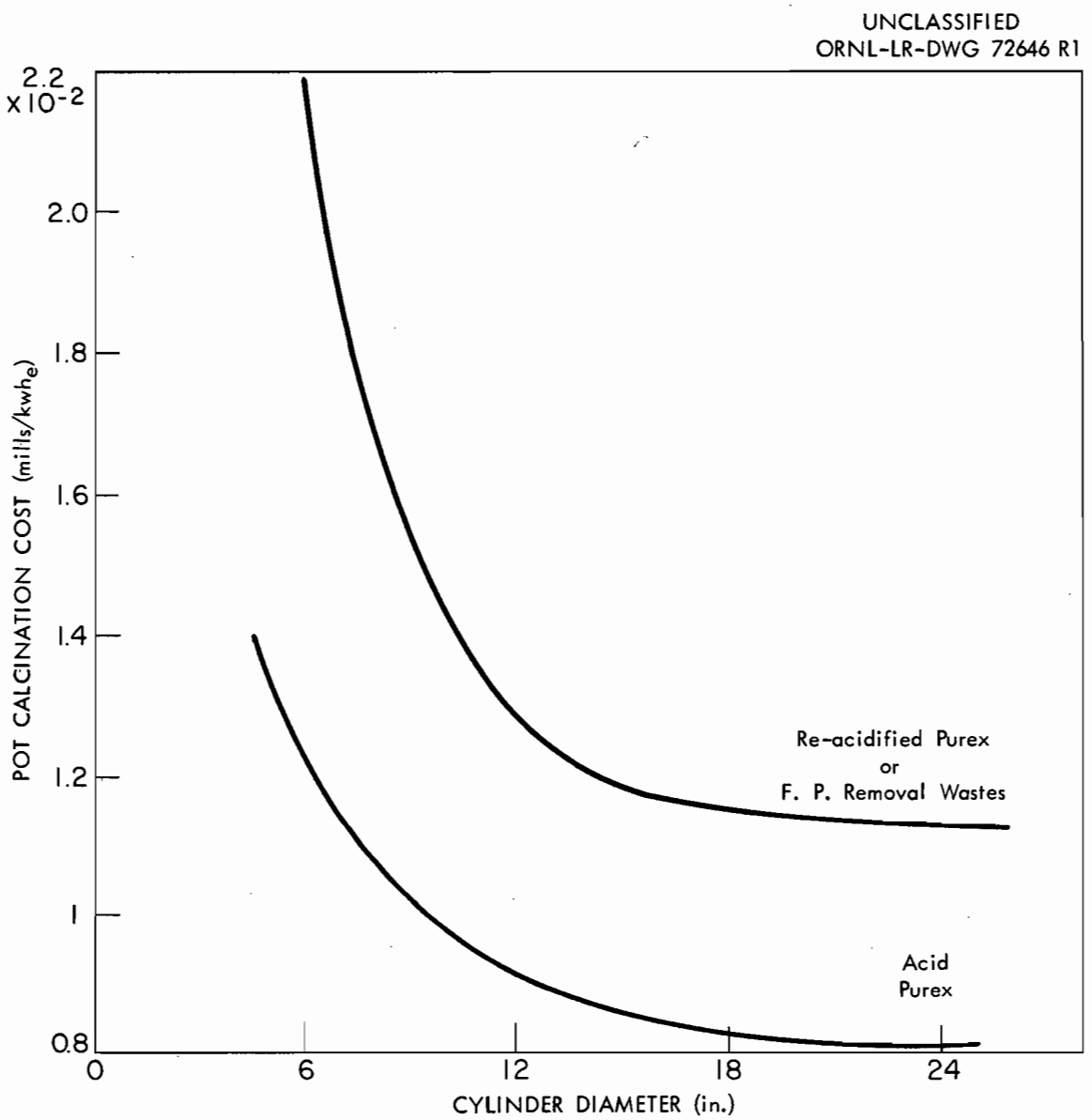

Fig. 7. Costs for Pot Calcination.

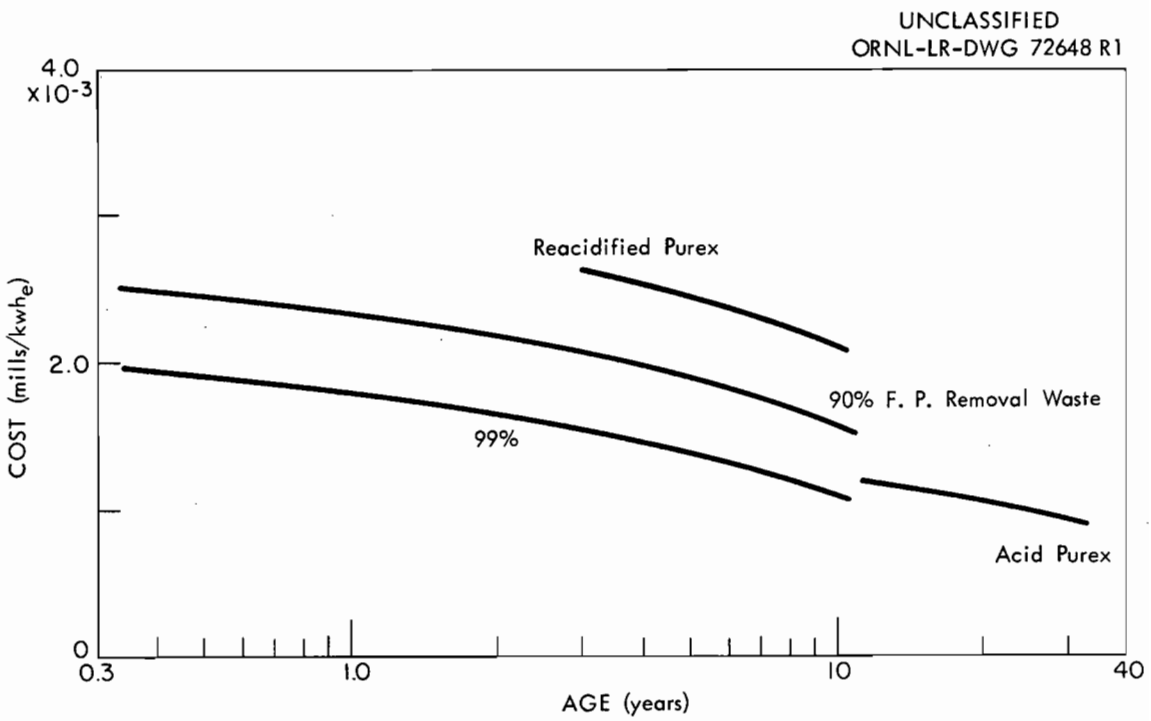

Fig. 8. Costs for Shipping the Calcined Wastes in 24-in.-diam Cylinders 1000 miles to a Disposal Site.

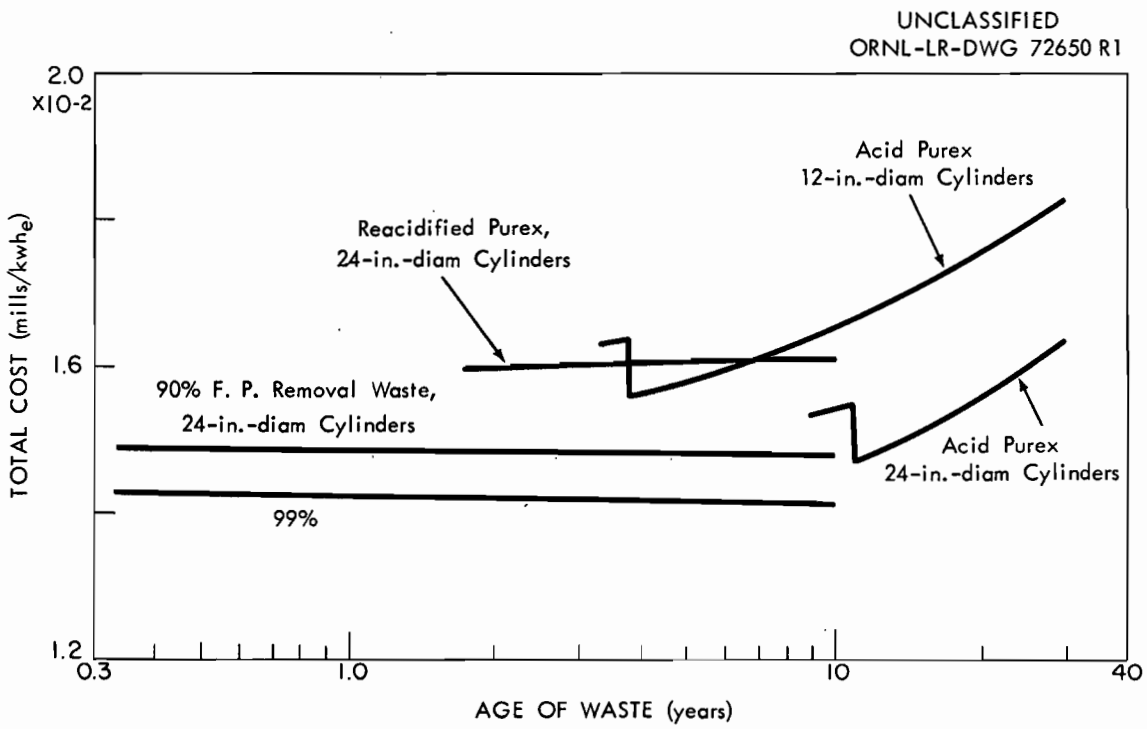

Fig. 9. Total cost of Interim Liquid Storage, Pot Calcination, and 1000-mile Shipment to a Disposal Site.

the Knox group, and the Chickamauga limestone. The Rome and the Chickamauga are classed as formations, because they have in the past been the basic units mapped from surface exposures in the field. The Conasauga and the Knox are classed as groups, because in other areas they have been subdivided for the purposes of surface mapping into six and five formations, respectively. These subdivisions of the Conasauga and Knox have not yet been identified or mapped in the Oak Ridge area, although it is apparent that some of them are present, and an attempt is being made to correlate the local rocks with the type areas. On the other hand, the local Chickamauga was subdivided by Stockdale[12] into eight members in the course of his mapping of the Laboratory area in 1951. The subdivisions of the formations and groups described below are based almost entirely on subsurface exploration for a special purpose, and they may or may not coincide with the subdivisions that can be recognized in surface exposures and which have, therefore, been used for surface mapping.

All the rock units outcrop at the surface and all dip to the southeast. Because the area is underlain by a series of great overthrust sheets, all the formations are repeated over and over in regular sequence as one moves across one thrust sheet and onto the next, and each formation may be said to be both underlain and overlain by each of the others. The total thickness of the units is about 6720 ft, of which the Rome comprises 360, the Conasauga 1500, the Knox about 3000, and the Chickamauga, 1860. In an area of gentle dips, therefore, a well starting at the surface would, at a depth of about 6720 ft, reach again the stratigraphic horizon at which it had started, and with deeper drilling would once more successively pass through the same units that it had already penetrated. Conversely, and of more interest to our problem, by selecting the surface location of the well, it is possible to find any required unit at any specified depth.

The site in Melton Valley (at the junction of Melton and White Oak Creeks) selected for the projected large-scale experimental waste injections, was chosen with the general geology already in mind but with the precise spot chosen in order to meet certain operational and administrative requirements. These requirements were: (1) the proximity to such operating waste disposal facilities as the burial ground and the seepage pits and trenches, (2) proximity to a waste-transfer pipeline, (3) distance from any existing or proposed facilities, and (4) within the drainage area of White Oak Lake, the discharge from which is already being monitored. The Knox and the upper Conasauga, a total of over 3000 ft of the stratigraphic column, had already been ruled out for disposal by fracturing, as they are largely thick bedded or generally very hard and brittle. The site is at a point stratigraphically just below these rocks and is immediately underlain, in consequence, by that part of the section of greatest interest.

In the summer of 1961 a test well was drilled at the site to a depth of 3263 ft to explore these rocks. The hole was cored

all the way, and gamma-ray and electric logs were made nearly to the bottom. A study of the data confirmed, incidentally, that this site is very nearly at the same stratigraphic position as the site of the second-fracturing experiment, which is 3000 ft away to the northwest. The log of the well may be summarized as follows:

Middle Conasauga

0 to 440 ft. Interbedded gray limestone and calcareous shale, beds 0.1 to 1.0 in. thick, except locally, 1 to 2 ft thick. Bedding irregular in detail and locally shows drag folds ranging from a few inches to several feet in amplitude. Does not appear well-suited for disposal by fracturing due to irregularities in bedding.

440 to 544 ft. Calcareous shale with less interbedded limestone than above. Bedding thin and regular; cores, in general, break evenly along bedding. Relatively little deformed -- this may be only local.

Unit probably would be suitable for disposal by fracturing where present at greater depth.

544 to 674 ft. Calcareous shale with some interbedded limestone. Bedding coarser and less regular than in overlying unit; locally deformed by drag folds. Probably poorly suited for disposal by fracturing.

674 to 692 ft. Three limestone beds in shale; significant as stratigraphic markers.

Lower Conasauga

692 to 1002 ft. Red noncalcareous shale, with a few thin, sandy beds in lower part. Bedding is irregular in detail and is locally deformed by minor folds and faults, but both cores and outcrops suggest it will, in general, fracture along the bedding planes. This appears to be one of the best units for disposal by fracturing, particularly where present at somewhat greater depths. This is the unit fractured in all experiments to date.

Rome Formation

1002 to 1360 ft. Well-indurated sandstone, generally thick bedded, locally shaly. Crushed and recemented in lower part. Too massive, hard, and brittle to fracture easily along the bedding, not suited for waste disposal.

Copper Creek Thrust Fault

1360 to 1362 ft. Shaly fault gouge. Soft, but very fine grained and apparently very nearly impermeable.

Chickamauga Limestone

1362 to 1700 ft. Limestone and shaly lime, in part with thin well-developed beds, in part with gradational or poorly developed bedding. With experience, perhaps, much of this will be found suitable for disposal by fracturing; at present, only limited section can be classed as suitable.

1700 to 1866 ft. Shaly limestone with thin well-developed bedding. This unit appears to be well-suited to disposal by hydraulic fracturing.

1866 to 1927 ft. Limestone and shaly limestone, generally unfavorable, but includes several short sections suitable for fracturing.

1927 to 2200 ft. Largely limestone, with relatively thick or poorly developed bedding. This general section is probably poorly suited to disposal by fracturing.

2200 to 2366 ft. Limestone and shaly limestone, generally unfavorable, but including several short sections suitable for fracturing.

2366 to 2648 ft. Largely limestone, with relatively thick or poorly developed bedding. This general section is probably poorly suited to disposal by fracturing.

2648 to 2852 ft. Calcareous shale with very uniform well-developed thin beds. This section gives every appearance of being excellently suited to disposal by hydraulic fracturing.

2852 to 3126 ft. Limestone, with many variations in texture and bedding, but, in general, relatively thick bedded or indistinctly bedded and therefore believed largely unsuited to disposal by fracturing.

Knox Group

3126 to 3263 ft. Thick bedded, structurally almost massive, coarsely crystalline dolomite. This rock, which probably extends to a depth of about 6000 ft, is clearly quite unsuited to disposal by hydraulic fracturing.

5.1.1 Evaluation of the Units with Respect to Suitability for Waste Disposal by Hydraulic Fracturing

The evaluation of these units is highly subjective, for it is possible only to guess at how a rock will fracture in depth from the appearance of a small sample. However, the suitability of the intervals between 692 and 1002 ft and between 2648 and 2852 ft

is almost certainly correctly evaluated, particularly in view of previous field testing of the upper unit. The interval between 1700 and 1866 ft is also almost certainly well-suited, although its range should, perhaps, be extended upward to 1640 ft. The evaluation of the rest of the Chickamauga limestone, while probably substantially correct as to the relative merit of the units, may be revised later because the cores and well logs are still under study. Field studies of the exposures of the Chickamauga, where the fracturing of larger masses of rock in place can be examined, will probably "upgrade" much of this formation. For example, the interval, 2366 to 2648 ft, classed as only partly suitable from a study of the well cores, appears much more promising where it is exposed in the walls of the recently abandoned quarry on Bethel Valley Road.

In general, however, the log does show the location of the best rocks, and it may be concluded that there are three intervals well-suited to disposal by hydraulic fracturing under the proposed site, and a considerable additional thickness of rock which, although apparently not as well-suited, may later prove to be usable.

The uppermost well-suited interval lies in the lower Conasauga shale between the depths of 692 and 1002 ft. This red, thin-bedded noncalcareous shale is the same rock and is at the same depth as that used in the second-fracturing experiment, and, even though there may be slight differences in the number of small-scale drag folds and faults, it may be expected to fracture in much the same way. It has been suggested, however, that for long-continued disposal of even moderate concentrations of radioactive materials, a deeper interval below the Copper Creek fault should be used. This fault, and the hard, massive Rome sandstone which overlies it, form a marked structural discontinuity that would hinder and probably prevent the formation of any continuous vertical fractures. The lower Conasauga at this site is regarded, however, as very well suited for even large-scale experimental injections containing real waste.

5.2 Liquid Injection into Permeable Formations

D. G. Jacobs

Exchange studies were extended to calcium-hydrogen-strontium exchange on the samples of Richfield sand. An "exercised" column of Richfield sand (that is, one that has been subjected to several saturation and leaching operations) was used to study the exchange of calcium and strontium from 0.01 N $CaCl_2$ tagged with Sr^{85} and brought to the desired pH with HCl. The results in Table 9 show that the sorption of both calcium and strontium are reduced by the same relative amounts as the pH of the influent solution is lowered. At an influent pH of 2, the dissolution of minerals in the exchange column caused interference with the EDTA titration of calcium. Redetermination of the exchange capacity at pH 7 indicated that a

Table 9. Calcium-Hydrogen-Strontium Exchange by Richfield Sand

Run	Influent pH	Calcium K_d (ml/g)	Strontium K_d (ml/g)	K_{Ca}^{Sr}
1	7	6.21	6.51	1.05
2	6	5.09	5.33	1.05
3	5	4.58	4.85	1.06
4	4	3.70	4.30	1.16
5	3	3.11	3.22	1.04
6	2		0.71	
7	7	2.67	3.65	1.37
8	2		0.38	

substantial portion of the exchange capacity had been lost due to the action of the acid. Dissolution of minerals in the column continued during a second operation at pH 2.

Attempts to arrive at a standard procedure for the exchange analysis of calcareous sandstones without alteration of the sample were continued. Five grams of Richfield sand and varying amounts of reagent grade $CaCO_3$ were weighed into 40-ml centrifuge tubes. Ten saturation steps were carried out with 25 ml of 0.005 M Ca^{2+} (chloride solution saturated with $CaCO_3$ at pH 7) tagged with Ca^{45}. Following saturation the samples were washed twice with 95% ethanol and leached ten times with 25 ml of untagged $CaCl_2$-$CaCO_3$ solution of the same concentration. Each leach solution was sampled for Ca^{45} counting, and the exchangeable calcium was determined. Strontium-85 exchange was then determined for the samples, employing solution of the same stable chemical composition. In the final step, the samples were leached five times with 1 N $NaC_2H_3O_2$, and the calcium was titrated with EDTA.

Because of dissolution of the slightly soluble $CaCO_3$, the sodium acetate determination does not give an accurate representation of the calcium exchange capacity of the Richfield sand (Table 10). The results obtained using Ca^{45} sorption from a $CaCO_3$ saturated solution are much more meaningful, although the $CaCO_3$ did exchange approximately 1.9 meq Ca^{2+} per 100 g and removed relatively less Sr^{85} from solution. (The strontium-to-calcium selectivity coefficient of the $CaCO_3$ was 0.31). This results in a decreasing apparent strontium-to-calcium selectivity coefficient with increasing amounts of calcium carbonate in the sample. When the exchangeable calcium and strontium values for the Richfield sand are corrected for the amounts held by the calcium carbonate, the resulting strontium-to-calcium selectivity coefficient for Richfield sand is quite constant.

Table 10. Calcium-Strontium Exchange by Mixtures of Richfield Sand and Calcium Carbonate

	Run							
	1	2	3	4	5	6	7	8
Weight of Richfield sand (g)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	
Weight of $CaCO_3$, g		0.0010	0.010	0.10	0.50	1.00	2.00	2.00
Ca^{45} exchange, meq	0.1415	0.1370	0.1575	0.1500	0.1580	0.1670	0.1770	0.0382
Ca^{2+} titrated by EDTA in $NaC_2H_3O_2$ leaches, meq	0.2530	0.2525	0.2790	0.4120	0.5845	0.5810	0.6280	0.1846
Sr^{85} exchanged, % of total in 100 ml	18.0	16.4	18.5	18.4	18.4	19.0	18.1	1.2
Ca^{45} exchanged by Richfield sand,[a] ml/g	2.83	2.74	3.15	2.96	2.97	2.96	2.78	
Sr^{85} exchanged by Richfield sand,[a] ml/g	4.38	3.92	4.54	4.49	4.46	4.58	4.18	
K_{Ca}^{Sr}[b]	1.55	1.43	1.44	1.52	1.50	1.55	1.51	0.31

[a]Corrected for amount exchanged by the added $CaCO_3$.

[b]The corrected values for Ca^{45} and Sr^{85} exchange were used in calculation for runs 1 through 7.

The exchange capacity of the Richfield sand determined in this series of measurements averaged 2.91 ± 0.11 meq per 100 g, and the strontium-to-calcium selectivity coefficient was 1.50 ± 0.04. This exchange capacity agrees very well with the value of 2.96 meq per 100 g, obtained previously in nonexercised columns of Richfield sand, and the strontium exchange was about the same as determined during the first column determination after the column had been exercised once.

The calcium-strontium exchange properties of numerous sandstone and clay samples were determined, using calcium carbonate saturated solution and the slurry method described above. The exchange capacities obtained for the clay minerals generally agreed quite well with those determined by Jackson's EDTA method,[13] and the strontium-to-calcium selectivity coefficient ranged from 1.03 to 1.52. In the case of the phosphatic minerals, variscite and crandallite, and the calcareous or dolomitic samples, exchange capacity determined by Ca^{45} sorption was much lower than that determined by EDTA titration. The samples taken from a Reagan sandstone "type" locality in Oklahoma by J. B. F. Champlin, U.S. Bureau of Mines, showed very low capacities for sorbing calcium and strontium (series Q, Table 11).

6. DISPOSAL IN NATURAL SALT FORMATIONS

6.1 High-Temperature Experiments

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

Both the array and cylinder tests II and III were started in July. Operation of the cylinder tests is proceeding normally, but the six peripheral heaters in the array failed during the first few days of operation, and the array is now functioning as a simple cylinder test.

6.1.1 High-Temperature Cylinders II and III

Both the floor and wall cylinder tests were started on July 18 with a power input of 3500 w each. Salt temperature rises in the plane perpendicular to the center of the heater are shown in Fig. 10, along with theoretical curves based on the 100°C salt thermal properties. After 45-hr of operation of the wall test, the power was turned off for 3 hr, during which time the heater was removed from the hole, and the hole diameter was calipered at 1-ft intervals. The floor heater was removed for 3 hr for calipering after 49 hr of operation. Both heaters were restarted at a power level of 5000 w, and the power has remained constant since that time, with the exception of a daily period of about 5 to 10 min when heater temperatures are recorded, and a period of about 45 min when the wall heater power was turned off for inspection of the hole.

Table 11. Strontium-Calcium Exchange by Various Sands and Minerals

	Exchange Capacity Determined by:				
	Jackson's EDTA Method[a] (meq/100 g)	EDTA Titration (meq/100g)	Ca^{45} (meq/100 g)	Sr K_d (ml/g)	K_{Ca}^{Sr}
Bentonite "BP"	61	103	74.4	76.5	1.03
Texas Bentonite	55	57.5	57.5	66.4	1.16
Metabentonite, H-42	36	30.4	28.0	33.1	1.18
Attapulgite	34	30.1	24.2	36.8	1.52
Halloysite, No. 12	16	13.8	12.9	16.6	1.29
Variscite	12	16.5	8.29	32.5	3.92
Georgia Kaolinite	9	6.72	6.74	7.29	1.08
North Carolina Kaolinite	5	4.42	4.11	4.76	1.16
Pennington sand	4	3.75	2.15	8.12	3.78
Crandallite	6	3.44	1.40	4.40	3.14
Noxie sand		1.73	1.87	4.09	2.19
Gilliland sand		2.30	1.71	6.34	3.71
Fowler sand		2.28	1.53	4.14	2.71
Crab Orchard sand no. 1		1.43	1.01	2.57	2.54
Crab Orchard sand no. 2		1.31	1.10	2.97	2.70
Berea sand		1.12	0.52	3.06	5.88
Bartlesville sand		2.73	0.49	1.50	3.06
Q-0, Honey Creek dolomite		7.75	1.53	2.19	1.43
Q-1, Honey Creek dolomite		1.94	1.38	3.82	2.77
Q-3, Weathered quartzitic sandstone with Feldspar		0.86	0.42	1.13	2.69
Q-5, Conglomerate sandstone		0.82	0.27	1.05	3.89
Q-6, Conglomerate, with feldspar and quartz		0.77	0.42	1.02	2.43
Q-7, Conglomerate, with feldspar, fine quartz, and Arkosic sand		1.46	0.59	1.22	2.07
Q-8, Conglomerate, with quartz, feldspar, and Arkosic sand		1.00	0.67	1.32	1.97

[a]Data supplied by T. Tamura

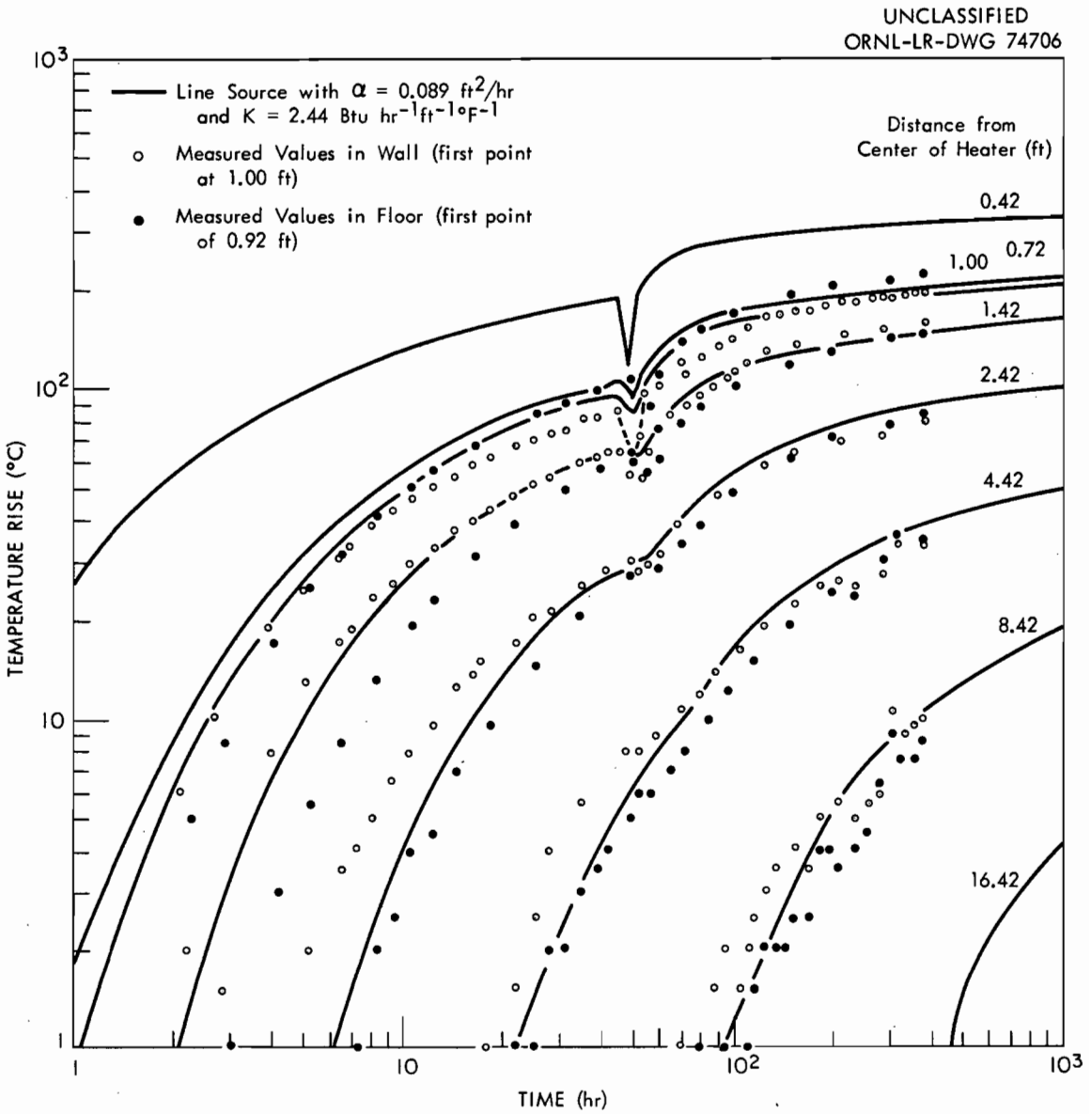

Fig. 10. Comparison of Temperature Rise in High-Temperature Cylinder Tests II and III with Theoretical for Line Source.

No thermocouples were installed at the periphery of the heater holes (0.42 ft from the center of the heater), but the theoretical salt temperature was about 210°C when the caliper measurements were begun. Maximum closure of the holes was about 0.4 to 0.5 in. at a depth of 8 ft (the center of the heater). Data on the floor hole was more variable, and fewer points were measured than on the wall hole, but there appears to have been little difference in the amount of closure of the two holes. Also, there does not appear to have been any significant difference in closure between the vertical and horizontal directions in the wall hole, indicating that the closure was primarily due to thermal expansion.

After about 69 hr of operation, the insulating plug was pulled from the wall hole, and a visual inspection was made. As the plug was being replaced, there was an explosion of sufficient violence to blow the plug from the hole. Within a half hour of the explosion, an explosion was heard in the floor test, which had not been disturbed since the completion of calipering. The theoretical peak temperature of the salt at the time of the first explosion was about 280°C. Since that time a number of additional explosions of various magnitudes have been heard in both wall and floor tests. They were not chemical explosions but were due to the pressure buildup in "negative" crystals containing trapped water. Laboratory tests had indicated that such explosions might be expected at salt temperatures about 250°C (see previous reports in this series). As may be seen from Fig. 10 the shattering of the salt does not appear to have had any significant effect on the heat transfer.

Both wall and floor tests had moisture-collection systems, consisting of a heated pipe extending down into the top of the annulus between the heater pipe and the wall of the heater hole, a condenser, a condensate trap, and a small vacuum pump. It was anticipated that several gallons of water would be driven from the shale bands in the floor test and that a small amount would be released from the salt in the wall if shattering took place. After 384 hr of operation the total condensate collected from the floor test was 10.6 liters, and from the wall, 0.2 liter.

6.1.2 High-Temperature Array

The array was started at 2:30 p.m. on July 23, and the peripheral heaters began to fail after about 8 hr of operation. Inspection of the first heaters to fail showed that the nickel connecting wires had broken for reasons that were not apparent. An investigation of the cause of the failure is underway.

Operation continues, with the central heater only, at a power level of 3700 w.

7. CLINCH RIVER STUDIES

7.1 Dilution Factors

P. H. Carrigan[14]

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

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

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

where

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

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

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

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

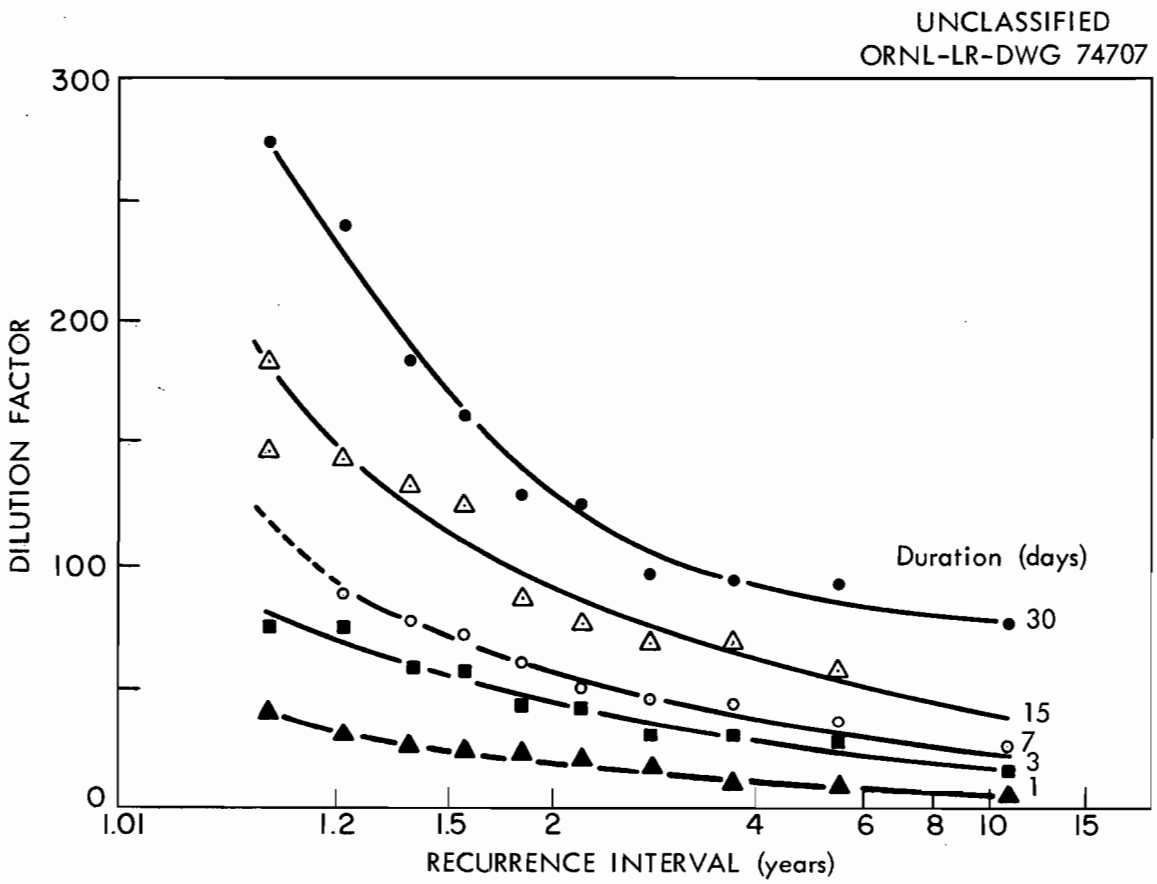

Fig. 11. Minimum Dilution Factor Frequency Curves for 1, 3, 7, 15, and 30 days, Annual Series.

7.2 Bottom-Sediment Sampling

R. J. Pickering[14]

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

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

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

8. FUNDAMENTAL STUDIES OF MINERALS

T. Tamura

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

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

8.1 Capacity of Heat-Treated Gibbsite for Cesium and Strontium

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

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

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

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

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

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

Table 13. Desorption of Cesium and Strontium from Heat-Treated Gibbsite

Cation Sorbed	N of $NaNO_3$ used for Desorption	pH of Solution	Total Na^+ used (meq)	Na^+ / Cs^+ or Sr^{2+}	Percentage Removed
Cesium	0.01	8	0.25	1.7	57
	0.01	8	0.50	3.3	83
	0.01	8	3.5	23	96
Strontium	0.01	8	3.5	7	22
	0.1	8	50	103	50
	1.0	8	352	733	77
	5.0	8	3540	7375	95

times the concentration of strontium on the sorbent, only 50% of the strontium was desorbed. After passage of sodium of over 730 times the strontium concentration, 77% was desorbed. Over 95% removal was not achieved until about 7000 times the concentration on the sorbent were used.

The difficulty with which strontium is desorbed is evidence of a strong bond between the sorbent and strontium. However, the strontium is desorbed quite readily if the pH is dropped below neutral. This rapid release with decrease in pH would indicate that the reaction is taking place on the surface of the sorbent, rather than as a separate discrete precipitate.

8.2 New Heat-Treated Materials as Strontium Sorbent

Several hydrous oxide minerals of iron and aluminum were heated to test whether they would show properties favorable for the sorption of strontium. Diaspore ($HalO_2$), goethite ($HFeO_2$), and limonite ($Fe_2O_3.xH_2O$) were used.

In Table 14 the results of surface area measurements and the strontium sorption tests are given for materials which had been heated at 500°C for 3 hr. In addition to the minerals, the results for reagent grade ferric oxide power is listed. In every case, the heated materials showed a higher surface area than the unheated mineral. The heat-treated materials were also superior to the unheated for removing strontium. The reaction reaches equilibrium in about 4 hr or less. Limonite showed a relatively high affinity for strontium even prior to heating, but the heat treatment produced a superior product. The high reactivity of limonite in the natural state is probably due to the initially high surface area.

Table 14. The Percentage Sorption of Strontium by Several Natural Materials from 0.1 M $NaNO_3$ Containing 1×10^{-5} M Sr^{2+} 0.25 g per 50 ml of solution

	Surface Area (m^2/g)	Contact Time (hr) 1		4		24		48		96	
		% sorbed	pH	% sorbed	pH	% sorbed	pH	% sorbed	pH	% sorbed	pH
Diaspore, <325 Mesh											
Unheated	6.6	16.33	9.85	17.30	9.91	18.64	9.69	17.51	9.98	17.40	9.65
Heated[a]	68.5	72.81	9.45	83.99	9.78	85.74	9.75	86.13	9.82	84.71[b]	9.21[b]
Goethite, <325 Mesh											
Unheated	3.3	15.76	9.80	18.33	9.69	17.85	9.80			17.72	9.59
Heated	62.1	95.49	9.75	97.62	9.77	98.13	9.79			97.30	9.59
Limonite, <325 Mesh											
Unheated	20.8	84.17	9.70	94.39	9.80	97.83	9.61	98.27	9.91	98.23	9.60
Heated	93.2	98.17	8.95	99.60	9.62	99.71	9.68	99.75	9.82	99.62[b]	9.16
Fe_2O_3											
Unheated		33.80	9.76	40.32	9.89	41.89	9.79	41.76	8.85	38.54[b]	9.11[b]

[a] 500°C for 3 hr.

[b] Sample contacted 144 hr.

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

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

9. WHITE OAK CREEK BASIN STUDY[16]

9.1 Movement of Radionuclides in White Oak Creek

T. F. Lomenick

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

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

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

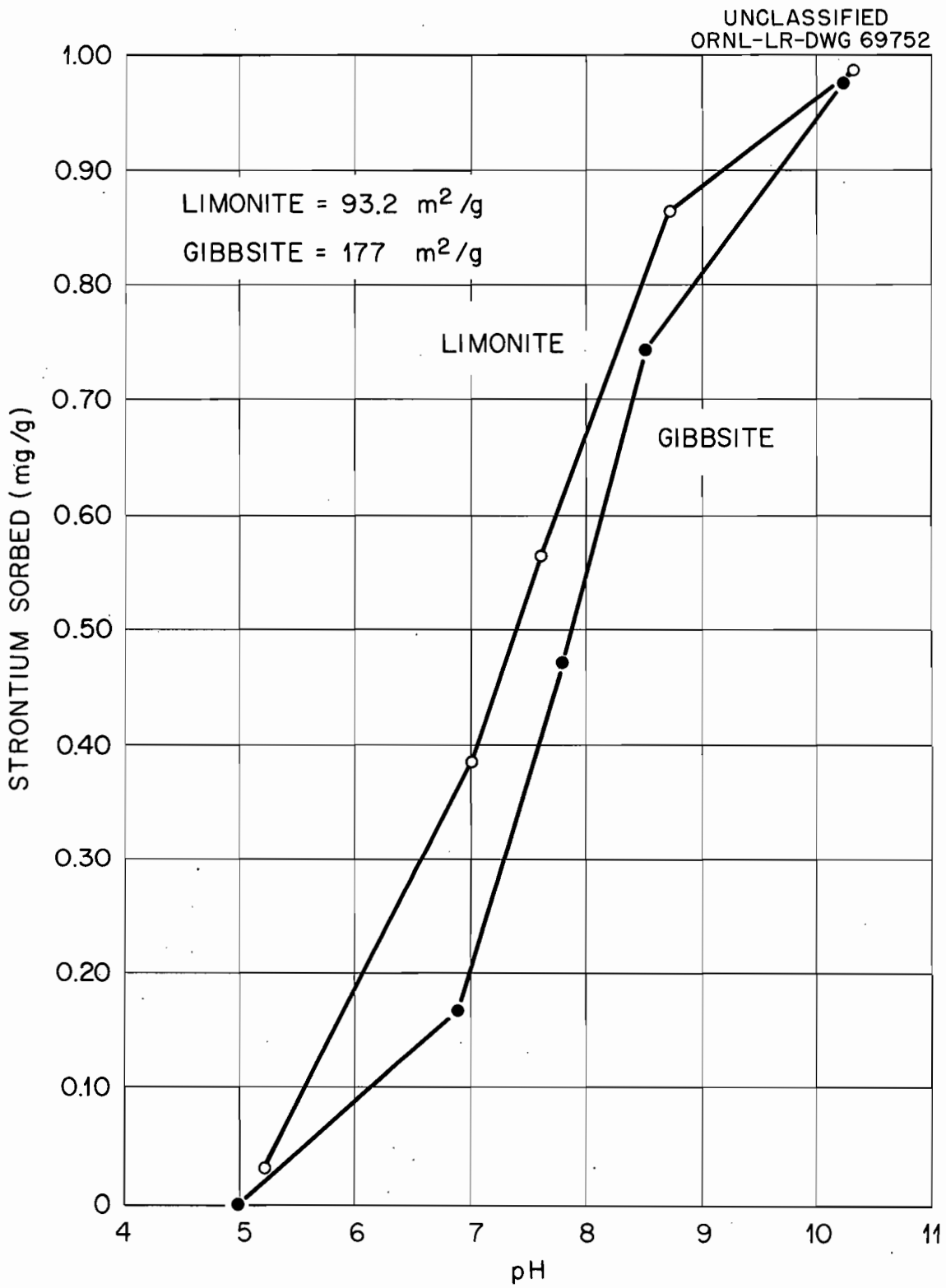

Fig. 12. Strontium Removed by Heat-Treated Minerals in 0.1 M $NaNO_3$.

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

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

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

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

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

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

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

10. FOAM SEPARATION

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

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

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

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

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

process. Strontium can be removed by factors of 100 to 1000 by foam separation from water with such low values of dissolved hardness.[19] Apparatus for the continuous runs (Fig. 13) was used to test the softening of this waste water by the addition of 0.004 M NaOH plus 50 ppm of Na_3PO_4 in a manner similar to that for the previous runs with 0.005 M NaOH--0.005 M Na_2CO_3 (Table 18). It may be seen that the phosphate precipitation process reduces dissolved hardness to 2 to 3 ppm; that is to say, to about the same level as that for the NaOH-Na_2CO_3 process. However, good operation of the phosphate process is rather critically dependent on pH and PO_4^{3-} concentration. The phosphate concentration in low-activity waste water used in the continuous runs was about 3 ppm, Table 19.

Beaker tests of the effects of individual impurities on the softening of ORNL tap water were extended to include 0.01 M NaOH--0.005 M Na_2CO_3 or 0.005 M NaOH--60 ppm PO_4^{3-} as precipitants (Table 20). These tests showed that precipitation of calcium as $CaCO_3$ from 0.01 M NaOH solution is inhibited by a few parts per million of Turco 4234, sodium hexametaphosphate, FAB, and sodium pyrophosphate, more so when Fe^{3+} is not used as a coagulating agent. The inhibition can be nearly eliminated by using 0.005 M NaOH--0.005 M Na_2CO_3 as precipitant or by using about 60 ppm of PO_4^{3-} in 0.005 M NaOH as precipitant.

The beaker tests suggest that Fe^{3+}, added as a coagulant, can act in two different ways. If slow stirring[17] is used the ferric oxide floc is voluminous and appears to cover $CaCO_3$ crystals, thereby reducing the speed of precipitation of more $CaCO_3$. At fast stirring rates, the floc is broken into smaller particles and the speed of $CaCO_3$ precipitation increases.

Results of other beaker tests showed that sodium dodecylbenzene sulfonate, which is typical of the surfactant used in many commercial detergent formulations, oxalate, fluoride, and copper ions do not interfere with the precipitation of calcium as $CaCO_3$; EDTA does not interfere with the portion of the dissolved calcium that is not chemically combined with EDTA (Table 20).

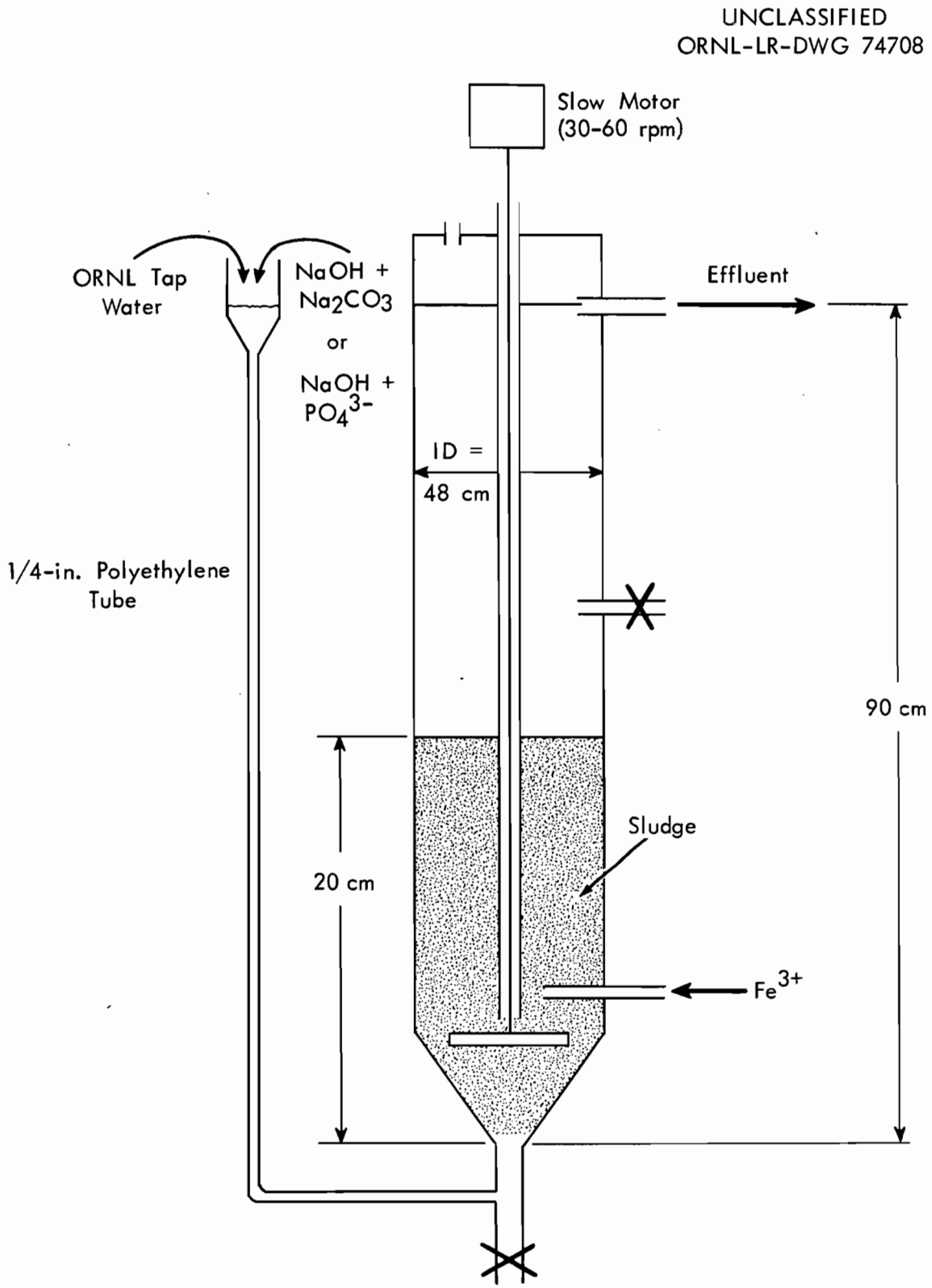

Fig. 13. Apparatus for the One-Step Pretreatment.

Table 18. Results of Continuous Runs with Low Activity Waste

Flow Rate of Feed (ml/min)	Sample Time (hr)	Type of Feed Water	Effluent from the Column: Ca in Soln.	Ca as Solids	Ca + Mg in Soln.	Ca + Mg in Solids	Sr DF: Soln.+ Solids	Soln. only	pH	Turbidity
		Precipitant: 0.005 M NaOH plus 0.005 M Na_2CO_3 Flocculating Agent: 2 ppm of Fe^{3+}								
10-6	48	Tap			1.2					
10-6	72	Tap			1.6				11.3	
11-0	80	Tap			1.5					
11-0	0	LLW 1							11.3	
11-2	20	LLW 1	1.1		1.8	0	10.2			
11-2	24	LLW 2	1.2	0.15	1.65	0.2	12.3	12.2	11.2	
11-2	27	LLW 2	1.05	0.2	2.05	0	10.2	12.0		
11-3	43	LLW 2	1.95		3.0		11.0	12.2		
11-3	45	LLW 3							11.3	
11-3	47	LLW 3	1.25		1.7	0.4	10.6	10.9		
11-3	49	LLW 3	1.2	0.25			10.6	11.1		
11-3	67	LLW 3	1.2		2.0		10.7	9.2	11.3	
11-3	67-1/2	LLW 4								
11-3	69	LLW 4	1.45		1.6	0.1	11.5	10.4		
11-3	74	LLW 4	1.30	0	1.65	0.3	10.1	12.2	11.3	
11-4	91	LLW 4	.95	0.2	1.80	0.15	10.0	10.4		
11-4	92	LLW 5							11.3	
11-4	99	LLW 5	1.50		1.80	0.15	10.0	10.0		
11-4	100	LLW 5	1.20		1.70	0	10.6	12.4	11.3	
		Precipitant: 0.004 M NaOH plus 50 ppm of PO_4^{3-} Flocculating Agent: 7 ppm of Fe^{3+}								
11-2	0	Tap							11.2	
11-2	48	Tap	1.50		1.8					3
11-0	0	LLW 6							11.2	
11-0	5	LLW 6					37.0	55		
11-0	24	LLW 6			2.2	0.2	20.7	24	11.15	
11-0	26	LLW 7								
11-0	28	LLW 7			2.2		18.7	23.4	11.0	
11-0	30	LLW 7			2.2	0.1	20.9	18.7		3
11-0	48	LLW 7			2.85	0.15	14.6	14.4	11.2	6
11-0	48-1/2	LLW 8								
11-0	52	LLW 8			3.2	0.3	11.2	12.5	11.2	5
11-0	54	LLW 8			1.2	0	20.7	19.0		

[a]ppm, as $CaCO_3$.

Table 19. Composition of ORNL Low-Activity Waste and Tap Water Samples

Sample	Date	Ca (ppm as $CaCO_3$)	Mg (ppm as $CaCO_3$)	pH	HCO_3^- (ppm)	Total P[a] as ppm PO_4^{3-}
LLW 1	5/21/62	65	39	7.5	76	3.4
LLW 2	5/22/62	68	37	8.0	88	2.6
LLW 3	5/23/62	61	39	8.0	88	2.6
LLW 4	5/24/62	64	38	8.3	88	2.8
LLW 5	5/25/62	60	36	8.0	83	3.0
LLW 6	6/13/62	63	34	8.2	102	2.0
LLW 7	6/14/62	63	35	8.8	100	3.0
LLW 8	6/15/62	63	33	8.0	108	3.0
ORNL Tap		~64	~35	~7.8	~90	-

[a]In the analysis, all phosphates are converted to orthophosphate.

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

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

[a]Noncomplexed (Ca + Mg).

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