80
10-25-65

ORNL-3811
UC-70 – Waste Disposal and Processing
TID-4500 (45th ed.)

LABORATORY DEMONSTRATION OF THE TWO-STEP PROCESS FOR DECONTAMINATING LOW-RADIOACTIVITY-LEVEL PROCESS WASTE WATER BY SCAVENGING-PRECIPITATION AND FOAM SEPARATION

W. Davis, Jr.
A. H. Kibbey
E. Schonfeld

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

Printed in USA. Price $2.00. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia

ORNL-3811

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

LABORATORY DEMONSTRATION OF THE TWO-STEP PROCESS FOR DECONTAMINATING LOW-RADIOACTIVITY-LEVEL PROCESS WASTE WATER BY SCAVENGING-PRECIPITATION AND FOAM SEPARATION

W. Davis, Jr. A. H. Kibbey E. Schonfeld

OCTOBER 1965

Oak Ridge National Laboratory
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

CONTENTS

LABORATORY DEMONSTRATION OF THE TWO-STEP PROCESS FOR DECONTAMINATING LOW-RADIOACTIVITY-LEVEL PROCESS WASTE WATER BY SCAVENGING-PRECIPITATION AND FOAM SEPARATION

W. Davis, Jr. A. H. Kibbey E. Schonfeld

ABSTRACT

The two-step process for decontaminating low-level radioactive waste water was demonstrated in two continuous runs on a laboratory scale. The process consists in first precipitating and eliminating most of the suspended solids and soluble hardness in a suspended-bed sludge column and then producing further decontamination in a counter-current foam column. Overall decontamination factors for Sr, Co, Ru, and Ce were $>3.7 \times 10^3$, 2.3 to 4, 2 to 5, and 50 to 180, respectively. The cesium decontamination factor was 20 when 60 ppm of grundite clay (baked at 600°C for 20 min) was added to the low-level waste (LLW) during the precipitation step. The ratio of surface to liquid flow rate is the crucial factor governing satisfactory strontium decontamination in the foam column. The metal ion decontamination factor in the foam-separation step is proportional to the metal ion distribution coefficient and inversely proportional to the volume reduction and liquid throughput. The cost of chemicals for this process is 26.6¢ per 1000 gal of LLW. Development of the process flowsheet required the study of several problems or variables. These included: (1) the effects of pH on precipitation of hardness ions; (2) the prevention of inhibitory effects of phosphates present in the waste water on the precipitation of calcium carbonate; (3) study of the sludge density as a function of liquid flow rate and bed depth; (4) the degree of biodegradability and fast quantitative analysis of surfactants; (5) the effect of splitting the feed of surfactant into the foam column; (6) volume reduction; and (7) recovery of surfactant.

1. INTRODUCTION

Some nuclear energy installations daily produce thousands of gallons of slightly radioactive "process water" which can be regarded as ordinary tap water that includes very small amounts of radioactive isotopes of elements such as Sr, Cs, Ce, Co, Ru, Zr, and Nb. The problem is to find an economical way to decontaminate the water to a sufficient degree that it may be released to the natural environment or returned to the plant for reuse as "industrial" water. The purposes of this report are to present a successful method for decontaminating water to a level that permits discharge to the environment and to present highlights of the developmental work.

Briefly, the method consists in first precipitating the hardness ions (calcium and magnesium) by simultaneously adding solutions of sodium hydroxide, sodium carbonate, and ferric chloride, the precipitated iron serving as a coagulant. The precipitation process also serves to scavenge some of the radioactive components (particularly strontium, cerium, and cobalt). Next, an appropriate detergent is added to the softened supernatant, which is fed to a foam column. Air is passed through a gas distributor in the liquid pool at the bottom of this column, thereby generating foam which carries off the rest of the strontium and most of the other remaining radionuclides.

The steps in developing the process were keyed to the removal of strontium, the most biologically hazardous radioisotope in the water. Of the factors that underlie the process, two are most important: (1) strontium, calcium, and magnesium combine with certain surfactants to form surface active compounds which concentrate in the foam phase created by bubbling air into the water; (2) to improve efficiency, the water should first be softened to remove calcium, which can greatly interfere with removal of strontium by foaming.

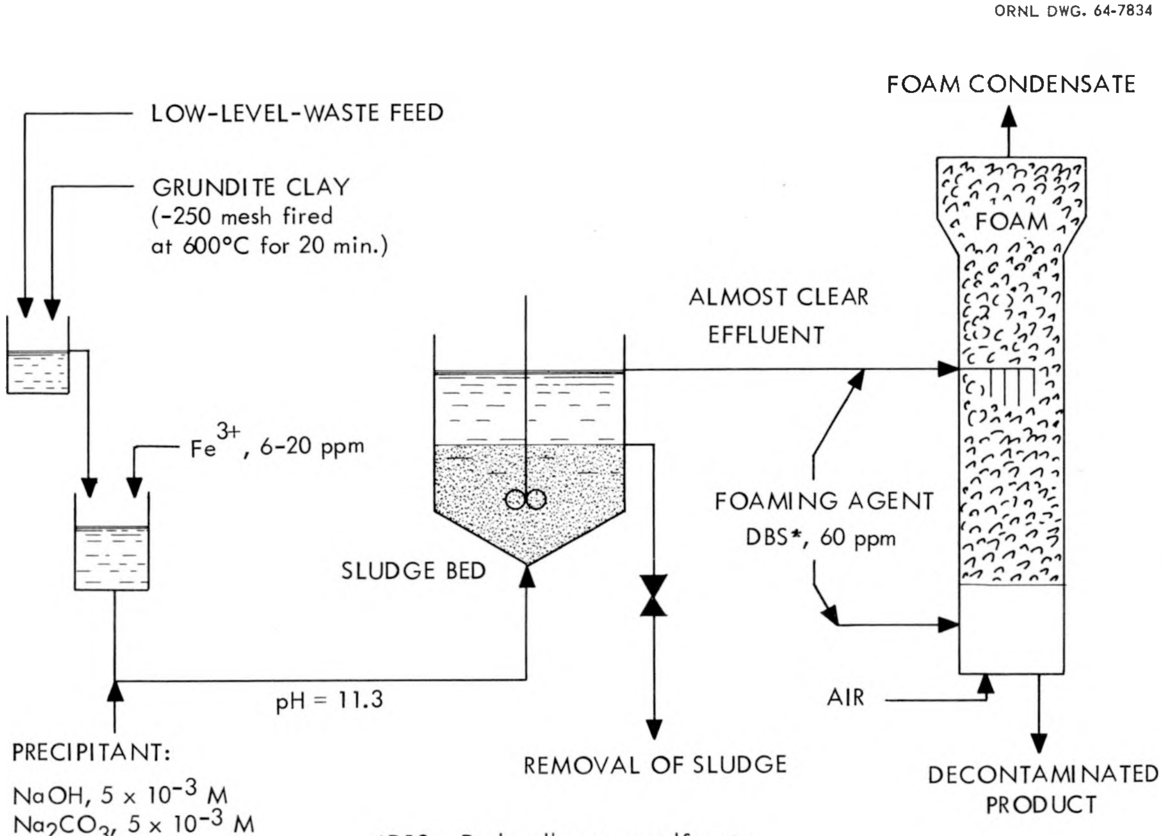
This report is divided into two parts: first, a discussion of laboratory demonstration runs; second, a summary of the developmental work.

2. GENERAL DISCUSSION OF FLOWSHEET

A diagram of the Two-Step Foam Separation Process for removing strontium and other radioactive elements from process solution is presented in Fig. 1; a picture of equipment used in some of the laboratory studies is shown in Fig. 2. In laboratory-scale flowsheet-development runs, synthetic feeds prepared from ordinary tap water were occasionally substituted for actual waste water, since both normally contain total hardness of about 100 ppm (as calcium carbonate).

2.1 Step 1: Scavenging-Precipitation of Hardness Ions Plus Most of the Strontium

In the first step (see Figs. 1 and 2), most of the calcium and magnesium are removed in a slowly stirred, up-flow, sludge precipitation column. Favorable, although possibly not optimum, conditions, as derived by laboratory experimentation, are attained by:



*DBS = Dodecylbenzene sulfonate

Fig. 1. Two-Step Process for Removing Strontium from Process Waste Water. First, the calcium and magnesium, and some radioactive strontium, are removed by adding NaOH, Na_2CO_3, and $FeCl_3$ solutions simultaneously to the waste water. On the way to the foam column, foaming agent is added to the softened water. At the foam column, air is bubbled through the pool of water in the bottom of the column, and the strontium salt of DBS is carried away in the foam, which moves on to a foam breaker and concentrator. DBS is also added to the pool. Decontaminated water is drawn off the bottom of the column.

PHOTO 60640R

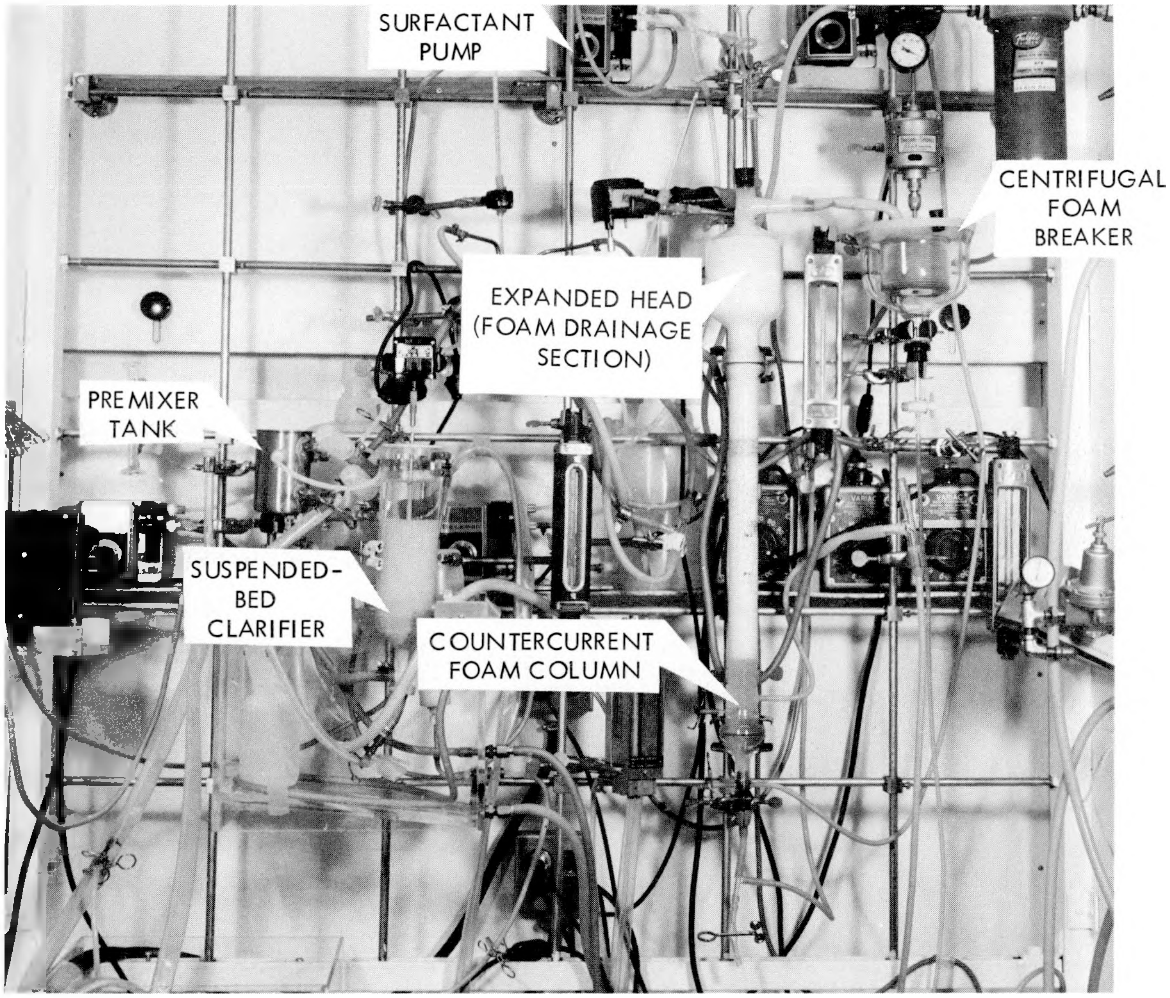


Fig. 2. Laboratory Equipment Used in Developing the Scavenging-Precipitation Foam-Separation Process for Decontaminating Low-Activity-Level Waste Water. This photograph shows the short column (50-cm height); the pumping system for grundite addition is omitted.

1. adding approximately 0.5 lb of baked grundite clay per 1000 gal of water for sorbing cesium, if desired (see Sect. 2.5.1);
2. maintaining the feed water flowrate at 20 gal per hr per sq ft of column cross-sectional area (however, flowrates as high as 60 gal ft^{-2} hr^{-1} are satisfactory[1]);
3. making the water 0.005 M each in sodium carbonate and sodium hydroxide (final pH 11.3); and
4. simultaneously adding sufficient ferric chloride to make the water 6 to 20 ppm in Fe^{3+} (depending on the phosphate concentration in the feed) as a scavenging agent and coagulant.

The softened, nearly clear supernatant solution, now containing less than 5 ppm of total hardness, is then fed to the foam column.

2.2 Step 2: Further Removal of Strontium from the Softened Water in the Foam Column

The hardness-removal step is followed by passing the water downward through a counter-current foam separation column in which further strontium decontamination is achieved. This is accomplished by:

1. pumping the softened water from the sludge column to the top of the foam column at a rate of about 60 gal per hr per sq ft of column cross-sectional area;
2. adding the surfactant (concentration: 5 g/liter sodium dodecylbenzene sulfonate solution) to foam column feed and liquid pool in the ratio 5/1 at a rate such that if it were all added to the feed, its concentration would be 60 to 100 ppm;
3. bubbling air through a gas disperser (extra-coarse sintered glass or 50- to 60-μ pore diameter platinum-rhodium spinerette) at a rate of 900 to 1200 cu ft per hr per sq ft of foam column area, which produces an upward linear flow of the foam phase of 1.5 to 2 ft per min; and
4. condensing the foam by allowing it to overflow into a foam breaker (we used a basket centrifuge, Fig. 2), the exit stream of which contains the highly concentrated, radioactive contaminants. The decontaminated waste water, containing 20 to 30 ppm DBS, emerges from the bottom of the foam column.

2.3 Cost of Chemicals

The reagents are commercially available and cheap. Also, since water from the sludge bed contains approximately a 15-fold molar excess of sodium hydroxide with respect to the number of moles of DBS added prior to foaming, the cheaper, acid form (DDBSA) should be used, rather than the sodium salt. List prices of reagents,[2,3] including \$0.005 per pound shipping costs (except for grundite clay[4]), and the calculated amounts of each required for processing 1000 gal of typical waste water, are given in Table 1. Total chemical costs of 26.6 to 29.7¢ per 1000 gal of water were obtained, depending upon the amount of surfactant recovery achieved (see Sect. 3.3.1) -- here the figures are for 30% recovery and no recovery, respectively.

Table 1. Costs of Chemicals for the Scavenging-Precipitation Foam-Separation Process

	Cost (\$/lb)	Usage (lb/1000 gal)	Chemical Cost (\$/1000 gal)
NaOH (ref 3)	0.03	1.67	0.067[a]
Na_2CO_3 (ref 3)	0.019	4.42	0.106[b]
$FeCl_3$ (ref 3)	0.095	0.15	0.015[b]
DDBSA (ref 4)	0.155	0.67	0.104[b]
Grundite (ref 5)	0.01	0.50	0.005[c]
		No surfactant recovery	\$0.297
		30% surfactant recovery	0.266

[a] Includes \$0.01/lb of contained NaOH for shipping 50% caustic.

[b] Includes \$0.005/lb shipping cost at essentially 100% purity.

[c] This value is assumed to include the shipping cost.

2.4 Correlation of Foam-Column Efficiency with $V/L\overline{D}$

The parameter $V/L\overline{D}$ is probably the most useful measure of foam column performance with respect to the strontium decontamination factor[5] (DF). Here V is the gas flowrate, L the liquid flowrate, and $\overline{D}$ an average bubble diameter (see Sect. 3.3.3).

From Fig. 3 we see that as $V/L\bar{D}$ increases almost threefold (from about 100 to nearly 300), the foam column strontium DF increases by a factor of roughly 100 (from about 2 to more than 200), even though some of the physical and chemical conditions differ. Apparently, the strontium DF is more or less independent of phosphate concentration (P indicates high phosphate concentration) and is not markedly affected by recycle of the condensed foam to the sludge-bed feed stream (recycle shown by squares except where none is indicated by NR). Foam condensate recycle was tested for two reasons: first, it would lower surfactant consumption and, second, the number of waste streams would be reduced to just one. (For further discussion of these two process variables see Sects. 3.1.2 and 3.3.1, respectively.) Slightly better strontium DF's were obtained for synthetic tap-water feeds than for actual waste water.

A comparison of these strontium decontamination factors in the foam column with those obtained for the overall process (Figs. 3 and 4), for all conditions studied, indicates that the overall strontium DF is about 10 times greater than that in the foam column alone at a given $V/L\bar{D}$; that is, the strontium DF in the sludge column is consistently close to 10.

2.5 Results and Discussion of Two Laboratory Demonstration Runs

Two laboratory demonstration runs with ORNL process waste water (only one of them with grundite clay present, at 0.5 lb/1000 gal of water) were made without the foam-recycle option. To ensure meaningful counting results in subsequent radiochemical analyses, the radioactivity levels of the isotopes of special interest - ^{85}Sr, ^{137}Cs, ^{106}Ru, ^{60}Co, and $^{141-144}$Ce - were boosted to the minimum reliable counting range by adding suitable amounts of each of the respective tracers. The total radioactivity processed in each run did not exceed 0.02 mc/liter. Since no ^{137}Cs tracer was added to the run in which grundite clay was omitted, the ^{85}Sr tracer required in this run was only 1/10 the amount used when ^{137}Cs was present. At maximum buildup of radioactivity, the precipitated sludge (less than 200 cc/day) was calculated to have a radioactivity concentration of less than 0.3 mc per liter of slurry. In actual practice, the accumulated slurry produced a radiation field less than 5 mr/hr at a distance of 1 ft.

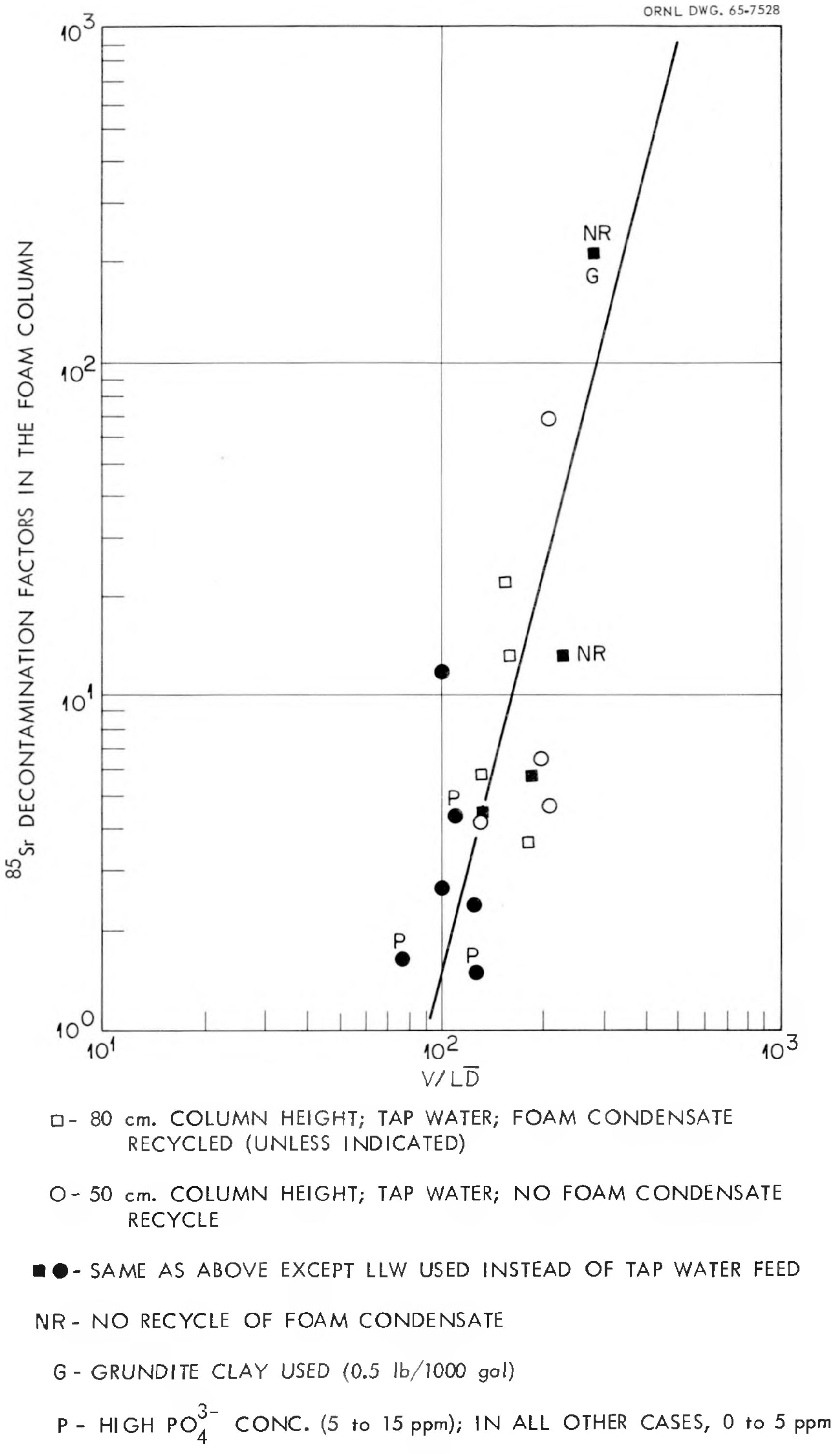


Fig. 3. Strontium Decontamination Factor in the Foam Column Increases as the Ratio V/L$\overline{D}$ Increases and Is More or Less Independent of Phosphate Concentration and/or Foam Recycle.

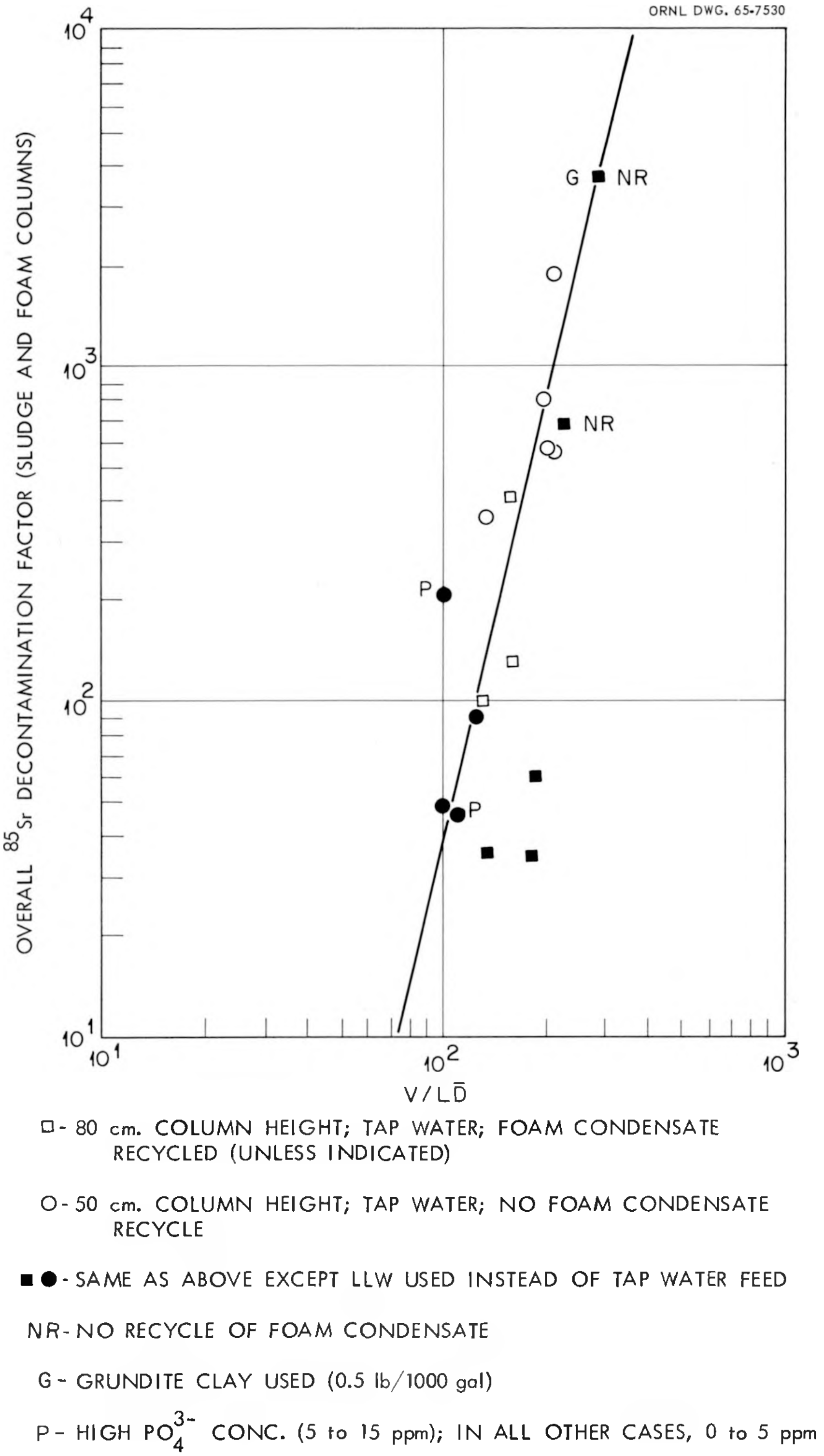


Fig. 4. The Total Strontium Decontamination Factor Over Both the Sludge Precipitator and Foam Column Is Ten Times Higher than for the Foam Column Alone (Compare with Fig. 3.).

The sludge and foam columns were, respectively, 76 mm ID x 25 cm high and 37 mm ID x 80 cm high (exclusive of foam drainage section which was 10 cm diam x 10 cm high), and the corresponding average liquid flowrates through these columns were 12.5 and 41 gal ft^{-2} hr^{-1}. The liquid pool depth was about 25 cm. Whether or not there is an advantage in using a foam column greater than 50 cm in length has not been determined.

The $V/L\bar{D}$ value was about 200 for the grundite run and about 270 for the run in which grundite was omitted. In both runs, the average bubble diameters, obtained from photographs taken during the runs, ranged from 0.06 to 0.08 cm. The surfactant added to the foam column, if added only to the feed, would have produced an average concentration of 90 to 100 ppm in the feed; the addition ratio (top/bottom) varied within the range 5 to 5.5 parts added to the foam column feed water for each part added to the liquid pool at the bottom of the column.

Samples of the process streams were taken from the line delivering water to the sludge column, from the sludge-bed supernatant overflow line, and from the decontaminated foam column effluent. A portion of each sample solution was filtered through No. 42 Whatman paper before analysis to enable us to distinguish between ionic contaminants and those entrained as solids. From the analytical results, various decontamination factors for calcium and total hardness and several radioactive elements were calculated (Table 2). Concentrations of individual radioactive nuclides were obtained by least-squares resolution of gamma-ray spectra.[6] Based on an estimated value of 2 for the strontium extraction factor (E), we calculated an HETS of 3 cm of foam for strontium removal. The uncertainty of this number is ±1 cm, or more.

2.5.1 Satisfactory Performance of Grundite Clay as a Cesium Sorber in the Precipitation Step

Overall strontium decontamination factors greater than 3.7×10^3 were achieved when 0.5 lb of baked grundite clay, a cesium sorber, was added per 1000 gal of water fed to the sludge precipitator unit. The strontium decontamination factor in the sludge precipitation step was lower when grundite was used than when it was not. However, the increased decontamination by the foam column when grundite was present more

Table 2. Decontamination of Spiked ORNL LLW Water by the Foam Process

Conditions: Feed: 0.005 M each NaOH and Na_2CO_3. ~60 ppm grundite clay (~0.5 lb/1000 gal) added in one run only. PO_4^{3-} <0.7 ppm in absence of grundite and 2.4 ppm with grundite present.

Flows: Surfactant feed ≈90 to 100 ppm in foam column, added in a split stream with the ratio top/bottom = 5 to 5.5/1.

Throughputs: sludge column = 12 to 13 gal ft^{-2} hr^{-1}
foam column = 40 to 42 gal ft^{-2} hr^{-1}

Average bubble diameter $\bar{D}$ = 0.06 to 0.08 cm

$V/L\bar{D}$: With no grundite = 273 cm^{-1}; with grundite present = 202 cm^{-1}

	Decontamination Factors											
	Sludge Column				Foam Column				Overall			
	With Grundite		No Grundite		With Grundite		No Grundite		With Grundite		No Grundite	
Component	Filt.[a]	Unfilt.[a]	Filt.[b]	Unfilt.	Filt.[b]	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.
Total Hardness	32	6	40	<8	~1.1	~9	~1	>9	41	53	30	43
Ca	29	5	34	<8	~1.3	~9	~1	>10	39	49	27	>40
^{85}Sr	20	16	70.5	42	338	212	12	13	7935	3725	630	705
^{137}Cs	25	21	1.6	1.3	~1	1	1	1	21	20	1.3	1.3
^{60}Co	2.5	2.9	4.5	4.1	1.3	1.1	1.1	1.0	2.4	2.3	3.5	4
^{106}Ru	1.7	1.8	1.3	1.5	3.5	3.8	1.4	1.3	4	6	1.8	2.0
^{144}Ce	44	24	> 775	75	6.4	4.4	~2.2	1.3	280	118	>49	118.6
$^{95}Zr-Nb$	(These activities were too low to measure)											

---

[a] Filtered effluents are expected to give higher DF's than unfiltered effluents, owing to precipitated solids removal; discrepancies are attributable to the standard deviations of the analytical and sampling techniques.

[b] These DF's are for soluble Ca^{2+} and total hardness ions only (no solids removal); this value is the ratio of filtered sludge effluent to filtered foam effluent analyses.

than compensated for the lower decontamination by the sludge column. (Omission of the grundite clay resulted in overall strontium DF's in the range of 600 to 700).

Cesium decontamination factors were about 20 with grundite present and only 1.3 when it was absent.

Overall decontamination factors obtained for other isotopes of interest, namely, ^{60}Co, ^{106}Ru, and ^{144}Ce, were 3 to 4, ~2, and 50 to 120, respectively, when grundite was absent, and ~2.35, ~5, and ~120 to 180 when grundite was used. All the foregoing data are summarized in Table 2.

3. DEVELOPMENTAL WORK

The developmental work entailed in putting the concept of foam separation to use in decontaminating low-level radioactive process waste water (LLW) was divided into two categories. The first, which arose from difficulties encountered in foaming small amounts of strontium out of solutions containing relatively large amounts of calcium and magnesium, dealt with reducing the total hardness in solution to an acceptable concentration (less than 5 ppm) in a head-end precipitation step. The second was confined to the various aspects of foam column operation and included: selection of a suitable surfactant, reduction of process costs, improvement of efficiency, testing related analytical procedures for quantitative determination of the surfactant (DBS), and optimizing the various operating parameters (liquid and gas flow rates and bubble diameters) to give satisfactory strontium decontamination with an acceptable volume reduction factor. These last two items vary in opposite directions as the process variables — throughput, distribution coefficient, and number of theoretical plates — are varied.

Much of this developmental work has been presented in detail elsewhere; therefore only brief summaries with appropriate references will be given here. In the few cases where new information has become available or where additional work has been done which has not been reported previously, a more complete discussion is offered. This is particularly true for the section dealing with the operating relationship $V/L\bar{D}$, and also for the more detailed treatment of the relation between volume reduction and strontium decontamination factor.

3.1 Scavenging-Precipitation Step

The removal of strontium from dilute, slightly basic waste-water solutions by foam separation was found to be an inverse function of the amount of calcium present.[7] Thus, to optimize strontium decontamination, calcium and magnesium were precipitated in a head-end step preceding foam separation.

3.1.1 Effects of pH on Precipitation of Hardness Ions

Early studies[1] showed that it is possible to reduce an initial hardness concentration (Ca/Mg mole ratio about 2) of about 100 ppm (expressed as $CaCO_3$) to the range of 2 to 5 ppm by using a slowly stirred, up-flow sludge precipitator in which pH is maintained at 11.3 in the presence of a few ppm of ferric-ion coagulant (Figs. 1 and 2). A mixture of sodium hydroxide and sodium carbonate was used as the precipitant because the solubility of calcium carbonate is at least a hundredfold less than that of calcium hydroxide, whereas the reverse is true of the corresponding magnesium salts.[8] Furthermore, a slight excess of sodium hydroxide prevents formation of the HCO_3^- ion, which effectively increases the solubility of calcium ion. (To minimize the amount of solids in solution, the excess caustic is limited to the amount necessary to maintain the pH at 11.3). Thus, under the chosen process conditions, calcium precipitates from solution as the carbonate while magnesium precipitates as the hydroxide.

3.1.2 Inhibitory Effect of Phosphates on Precipitation of Calcium Carbonate and Its Prevention

Phosphate ions in the few-parts-per-million range are known to inhibit calcium precipitation from dilute caustic solution.[9,10,11] Since LLW normally contains mixed phosphates equivalent to 2 to 5 ppm when measured as the orthophosphate,[12] a series of beaker tests and column runs[5] were performed to study the behavior of hardness ions (primarily calcium and magnesium) under various conditions of carbonate, phosphate, iron, and hydrogen ion concentrations.

A solution 0.005 M each in sodium carbonate and sodium hydroxide and 4 ppm in ferric iron (pH = 11.3) was very effective for precipitating calcium and magnesium in the presence of low phosphate concentrations[10] (total phosphorus equal to 1 to 3 ppm of orthophosphate). Experiments in which the total phosphorus concentrations (expressed as orthophosphate) were near 5 ppm showed that adding 10 ppm of ferric ion to the neutral water solution (that is, prior to adjusting the pH to 11.3 by adding the caustic-carbonate) effectively removed the soluble, calcium-complexing phosphates from solution within 4 min, thus permitting almost complete calcium precipitation upon subsequent addition of the precipitant. Even as much as 15 ppm mixed phosphate can be temporarily removed from solution in this way. However, after a prolonged period, owing to the higher solubility of ferric phosphate at pH 11.3 than at pH 7 to 7.5, an equilibrium condition between calcium, phosphate, and iron is reached in which the beneficial effects of separate iron addition are lost.[5] The method is still useful, however, for handling the occasional large concentrations of phosphates that occur briefly in ORNL LLW when extra-large quantities of certain cleaning and/or decontaminating compounds are used at the site.[13]

3.1.3 Sludge Density as a Function of Liquid Flow Rate and Bed Depth[14]

Densities of the sludge in a suspended-bed clarifier were measured under flowsheet conditions (0.005 M each NaOH and Na_2CO_3) for a bed 10 to 13 cm deep at a water flowrate of 20 gal ft^{-2} hr^{-1}. Calcium and magnesium concentrations decreased by a factor of 5 to 5.5 from the bottom to the top of the bed, while the concentration of ferric ion decreased by a factor of 3.5. The analytical results obtained on samples taken at the bottom, middle, and top of the bed are summarized in Table 3.

Table 3. Distribution of Iron and Total-Hardness Cations in the Sludge Bed
Conditons: Flow rate, 20 gal ft^{-2} hr^{-1}
0.005 M NaOH--0.005 M Na_2CO_3, except where noted

Sample Point	Total Hardness (as $CaCO_3$) (g/liter)	Calcium (as $CaCO_3$) (g/liter)	Iron (g/liter)	$CaCO_3$ in Total Hardness (%)
Bottom	16.70	12.02	1.355	73
Middle	11.34	6.66	0.845	59
Top[a]	3.35	2.19	0.390	65

[a] 0.01 M NaOH; no carbonate.

In a similar experiment in which the water flow rate was varied over the range 20 to 60 gal ft^{-2} hr^{-1} while samples were taken only within the top centimeter of the sludge bed, analytical results showed that the bed density decreased by a factor of 2 to 2.5 with the threefold increase in flow rate. In this experiment no sodium carbonate was added, but the sodium hydroxide concentration was increased to 0.01 M. The amounts of hardness and ferric iron in the slurry samples are given in Table 4.

Table 4. Effect of Increasing the Water Flow Rate on Density of the Sludge Bed

Precipitant: NaOH, sufficient to make the feed 0.01 M

Water Flow Rate (gal ft^{-2}hr^{-1})	Total Hardness (as $CaCO_3$) (g/liter)	Calcium (as $CaCO_3$) (g/liter)	Ferric Iron (g/liter)	$CaCO_3$ in Total Hardness (%)
20	3.35	2.19	0.39	63
47	2.00	1.25	0.28	62.5
60	1.40	0.88	0.20	62.5

3.1.4 Selective Cesium Removal and the Merits of Grundite Clay[5]

Cesium ion is not precipitated or scavenged by the caustic-carbonate and ferric iron in the head-end precipitation step. Further, it cannot readily be removed by foaming in the countercurrent foam column in the presence of such a large concentration of sodium ion (0.015 M). Because of the great interference by sodium, a suitable "cesium-specific" reagent was sought for eliminating this nuclide from the waste water.

On the basis of past experience,[15-19] grundite clay (-230 mesh) was tested as a selective sorber for cesium ion in batch-type beaker tests and in continuous column runs. Baking the clay briefly (20 min) at 600°C, as suggested by Tamura,[19] doubled its cesium-sorbing capability. A concentration equivalent to 0.4 to 0.6 lb/1000 gal of process water, added to the water before the addition of caustic-carbonate and ferric reagents, increased the cesium decontamination factor from 1.3 to 20 in laboratory-scale flowsheet demonstration runs (see Table 2, Sect. 2.5.1). The overall decontamination factors obtained for strontium, ruthenium, and cerium were also higher when grundite was present. The clay and the radioactivity associated with it are almost entirely removed in the sludge bed clarifier, but any solids entrained in the foam column report to the foamate.

As a cesium scavenger under process conditions, grundite clay was superior to two other materials tested: magnesium ammonium phosphate powder and a refined asbestos, Asbestos CMS, a product of Union Carbide Corporation.

3.2 Selection of Surfactant for Strontium Removal in the Foam Column

The choice of dodecylbenzene sulfonate (DBS) as the foam column surfactant was the result of an extensive screening process in which over 100 surfactants were tested.[18,20]

3.2.1 Criteria

To be considered an acceptable reagent, a surfactant should be readily available, cheap, and an effective strontium remover. In addition, its physical properties under process conditions -- for example, solubility, foam stability at low surfactant concentration, and critical micelle concentration -- are important. DBS met all these requirements better than any others tested. However, a continued search for a suitable, more biodegradable surfactant recently indicated that Alipal LO 436* and Nacconol 40 FX** have the desirable physical and chemical properties and are available at low cost. Because of their purported biodegradability, they may be preferable to DBS.[21]

Biodegradability of Alklybenzene Sulfonates.--A semiquantitative study of the biodegradability of the branched-chain alkylbenzene sulfonates (ABS) present in ORNL process waste water, in the commercial cleaner Fab, and in Trepolate F-95 (nearly pure sodium dodecylbenzene sulfonate) showed that 2 to 3 weeks were required for roughly 50% degradation to occur.[22]

---

*Product of General Aniline and Film Corp.

**Product of National Aniline Div., Allied Chemical Corp.

3.2.2 Quantitative Analysis of Surfactant

The recommended standard procedure for determining dodecylbenzene sulfonate[23] (or any alkylbenzene sulfonate, ABS) is a spectrophotometric method based on extraction of the methylene-blue complex of the surfactant from a Na_2HPO_4-buffered aqueous phase into chloroform. The optical density of this chloroform solution is determined at the characteristic absorption peak of the methylene-blue--ABS compound, which occurs at 652 mμ.

A modified colorimetric method, involving a single chloroform extraction of the methylene-blue--ABS complex was also tested. Here, the surfactant concentration of the chloroform phase was read directly from a calibrated standard color wheel in a Hellige Comparator.[24] Total analysis time was about 2 min per sample, and the range of greatest accuracy was around 1 ppm.[25] This method is the one finally used for process control in the ORNL foam-separation pilot plant.[26]

3.3 Optimization of Operating Variables for the Foam Column

The main physical variables discussed in this report, $V/L\bar{D}$ and volume reduction, have direct bearing on process efficiency and cost. The first-mentioned variable is related to element decontamination factors in the foam column, while the latter is related to the cost of ultimate disposal of the concentrated intermediate-radioactivity-level waste produced by the process. The flowsheet values (see Sect. 2.4) for these variables were selected on the basis of previous experience.[18,22] Although they were not necessarily optimum operating conditions, they probably were nearly so.

3.3.1 Reduction of Process Costs

Two of the more obvious methods of cutting process costs are recovery of surfactant from the decontaminated foam-column raffinate stream and recycle of the foam condensate (foamate) to the sludge-column feed stream.

Surfactant Recovery.--No difficulty is anticipated in removing residual DBS from the decontaminated foam-column raffinate stream. Experience at ORNL has shown that 90% of the DBS in an aqueous solution 0.005 $\underline{M}$ in NaOH and 0.005 $\underline{M}$ in Na_2CO_3

(pH 11.5) can be recovered in a multistage foam column at a throughput rate of 7.5 gal ft^{-2} hr^{-1}. This has been shown with columns 1.5 in. and 6 in. diameter.[28] Other investigators[29] have also been studying the removal of surfactants from sewage and industrial wastes by foaming.

Recycle of Foam Condensate.[30]--Recycle of collapsed foam to the sludge column presented no mechanical problems. Chemical analyses showed that the recycled DBS accumulates in the solid phase of the sludge bed, probably as an insoluble calcium and/or magnesium salt. Based on DBS material balances, we estimated that about 50% of the recycled surfactant is so precipitated. Development work would be required to devise a satisfactory method for recovering the surfactant from these solids. If the foam condensate is recycled, then the waste-volume reduction factor is in the range of 1000 or greater after decantation, whereas separate sludge and foam waste streams would give values in the range of 30 to 40. (Further discussion of volume reduction is presented in Sect. 3.3.4.)

3.3.2 Improving Process Efficiency by Adding Surfactant Simultaneously to Top and Bottom of Foam Column

By splitting the surfactant feed stream to provide addition at the top of the column and at the bottom, a more uniform DBS distribution throughout the column was attained.[27] For the present flowsheet, addition of about 85% of the DBS to the top resulted in better column operation and higher strontium decontamination factors than when the total surfactant addition was made at a single point.[25]

3.3.3 Importance of the Ratio V/L$\bar{D}$ in Process Control

The factor V/L$\bar{D}$ (foam flowrate divided by the product of liquid flowrate and average bubble diameter) is related to the extraction factor E in the equation:[27]

$$E = \left(\frac{\text{Total surface area flow rate of foam}}{\text{Liquid feed flow rate}} \right) \left(\frac{\Gamma}{x} \right) , \qquad (1)$$

where Γ is the excess surfactant concentration in the surface phase (moles/cm^2), and x is the concentration of this component in the bulk phase (moles/cm^3). When the extraction factor is greater than 1, a decontamination factor in excess of 1 can be obtained (see Sects. 2.4 and 2.5). A derivation of the expression relating E and V/L$\bar{D}$ follows:

Let

S_T = surface area per unit volume of foam,

f = total volume of bubbles per unit volume of foam (i.e., the gas fraction),

n = number of bubbles per unit volume of foam, and

D_i = measured diameter of each individual bubble from Polaroid camera photographs.

Then

$$S_T = \sum_{i=1}^{n} \pi D_i^2 \quad , \tag{2}$$

and

$$f = \frac{1}{6} \sum_{i=1}^{n} \pi D_i^3 \quad . \tag{3}$$

Combining Eqs. (2) and (3) we have:

$$S_T = \frac{f \sum_{i=1}^{n} \pi D_i^2}{\frac{1}{6} \sum_{i=1}^{n} \pi D_i^3} = \frac{6f}{\sum_{i=1}^{n} D_i^3 \Big/ \sum_{i=1}^{n} D_i^2} \quad .$$

If we define

$$\bar{D} = \frac{\sum_{i=1}^{n} D_i^3}{\sum_{i=1}^{n} D_i^2} \tag{4}$$

then

$$S_T = \frac{6\,f}{\bar{D}} \quad . \tag{5}$$

By making the assumption that $f \simeq 0.8$ (which is a fairly good estimate for wet foam),[27] we can immediately obtain the value:

$$S_T \simeq \frac{5}{\bar{D}} \quad . \tag{6}$$

The surface area flow rate A_R may then be expressed by the equation:

$$A_R = V\,\frac{5}{\bar{D}} \quad , \tag{7}$$

where V is the volume of foam passing up the column per unit time.

By substituting Eq. (7) into Eq. (1):

$$E = \frac{5\,V}{L\bar{D}}\left(\frac{\Gamma}{x}\right) \quad \text{and} \quad E \propto \frac{V}{L\bar{D}}\left(\frac{\Gamma}{x}\right) \quad , \tag{8}$$

with L representing the liquid throughput rate. From Eq. (8),

$$\propto \left(\frac{L\bar{D}}{V}\right) E\,x \quad . \tag{9}$$

Now the McCabe-Thiele diagram for foam separation is obtained by plotting Γ vs x for the equilibrium line and for the operating line. The slope of the former, from Eq. (8), is proportional to $L\bar{D}/V$, i.e., the reciprocal of $V/L\bar{D}$, as is shown in Fig. 5. Typical experimental Γ/x values for strontium in DBS solutions at various calcium concentrations are given[31] in Table 5. An ALGOL program for the CDC-1604 computer was written to calculate $V/L\bar{D}$ from gas and liquid throughput rates and individual bubble diameters. (Bubble diameters are obtained by taking a Polaroid Land camera picture of the bubble column at magnification of 3.63, measuring the apparent diameter of about 20 bubbles, and using these data as input for the computer program.)

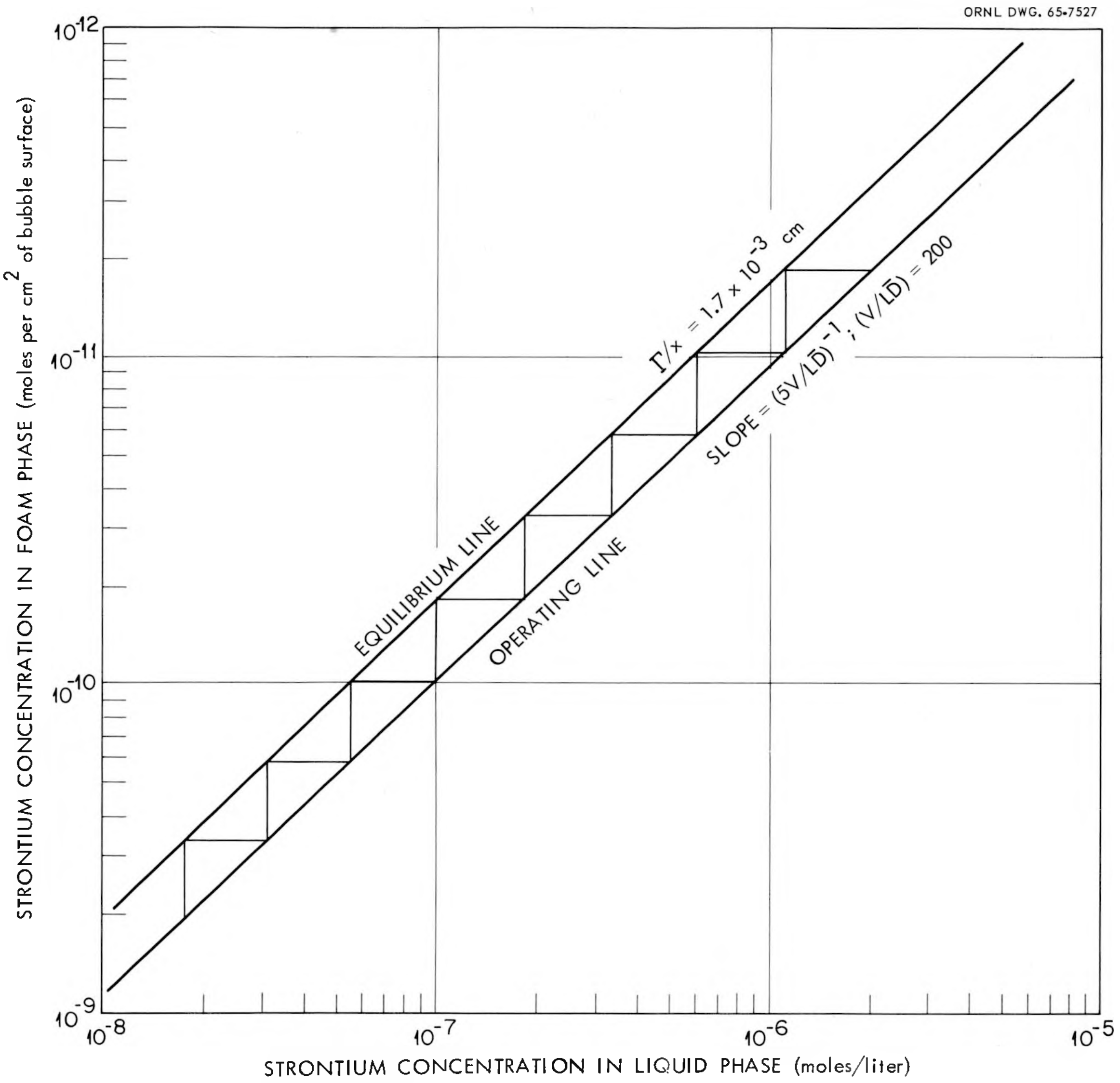


Fig. 5. The McCabe-Thiele Diagram for Foam Separation Is Obtained by Plotting Γ vs x for the Equilibrium Line and for the Operating Line. The Slope of the Equilibrium Line Is Proportional to the Reciprocal of $V/L\bar{D}$.

Table 5. Strontium Distribution Coefficients in Alkaline ORNL Tap Water with the Surfactant Dodecylbenzene Sulfonate (DBS)

Surfactant Conc. (mg/liter)	Sr^{2+} Conc. x 10^6 (moles/liter)	NaOH Conc. x 10^3 (moles/liter)	pH	Ca^{2+} Conc. (ppm)	Sr^{2+} Distribution Coefficient (Γ/x) x 10^3 cm
250	2	1	~11	0	17.
62	1	1	~11	0	20.
62	1	10	~12	0	8.7
62	1	10	~12	0.4	8.5
62	1	10	12	2.0	2.2
62	1	10	12	4.0	1.25
125	1	10	12	4.0	1.40

3.3.4 Volume Reduction and Its Relation to Strontium Removal

The relation of volume reduction to process cost has already been discussed in Sect. 3.3.1 (see Surfactant Recycle). The volume-reduction factor obtained in the foam column is also related to liquid throughput, foam density, linear velocity, strontium distribution coefficient, and strontium decontamination factor.[18,32] Values for strontium Γ/x are given in Table 5 (see Sect. 3.3.3, above). Because no experimental data on foam density at various linear velocities are available for sodium dodecylbenzene sulfonate in ORNL LLW, the foam-density data obtained under such conditions with sodium dodecyl sulfate (1.6 g/liter)[33] are used to illustrate the relationship when Γ/x for strontium is assumed to be either 1.7 x 10^{-3} cm or 3.4 x 10^{-3} cm (see Figs. 6 and 7). Each curve in the family of curves represents a different water feed rate.

The equations from which these curves were calculated are as follows:

(1) Data on the linear foam flow rate, dz/dt, in the expanded head and the foam ratio, I_e, which is the ratio of foam condensate to foam rate in the expanded head, are empirically correlated by

$$\frac{dz}{dt} = 494\, I_e^{0.82} \quad . \tag{10}$$

If we avoid assigning a specific value to the ratio, f, of gas volume rate to foam rate, then

$$E = \frac{6fV}{L\bar{D}} \left(\frac{\Gamma}{x} \right) \quad . \tag{11}$$

Defining the volume reduction, VR, as the ratio of liquid feed rate to foam condensate rate, we have:

$$VR = \frac{L}{VI_e} = \frac{6\,f}{\bar{D}\,E\,I_e} \left(\frac{\Gamma}{x} \right) \quad , \tag{12}$$

where we have neglected the small decrease in foam rate in the expanded head due to liquid drainage.

(2) Now, in terms of foam flow rate in the expanded head, of cross sectional area A_e, instead of in the column, Eq. (11) can be rewritten as:

$$L = \left(\frac{\Gamma}{x} \right) \frac{6f}{\bar{D}\,E} \left(A_e \frac{dz}{dt} \right) \quad . \tag{13}$$

(3) By substituting Eqs. (10) and (12) into (13), we obtain for sodium dodecyl sulfate:

$$E = \left(\frac{\Gamma}{x} \right) \frac{6f}{\bar{D}} \left(\frac{494\,A_e}{L} \right)^{1/1.82} \frac{1}{(VR)^{0.82/1.82}} \quad . \tag{14}$$

(4) Finally, the strontium decontamination factor is given by[27]

$$DF = \frac{E^2 e^{n(1-1/E)} - 1}{E - 1} \quad , \tag{15}$$

where n is, as usual, the number of transfer units (including the pot) from the differential model of foam column operation.

Conditions of interest in foam separation include $E > 1$, $n > 10$, in which case, from Eq. (15), DF is roughly proportional to E. Since, by Eq. (14), E is proportional to Γ/x, but inversely related to VR and L, so also is DF roughly proportional to Γ/x and inversely related to VR and L. These relations are more easily seen in Figs. 6 and 7, which were drawn for the case $f = 0.8$ to be compatible with Eq. (6) and Fig. 5.

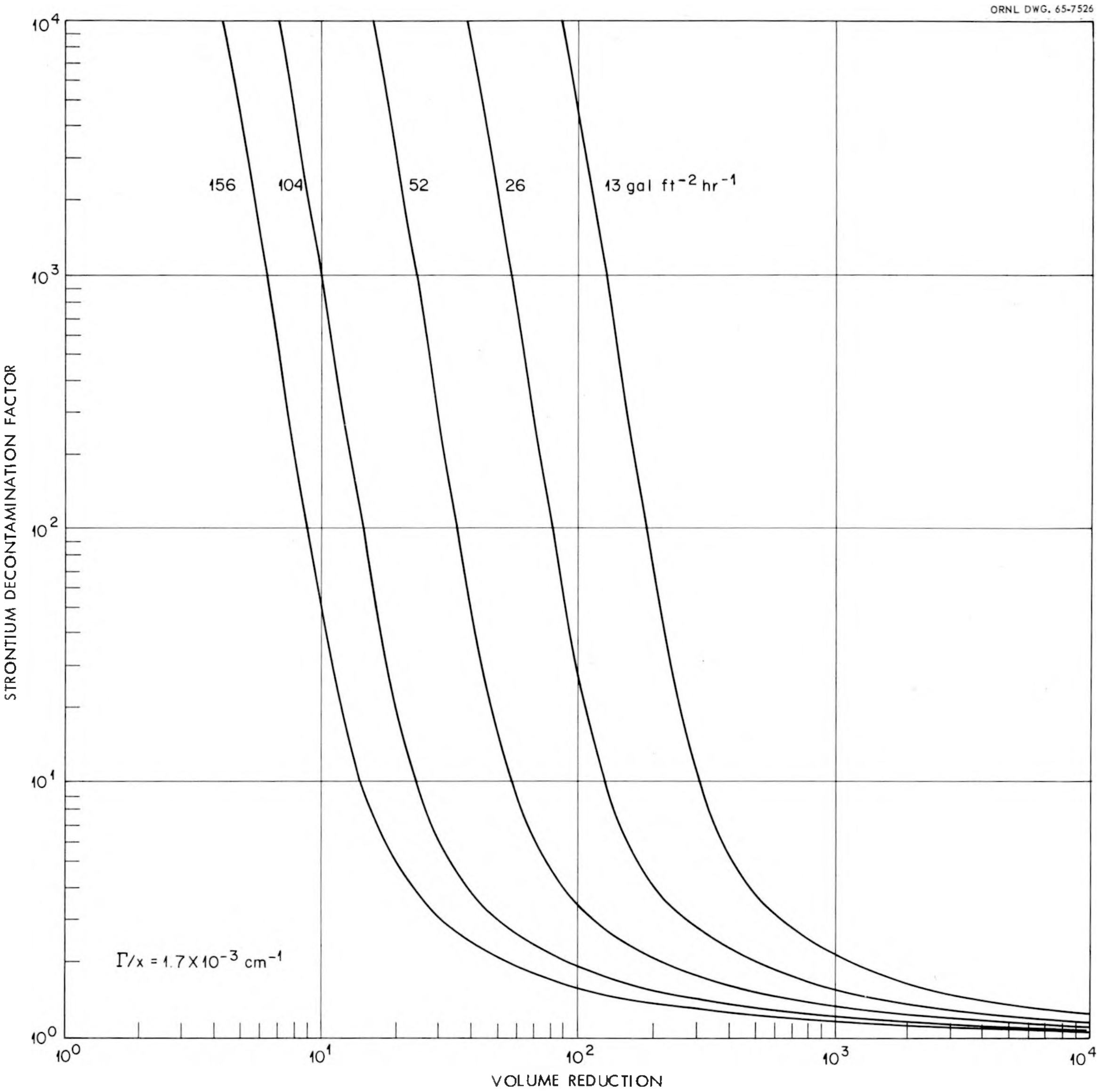


Fig. 6. The Strontium Decontamination Factor Is Inversely Proportional to the Volume Reduction and the Throughput, but Directly Proportional to the Distribution Coefficient, as Can Be Seen by Comparing Fig. 6 with Fig. 7.

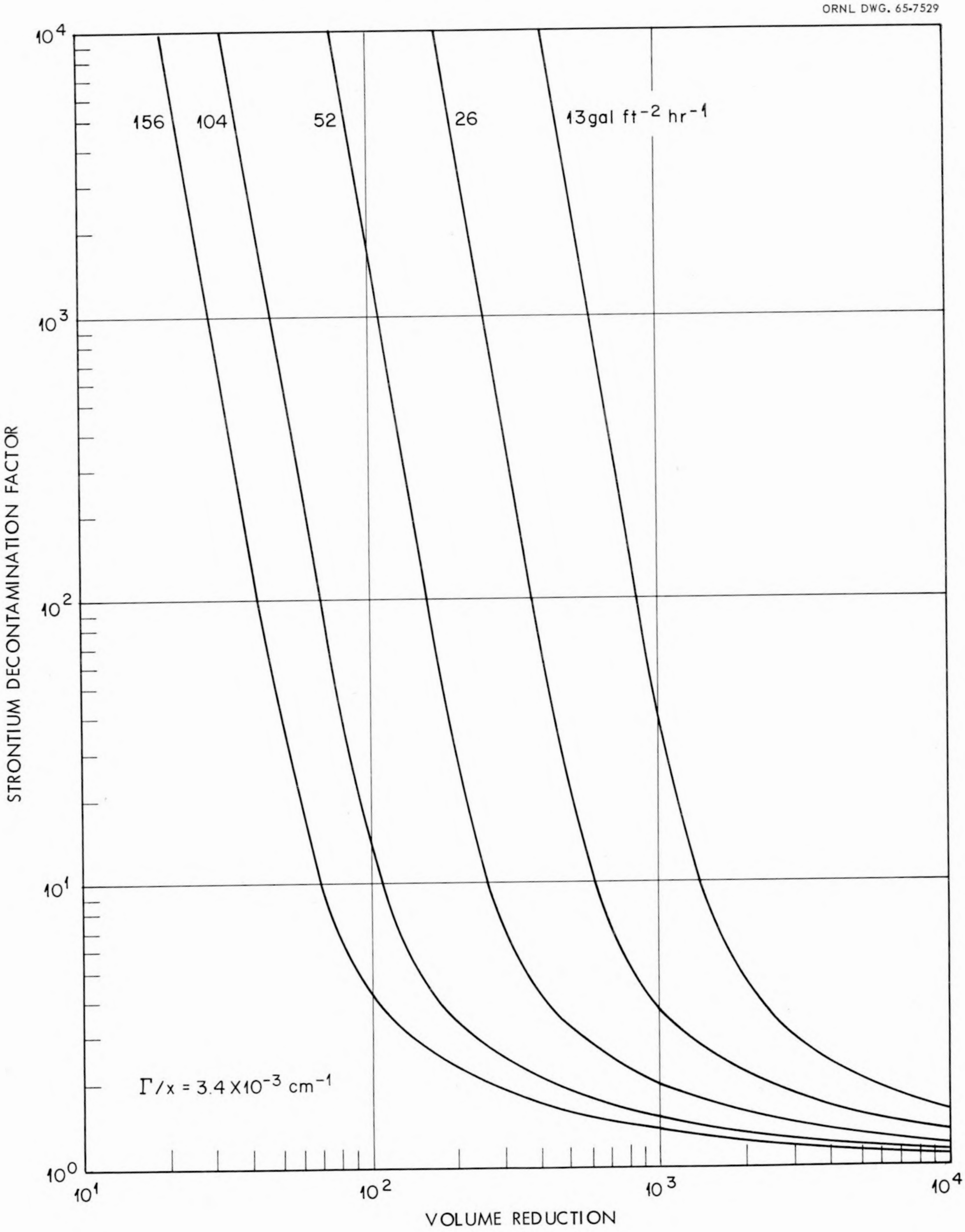


Fig. 7. The Strontium Decontamination Factor Is Inversely Proportional to the Volume Reduction and Throughput, but Directly Proporational to Distribution Coefficient (Compare with Fig. 6.).

REFERENCES

1. E. Schonfeld and W. Davis, Jr., Softening and Decontaminating Waste Water by Caustic-Carbonate Precipitants and Filtration in a Slowly-Stirred Sludge-Blanket Clarifier: Laboratory Development and Semi-Pilot-Plant Testing, ORNL-TM-835 (January 1964).

2. Oil, Paint, and Drug Reporter, (see Anhyd. Ferric-Chloride, Soda Ash, and Soda Caustic), Feb. 15, 1965.

3. Semiannual Report on Current Chemical Prices, (see DDBSA), C and EN (Aug. 3, 1964).

4. Supplier's Price List (1961), Illinois Clay Products Co., 208 So. Lasalle St., Chicago 4, Ill.

5. E. Schonfeld, A. H. Kibbey, and W. Davis, Jr., in Waste Treatment and Disposal Progress Report, May-October 1963, ORNL-TM-757, pp. 63-72.

6. E. Schonfeld, A. H. Kibbey, and W. Davis, Jr., Determination of Nuclide Concentrations in Solutions Containing Low Levels of Radioactivity by Least-Squares Resolution of the Gamma-Ray Spectra, ORNL-3744 (January 1965).

7. R. W. Schnepf, E. L. Gaden, Jr., E. Y. Mirocznik, and E. Schonfeld, "Foam Fractionation: Metals," Chem. Eng. Prog. 55, 42 (1959).

8. Handbook of Chemistry and Physics, (see "Physical Constants of Inorganic Compounds"), Chemical Rubber Publishing Co., Cleveland, Ohio.

9. G. B. Hatch and O. Rice, "Surface Active Properties of Hexametaphosphate," Ind. Eng. Chem. 31, p. 51 (1939).

10. E. Schonfeld, "Effect of Impurities on Precipitation of Calcium," J. Am. Water Works Ass'n., Vol. 56, No. 6, p. 767 (June 1964).

11. J. B. Nesbitt, W. J. Kaufman, R. F. McCauley, and R. Eliassen, The Removal of Radioactive Strontium from Water by Phosphate Coagulation, NYO-4435, USAEC (Feb. 15, 1952).

12. W. Davis, Jr., E. Schonfeld, and A. H. Kibbey, in Waste Treatment and Disposal Progress Report for November-December 1962 and January 1963, ORNL-516, pp. 118-1

13. E. Schonfeld, W. Davis, Jr., and P. A. Haas, in Waste Treatment and Disposal Progress Report, April-May 1962, ORNL-TM-376, p. 68.

14. Chem. Technol. Div. Ann. Progr. Rept. for Period Ending May 31, 1964, ORNL-3627, pp.104-105.

15. K. E. Cowser, R. J. Morton, E. J. Witkowski, "The Treatment of Large Volumes of Low-Level Waste by the Lime-Soda Softening Process," Proc. of the 2nd Internat'l. Conf. on the Peaceful Uses of Atomic Energy, P/2354, Vol. 18, p. 161, Geneva, Switzerland (1958).

16. Chem. Technol. Div. Ann. Progr. Rept. May 31, 1961, ORNL-3153 (see "Froth-Foam Decontamination of ORNL Low-Activity Waste").

17. E. Schonfeld and W. Davis, Jr., Head-End Treatment of Low Level Wastes Prior to Foam Separation, ORNL-TM-270 (May 1962).

18. E. Rubin, E. Schonfeld, and R. Everett, Jr., The Removal of Metal Ions by Foaming Agents and Suspensions: Laboratory and Engineering Studies, RAI-104, New York, N.Y. (October 1962).

19. T. Tamura, "Cesium Sorption Reactions as Indicator of Clay Mineral Structures," Clays and Minerals 10, 389-398 (1963).

20. J. J. Weinstock, E. Rubin, E. Schonfeld, and S. Mook, Foam Separation, RAI-100, New York, N.Y. (October 1961).

21. J. J. Weinstock, The Removal of Metallic Ions by Foaming Agents and Suspensions: Laboratory and Engineering Studies, RAI-350, New York, N.Y. (March 1965).

22. W. Davis, Jr., E. Rubin, E. Schonfeld, and A. H. Kibbey, in Waste Treatment and Disposal Quarterly Progress Report, February-April 1963, ORNL-TM-603, pp.40-41.

23. Standard Methods for the Examination of Water and Waste-Water, 11th ed., pp.245-48, Am. Public Health Assn., Inc., 1790 Broadway, New York, N.Y.

24. "The Determination of Alkyl Benzene Sulfonate," Technical Information Procedure No. 367-D, Hellige, Inc., 877 Stewart Ave., Garden City, N.Y.

25. W. Davis, Jr., A. H. Kibbey, E. Schonfeld, and P. F. Wace, in Waste Treatment and Disposal Semiannual Progress Report, July-December 1964, ORNL-TM-1081, pp. 61-74.

26. L. J. King, A. Shimozato, et al., Low-Radioactivity-Level Waste Treatment. Pilot Plant Studies of the Removal of Activity from Low-Level Process Waste by a Scavenging-Precipitation Foam Separation Process, ORNL-3803 (in prep.).

27. E. Schonfeld, D. Ghosh, R. Sanford, S. Mook, and G. Mazzella, The Removal of Strontium and Cesium from Nuclear Waste Solutions by Foam Separation, NYO-9577, Radiation Applications, Inc., New York, N.Y. (July 1960).

28. P. A. Haas, Engineering Development of a Foam Column for Countercurrent Surface-Liquid Extraction of Surface-Active Solutes, ORNL-3527 (see "DBS Recovery"), pp. 162-67 (June 1965).

29. R. B. Grieves, C. J. Crandall, and R. K. Wood, "Foam Separation of ABS and Other Surfactants," Int. J. Air Wat. Poll., Vol. 8, pp. 501-13, Pergamon Press, Gt. Britain (1964).

30. W. Davis, Jr., E. Schonfeld, P. F. Wace, and A. H. Kibbey, in Waste Treatment and Disposal Quarterly Report for November 1963—January 1964, ORNL-TM-830, pp. 49-58.

31. E. Schonfeld and W. Davis, Jr., in Chem. Technol. Div., Chem. Dev. Sect. B, Quarterly Progr. Rept., July-September 1961, ORNL-TM-81, pp. 37-42.

32. E. Schonfeld and W. Davis, Jr., in Chem. Technol. Div., Chem. Dev. Sect. B, Quarterly Progr. Rept., October-December 1961, ORNL-TM-177, pp. 73-76.

33. E. Schonfeld and W. Davis, Jr., in Chem. Technol. Div., Chem. Dev. Sect. B, Quarterly Progr. Rept., April-June 1961, ORNL-TM-1, pp. 68-69.

ORNL-3811
UC-70 – Waste Disposal and Processing
TID-4500 (45th ed.)

INTERNAL DISTRIBUTION

1. Biology Library
2-4. Central Research Library
5. Reactor Division Library
6-7. ORNL – Y-12 Technical Library
Document Reference Section
8-27. Laboratory Records Department
28. Laboratory Records, ORNL R.C.
29. R. E. Blanco
30. J. O. Blomeke
31. R. E. Brooksbank
32. W. E. Clark
33. F. L. Culler
34-38. W. Davis, Jr.
39. D. E. Ferguson
40. H. E. Goeller
41. A. H. Kibbey
42. L. J. King
43. C. E. Larson
44. T. F. Lomenick
45. H. G. MacPherson
46. F. L. Parker
47. J. T. Roberts
48. E. Schonfeld
49. M. J. Skinner
50. E. G. Struxness
51. T. Tamura
52. A. M. Weinberg
53. M. E. Whatley
54. P. H. Emmett (consultant)
55. J. J. Katz (consultant)
56. C. W. J. Wende (consultant)
57. C. E. Winters (consultant)

EXTERNAL DISTRIBUTION

58-61. W. G. Belter, AEC, DRD
62. E. W. Bloore, AEC, DRD
63. W. K. Eister, AEC
64. W. H. Regan, AEC, DRD
65. E. C. Van Blarcon, AEC, DRM
66. E. R. Irish, Hanford
67. W. H. Reas, Hanford
68. C. M. Patterson, Savannah River
69. J. H. Horton, Savannah River
70. T. H. Siddall III, Savannah River
71. C. E. Crouthamel, ANL
72. S. Larowski, ANL
73. B. Manowitz, BNL
74. C. E. Christenson, LASL
75. L. P. Hatch, BNL
76. J. A. McBride, Idaho
77. C. Straub, USPHS
78. D. G. Stephan, USPHS (Division of Water Supply and Pollution Control)
79. C. H. Ice, Savannah River
80. S. J. Arditti, RAI, New York
81. J. J. Weinstock, Uniprocess Co., New York

82. H. M. Schoen, General Foods Corp., Tech. Center, White Plains, New York New York
83. E. Rubin, Department of Chem. Engineering, Israel Institute of Technology, Haifa, Israel
84. K. D. B. Johnson, UKAEA, Harwell, England
85. P. F. Wace, UKAEC, Harwell, England
86. F. Sebba, University of Witwatersrand, Department of Phys. Chem., Johannesburg, South Africa
87. C. A. Brunner, Robert A. Taft Sanitary Engineering Center, Cincinnati
88. R. B. Grieves, Illinois Institute of Technology, Chicago
89. R. K. Wood, Department of Chem. Engineering, University of Ottawa, Ottawa, Canada
90. Research and Development Division, AEC, ORO

91-404. Given distribution as shown in TID-4500 (45th ed.) under Waste Disposal and Processing category (75 copies – CFSTI)