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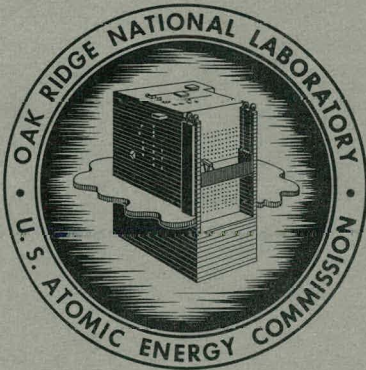
ORNL-3322

UC-70 - Waste Disposal and Processing
TID-4500 (20th ed.)

MASTER

LOW-RADIOACTIVITY-LEVEL WASTE TREATMENT.
PART I. LABORATORY DEVELOPMENT OF A
SCAVENGING-PRECIPITATION ION-EXCHANGE
PROCESS FOR DECONTAMINATION OF
PROCESS WATER WASTES

Rowland R. Holcomb



OAK RIDGE NATIONAL LABORATORY
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ORNL-3322

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

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DATE ISSUED

JUL 10 1963

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ABSTRACT

A scavenging-precipitation ion-exchange process using phenolic (organic) resins was developed to decontaminate low-radioactivity-level process water waste prior to discharge to the environment. In laboratory and small engineering-scale tests, greater than 99.9% of the cesium and strontium the principal biological hazards, were removed from ORNL low-level waste, and the total activity level was lowered to less than the maximum permissible concentration (for example, Sr^{90} is 10^{-7} $\mu\text{c}/\text{ml}$) recommended for populations in the neighborhood of atomic energy installations.

The water was treated by a scavenging-precipitation with sodium hydroxide (pH 11.7) and ferrous sulfate (copperas-5 ppm Fe) to remove suspended solids and soluble hardness (calcium, magnesium, etc.), clarified, and then passed through a carboxylic-phenolic ion-exchange resin to sorb the remaining radionuclides. After passage of 1,500 to 2,000 resin-bed volumes, the resin was eluted with 10 volumes of 0.5 M HNO_3 . Sodium carbonate can be added in the precipitation step to aid the quantitative precipitation of calcium for wastes that contain small amounts of phosphates, or alternatively, an extra ion-exchange column of carboxylic resin can be used to remove calcium and thus conserve the capacity of the phenolic resin for cesium and strontium. Three kinds of studies were made: batch laboratory-scale studies, continuous nonradioactive runs at 15 liters/hr, and runs with radioactive waste at 60 liters/hr. These studies led to a pilot-plant demonstration of the process (Part II of this

report, ORNL-3349). The process is similar to that reported in ORNL-3036, which describes the use of a sulfonic-phenolic resin and a 5 M HCl regenerant.

1. INTRODUCTION

The objective of the work reported here was to develop an improved, economical method with possible universal applicability to the decontamination of low-radioactive-level process water waste prior to its discharge to the environment. It is desirable to reduce the radioactive content of this water as much as possible, preferably to less than the maximum permissible concentrations for water (MPC_w) recommended for populations in the neighborhood of atomic energy installations.^{1,2} This report describes the development of a scavenging-precipitation ion-exchange process that produced water which exceeded radiological safety requirements and that advanced from laboratory-scale work to a 15,000 gal/day pilot-plant process.

Atomic energy installations usually produce large volumes of process wastes whose macrochemical composition is not very different from tap water but which contain micro amounts of radioisotopes. These so-called "low-level" wastes represent a unique disposal problem. Processes, such as evaporation, may not be economical for treating such large volumes, and the standard precipitation softening processes for treating large volumes of water do not always afford sufficient decontamination to meet requirements for environmental discharge.

At ORNL, low-level waste water is currently treated by a standard horizontal-flow lime-soda softening process, with a decontamination factor of at best 10 to 20.³⁻⁵ Grundite clay is added to increase cesium removal by adsorption. The radionuclides are concentrated in a sludge composed of calcium carbonate, magnesium hydroxide, clay, algae, etc., which settles out of the water, and the effluent water is discharged to area streams. A process developed at Harwell in the United Kingdom, uses

a precipitation step followed by ion exchange on vermiculite for high decontamination prior to discharge. The vermiculite is not regenerated and must be replaced after each treatment cycle, constituting a solid waste which must be disposed of. Desirable improvements in low-level waste treatment processes include increased decontamination but lower operating costs. A particular objective of the development program was to minimize the amount of solid producing additives and to reuse the exchange media, minimizing the volume and cost of concentrated solid or slurry disposal.

Accordingly, a scavenging-precipitation ion-exchange process was developed at ORNL for decontaminating low-level waste water, which used a sulfonic-phenolic ion-exchange resin⁶, however, this report describes an improved process, characterized by the use of better precipitation-clarification procedures and the use of a weak-acid carboxylic-phenolic ion-exchange resin.⁷⁻¹¹ In both processes, the resin is not discarded after each cycle but is eluted for reuse with acid to remove the radioactivity. The use of a weak-acid resin permits elution with an essentially stoichiometric equivalent of dilute nitric acid. The sulfonic-phenolic resin previously used gave equally satisfactory decontamination of process water but was unstable in the concentrations of nitric acid (about 5 M) required for efficient elution, thus hydrochloric acid was required. The resin eluate solution from either process can be evaporated for added volume reduction.

The new process was successfully demonstrated in a 600-gal/hr pilot plant to treat ORNL low-level process-water waste as reported in Part II of this two-part report.¹² A cost estimate showed that 750,000 gal/day of ORNL low-level waste can be treated with the scavenging-precipitation ion-exchange process at a cost of \$0.716 per thousand gallons,¹² including \$0.07 for equipment amortization and \$0.06 for burial of the solid residues.

Acknowledgment is made to R. E. Blanco, R. E. Brooksbank, J. M. Holmes, J. T. Roberts, and W. E. Clark for technical assistance, and also E. I. Wyatt, W. R. Laing, and C. L. Burros of the Analytical Chemistry Division, for analytical assistance.

2. FLOWSHEET DISCUSSION

Ion exchange with phenolic cation-exchange resins was selected for evaluation as a method of process-water decontamination because the phenolic group is highly selective for cesium and strontium, though the useful capacity is large only at pH values high enough to cause a significant fraction of these groups to be ionized. The use of a carboxylic-phenolic resin, Duolite CS-100, will not essentially alter the flowsheet proposed⁶ for the sulfonic-phenolic resin, Duolite C-3, which was a conservative first choice because of its high cesium and strontium capacities, resistance to shrinking and swelling, and low cost.

ORNL low-level process waste, (Table 1) typical of low-level waste produced at many nuclear installations, was used as the waste media for study throughout this development program. Since the process water is usually neutral, it was necessary to make the waste 0.01 M in NaOH to raise the pH to about 12, which is near optimum for cesium and strontium removal from dilute solutions with phenolic resins (Fig. 1). This pH-adjustment step is followed by a clarification step because when the low-level waste is made alkaline, most of the dissolved calcium and magnesium precipitate, carrying with them the dirt, algae, and other suspended solids and a substantial fraction of the radioactivity to such an extent that clarification removes 1 to 10% of the cesium, 30 to 70% of the strontium, 70 to 90% of the ruthenium and cobalt, and greater than 90% of the rare earths. In the ion-exchange step that follows this clarification, 1500 to 2000 volumes of waste are passed through one volume of phenolic resin on a three day exhaustion cycle. Decontamination factors (DF's) were: ruthenium and cobalt, 10; rare earths, 100; cesium, 100 to 1000; and greater than 1000 for strontium. Fortunately, the elements for which ion-exchange is less effective (e.g., ruthenium, rare earths, cobalt) are effectively precipitated and those that are poorly scavenged (cesium and strontium) were efficiently removed during the ion-exchange step. Thus, no great difficulty was encountered in reducing the major biological-radioactive hazards in the waste to less than the present maximum permissible concentration levels for environmental discharge.¹³

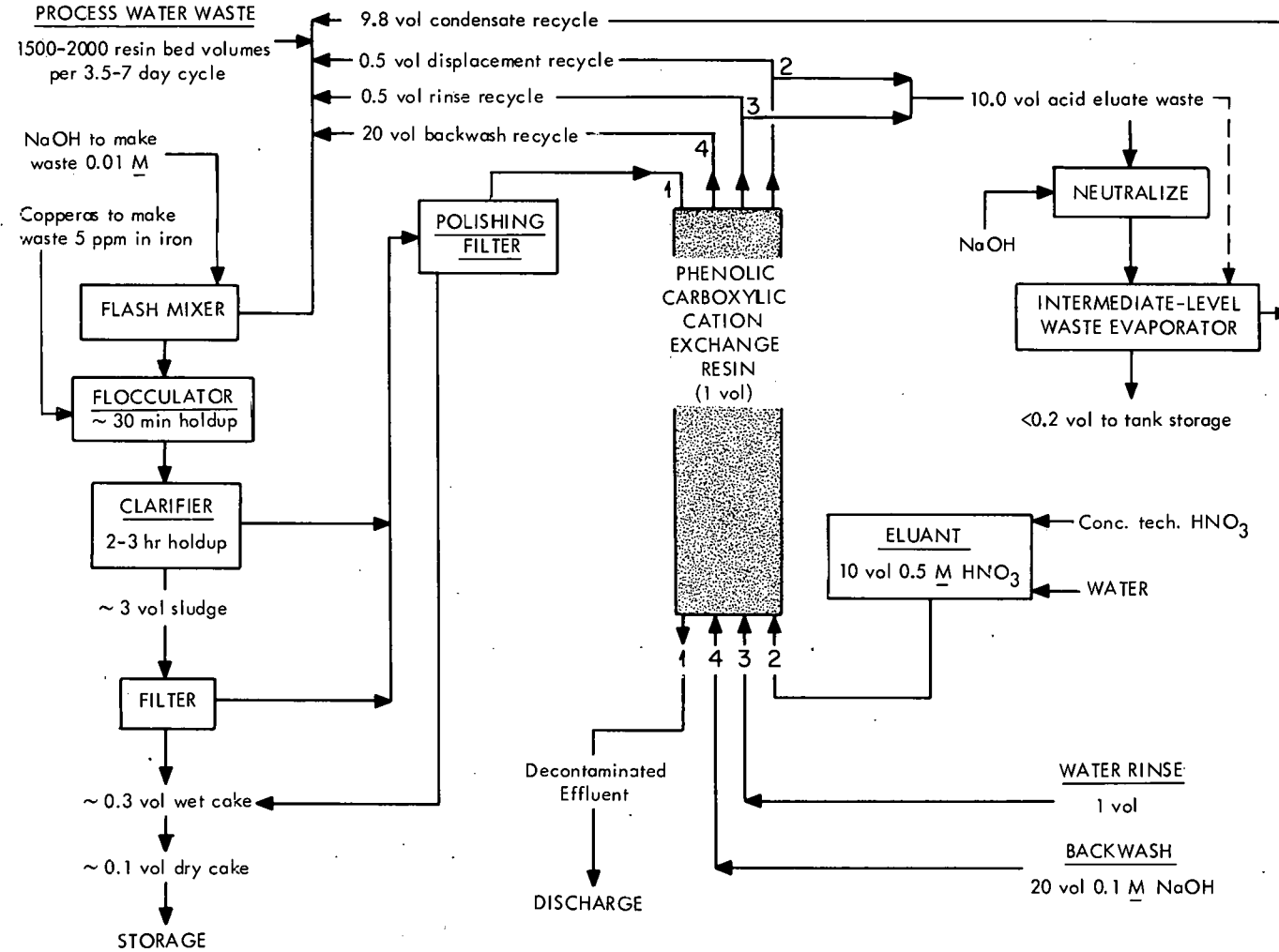


Fig. 1. Flowsheet for Decontamination of Process Water with Carboxylic-Phenolic Ion-Exchange Resin.

Table 1. Typical Analysis of ORNL Low-Level Waste*

Constituent	ppm	Constituent	ppm
Total Hardness	100-120	Dissolved CO ₂	10
Calcium Hardness	60- 85	Bicarbonate	50-80
Total Alkalinity	80- 95	Carbonate	<1
Calcium	20- 30	Phosphate	0.89-3.3
Magnesium	2- 10	Sulfate	12
Sodium	25- 30	Flouride	7
Uranium	0.01	Nitrate	26
Copper	0.05	Chlorine	5
Aluminum	<0.01	Total solids	180
Silicon	2.6		
Iron	0.1	pH 7-8	
Nickel	0.03	Specific Resistance	4 x 10 ³ ohms
Chromium	0.05		

* A range is given where sufficient analyses were obtained to establish limits -- other figures are the result of a single analysis.

Fortunately, calcium and magnesium hardness was removed in the scavenging-precipitation step since these ions are also sorbed on the resin and could have caused premature breakthrough of radioactivity. (Hardness, unless otherwise specified is expressed in terms of ppm as CaCO₃). The precipitation was aided by contacting the waste with preformed particles by recirculating the sludge in order to seed the new precipitate. Also, since the formation of large floc particles reduces the surface area available for the seeding effect, the hardness was more completely precipitated in the flash-mixing stage before the small floc particles aggregated. The precipitation kinetics were improved by increasing the water temperature from the normal 11 to 18°C to about 26°C, but was probably uneconomical. Phosphates interfered with precipitation by inducing supersaturation, but this effect was overcome by the addition of sodium carbonate in the head-end treatment during periods of increased use of detergents and decontaminating solutions which contain phosphate.¹⁴

The solids produced in the precipitation step were removed with a sludge blanket or suspended-solids contact clarifier. The addition of 5 to 10 ppm iron is desirable for floc formation in the clarifier, particularly during periods of low hardness in the feed and when algae concentrations are high. The solids collected in the clarifier were withdrawn either continuously or periodically and then dewatered by filtration in preparation for disposal by burial. The clarifier effluent was passed through a polishing filter, either sand or anthracite beds, to remove the last traces of particulate matter and the associated radioactivity; then, the water was sent to the ion exchangers for further decontamination.

After exhaustion of the resin, the activity was eluted from the resin with 10 resin-bed volumes of 0.5 M HNO_3 , washed with water, and regenerated to the Na^+ form by a 20-volume backwash with 0.1 M NaOH . The acid eluant requirement was halved by employing a split-elution procedure, in which the second 5 volumes of acid were held for use as the first 5 volumes in the subsequent cycle. The first 5 volumes of eluate in each cycle was evaporated in either the acid or neutralized form. Volume reductions of at least 30 to 1 were achieved, producing less than 0.2 volume of concentrate per cycle. The combined volume of the evaporator concentrate and the 0.1 to 0.3 volume of solids from the precipitation step represented an overall volume reduction from the original water of greater than 3000.

3. PROCESS DEVELOPMENT

The development of the process using precipitation scavenging and a weak acid carboxylic-phenolic ion-exchange resin, Duolite CS-100, to decontaminate low-level process water wastes followed a logical progression from batch laboratory-scale experiments to an engineering-scale pilot plant demonstration. The ion-exchange process will be discussed first, and the head-end step (scavenging by precipitates) will be discussed in a description of the integrated process.

3.1 Batch Laboratory Experiments with the Ion Exchanger

The ion-exchange capacity of the resin for cesium is controlled by the ionized phenolic groups because of their cesium selectivity, which is 10

to 100 times greater than that of the carboxylic groups. Strontium was sorbed effectively on both the phenolic and carboxylic groups, and when cesium exceeded the 1%-breakthrough level, the proposed end point of a loading cycle in plant operation, strontium was still being removed from solution with a DF of more than 1000 and could not be detected in column effluents. Since the cesium content of the waste is already below MPC_w levels, strontium could have been employed as the controlling isotope; increasing the amount of waste which could be treated per cycle and thus reducing the operating costs. However, the cesium cycle was used in this study for the benefit of installations where cesium may be of major importance. Consequently, the results presented here represent the minimum efficiency which can be assigned to this ion-exchange process.

3.1.1 Sorption

Gross-gamma breakthrough curves obtained during four separate batch loading runs with Duolite CS-100 showed that 1600 to 1900 bed volumes of waste had been treated prior to exceeding the 1%-breakthrough level (Fig. 2). While the effect of residual hardness on the resin capacity was not considered during these batch experiments, later results (Sec 3.4.2, Fig. 11) would indicate a probable total hardness of 1 to 3 ppm in this feed.

The data were obtained from fixed-bed runs on 0.5-in.-diam columns, 6 in. high, containing 19.2 ml of sodium-form resin at flow rates of about 625 bed volumes per day. Fifty-liter samples of actual process water waste taken at the waste treatment plant inlet, except in run 27 which was made with tap water, were spiked with Cs¹³⁷, Sr⁸⁵, and Ce¹⁴¹ to a concentration of 0.1 mc/liter for each isotope in order to raise the radioactivity high enough above background for accurate decontamination factor (DF) measurement and identification of radioactive species in effluents by gamma-energy spectrometry.

Following flowsheet conditions, the waste samples were made 0.01 M in NaOH, stirred vigorously for 2 to 3 min, stirred slowly for 30 min to provide for floc formation, and settled for 3 to 24 hr. This long settling period accounts for the low (1 to 3 ppm) hardness estimated for

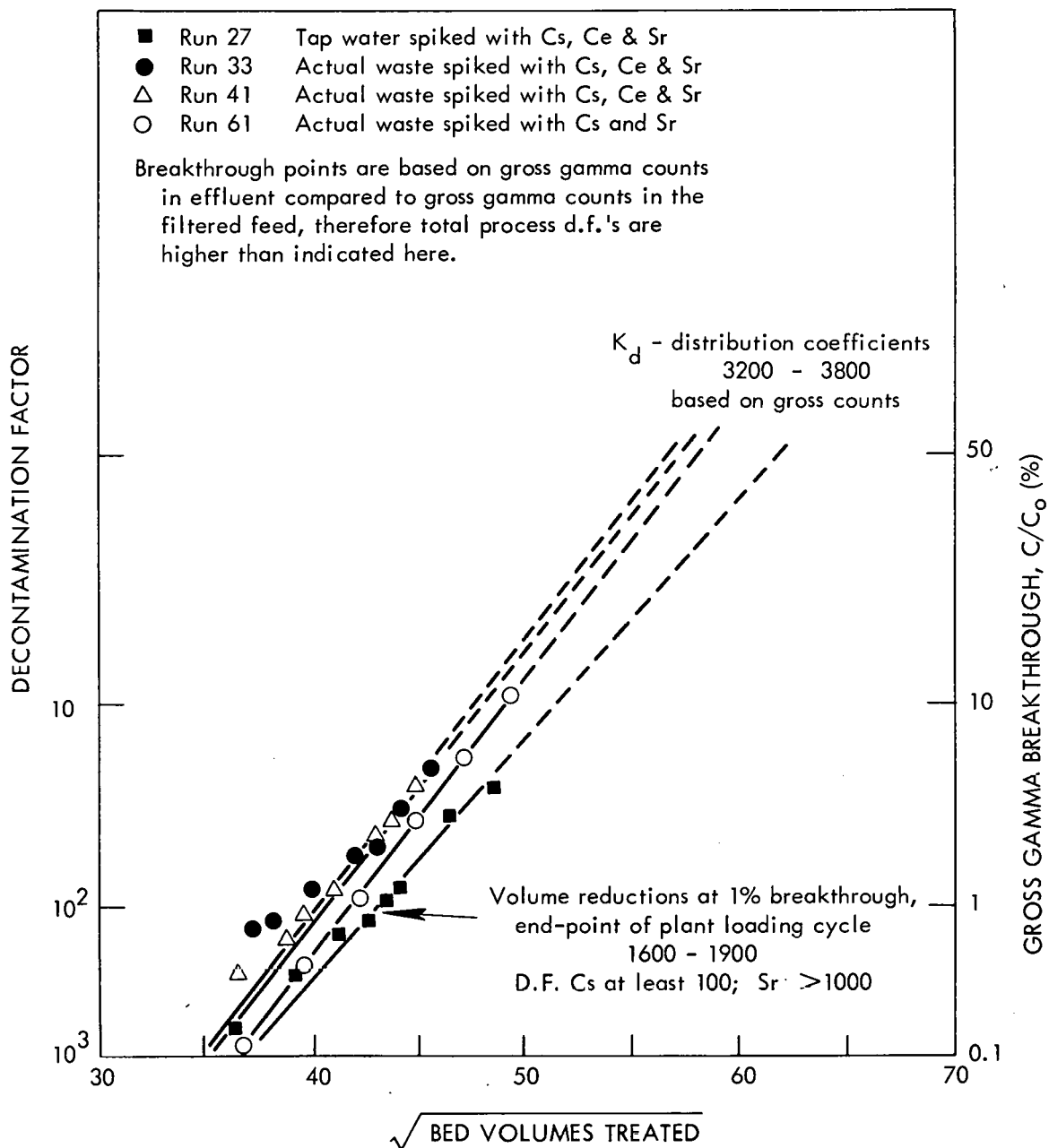


Fig. 2. Loading of Duolite CS-100, Carboxylic-Phenolic Ion-Exchange Resin.

these solutions. The supernatant solution was pumped through a 5- μ -pore compacted cellulose-fiber filter and the ion-exchange column in series. The individual points on the breakthrough curve are based on gross gamma counts per minute per milliliter above 40-keV energy and represent the ratio of the radioactivity in the effluent from the ion-exchange column to the radioactivity in the effluent from the filter as a function of the number of bed volumes treated. Since these DF's are based on the radioactivity remaining after filtration, the overall process DF's would be higher than indicated, depending on the amount of activity removed in the scavenging-precipitation step. Gamma-energy scans of the effluent samples taken prior to gross gamma breakthrough indicated that little or none of the total radioactivity in them was due to cesium and strontium, and this portion of curves was not plotted. This background "hash", over and above actual counting background, consists primarily of anionic, nonionic, and colloidal active material initially in the waste and possibly present as impurities in the tracers used.

Extrapolation of the gross gamma breakthrough curve which exceeded the 1%-breakthrough level after treatment of 1600 to 1900 resin bed volumes of waste showed gross gamma distribution coefficients, K_d , of 3200 to 3800, based on a volumetric comparison. These K_d 's are due primarily to cesium and not at all to strontium, since strontium was not present to detectable levels in any of the effluent samples. Thus, strontium distribution coefficients were much higher, but were not considered here since by choice cesium will control the loading-cycle end point. Cerium ion-exchange results were uncertain since little remained in the feed after pH adjustment precipitation, and clarification; however, the overall process decontamination factor for cerium was about 1000.

3.1.2 Resin Regeneration

Ten resin-bed volumes of 0.5 to 1.0 M HNO_3 eluted 99.9% of the capacity of the weak-acid carboxylic-phenolic resin Duolite CS-100 (Fig. 3); the same level of elution as was obtained for the sulfonic-phenolic resin Duolite C-3 with 10 bed volumes of 5 M HCl . Upflow elution was used in these experiments to minimize leakage of radioactive ions in the subsequent

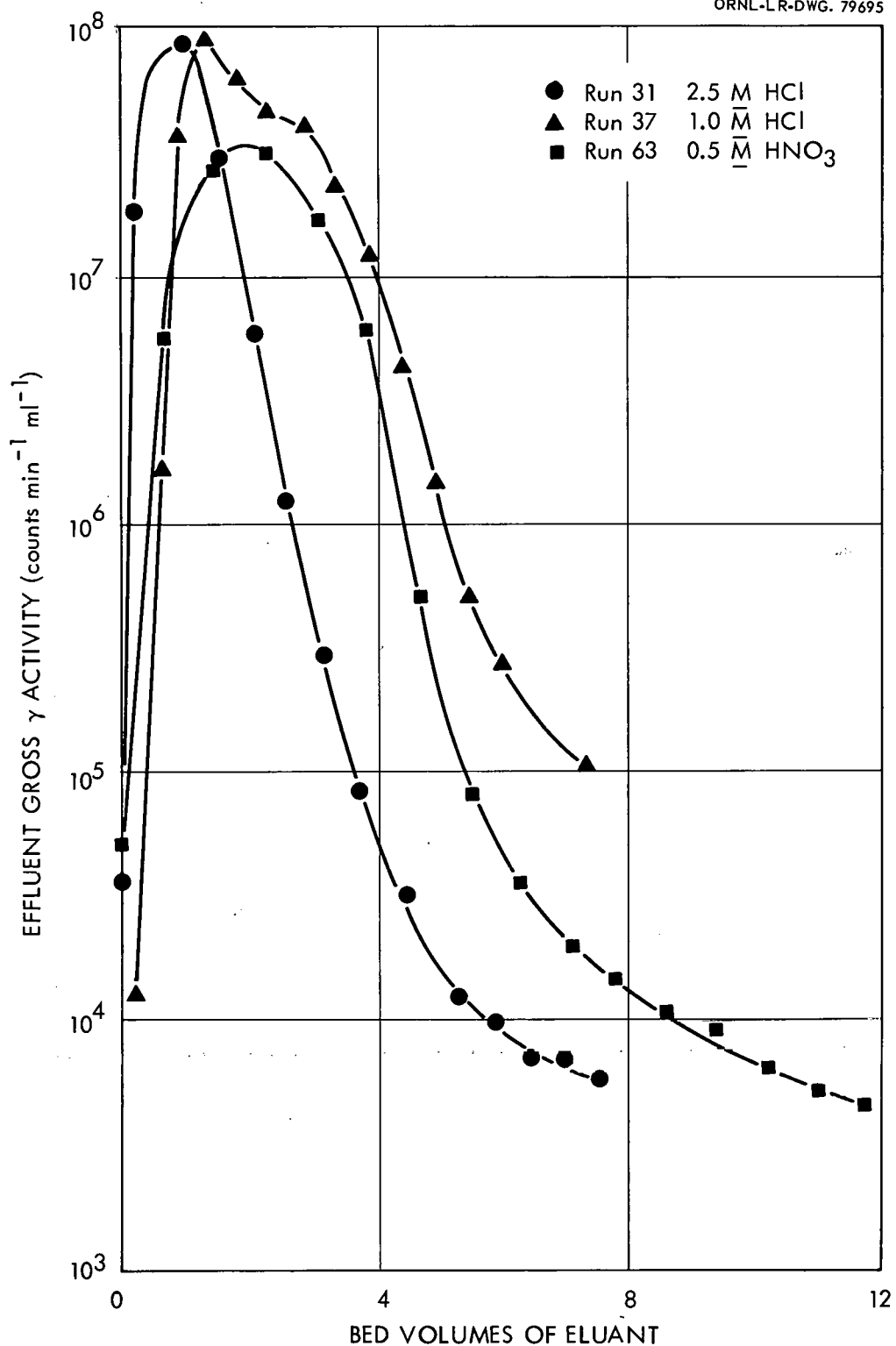
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Fig. 3. Elution of Duolite CS-100 Resin. Each, 19.2 ml (6 in. of a 1/2-in.-ID column) of Duolite CS-100 eluted upflow at 30 to 50 ml/min.

downflow loading cycle. The fresh eluant contacted the ions in the bottom of the bed first, displacing them upward, so that the most thoroughly eluted portion of the bed was at the bottom. Because of variations in tracers used, composition of ORNL process water waste, and degree of saturation during the loading cycles, the three resin beds did not contain exactly the same amount of radioactivity. Therefore, the effectiveness of this operation was best compared by relating effluent activity during an elution with the peak effluent activity during the same elution. As a rough approximation, the degree of resin elution was indicated by the degree to which the eluate waste activity dropped from its peak value. Thus in the three runs (Fig. 3), a 1000-fold decrease in effluent activity, about a 99.9% elution, was obtained within 10 resin-bed volumes of eluant.

A savings in eluant requirement can be realized by employing a split elution procedure, in which the second 5 volumes of acid, containing relatively little radioactivity, is stored and used as the first 5 volumes in the following cycle.

In the elution of Duolite CS-100 with 1.0 and 2.5 M acid (Runs 31 and 37), a shrinking and swelling of 30% was noted between the acid and base forms. However, with 0.5 M acid this was decreased to 10%, about the same as for Duolite C-3 when 5 M acid eluant was used. Elution with greater than 1 M HNO_3 causes gassing, color throw, and loss of capacity in subsequent loading cycles. This will also occur if 0.5 M HNO_3 is allowed to remain in stagnant contact with the resin. In a deliberately extreme test, about half of the loading capacity was lost (Fig. 4) when the resin eluted in Run 63 (Fig. 3) was left in contact with the 0.5 M HNO_3 eluant in a closed column. After two months of contact it was rinsed with water, converted to the sodium form with 0.1 M NaOH, and reloaded under conditions identical to the previous loading. The capacity loss can be eliminated by preventing contact of the phenolic resin with concentrated nitric acid or stagnant contact with 0.5 M acid for extended times.

The final step in the regeneration cycle was reconversion of the resin to the sodium form with 0.1 M NaOH. Since the resin swells about 10% during this conversion, the solution must be passed through the resin upflow at a rate sufficient to slightly fluidize the bed.

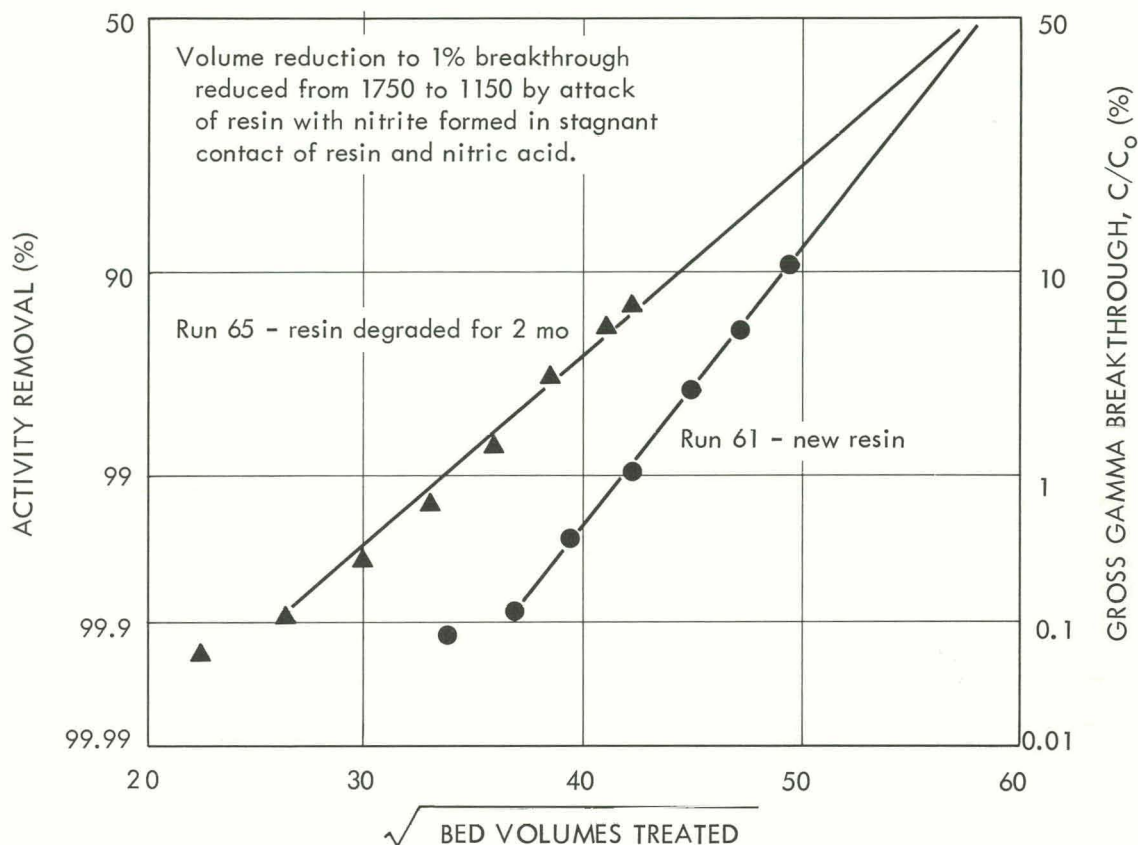
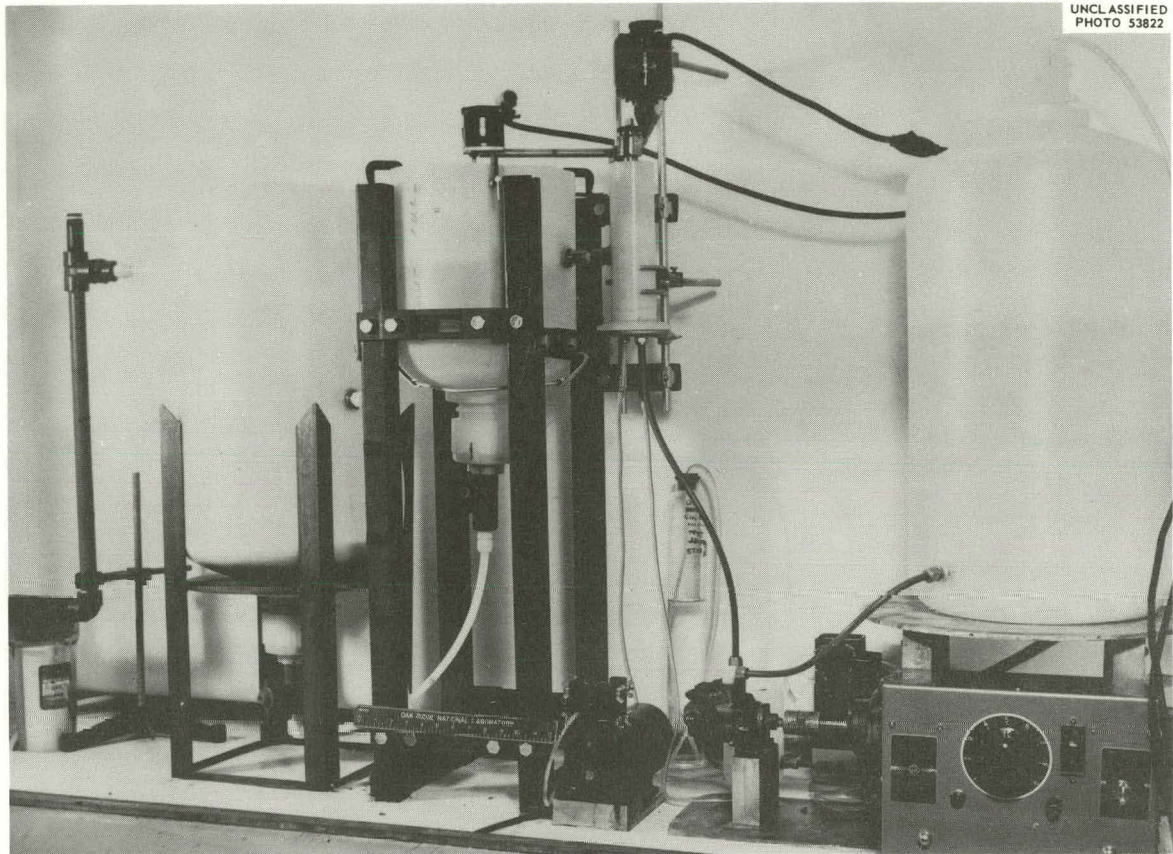


Fig. 4. Loss in Breakthrough Capacity Resulting from Nitric Acid (0.5 M) Attack of Phenolic Resin for a Period of Two Months.

The 10 volumes of nitric acid eluate waste was volume reduced at least 30-fold by evaporation without solids forming on cooling. The overall volume reduction was more than 3000 from original waste water to the concentrated eluate waste plus the filtered solids from the scavenging-precipitation step. With the previous hydrochloric acid process, the volume reduction by evaporation was 20-fold, for an overall volume reduction factor of 2000 to 2500.

3.2 Integrated Solids Handling System

The pretreatment steps of the process were demonstrated in an integrated operation in laboratory-scale polyethylene equipment (Fig. 5) to show that the solids handling could be accomplished on a continuously



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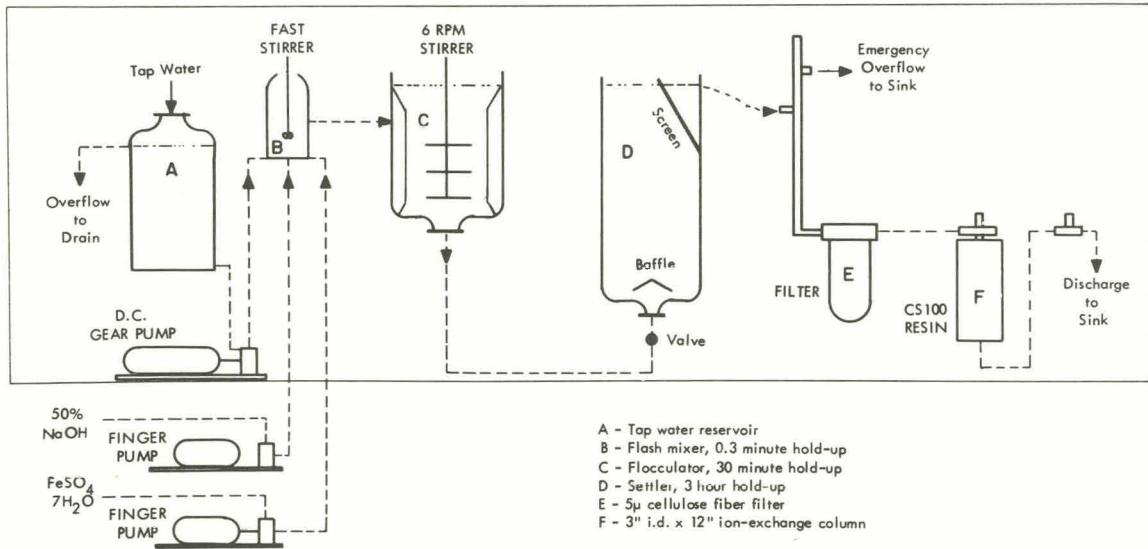


Fig. 5. Bench-Scale Equipment (250 ml/min) for Demonstration of the Head-End Portion of the Scavenging-Precipitation Ion-Exchange Process.

flowing stream. The final design of the system and the operating conditions were derived during 17 demonstration cycles, in which various flow rates, hold-up times, equipment, and vessel designs were employed. The final operating flow rate was 250 ml/min of tap water of the following composition: 90 to 100 ppm total hardness as CaCO_3 ; 25 to 29 ppm of calcium; 2 to 8 ppm of magnesium; 70 to 100 ppm of bicarbonate; 3 to 6 ppm of chloride; and 70 to 170 ppm of total dissolved solids. Of the solids produced by precipitation, 90% was retained in the clarifier and had a dry bulk density of 1.25 g/cc; the remaining 10% was caught by the filter and had a dry bulk density of 0.8 to 0.9 g/cc.

3.2.1 Flash Mixing

The time needed for flash mixing to distribute the chemicals through the water and bring about complete reaction varies from 10 to 60 sec in standard water-treatment practice, depending on the mixer used and the characteristics of the feed. Approximately 18 sec was sufficient for the pretreatment of ORNL tap water in the above system, but with ORNL waste (Secs 3.3 and 3.4) from 15 to 30 min of mixing was necessary to break a stabilized hardness supersaturation that resulted from complexing agents and other materials in the waste.

3.2.2 Flocculation

Floc growth is encouraged by slow and gentle stirring, which increases the number of collisions that produce floc masses. A 30-min flocculation period, with a three-blade sweep agitator rotating at 6 to 10 rpm in a vessel with four periphery baffles, gave a satisfactory, rapid-settling floc. When 19 M NaOH was metered to the flash mixer at a rate sufficient to maintain the water at 0.01 M in NaOH (pH about 11.7), the resulting precipitate was not sufficiently large after flocculation to maintain a stable sludge blanket. This was corrected by adding 5 ppm of iron in the form of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (copperas) which improved floc formation and increased floc size to that required for sludge blanket stabilization.

3.2.3 Clarification

Removal of solids to produce clear water was best accomplished with a sludge blanket or suspended-solids contact clarifier as opposed to a

simple settling chamber. The unit consisted of a vertical-flow, circular tank with a 3-hr hold-up volume. The coagulant-water mixture entered the bottom with a decelerating velocity through a layer of suspended flocculent particles, which acted as a screen to hold suspended matter. The line of demarcation of the sludge blanket was usually well defined, the water above it being clear and containing as little as 3 to 10 ppm of turbidity. Since the blanket itself represented only a small percentage of the total volume holdup, and since little or no clarification occurred above the blanket, the size of this piece of equipment could be reduced. Later studies (Sec 3.4) showed that the size reduction could be as much as 10- to 20-fold.

3.2.4 Filtration

The last traces of solids were removed with a 5- μ -pore compacted cellulose fiber (Cuno) filter. The water overflowing the clarifier was passed through the filter to the resin column with an initial head loss of only 1 or 2 in. The head loss increased at a rate of 1 ft per 8 hr, plugging the filter completely in 16 to 24 hr. After drying, the solids collected from the clarifier and filter represented only 0.006 to 0.008 vol % of the total water treated, that is, less than 0.1 bed volume.

3.3 Process Demonstration on Actual Low-Level Waste

Based on the equipment design developed in the integrated laboratory system (Sec 3.2), a small-scale, 60-liter/hr, demonstration unit⁸⁻¹¹ (Figs. 6 and 7) was constructed in the basement of the present process waste treatment plant for treating actual low-level liquid waste. In the initial run, two problems were apparent: (1) The clarifier did not produce sparkling water, thus the burden of clarification was placed on the filters, and (2) the small-pore cellulose filters coated easily with sludge, resulting in complete stoppage in about 8 hr. The clarification problem was remedied by the formation, after three to four days, of a cone-shaped dike of solids in the clarifier which improved sludge distribution and decreased channeling through the blanket. To reduce the time required to come to steady-state operation, an inner metal cone was installed. It approximated the size of the cone of solids mentioned above. The filter difficulty was

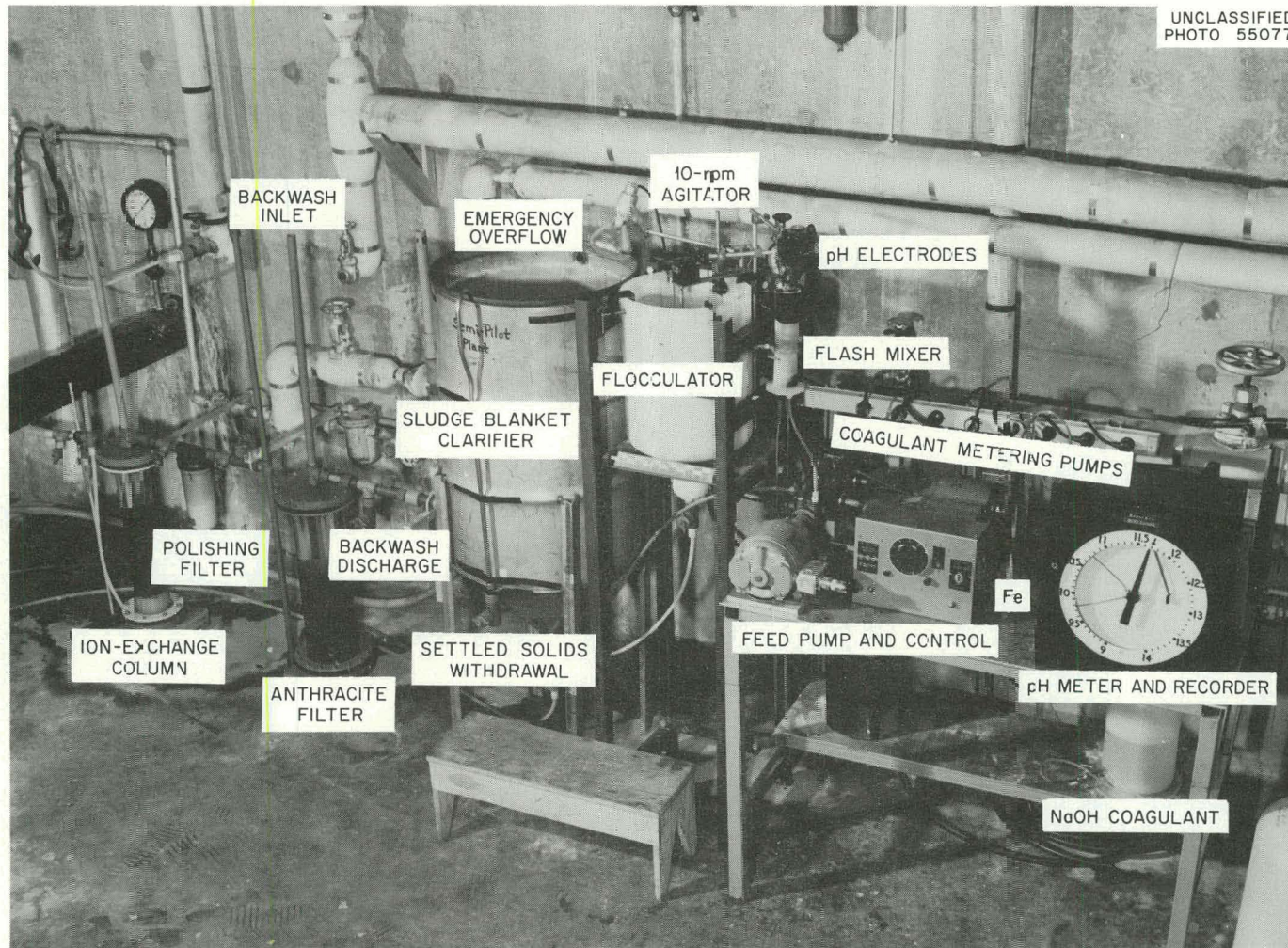


Fig. 6. Semi-Pilot Plant for Demonstration of the Ion-Exchange Treatment of Low-Level Process Water Waste. The size of the equipment is indicated by the size of the sludge-blanket clarifier, which is a 55-gal drum.

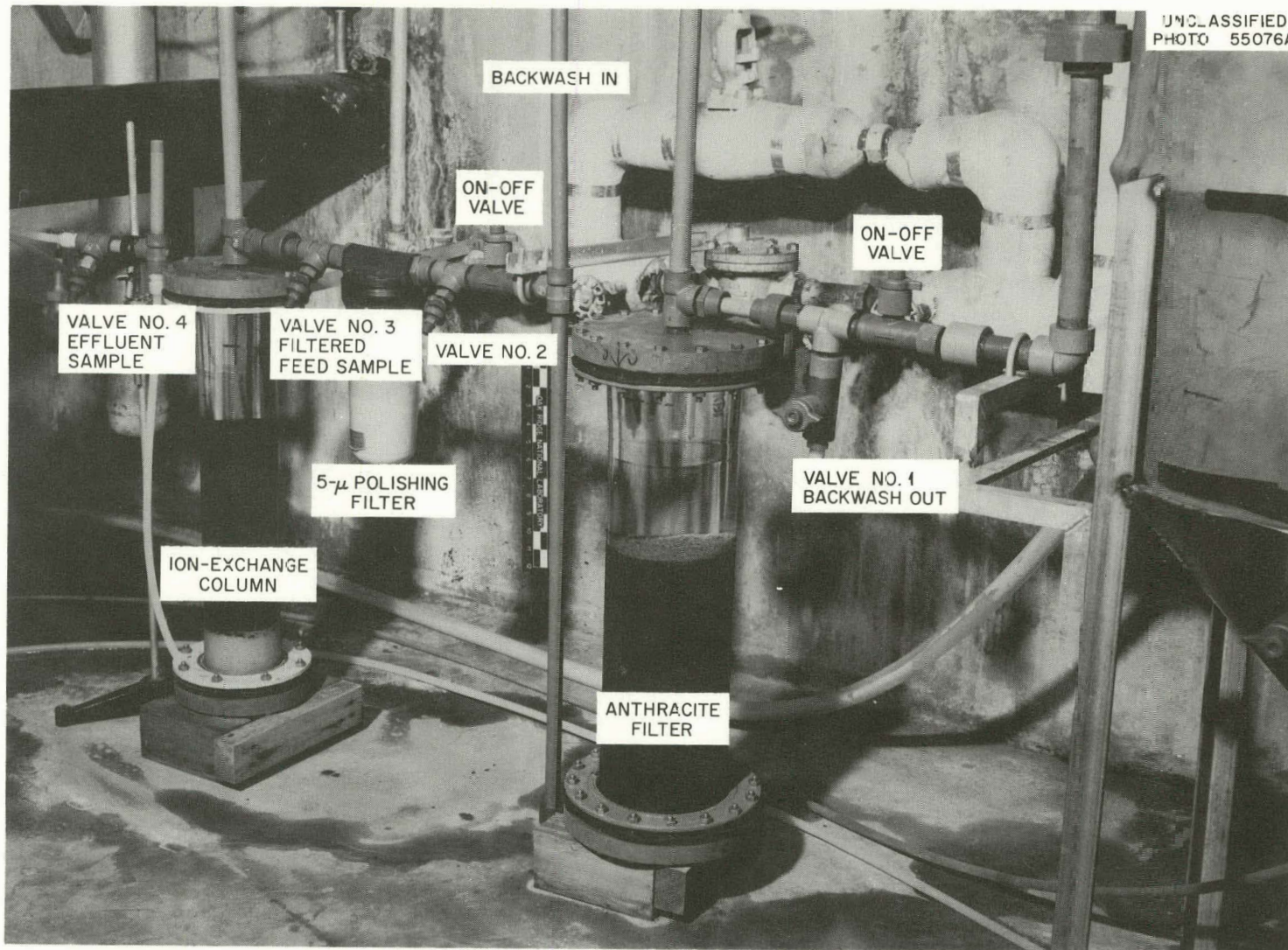


Fig. 7. Filtration and Ion-Exchange Equipment Portion of Semi-Pilot Plant Unit.

eliminated by replacing the two cellulose-fiber filters with a 6-in. ID by 12-in.-high anthracite coal, 6 to 18 mesh filter for longer life. The results were excellent. The clarifier overflow water produced after steady-state was established had only 3 to 10 ppm of turbidity, and the filter held up well for 36 to 48 hr before a rapid backwash under fluidized conditions was required. The backwash required 7 volumes of tap water and was accomplished in 1 to 1-1/2 min with the bed expanded 50 to 100%. Under continuous operating conditions no more than two and perhaps only one filter backwash per three-day cycle would be required.

Operation of this demonstration unit under flowsheet conditions successfully demonstrated the process -- decontamination factors and volume reductions were equal to or better than design specifications and confirmed the laboratory results. The necessary DF's, more than 1000 for strontium, 100 for total rare earths (TRE's), and greater than 100 for cesium prior to breakthrough at about 1500 bed volumes of waste were demonstrated (Table 2), thus guaranteeing discharge of the process waste stream at less than the MPC_w , for environmental discharge, with overall volume reduction approaching 3000.

During these runs, ruthenium and cobalt decontamination factors were only about 2 to 5. However, these nuclides during the period of study were already well below MPC_w levels in the untreated waste stream, and usually below the limits of detection.¹² Because of these low concentrations in the entering stream, exact ion-exchange decontamination factors were difficult to obtain. The distribution of ruthenium and cobalt between the precipitation and cation-exchange removal varied, depending on the species of the nuclides present. When ruthenium and cobalt were still detectable in the effluent from the above two treatments, they were reduced to below detectable limits by an anion-exchange resin in the hydroxyl form. Since principal anion is hydroxyl from the sodium hydroxide treatment, the use of an anion resin would not represent complete demineralization. Thus, the use of an anion-exchange step could be employed at installations where these nuclides contribute significantly to the total radioactivity.

Table 2. Decontamination of ORNL Low-Activity Waste by Phenolic-Ion Exchange Process

Semi-pilot plant operating rate: 60 liters/hr

Code	Bed Vols	Radioactivity, (dis min ⁻¹ ml ⁻¹)								
		By Radiochemical Analyses			By Gamma Spectrometry					
		Gr β	TRE β	Sr β	Ru ¹⁰⁶	Cs ¹³⁷	Co ⁶⁰	Zr ⁹⁵ -Nb ⁹⁵	Zn ⁶⁵	Sb ¹²⁵
MPC _w (168 hr week)		--	66.6	0.222(Sr ⁹⁰)	22.2	44.4	111.0	--	--	--
SPP Run 1										
Feed		280	135	92	6.6	20	5.4	--	7.4	--
Effluent	300	11	0.85 (DF 158)	0.02 (DF 4600)	2.1	n.d. (DF >10 ³)	2.1	--	n.d.	--
SPP Run 2										
Feed		353	160	94	6.5	21	4.6	10	trace	--
Effluent	1398	13	1.5 (DF 107)	0.04 (DF 2700)	1.8	n.d. (DF >10 ³)	2.4	n.d.	n.d.	--
SPP Run 3										
Feed		462	129	110	3.10	19.44	8.53	9.81	2.78	1.55
Effluent	1156	99	1.98 (DF 65)	0.04 (DF 2750)	3.73	0.09 (DF 216)	3.70	0.60	1	n.d.
Feed		460	--	123.2	6.24	22.14	6.74	--	trace	8.64
Effluent	1587	61	--	0.07 (DF 1760)	1.97	0.24 (DF 92)	2.94	--	n.d.	4.82
Feed		440	199	122	5.47	29.0	7.49	13.1	1.40	4.48
Effluent	1876	26	1.58 (DF 126)	0.05 (DF 2440)	1.65	0.74 (DF 39)	1.46	trace	n.d.	2.54

TRE results are biased by yttrium produced in effluent samples prior to analysis, thus TRE decontamination factors are actually much higher than indicated here.

The final demonstration run (SPP 8, Table 4) in the semi-pilot plant showed the excellent decontamination discussed above for strontium and total rare earths prior to cesium breakthrough at about 1500 bed volumes. While the cesium decontamination factors were somewhat low, the effluent contained only a fraction of the MPC_w for that isotope. Later results¹² supported the opinion that these analyses were in error. Neither strontium nor total hardness breakthrough to the 1% level was detected up to 2000 bed volumes. Total hardness in the overflow from the sludge-blanket clarifier averaged about 20 ppm as $CaCO_3$, compared with 60 ppm in the previous run (SPP 7, Table 3), in which a premature breakthrough of activity and hardness occurred at about 600 bed volumes. Later studies (Sec 3.4) indicated this high effluent hardness was the result of 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 (3) the presence of other materials in addition to phosphates, for example, dirt, algae, and detergents, which produce a physically different floc from that obtained with tap water.

Following the loading cycle, the 3-liter resin bed was eluted upflow with 30 liters of 0.5 M HNO_3 . The bed contracted about 10% during the acid treatment. The eluate was volume reduced to about 900 ml by evaporation, but not to the point of formation of solids on cooling to room temperature. Thus, a volume reduction of greater than 30 can be achieved and still permit the use of liquid-handling procedures. The resin was converted to the sodium form with 60 liters of 0.1 M $NaOH$ after a 3- to 6-liter rinse with water. Subsequent loading cycles showed no loss in the capacity of the ion-exchange resin.

3.4 Pilot Plant Support Studies

Demonstration of engineering-scale equipment was necessary to provide confidence in the design scaleup and cost estimate of a full-scale low-level waste treatment plant for handling up to 750,000 gal/day of process waste. A pilot plant sized for a capacity of 15,000 gal/day, a fiftieth of the size required to handle the entire waste stream, was designed, constructed, and operated for this purpose. The results of this demonstra-

Table 3. Decontamination of Low-Level Waste in Demonstration Run SPP 7

Code ^a	Bed Vols	Activities (dis min ⁻¹ ml ⁻¹)				
		Gr β	TRE	Sr	Cs	Co
F-	100	351.60	141.78	129.85	86.76	46.43
FF-		229.1	47.41	85.23	19.26	1.84
Eff-		16.67	0.344	0.01	n.d.	1.62
F-	500	460.30	146.85	151.42	111.20	76.19
FF-		229.1	43.87	100.80	39.96	3.03
Eff-		25.00	0.441	0.56	0.36	1.81
Eff-	600	--	--	8.59	1.08	1.46
Eff-	700	--	--	29.9	3.25	4.47
Eff-	800	--	--	59.59	5.30	10.12
Eff-	900	--	--	80.72	7.79	6.65
F-	1000	304.70	96.04	159.81	66.06	46.76
FF-		134.60	36.39	70.11	52.56	10.14
Eff-		123.20	44.73	95.24	7.61	8.01
Eff-	1200	--	48.8	69.1	13.57	5.82
F-	1500	186.70	61.75	136.40	50.04	35.78
FF-		90.25	15.82	62.09	27.0	3.53
Eff-		81.30	14.04	52.51	25.02	3.30
F-	2000	248.30	97.52	151.13	24.52	21.68
FF-		69.84	20.93	49.49	19.80	2.08
Eff-		62.36	12.1	36.40	11.66	1.91

^a F = feed; FF = precipitated-filtered feed; Eff = effluent.

tion are reported in Part II (ref 12) of this report. An economic evaluation of the process, based on both laboratory and pilot-plant studies, is included in that report.

During operation of this 15,000 gal/day pilot-plant, several problems were encountered which suggested the need for further laboratory investigation of process variables. For example, difficulty was encountered in reducing the total hardness content of the water exiting the sludge-blanket clarifier (about 70 ppm), however, the hardness was reduced to an acceptable level (less than 10 ppm) by the subsequent anthracite polishing filter. In later runs, the hardness of the water leaving the polishing filter was excessively high (greater than 60 ppm), causing premature breakthrough of the ion-exchange resin. Initially, a comparison of treatment methods,^{15,16}

Table 4. Decontamination of Low-Level Waste in Demonstration Run SPP 8

Code ^a	Bed Vols	Activities					
		counts ml ⁻¹ min ⁻¹		dis ml ⁻¹ min ⁻¹			
		Gr β	Gr γ	TRE	Sr	Cs	Co
F-	1000	30.2	14.7	10.34	134.32	27.18	18.86
FF-	1000	5.8	6.3	2.25	48.02	25.74	2.85
Eff-	1000	0.3	0.92	0.015	0.0	trace	4.35
Eff-	1200	0.38	1.60	--	--	0.8	--
Eff-	1300	0.37	2.11	--	--	1.45	--
Eff-	1400	0.13	1.56	--	--	2.75	--
F-	1500	25.3	13.8	7.89	161.39	23.58	16.91
FF-	1500	6.8	6.3	1.69	48.2	21.96	3.60
Eff-	1500	0.43	2.3	0.024	0.05	4.82	4.64
Eff-	1700	1.03	3.01	--	--	7.48	--
F-	2000	21.1	12.4	6.92	156.20	24.84	18.60
FF-	2000	5.4	5.02	1.02	41.65	22.86	3.12
Eff-	2000	1.15	3.3	0.024	0.16	14.78	2.32

^a F = feed; FF = precipitated-filtered feed; Eff = effluent.

using tap water in batch jar tests showed that the lowest residual hardness (less than 18 ppm without filtration) was obtained when the water was made 25 ppm in Ca(OH)₂ and 0.01 M in NaOH (Fig. 8). Optimum results were achieved at about 26°C, since the reaction is temperature dependent (Fig. 9). However, when this treatment was applied to the low-level waste stream in the pilot-plant, the hardness exiting the clarifier was reduced to only 56 ppm. This relatively high hardness was attributed to the three causes mentioned previously (Sec 3.3): improper equipment, complexing agents, and type of floc. These problems were studied in a laboratory-support program aimed at describing and counteracting their effects, thus allowing removal of hardness in the clarifier.

3.4.1 Improved Clarification Equipment

The precipitation of hardness by sodium hydroxide is not very effective in the cold with waters containing less than 100 to 150 ppm of hardness unless a sludge blanket or sludge recirculation type of plant is employed. The rate of precipitate formation is of great importance in the

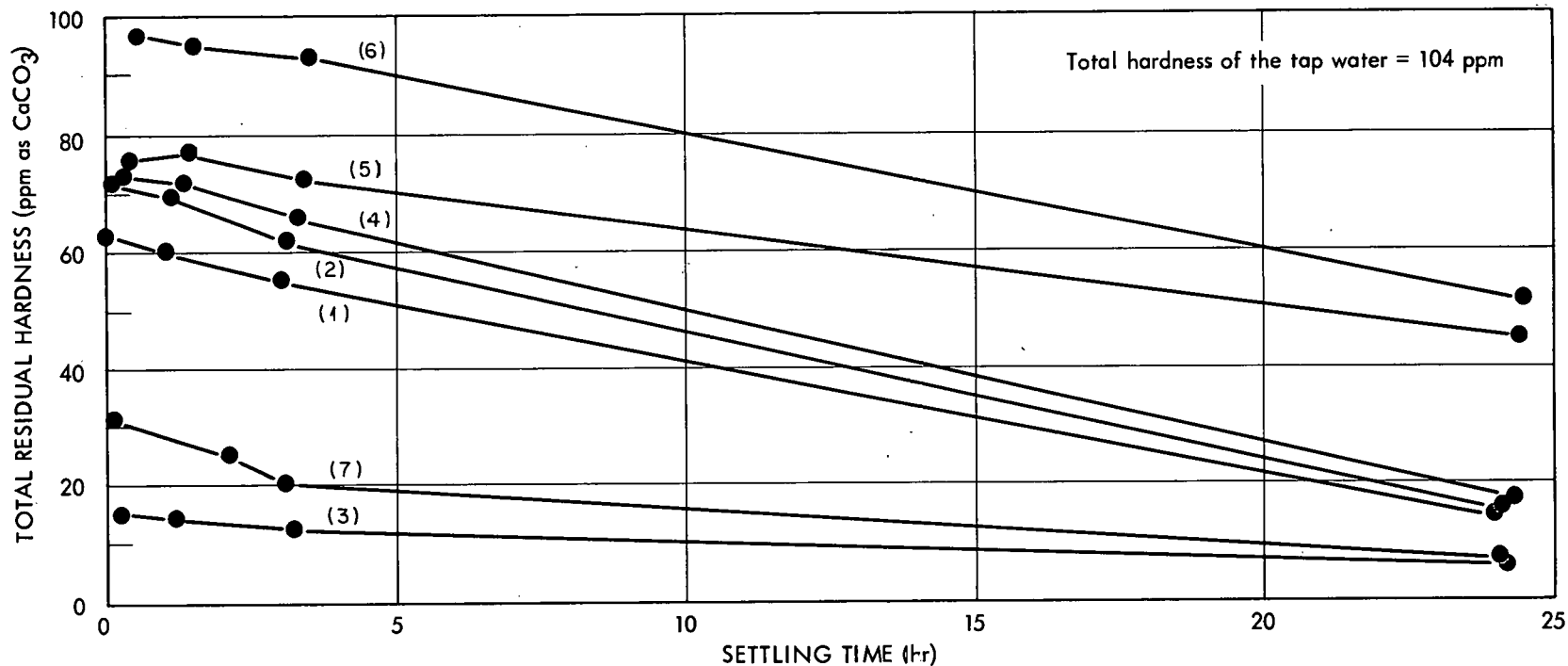


Fig. 8. Results of Standard Jar Tests, Employing Various Treatments on ORNL Tap Water. (1) 0.01 M NaOH and 5 ppm iron; (2) 0.01 M NaOH, 100 ppm $\text{Ca}(\text{OH})_2$, and 5 ppm iron; (3) 0.01 M NaOH and 25 ppm $\text{Ca}(\text{OH})_2$; (4) 0.01 M NaOH and 100 ppm $\text{Ca}(\text{OH})_2$; (5) 100 ppm $\text{Ca}(\text{OH})_2$ and 5 ppm iron; (6) 100 ppm $\text{Ca}(\text{OH})_2$; and (7) 0.01 M NaOH, 25 ppm $\text{Ca}(\text{OH})_2$, and 5 ppm iron.

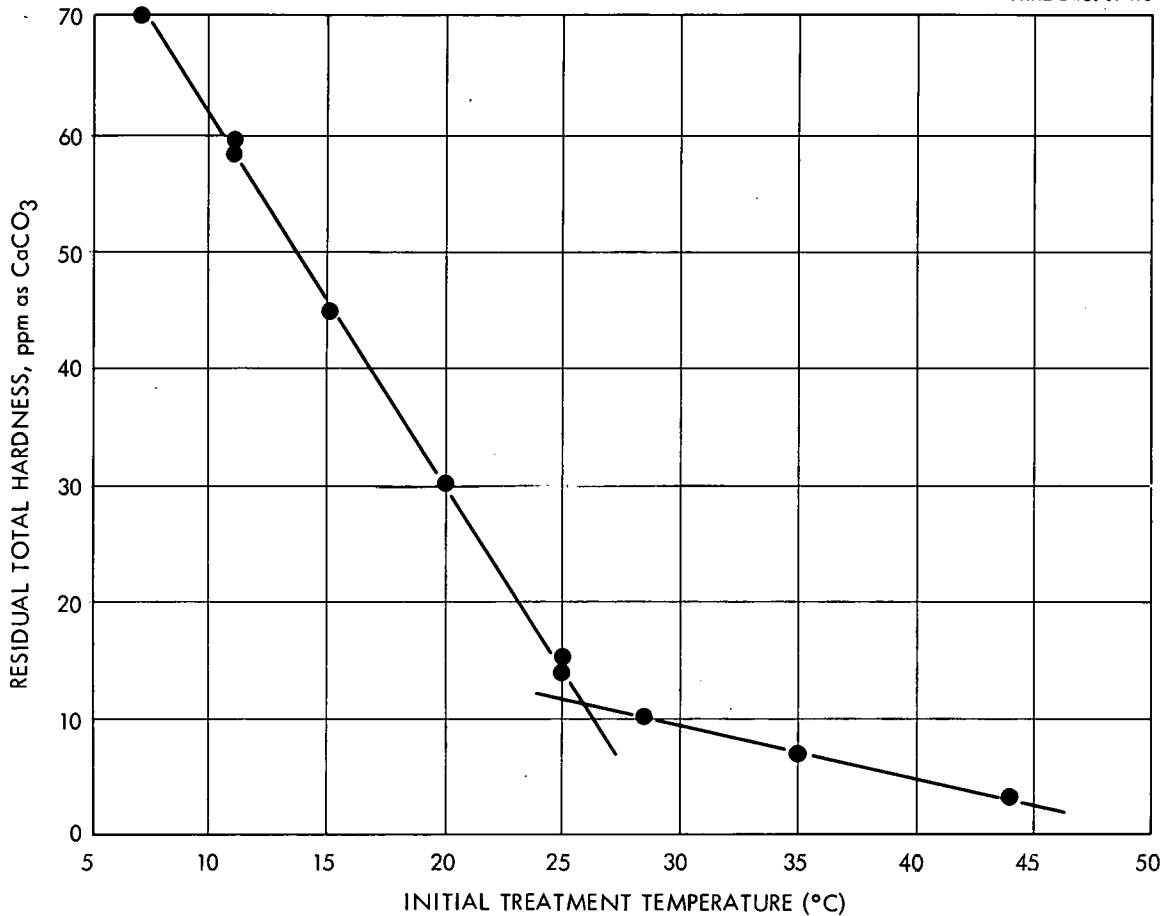


Fig. 9. Temperature Dependence of the Caustic (0.01 M NaOH)—Lime [25 ppm Ca(OH)₂] Treatment of ORNL Tap Water in Standard Jar Tests.

effectiveness of such a softening process, and unless precipitation is rapid, the softening obtained is poor, and the softened water will be supersaturated with hardness salts — so called "unstable" water. The rate of formation of the precipitate can be increased by the following means:¹⁸

"(1) increasing the temperature, which hastens crystallization and reduces the solubility of the precipitates; (2) using an excess of the reagents to reduce the solubility; (3) mixing the reagents well with the water; (4) stirring or agitating the water to bring supersaturated solution to the solid surfaces; and (5) bringing the water into contact with preformed particles of precipitate or grains of sand (the Spiractor process) which can act as nuclei for the precipitation."

The rate of settling is also important in precipitation softening since this is the principal way in which the precipitate is separated from the water, though filtration may also be necessary. The rate of settling may be increased by the following methods:¹⁸

"(1) increasing the precipitation temperature; (2) stirring gently in the precipitation zone to increase particle size; (3) bringing the water into contact with preformed precipitate while adding the precipitants; (4) adding the precipitants in the presence of calcium carbonate and magnesium hydroxide crystals and stirring vigorously; (5) passing the water upwards through a zone of suspended floc to entrap the smaller particles; and (6) using coagulants."

A continuous laboratory-model head-end treatment system (Fig. 10) was built incorporating some of the above features to improve softening and to rapidly evaluate new process improvements in support of the pilot-plant program. The clarifier unit used in the new system employed the "inner-cone" developed in the operation of the semi-pilot-plant (Sec 3.3). The use of this unit over a six-months' period of almost continuous operation verified the possibility of reducing the size of the present pilot-plant clarifier and proposed plant clarifier to a tenth or twentieth of its present size. Initial operation of the new unit with the standard caustic-copperas treatment (0.01 M NaOH and 5 ppm Fe) reduced the hardness of tap water from 100 ppm to 8 to 12 ppm with less than 1 min of flash mixing and 2 min of flocculation. This indicated the possibility of eliminating the flash-mixing and flocculation steps as separate steps, each requiring separate equipment, and performing the head-end treatment in a single clarification unit. The single unit worked well with tap water in the laboratory and with actual waste containing low phosphate (Sec 3.4.2) concentrations, producing about 10 ppm of residual hardness when the sludge blanket was stable. However, minor variation in the depth or density of the sludge blanket produced major fluctuations in the residual hardness exiting the clarifier unit. Thus, a separate flash-mixing vessel was preferred to accomplish the precipitation of hardness, depending on the clarifier for removal of turbidity only. The precipitation of hardness

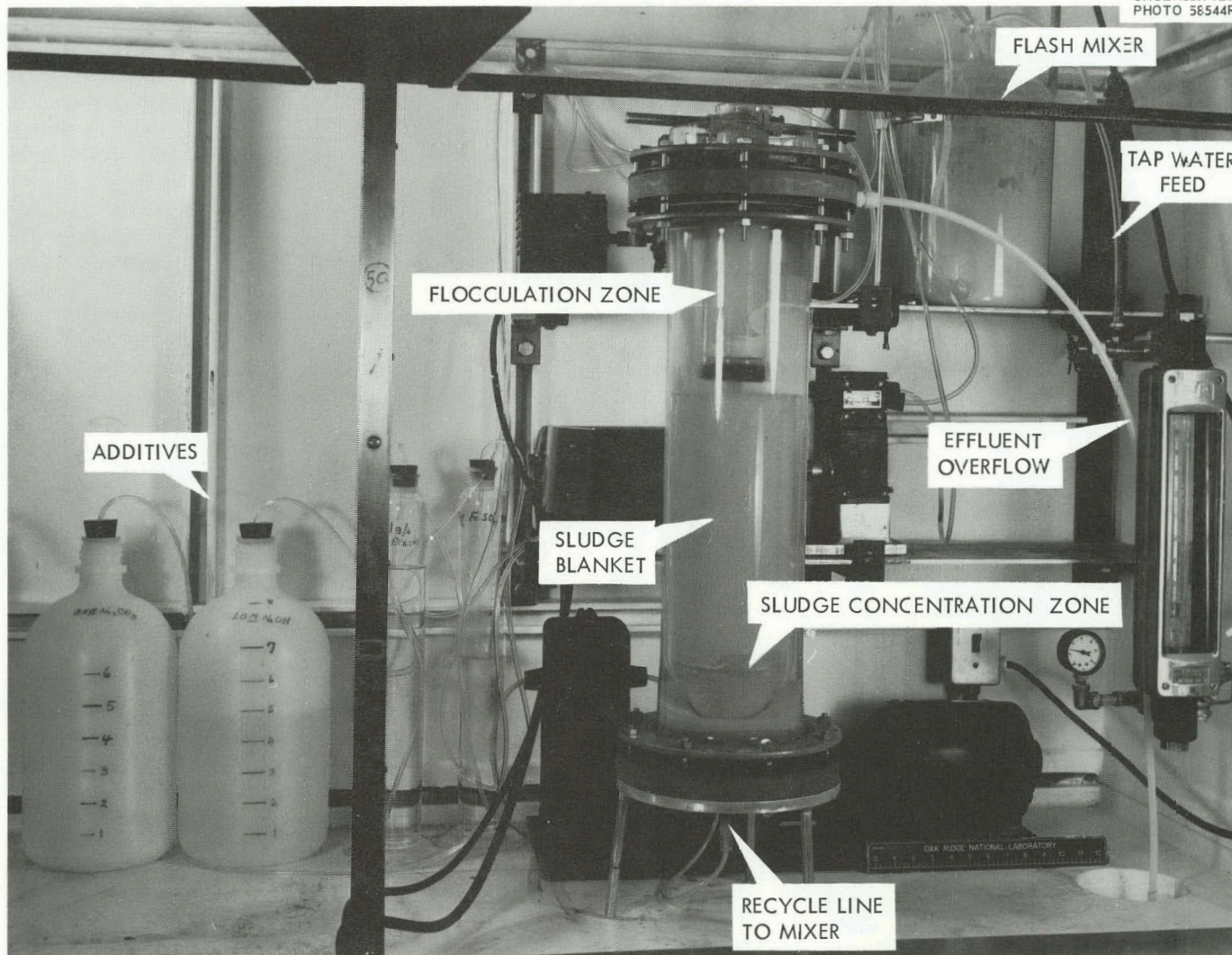


Fig. 10. Continuous Clarification Equipment, Laboratory Scale.

was also aided by the presence of preformed particles, which seeded precipitation. (In the flash-mixing vessel, rapid agitation prevented the coalescence of small floc and thus afforded more surface area to induce seeding.) Operation of the two-unit system (Fig. 10) consistently reduced the hardness of tap water from 100 to less than 2 ppm as compared to about 10 ppm obtained with the single-unit system.

3.4.2 Effect of Phosphates

The presence of complexing agents such as phosphates, in the waste stream hindered complete precipitation of hardness. This supersaturation encountered in the treatment of low-level waste was initially attributed to hexametaphosphate,¹⁴ a constituent of detergents and decontaminating solutions such as "Turco No. 4324". Precipitation of calcium carbonate was prevented because the phosphates at very low concentrations segregated nuclei of calcium carbonate as they developed.^{18,19} The effect is the same as the "threshold" treatment²⁰ of water with very low concentrations of Calgon. This treatment depends upon surface phenomena rather than stoichiometric chemical reactions. The concentration of hexametaphosphate (Calgon) is accordingly a great deal less (1 to 5 ppm) than would be required if sequestration (more than 100 ppm) of metal ions were accomplished. This remarkable property of hexametaphosphate depends on its ability to isolate any nuclei from which crystals of calcium carbonate might grow. The precipitation or crystallization which normally starts upon the surfaces of these nuclei is stopped, so that conditions of marked supersaturation are stabilized. The effect was studied in the laboratory-model clarification system (Fig. 10) treating tap water with a usual phosphate concentration of 0.02 ppm. The standard caustic-copperas treatment of the water produced a residual hardness of 1 to 3 ppm. The residual hardness or degree of supersaturation increased as the concentration of hexametaphosphate was increased, showing steady state values of 8-9, 30-40, and 60-70 ppm at hexametaphosphate concentrations of 1, 2, and 3 ppm, respectively. However, exactly the same residual hardness results were obtained when ortho-, pyro-, or polyphosphate was used in place of hexametaphosphate at the same concentration with respect to PO_4^{3-} . Apparently all phosphates at low concentrations have the same effect on supersaturation.

In waste containing phosphate concentrations of less than 2 ppm, the detrimental effect was seen as high clarifier-effluent hardness in the pilot plant (Table 5). However, the supersaturation was broken in the polishing filter by intimate contact with the calcium carbonate coated anthracite particles. This study showed that complete precipitation was also aided by the addition of calcium carbonate to the clarifier or by the intimate contact with finely divided recirculated sludge in the flash mixer. With concentrations of 3 ppm and above, the phosphates not only prevented seeding but dissolved predeposited calcium carbonate particles. This accounted for the failure of the polishing filters to remove hardness (line 7, Table 5) in some of the pilot plant runs. In this case (3 ppm of phosphate), making the water 0.005 M in Na_2CO_3 furnished sufficient carbonate to overcome the phosphate "threshold" effect. With 4 to 5 ppm of phosphate, the water had to be made 0.01 M in Na_2CO_3 . The complete precipitation of hardness was necessary because of the competition between hardness ions and strontium and cesium for resin exchange sites. In the pilot plant, the hardness in the feed to the ion-exchange resin column reduced the break-through volumes of cesium and strontium considerably.¹² Making the water 0.005 M in Na_2CO_3 in the precipitation stage reduced the hardness and thus restored the original break-through volume of about 3000 bed volumes for strontium. However, the cesium break-through was still about 50% of the expected 2000 bed volumes because of the competition between sodium and cesium for exchange sites. When the water was made 0.005 M in Na_2CO_3 , it doubled the Na^+ concentration and consequently reduced the cesium loading 50% (Fig. 11).

Another approach to the supersaturation problem was to accept the high hardness in the effluent from the precipitation-clarification step when phosphates were present and to remove the hardness by ion exchange. In this case more frequent regeneration of the resin is required. A residual hardness of about 20 ppm reduced the break-through capacity of the carboxylic-phenolic resin by 50% (Fig. 11). Thus, two regenerations were required at an added cost of 25.4 cents per 1000 gal.¹² Economically, this did not compare favorably with making the water 0.005 M in Na_2CO_3 at a cost of 11 cents per 1000 gal. However, the cost of removing the

Table 5. A Comparison of Laboratory and Pilot-Plant Results in the Head-End Treatment of Low-Level Waste by the Scavenging-Ion Exchange Process

Line No.	Feed Medium	Concentration of Coagulants			pH	Average Steady-State Residual Hardness in Effluent (ppm as CaCO ₃)		
		NaOH (M)	Na ₂ CO ₃ (M)	Fe ²⁺ (ppm)		Lab.- Model Clarifier	Pilot Plant	
						Clarifier	Clarifier	Polishing Filter
1	Tap H ₂ O	0.01	0	5	11.8	<5	11-12	11-12
2	Tap H ₂ O plus: 1.7 ppm Turco*	0.01	0	5	11.8	<5	---	---
3	2.4 ppm Turco	0.01	0	5	11.8	<5	---	---
4	3.2 ppm Turco	0.01	0	5	11.8	40	---	---
5		0.01	0.005	5	11.9	<5	---	---
6	Waste H ₂ O (Early Runs), <3 ppm PO ₄	0.01	0	5	11.8	---	60-70	8-10
7	Waste H ₂ O (with ~3 ppm PO ₄ ³⁻)	0.01	0	5	11.8	40-50	60-70	50-60
8	Runs 7-13	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	---	---

* Turco is a phosphate containing, decontaminating solution in use at ORNL.

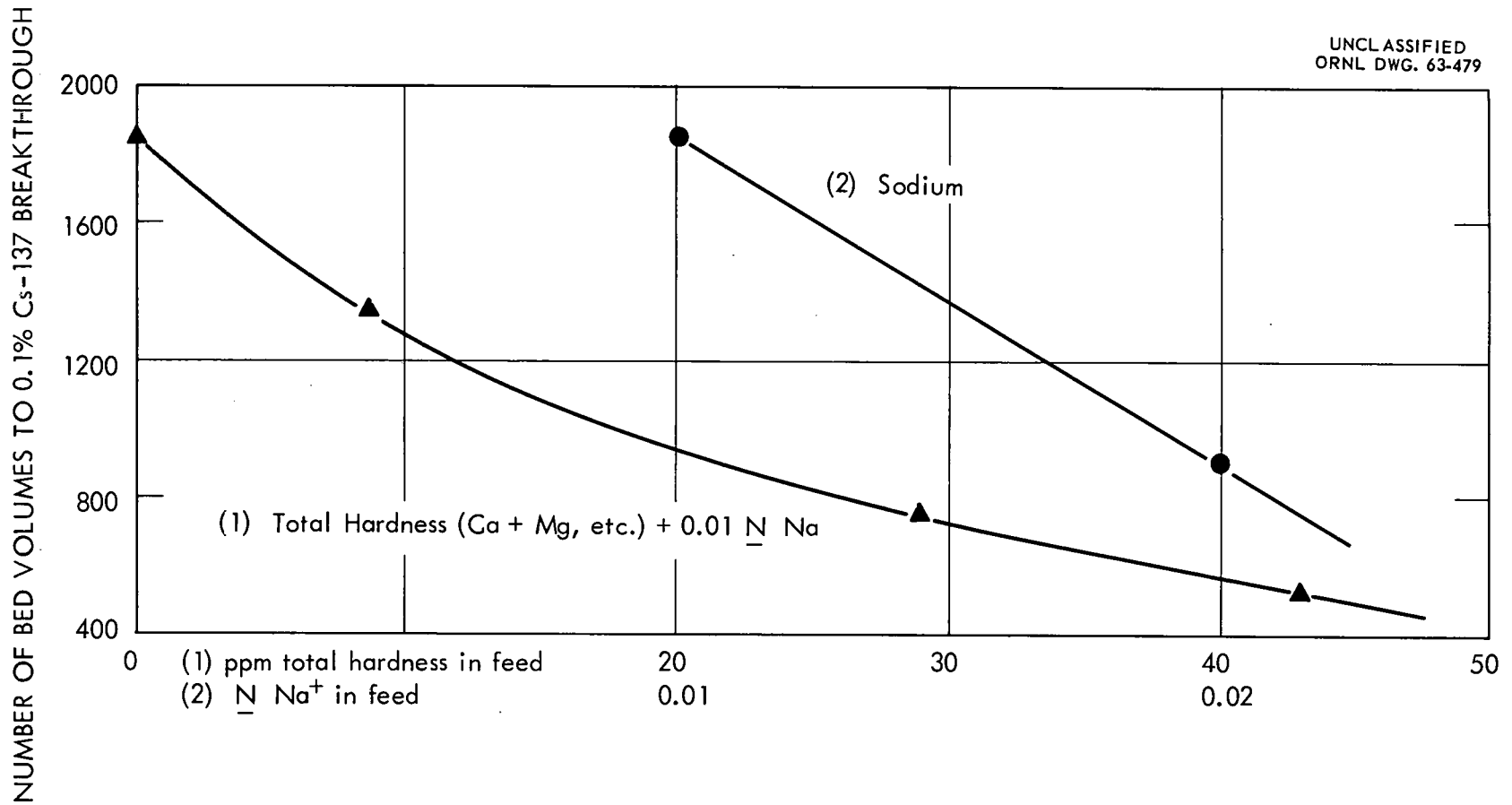


Fig. 11. The Effect of: (1) Total Hardness on Cs¹³⁷ Breakthrough Capacity in Presence of 0.01 N Sodium Ion, and (2) Sodium Ion on Cs¹³⁷ Breakthrough Capacity in the Absence of Total Hardness.

hardness with the ion-exchange resin was based on the carboxylic-phenolic resin, which had a capacity of 0.4 to 0.5 meq of calcium per ml of sodium-form resin. Another carboxylic resin, Amberlite IRC-50, achieved a loading of 1.45 meq of calcium per ml of sodium-form resin. While this resin had little capacity for cesium and thus could not be used as the principal resin; when used as a pretreatment column, it would protect the capacity of the phenolic resin for cesium and strontium. Since this pretreatment column could also be eluted with essentially a stoichiometric quantity of 0.5 \underline{M} HNO_3 , the cost of removing hardness by ion exchange would probably compare with the sodium carbonate method. It should be emphasized that the sodium carbonate method involved the addition of excess Na^+ , which competed with cesium for exchange sites. On the other hand, the ion-exchange method introduced only stoichiometric Na^+ and thus protected the loading capacity of the phenolic resin for cesium (Fig. 12). The life of the pretreatment column was dependent on the concentration of residual hardness (Table 6) in the clarifier effluent, which was a function of the phosphate concentration in the waste stream. Since the residual hardness reached a maximum at 70 ppm (the fraction of hardness due to calcium), the ion-exchange method of removing hardness was independent of phosphate concentrations over 4 ppm. Conversely, the sodium carbonate requirement was dependent on the phosphate concentration, doubling to 0.01 \underline{M} at 4 to 5 ppm of phosphate and trebling to 0.015 \underline{M} at 5 to 6 ppm of phosphate. This tended to make the ion-exchange method more attractive than the other, in which sodium carbonate was added to the water.

3.4.3 Improved Floc Distribution

Phosphates also contributed to the production of a large, light floc that promoted channeling in the sludge blanket and hindered the recirculation of sludge to the flash mixer in the laboratory-model treatment system. The increase in size of floc particles became apparent at the 3-ppm-of-phosphate level with tap water. Difficulty with recirculation and channeling occurred with more than 4 ppm of phosphate. During the treatment of the actual waste stream, the problem was compounded by the presence of algae and detergents, causing difficulty with less than 3 ppm of phosphate. A larger recirculation line permitted the return of floc to the flash mixer,

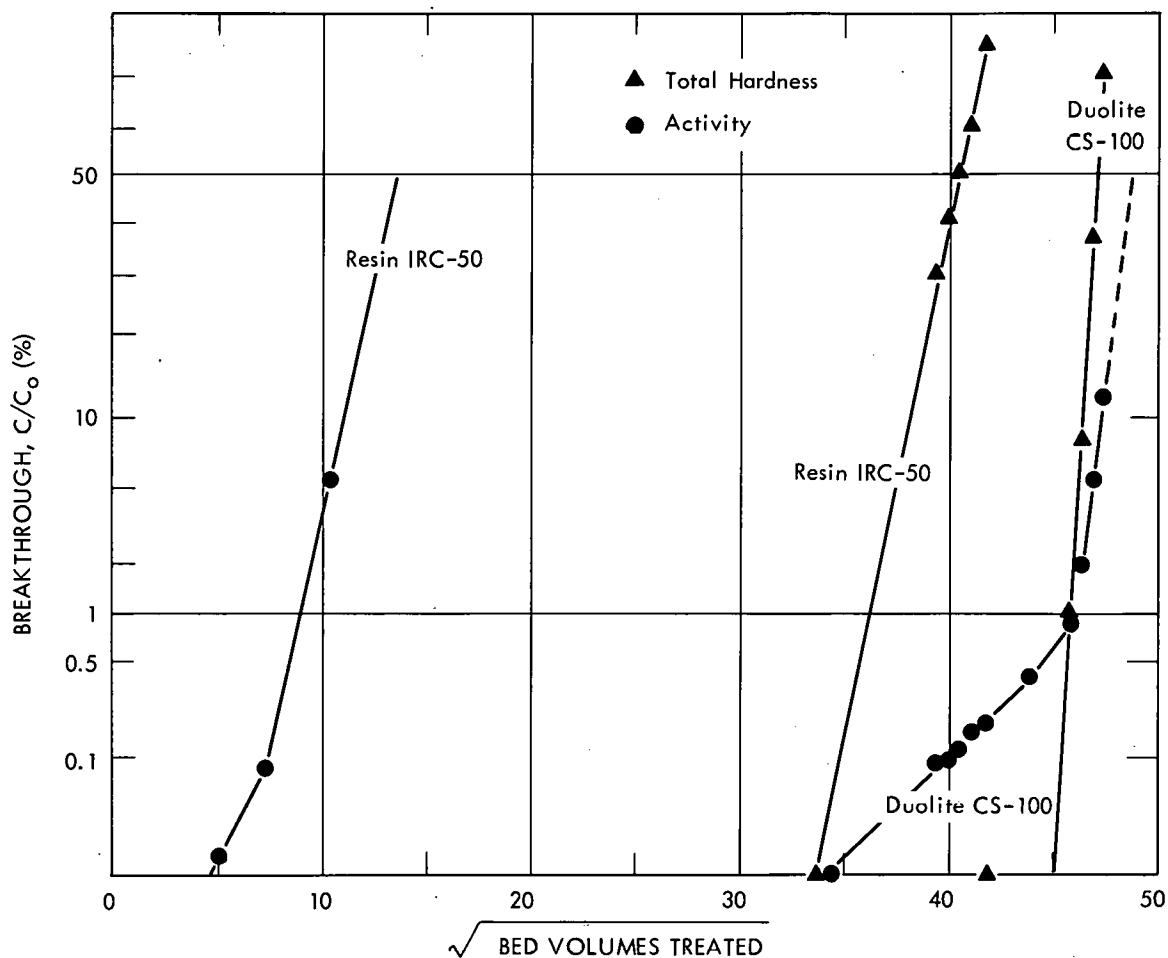


Fig. 12. Cesium-137 Loading of Amberlite IRC-50 Pretreatment Column for Removal of 60 to 70 ppm of Total Hardness and Duolite CS-100 Resin Column in Series.

Table 6. Removal of Residual Hardness from the Headend Treatment Effluent with Sodium Form, Amberlite IRC-50.

Phosphate in Waste (ppm)	Residual Hardness in Clarifier Effluent (ppm)	Bed Volumes to Hardness Breakthrough
0	0-2	$>10^4$
1	8-9	$>10^4$
2	30-40	8400
3	60	2400
4-5	70	1200
>5	70	1200

where the particle size was reduced by the rapid agitation. While the addition of calcium carbonate to the system (Table 5) densified the blanket, the best solution to the channeling problem was the installation of a 3-rpm stirrer in the bottom of the sludge blanket.

4. CONCLUSIONS AND RECOMMENDATIONS

The scavenging-precipitation ion-exchange process for decontaminating low-level process water waste was successfully demonstrated, exceeding radiological safety requirements. Part II of this report (ORNL-3349) describes the large-scale work.

Normal flowsheet treatment (making the water 0.01 M in NaOH and 5 ppm in iron) produced excellent results in the majority of demonstration cycles in both the laboratory and pilot-plant studies. However, occasional surges of complexing agents such as phosphates due to the occasional increased use of detergents and decontaminating solutions hindered complete precipitation of hardness in the head-end system and tended to shorten the life of the ion-exchange system. This detrimental effect can be overcome by preferably restricting the use of phosphate-containing detergents and decontaminating solutions, or by employing a special pretreatment column of ion-exchange resin for the removal of residual hardness, or by adding sodium carbonate to the waste in the headend treatment to aid the removal of hardness by precipitation prior to ion exchange. While chemical additives along with increasing temperature and improved clarification equipment (Sec 3.4.1) should improve the softening, their benefit can be completely masked by phosphate concentrations over 3 ppm, thus emphasizing the need to eliminate phosphates from the waste or to apply ion-exchange for removal of the resulting high residual hardness. Breakthrough of hardness and the accompanying activity can be detected by a continuous total-hardness measuring instrument or counter on the discharge stream in order to signal the impending escape of radioactive contaminants to the environment.

The floc particles formed during the treatment of actual waste were much larger and less dense than those obtained with tap water. Floc forma-

tion was accomplished in the sludge blanket itself, eliminating the need for a separate flocculation vessel. This large floc, while excellent for producing clear, low-turbidity water, did not aid hardness precipitation because of the reduced surface area available for seeding new precipitate. Thus, hardness could be precipitated more completely in a separate flash-mixing vessel where the particles were finely divided by rapid agitation. The large floc also created channeling, which required the use of an agitator in the sludge blanket for proper distribution. An agitator in the bottom of the sludge blanket is recommended for treating waste high enough in phosphate to produce the large floc which creates channeling.

The laboratory-model clarification unit utilizing an inner cone was operated almost continuously for over six months. The unit operated at $45 \text{ gal hr}^{-1} \text{ ft}^{-2}$, with only a 10-min holdup in the inner-cone sludge blanket, representing an equipment size reduction of 10- to 20-fold over the previous laboratory units and the pilot-plant clarifier, which offered a 3-hr holdup. This decrease in equipment size will result in a reduction in capital cost of equipment for a full-scale plant.

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