

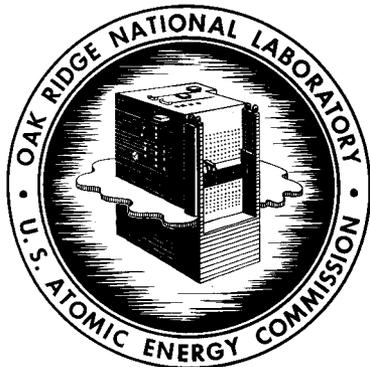
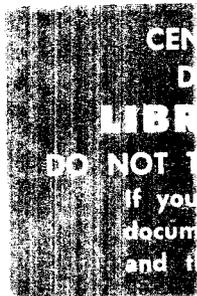


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ORNL-3036
UC-70 - Waste Disposal and Processing

A PHENOLIC RESIN ION EXCHANGE
PROCESS FOR DECONTAMINATING
LOW-RADIOACTIVITY-LEVEL
PROCESS WATER WASTES

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price **\$0.75**. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D. C.

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ORNL-3036

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION B

A PHENOLIC RESIN ION EXCHANGE PROCESS FOR
DECONTAMINATING LOW-RADIOACTIVITY-LEVEL PROCESS WATER WASTES

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DATE ISSUED

MAY 22 1961

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
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ABSTRACT

A process was developed on a laboratory scale to decontaminate large volumes of low-radioactivity-level process water wastes having a macro-chemical composition not very different from tap water but containing more than the maximum permissible concentration of radioisotopes for unrestricted discharge. The water is adjusted to 0.01 M NaOH (pH slightly under 12), clarified to remove the small amount of solids, and passed through a bed of phenolic cation exchange resin. With typical Oak Ridge National Laboratory waste, when the water is made alkaline, more than half the radioactivity is removed by coprecipitation with the calcium and magnesium already present and most of the remaining radioactivity is removed by the resin. About 99.9% of the Sr-90 and Cs-137, the greatest health hazards, can be removed from 1500-2000 volumes of the alkaline water by passage through one volume of phenolic resin (Duolite CS-100 or C-3) on a 3.5-7 day cycle. Phenolic resins are much more selective for cesium at high pH than other resins. The resin can be regenerated with 10 volumes of 1-5 M HCl, removing 99.9% of the strontium and cesium. The waste regenerant can be evaporated to one-half resin volume of concentrated radioactive waste to be stored, representing an over-all volume reduction factor of 3000-4000 for the ion exchange and evaporation steps.

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1.0 INTRODUCTION

Atomic energy installations usually produce large volumes of process water waste from such sources as equipment cooling systems, floor drains, decontamination pad drains, storage canals, laboratory sinks, and discharges from low-level radioactive operations. These low-radioactivity-level wastes have a macrochemical composition not very different from tap water but may contain micro amounts of radioisotopes in excess of the maximum permissible concentrations (MPC) for unrestricted discharge to the environment (1,2). In some cases the volume and radioactivity of the waste are such that little or no treatment other than dilution is required prior to discharge. In other cases chemical and physical treatments must be used to reduce the radioactivity by factors of 2 to 1000, depending on the waste, the radioisotopes involved, and the environment of the waste-producing installation.

The objective of the work reported here was to develop an economical method for treating Oak Ridge National Laboratory (ORNL) process water waste which would reduce its radioactivity to below MPC levels. Such a new method could be used at ORNL if the present practice of dilution and dispersal should be restricted or if it provided higher decontamination at a cost comparable to that of the present ORNL lime-soda-clay treatment (see below), and at similar installations where dilution and dispersal are not practical. Evaporation can give excellent decontamination and volume reduction factors but is also comparatively expensive for large volumes. The phosphate-sulfide-vermiculite process (see below) appears to give acceptable decontamination factors, but a simpler chemical and engineering flowsheet and/or a lower final waste volume to be stored would reduce costs.

Laboratory scale work indicates that a phenolic-resin ion exchange process should provide higher decontamination factors and volume reductions than other current processes. A small pilot plant demonstration of the phenolic ion exchange process is planned to confirm these results under actual operating conditions.

1.1 Present ORNL Treatment

At ORNL the low-level process water waste has averaged about 700,000 gal/day. This waste is continuously monitored and, depending on its radioactivity level, either diverted for discharge without treatment or passed through the ORNL low-level waste water treatment plant (3). As shown in Fig. 1, waste containing less than about 50 c/m/ml gross beta (referred to second-shelf counting using an end-window Geiger counter) passes through a 1,500,000-gal settling basin which overflows into White Oak Creek. Wastes containing more than this, averaging 100-200 c/m/ml with occasional transient levels above 1000, pass through a 1,000,000-gal equalization basin and a treatment plant before being discharged to the creek.

The ORNL low-level waste water treatment plant uses a horizontal-flow lime-soda softening process with the addition of grundite clay to increase cesium removal (4,5). The reduction of gross radioactivity depends on the radionuclide composition of the waste and the types and amounts of chemicals present or added. The radionuclides removed are associated with the "sludge" (calcium carbonate, magnesium hydroxide, clay) which settles out of the water. The sludge is transported by tank truck to waste seepage pits, bulldozed in a Conasauga shale formation.

The design capacity of the plant is 500,000 gal/day. In the first 14-month period of continuous operation the plant treated an average of 414,000 gal/day, 62% of the total process water waste during this period, and produced an average of 1210 gal/day of sludge containing an average of 51% solids by volume. During the last 6 months of this period the plant removed 83-90% of the gross beta activity, 79-90% of the Sr-89-90, 71-95% of the total rare earths, 80-86% of the Cs-137, 65-82% of the Co-60, and 47-84% of the Ru-106. The influent and effluent concentrations, expressed in percent of the MPC for a 168-hr week, were:

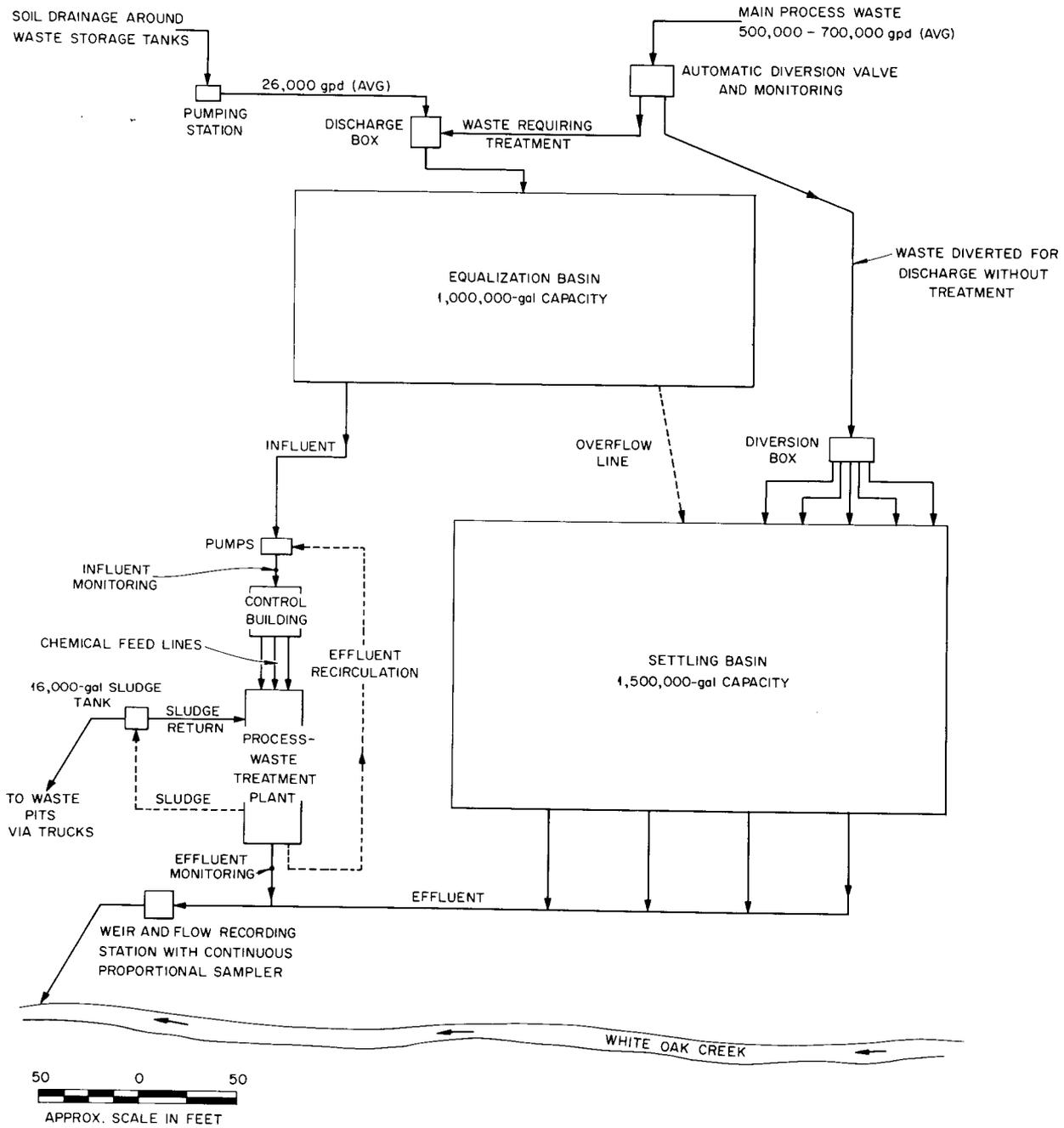


Fig. 1. Flow diagram of process waste system.

Isotope	MPC _w (168 hr), d/m/ml	Activity, % of MPC		Decontamination Factor
		Influent	Effluent	
Sr-89	222	7-21	1-4	5-10
Sr-90	2.22	13,000-17,600	1600-2800	5-10
TRE (figured as Y-91)	666	66-180	7.5-22	3.5-20
Cs-137	444	56-151	9-36	5-7
Co-60	1110	2.6-24	0.5-5	3-6
Ru-106	222	3-30	0.5-9	2-6

The 700,000 gal/day total of treated plus untreated waste water is diluted by a factor of about 5 by the flow in White Oak and Melton Creeks before being discharged into the Clinch River, and by another factor of about 1000 by the river before leaving the AEC restricted area, so that the downstream radioactivity is only a small percentage of the MPC.

1.2 Present AERE Treatment

In a location less suitable for environmental dilution than ORNL, however, an installation producing a similar waste might well have to treat all of it and also remove a larger fraction of at least the strontium and cesium. At the Atomic Energy Research Establishment at Harwell, England, for example, the process water waste is treated by a calcium iron phosphate precipitation at pH 11.5 followed by an iron sulfide precipitation and then passage through a bed of vermiculite (6-8). The sludge from the two precipitation steps is frozen and then thawed, and the resultant liquor filtered on a vacuum filter. The freezing step makes the filtration easier and gives a smaller final volume of solids, about 0.56 ml (0.7 g) of cake (68 wt % water) per liter of original waste. One volume of vermiculite per 650 volumes of solution is used in the final step in the process. The exhausted vermiculite and the cake from the sludge filtration constitute a concentrated waste, volume-reduced by a factor of about 480 compared to the original process water waste, which is transferred to mild steel drums, sealed, and dumped at sea in specially selected areas. The percent removal of radioactivity in this process is:

Treatment	Gross α	Gross β	Ru	Cs
Phosphate only	98	86.91	47-70	16-33
Phosphate + sulfide	99.47-99.92	86.58-94.54	69-83	32-49
Phosphate + sulfide + vermiculite	99.83-100	99.17-99.67	69-83	~ 100

The over-all removal of strontium was reported to be >97% in an early paper (9).

2.0 PHENOLIC RESIN PROCESS FLOWSHEET

Ion exchange with phenolic cation exchange resins was selected for evaluation as a method of process water decontamination (Fig. 2). Most cation exchange resins offer good decontamination factors and high capacity for strontium, the greatest hazard in ORNL waste, but only the phenolic types are effective for cesium, the next greatest hazard. The phenolic resins are highly selective for cesium at pH values high enough to cause a significant fraction of the phenolic groups to be ionized (10-15). Since ORNL process water waste tends to average about neutral, it is necessary to make it about 0.01 M in NaOH to raise the pH to about 12, which is near optimum for cesium removal from dilute solutions with phenolic resin (16).

When typical ORNL low-level waste water is made alkaline, most of the dissolved calcium and magnesium precipitate, carrying down with them the dirt, algae, and other suspended solids and a substantial fraction of the radioactivity, such that filtration removes about 1-10% of the cesium, about 30-70% of the strontium, about 70-90% of the ruthenium and cobalt, and greater than 90% of the rare earths. The settled solids have a volume of about 0.2% of the original waste volume and the filtered solids about 0.02%, even less after drying. The subsequent ion exchange step removes part of the residual cobalt and ruthenium, most of the residual rare earths, and nearly all of the remaining cesium and strontium. For 1500 volumes of waste passed through one volume of phenolic-sulfonic or phenolic-carboxylic resin on a 3-day exhaustion cycle, the over-all process decontamination factors were about 10 for ruthenium and cobalt, about 100 for rare earths, and about 1000 for cesium and strontium.

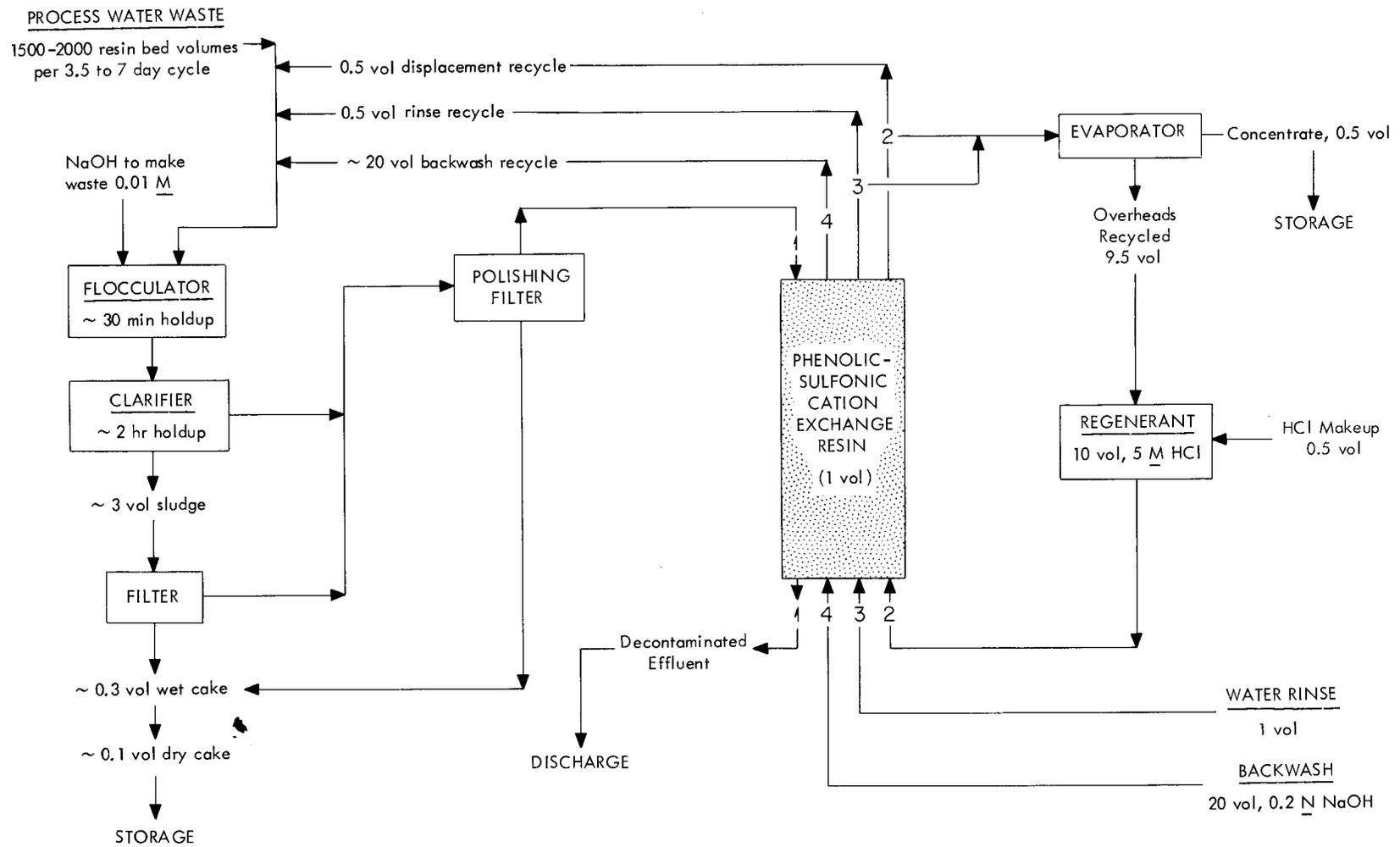


Fig. 2. Process water decontamination with phenolic resin.

Duolite C-3, a phenolic-sulfonic resin, and Duolite CS-100, a phenolic-carboxylic resin, were about equally effective in the exhaustion cycle. Both were about as effective as the standard polystyrene-sulfonic resins for polyvalent radioisotopes but were much more effective for cesium since the phenolic group, ionized only at high pH, is unusually selective for cesium in the presence of sodium and other cations.

Greater than 99.9% of the cesium and strontium can be removed from the resin by upflow regeneration with 10 resin volumes of 5 M HCl for Duolite C-3 or with 10 resin volumes of 1 M HCl for Duolite CS-100. Duolite S-30, a phenolic-only resin, has about half the breakthrough capacity of C-3 or CS-100 but can be regenerated with even less acid than CS-100. A large volume change between the acid and alkaline forms of CS-100 and S-30 is an operational disadvantage of these weak-acid resins. Sulfuric acid regeneration is probably not desirable because of the possibility of calcium sulfate precipitation and smaller volume reduction factors on evaporation. Regeneration with concentrated nitric acid is precluded since it vigorously attacks phenolic resins, but dilute nitric acid might be used to regenerate CS-100 or S-30 under carefully controlled conditions.

The 10 volumes of HCl regenerant waste can be evaporated by a factor of about 20, to give a volume reduction factor from original waste water to concentrated regenerant waste of about 3000. The condensate from the regenerant waste evaporation can be reused as regenerant after butting up to original strength with fresh acid.

3.0 EXPERIMENTAL

3.1 Effect of pH on Radioactivity Removal with Phenolic Resins

Figure 3 shows the effect of pH on the trace concentration Cs-137 distribution coefficient of Duolite S-30, a phenol-formaldehyde resin in which all of the ion exchange capacity is associated with the phenol groups (16). In the two dilute solutions (distilled water or 0.01 M NaNO₃, plus NaOH to adjust the pH) the distribution coefficient increased sharply with pH up to about pH 12 and then leveled out or dropped somewhat. From these data

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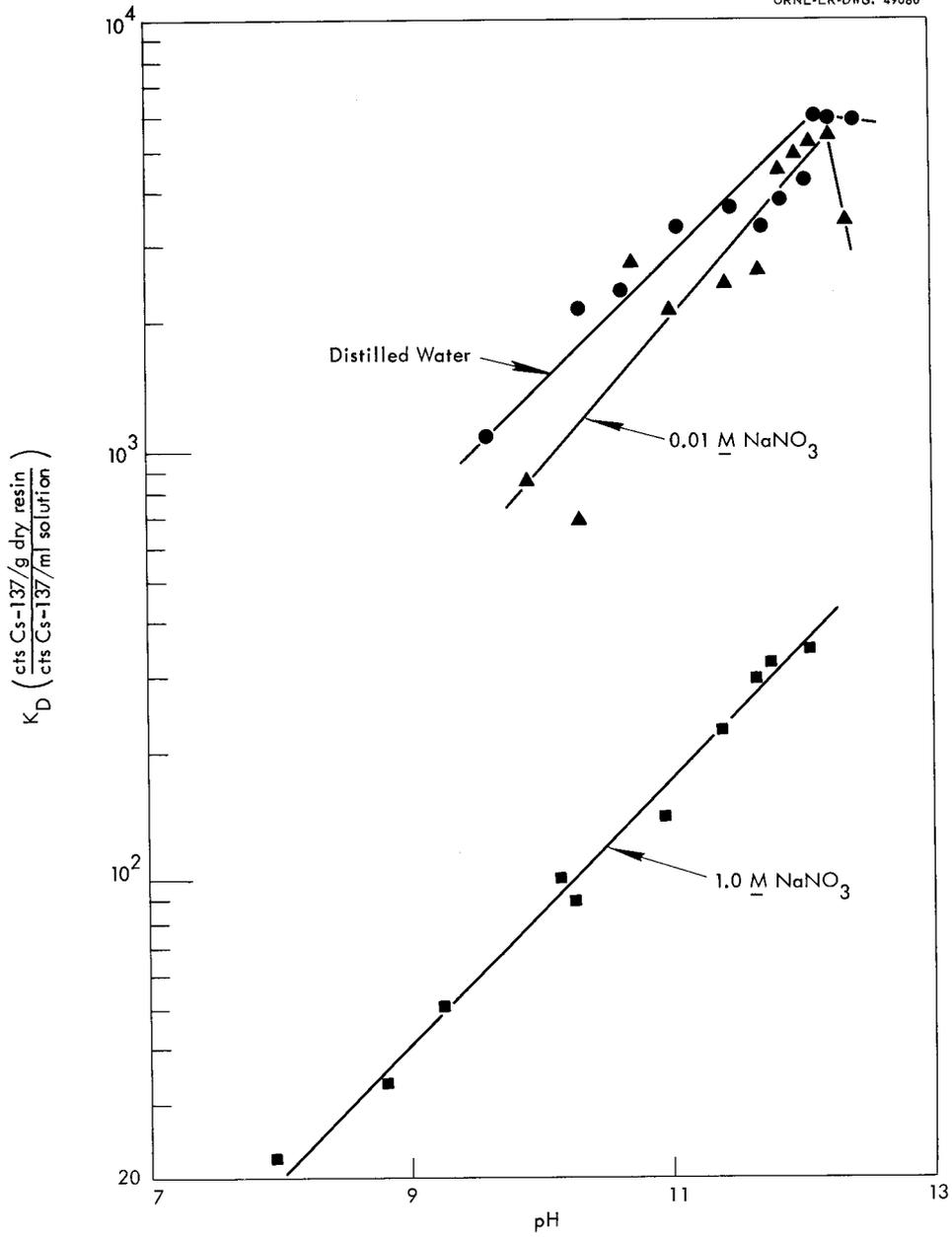


Fig. 3. Cesium distribution coefficient for Duolite S-30 resin in alkaline solutions. Sodium hydroxide added to adjust pH.

the cesium-sodium separation factor is calculated to be about 160 for the phenolic group. Presumably, up to about pH 12 the increased ionization of the phenolic group is controlling, but above this point the increasing sodium ion concentration begins to be competitive. In the 1 M NaNO_3 solution (plus NaOH to adjust the pH) the distribution coefficients are lower because of the much greater competition from sodium ion, and the pH corresponding to a maximum value of the distribution coefficient presumably is shifted to above 12 since the amount of NaOH added at this point (about 0.02 M) contributed little to the total sodium ion concentration.

Figure 4 shows the effect of pH on radioactivity removal in fixed-bed tests with spiked ORNL process water waste and Duolite C-3, a sulfonated phenol-formaldehyde resin. With this resin most of the total ion exchange capacity is due to the sulfonic groups but the cesium capacity is controlled by the phenolic groups because of their much greater cesium selectivity (a factor of 10-100 times greater than for sulfonic or carboxylic groups). The runs were made on 0.5-in.-dia beds, 6-7 in. long (19.2-22.5 ml of resin), at flow rates of 575-1090 bed volumes per day. Samples of ORNL process water waste, taken at the waste treatment plant inlet, were spiked with about 0.01-0.1 mc/liter each of Cs-137, Sr-85, and Ce-144-Pr-144 to raise the radioactivity high enough above background to facilitate accurate measurement of decontamination factors and identification of radioactive species in effluents by gamma energy distribution measurement. In run 4 the solution was spiked with cesium and strontium tracers, filtered, and passed through the ion exchange bed at its unadjusted pH of 7.3. Run 5 was similar except that the pH was adjusted to 10.6 after spiking and before filtration. Run 22 was similar except that cerium tracer was also added and the pH was adjusted to 11.7 (NaOH added equivalent to 0.01 M). The pH adjustment and filtration resulted in partial removal of the radioactivity from solution (Sect. 3.5). The curves in Fig. 4 are based on gross gamma counts per minute per milliliter above 40 kev energy. Gamma energy scans of the samples on the initial level portions of the curves indicated that no more than a minor fraction of the total radioactivity in them was due to cesium and strontium. This "background

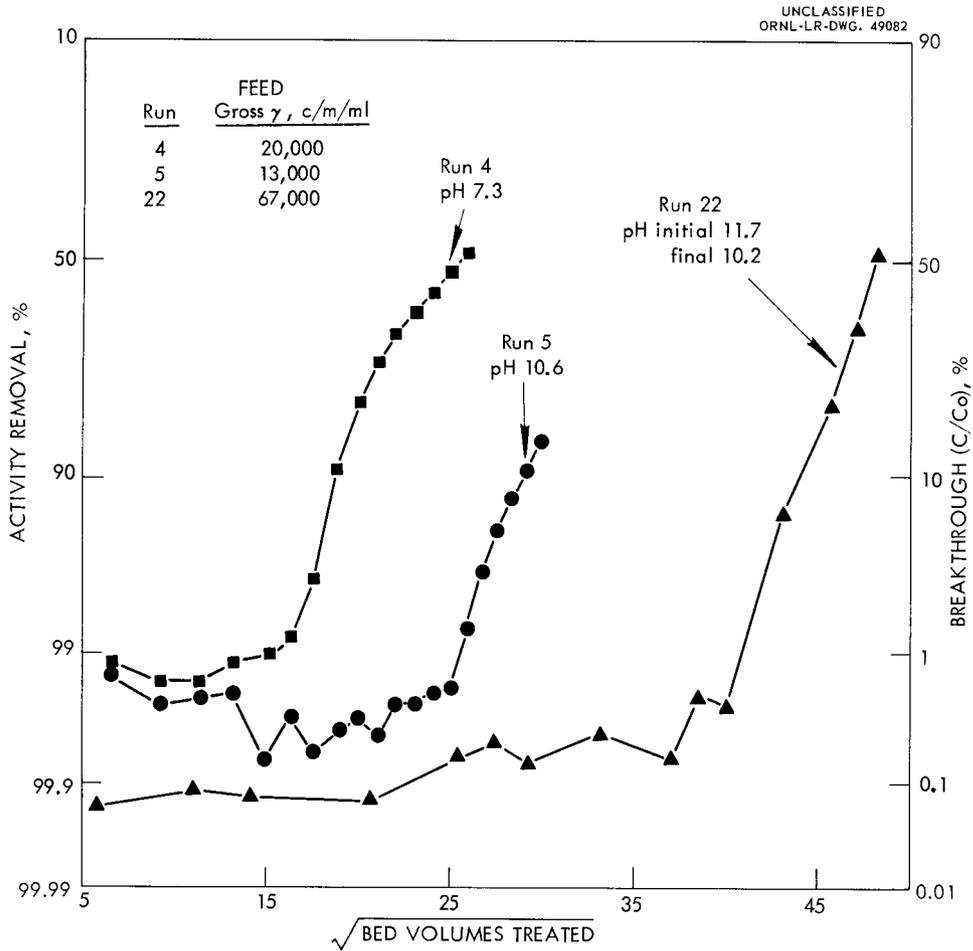


Fig. 4. Low-radioactivity-level waste treatment with Duolite C-3 sulfonic-phenolic exchanger as a function of pH. Runs 4 and 5: Cs-137 and Sr-85 spike; 22.5 ml of Na⁺ form Duolite C-3, 0.5 in. i.d. x 7 in. column, 17 ml/min flow rate. Run 22: Cs-137, Sr-85, and Ce-141 spike; 19.2 ml Na⁺ form Duolite C-3, 0.5 in. i.d. x 6 in. column, 9 ml/min flow rate.

hash" (over and above actual counting background) consists primarily of anionic, nonionic, and colloidal activities initially in the waste and possibly present as impurities in the tracers used, including Ru-103-106, Zr-Nb-95, Co-60, and Ce-141-144. Cesium broke through sharply when it finally appeared in the effluent, after about 225 bed volumes at pH 7.3, 650 volumes at pH 10.6, and 1600 volumes at pH 11.7. Strontium broke through close behind cesium at pH 7.3, further behind cesium at pH 10.6, and did not break through to a detectable level after 2300 volumes at pH 11.7 (see also Sect. 3.4). No real cerium breakthrough was noted in run 22 but there was not much left in the feed after pH adjustment and filtration and thus the analytical uncertainty is large. The over-all precipitation-filtration-ion-exchange decontamination factor for cerium was 100-1000, however. In run 22 the pH dropped gradually from 11.7 initially to 10.2 finally, presumably due to absorption of CO₂ from the air, but the drop was not rapid enough or large enough to overcome the advantage of the higher starting pH.

3.2 Comparison of Different Resin Types

Figure 5 shows breakthrough curves for four different resins. Runs 40 and 41 were made simultaneously with the same batch of feed and the same flow rate. Runs 42 and 43 were also made simultaneously but at a later date than 40-41 and with a different batch of feed and at a slower flow rate. Both batches of feed were spiked with 0.1 mc/ml each of Cs-137, Sr-85, and Ce-141, made 0.01 M in NaOH and filtered before being passed through the ion exchange resin.

Run 40 was made with Duolite C-20, a sulfonated styrene-divinylbenzene resin. The Cs-137 activity broke through rapidly, reaching 1% breakthrough at about 60 resin bed volumes throughput, and leveled off at its feed concentration, about 70% of the total feed activity. Most of the rest of the feed activity was due to Sr-85, which did not break through significantly during the run (>2000 volumes throughput). After pH adjustment and filtration neither the feed nor the effluent contained enough Ce-141 to detect in the presence of the Cs-137.

The other runs were made with three different phenolic resins. Run 41 was made with Duolite CS-100, a phenolic base resin with most of its total ion exchange capacity due to carboxylic groups. Run 42 was made with

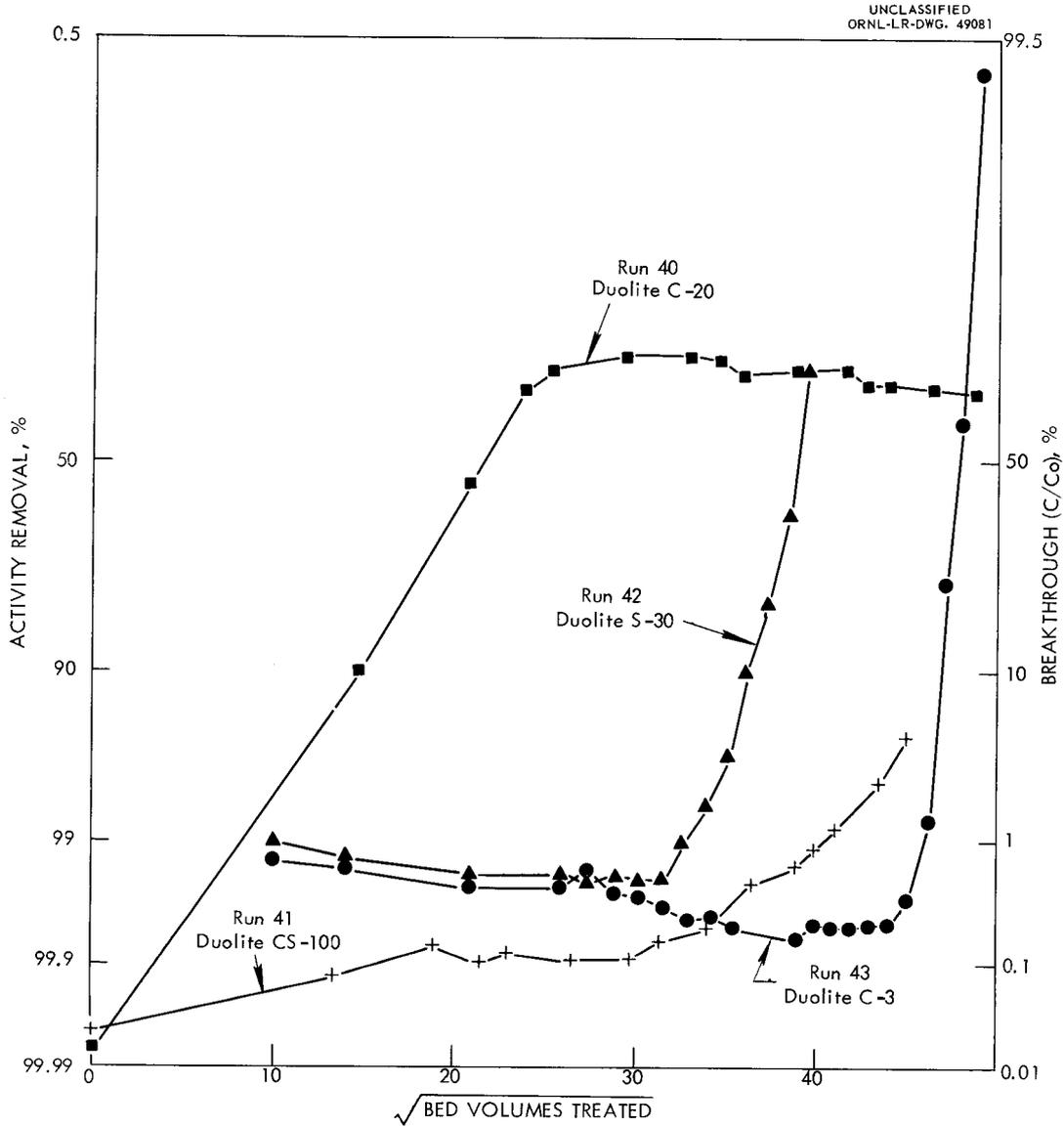


Fig. 5. Loading of trace activities on various resins from spiked ORNL process water waste at pH 11.7. All runs: 19.2 ml of resin, 0.5 in. i.d. x 6 in. column; Na⁺ form resin; flow rate ~8 ml/min in runs 40, 41, and ~3 ml/min in runs 42, 43.

Duolite S-30 whose ion exchange capacity is all due to phenolic groups. Run 43 was made with Duolite C-3, a phenolic base resin with most of its total ion exchange capacity due to sulfonic groups. The 1% activity breakthrough capacity was about 1000 resin bed volumes for S-30, 1600 for CS-100, and 2000 for C-3. With S-30 resin the Sr-85 broke through not too far behind the Cs-137, but with CS-100 and C-3 strontium breakthrough was negligible up to 2000 volumes treated. The 0.1-1% activity of the initial level portion of the breakthrough curves was indicated by its gamma energy spectrum to be mostly cerium. The differences between the CS-100 and C-3 curves in Fig. 5 are thought to be mainly due to the difference in flow rates but possibly also to differences in composition of feed batches. In other runs with these two resins, made at the same time and flow rate with the same feed, differences in the breakthrough curves were small.

3.3 Regeneration of Exhausted Resin

Figure 6 shows the results of upflow regeneration of Duolite C-3 (run 25) CS-100 (run 31), and S-30 (run 45) with 5 M, 2.5 M, and 1 M HCl, respectively. The different acid concentrations were used in an attempt to get roughly similar elution behavior from the "strong acid" sulfonic resin, the "weak acid" carboxylic resin, and the "very weak acid" phenolic resin. The resin beds were exhausted under similar but not identical conditions with spiked ORNL process water waste at different times. Run 25 was made with resin exhausted in run 22 (Fig. 4). Run 31 was made with resin exhausted in run 27, not illustrated here but similar to run 41 (Fig. 5). Run 45 was made with resin exhausted in run 42 (Fig. 5).

Due to variations in tracers used, composition of ORNL process water waste, and degree of saturation during the exhaustion, the three resin beds did not contain exactly the same amount of radioactivity and are best compared by relating regenerant waste activity during a run with the **peak regenerant** waste activity during the same run. As a rough approximation the degree of resin regeneration is indicated by the degree to which the regenerant waste activity has dropped from its peak value. Thus, Fig. 6 indicates that a 99.9% regeneration level was reached after 8.3 resin bed volumes of regenerant for the C-3 resin, 4.0 volumes for CS-100, and 3.4 volumes for S-30.

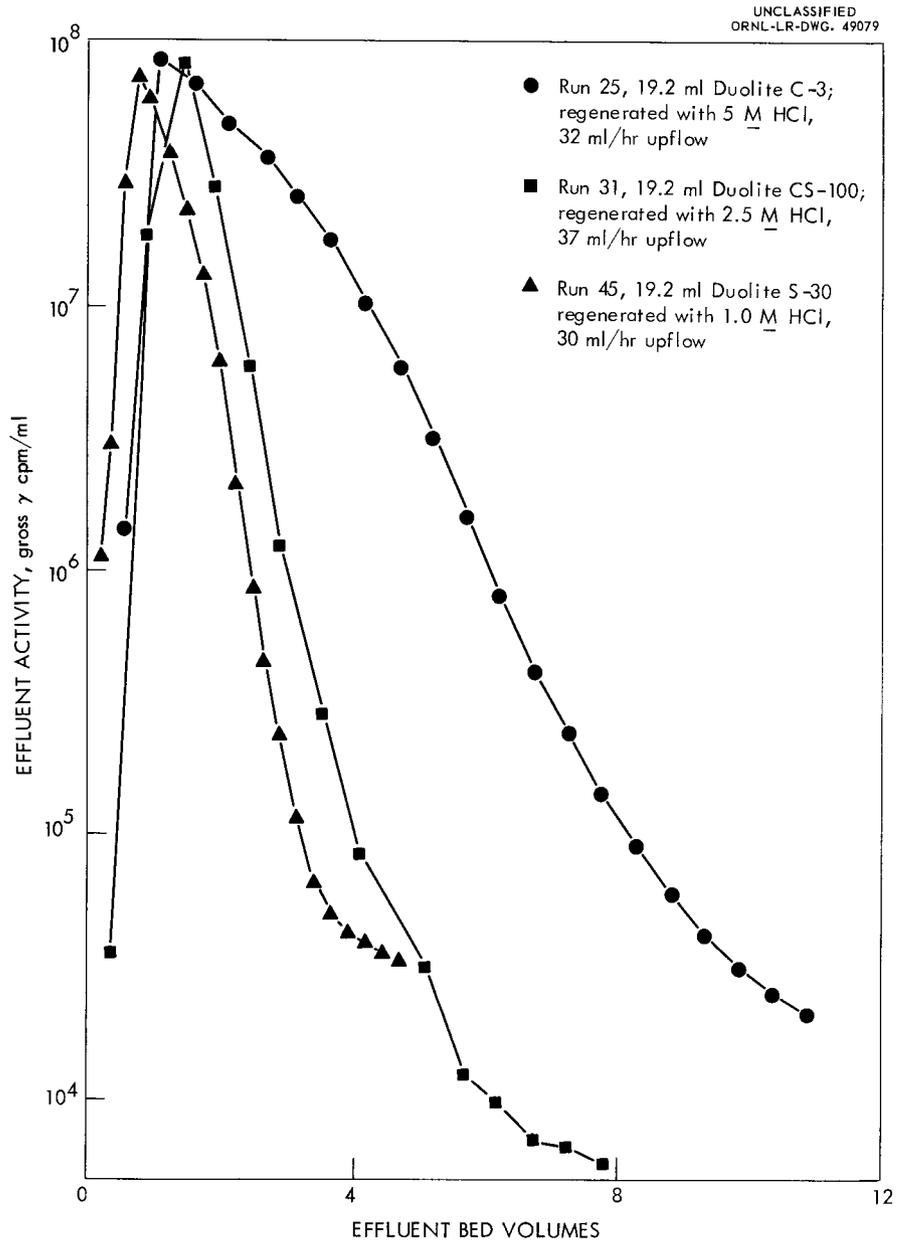


Fig. 6. Elution of tracer activities from resins exhausted with spiked ORNL process water waste.

In other runs, not illustrated, 99.9% regeneration was achieved with 9.8 volumes of 4.0 M HCl for C-3 resin and with about 8 volumes of 1.0 M HCl for CS-100 resin. In all cases the gamma energy spectrum of samples along the tail of the elution curve indicated that cesium was being removed from the resin somewhat more slowly than the strontium.

These results indicate that the weak acid resins CS-100 and S-30 are regenerated with about the same or smaller volume of 1 M HCl as is the strong acid C-3 with 5 M HCl. The CS-100 and S-30 resins have the disadvantage, however, of shrinking about 30% in volume during regeneration. This shrinkage might result in inefficient regeneration due to channeling in large size beds. It is necessary to re-swell the bed before it is reused in order to prevent possible plugging, or even equipment rupture, during the subsequent cycle. The re-swelling can be accomplished with an alkaline backwash at sufficiently high flow rate to fluidize the bed slightly. This alkaline backwash is desirable even in the case of C-3 resin, but the problem is much less severe since the shrinking and swelling is only about 10%. The CS-100 resin has the further disadvantage that it is not a standard commercial resin, though it is available on special order (about \$50 per cubic foot, vs \$20-25 for C-3 and S-30).

Because of the shrinkage-swelling problem, the lower exhaustion capacity of S-30 (Fig. 5), and the noncommercial status of CS-100, the C-3 resin is probably the conservative choice of the three. The other two deserve further consideration, however, because of their advantage of easier regeneration. One possible advantage which will be investigated is the use of dilute nitric acid as regenerant. Concentrated nitric acid attacks the phenolic resins, but it may be possible to use dilute nitric acid to regenerate the weak acid CS-100 and S-30, in which case a stainless steel evaporator could be used instead of the more exotic materials required for an HCl evaporator.

3.4 Demonstration of High Decontamination Factors for Strontium and Cesium

The phenolic resin loading curves (Figs. 4 and 5) were characterized by a level initial portion at 0.1-1% of the feed radioactivity followed by a sharp rise. Gamma energy analysis of samples taken along the level portion indicated that the cesium and strontium were present at less than 0.1% of

the feed concentration and that the balance of the activity was due to cerium, praseodymium, barium, lanthanum, ruthenium, zirconium, niobium, cobalt, etc., either present in the original waste water or added in the cesium-strontium-cerium spike. Since increasing the spike level in general decreased the percentage breakthrough along the level portion of the curve, it was concluded that most of the activity in this region was due to colloidal or anionic activities in the unspiked waste feed. The sharp rise in activity was associated with the cesium breakthrough. The 1% breakthrough was taken as an end point for a run since a decontamination factor of 100 is more than sufficient for cesium in typical ORNL waste and since gamma analysis indicated that the strontium was still below 0.1% at this point.

It was felt desirable, however, to demonstrate an actual gross decontamination factor of 1000 for cesium and strontium along the initial level portion of the curve in order to remove any doubts about interference of impurities. The most straightforward way to do this would be to simply increase the amount of tracer used by a factor of about 10, but this was ruled out on the basis that the total amount of activity being used was already as high as desirable for the direct handling techniques being used. A compromise was made by adding the total amount of Cs-137-Sr-85 tracer normally used for a run to the first 10% of the feed and following this with unspiked feed. According to simple chromatographic theory (linear sorption isotherms, linear kinetics), the initial portion of breakthrough curve for such a run should be approximately the same as if the spiked feed had been continued throughout the run. As can be seen in Fig. 7, in this run the effluent radioactivity stayed below 0.1% of the feed for about 2000 resin volumes throughput.

3.5 Precipitation and Filtration

This study stressed the ion exchange step primarily, with only enough attention paid to the precipitation and filtration steps to ensure that the ion exchange step could be fairly evaluated. The ion exchange results indicate that this step is highly effective for removing cationic radioactive species in solution but not for colloidal or anionic species. Thus the effectiveness

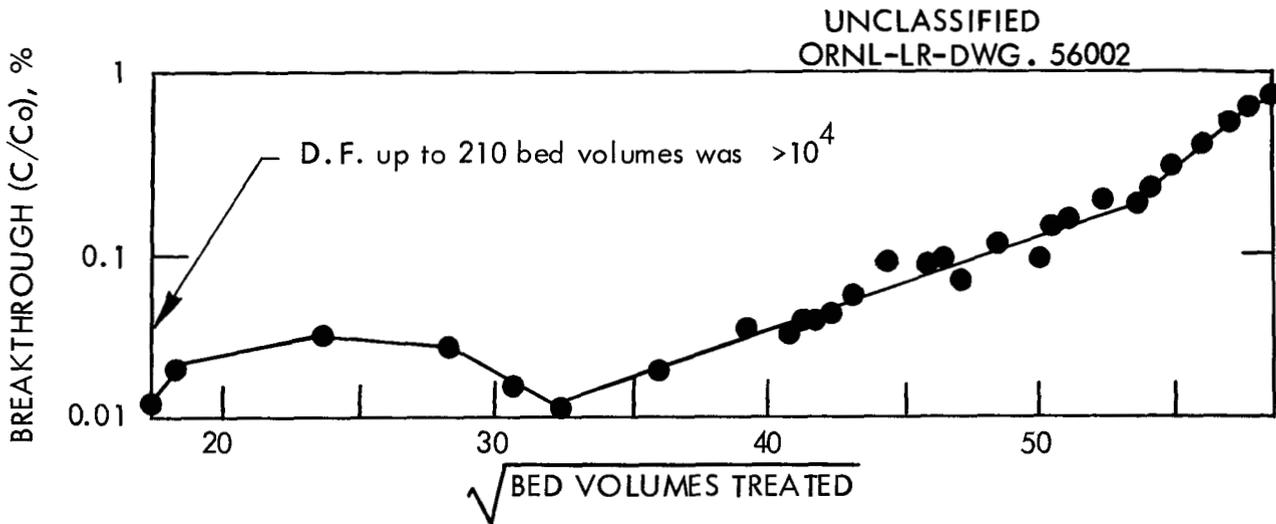


Fig. 7. High decontamination factor demonstration with Sr-85 and Cs-137 in actual process water waste on Duolite C-3, run 48. Feed: (1) 3750 ml of process water waste spiked with 5 mc of Sr-85 and 2 mc of Cs-137 (7×10^5 gross γ c/m/ml), made 0.01 M in NaOH, stirred 30 min, and filtered with fine porosity fritted glass filter; (2) followed with unspiked 0.01 M NaOH process waste water which was filtered with a medium porosity fritted glass filter. Flow rate: 312 ml/hr. Column: 0.5 in. i.d. x 6 in. glass pipe. Resin: 19.2 ml of Na⁺ form Duolite C-3, sulfonic-phenolic resin.

of the precipitation and filtration steps controls the over-all process gross decontamination factor with typical ORNL process water waste. Fortunately, the usual mixture of radioisotopes in this ORNL low-level waste is such that no great difficulty was encountered in decreasing each of the major biological hazards to the order of 10% of the MPC. Further study of the precipitation and filtration steps in the interest of process optimization is indicated, however. Process water wastes at other sites might contain more Ru-106 or Co-60, for example, or might require the addition of enough calcium and/or magnesium to get the desired precipitate formation.

Flocculation time, the period of agitation after addition of the NaOH to the water, has not yet been studied in detail, but indications are that about 30 min should be allowed. In one test, ORNL waste water was spiked with Cs-137 and Sr-85, made 0.01 M in NaOH, stirred for about 1 min, and allowed to settle overnight; the supernatant was filtered through medium-porosity fritted glass and passed through a Duolite C-3 column. About 5% of the strontium that passed through the filter soon broke through the ion

exchange column. The test was repeated with the same water and under the same conditions except that 30 min flocculation time was allowed and a fine-porosity glass frit was used. In this case the strontium breakthrough stayed below 0.1% for 2000 resin bed volumes of feed (Sect. 3.4). In other runs, with 20-60 min flocculation time and a fiber cartridge filter, the strontium breakthrough also stayed below 0.1%. It was indicated qualitatively, though not studied quantitatively, that flocculation time may be as important as filter porosity in the 5-10 μ range.

The settling time, the period after flocculation and before filtration, was not studied in detail, either. It did not appear to be critical when followed by filtration immediately before ion exchange. The bulk of the solids settled out in about 30 min and practically all the remainder in 2 hr, but even after 24 hr a few fine particles could be seen in the supernatant.

Since 2-hr settling removed only 95-99% of the total radioactivity that could be removed by filtration, and since part of both the strontium and cesium as well as most of the other activities are associated with the solids, filtration seems to be required in order to achieve the desired d.f. of 10³ for Sr-90. Neither small sand bed filters (about the same size as the ion exchange beds) nor the ion exchange beds themselves were highly effective for this purpose. Particularly when the feed water solids content was high, the sand or resin beds "leaked" solids and also built up high pressure drops. In most of the ion exchange studies settling was used to separate most of the solids, and paper, fritted glass, or Cuno fiber cartridge filters were used for polishing. Filtration immediately ahead of the ion exchange beds seems desirable. Some trouble with solids depositing in the beds and pressure drop buildup was experienced when an entire batch of feed was filtered first and then passed through ion exchange after standing. This possibly was due to further precipitation of calcium and magnesium, as a result of supersaturation, on standing. This point will be studied further.

When Oak Ridge tap water is made 0.01 M in NaOH a small amount of precipitate forms. In one test, after flocculation, the precipitate settled to about 1.3% of the original water volume fairly rapidly, then to about 0.35% in 30 min, about 0.15% after 2.5 hr, and about 0.11% after 24 hr. In a test

with actual ORNL process water waste, containing small amounts of algae and mud, after pH adjustment and flocculation the solids settled rapidly to about 2.3% of the original waste volume, then to about 0.3% after 20 min, and 0.2% after 2 hr. The settled slurry filtered cleanly but slowly on a medium-porosity fritted glass filter to give a wet cake with about 0.02% of the original waste volume after 3 hr. Air drying overnight decreased the cake volume to less than 0.01% of the original waste volume.

When ORNL process water waste was spiked with mixed fission products, stirred, and filtered without pH adjustment (pH 7.3), about 34% of the gross activity was filtered out, including 50% of the ruthenium and 81% of the cerium. When the same waste was spiked and the pH adjusted to 11.3 before filtration, greater than 90% of the gross activity was removed, including ~92% of the ruthenium, 97% of the cerium, and ~50% of the zirconium-niobium. After filtration at pH 11.3, Duolite C-3 resin removed 92-96% of the remaining activity (mostly Cs-137), giving an over-all d.f. for pH adjustment, filtration, and ion exchange of about 200. The remaining activity was mostly ruthenium, zirconium-niobium, and cerium. In another experiment with a different batch of waste water and a different batch of mixed fission products, adjustment to pH 11.4 and filtration again removed about 90% of the gross activity but the ion exchange step removed only about 75% of the balance, the residual activity being mostly ruthenium and zirconium-niobium.

In a separate experiment with ORNL waste water spiked with Co-60, filtration before pH adjustment removed only 10% of the activity. After adjustment to pH 11.75, 95% of the remaining activity was filtered out and ion exchange removed less than 10% of the balance. The over-all process d.f. was about 40.

Ordinary filtration removed little activity from ORNL waste spiked with Cs-137 with or without pH adjustment. Typical results varied from 1 to 10%, corresponding roughly to the amount of "mud" in the waste. At pH 11-12, cesium was found to be partly removed by Cuno cellulose filter cartridges (5- μ size), apparently by an ion exchange process. The capacity and efficiency of the cartridge were much less than for the phenolic resin beds,

but large enough that it was necessary to base the ion exchange performance calculations on feed samples taken after filtration.

Adjustment to 0.01 M NaOH and filtration removed 70-90% of the activity from Sr-85 spiked Oak Ridge tap water. In similar experiments with ORNL process water waste 30-70% was removed. The difference may be due to the presence of small amounts of complexing agents in the waste, but little difference in strontium removal by either filtration or ion exchange resulted when 10 ppm of EDTA was added to Oak Ridge tap water.

Greater than 90% removal of cerium activity by filtration after pH adjustment has been achieved consistently. As yet these experiments with cerium (or other rare earths) have not been done in the absence of other radioelements, and the upper limit on removal by pH adjustment and filtration is not yet known. For the over-all process, including ion exchange, however, gross cerium d.f. values of 100 or better were typical.

4.0 FULL-SCALE EQUIPMENT REQUIREMENTS

A process demonstration with engineering-scale equipment is planned in the near future, so that a full-scale plant can be designed and cost-estimated with confidence. For purposes of preliminary economic evaluation, the size of a full-scale ion exchange plant has been estimated based on data obtained in laboratory equipment.

Most of the ion exchange runs made in the laboratory study were carried out at a waste feed rate of 500 resin bed volumes per day, corresponding to two complete cycles per week with each cycle consisting of 3 days exhaustion time and 0.5 day regeneration time. A few runs were made at about 308 bed volumes per day feed rate, corresponding to one complete cycle per week with a 6.5-day exhaustion time and a 0.5-day regeneration time. The higher exhaustion capacity for the longer cycle, about 2000 bed volumes for the 7-day cycle compared with about 1500 bed volumes for the 3.5-day cycle, results from a steeper breakthrough curve for the slower contact rate. The contact time range studied corresponds approximately to the 2 gal/min/cu ft flow rate (384 bed vol/day), recommended by the manufacturer.

For an average of 700,000 gal/day of ORNL process water waste, about 218 cu ft of resin would be required for a 3.5-day cycle or about 327 cu ft for a 7-day cycle. A choice of the longer cycle would give a higher capital cost (because of the larger ion exchange beds) but a lower operating cost (because of less frequent regeneration, lower regenerant consumption, and lower waste storage volumes). A choice of the longer cycle time would be more conservative but might be more expensive. For the 3.5-day cycle, two beds of resin in parallel might be used, each 4.11 ft dia by 8.22 ft deep. For the 7-day cycle three such beds in parallel could be used. Allowing 50% freeboard, the gross height of the beds would be over 12 ft. For the 3.5-day cycle the ion exchange pressure drop would be in the 17.5-35 psi range, and for the 7-day cycle would be 11-22 psi. The unusually deep ion exchange beds are responsible for the moderately high pressure drop. The pressure drop could be reduced, if necessary, by using more beds in parallel or by choosing a length/diameter ratio smaller than 2/1. The latter alternative is not recommended since this process requires a much higher degree of performance, both in exhaustion and regeneration, than conventional water softening, and a higher L/D ratio will give more uniform flow distribution.

Engineering-scale studies of clarification and filtration are needed before scaling up these steps. As indicated in Sect. 3.5, a high degree of solids removal is desirable, probably 99% over-all and possibly 90% for 10- μ size particles.

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