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TITLE: Low Level Waste Treatment by Ion-Exchange, II. Use of a Weak Acid, Carboxylic-Phenolic Ion-Exchange Resin

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ABSTRACT

Laboratory results are presented for a flowsheet study of a process for decontaminating ORNL low level waste water. The water is adjusted to approximately pH 12 with NaOH, clarified, and passed through a bed of phenolic cation exchange resin. This study, using a phenolic-carboxylic resin, showed essentially the same results as those previously reported using a phenolic-sulfonic resin, i.e., radioactivities in ORNL waste were reduced to the order of 10% of MPC. The phenolic-carboxylic resin has the advantage that it can be regenerated with 0.5 M HNO₃ instead of the 5 M HCl required for the phenolic-sulfonic resin. Volume reduction factors of 2000-3000 were achieved.

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1.0 INTRODUCTION

At Oak Ridge National Laboratory (ORNL) large volumes of process water are discharged routinely to area streams. This water represents a waste having a macro chemical composition not very different from tap water but usually containing micro amounts of radioisotopes, at times in excess of maximum permissible concentration (MPC_w) limits. Presently, 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, a horizontal flow lime-soda softening process. The objective of the work reported here was to develop an economical method of treating the entire flow of ORNL process water waste, approximately 750,000 gal per day, which would reduce its radioactivity to below MPC_w levels prior to discharge, without dependence on dilution in the area streams.

As previously reported (1), the phenolic resin ion-exchange process proposed for this treatment should provide higher decontamination factors and volume reductions than other current processes. In the previous report, the use of a strong-acid sulfonic-phenolic resin (Duolite C3, Chemical Process Company, Redwood City, Calif.) was described. Because of its high cesium and strontium capacity, resistance to shrinking and swelling, and low cost it was thought to be the most conservative "first choice." The laboratory results during the development of the process using this resin have shown it to be highly effective and have been very encouraging. However, one serious disadvantage was evident, the regeneration of this type resin required the handling of 4-5 M HCl, which means that rubber or plastic lined equipment must be used along with other "exotic" and expensive materials such as a tantalum and Karbate evaporator to reclaim acid values. A stainless steel-nitric acid system would be more desirable from the standpoint of compatibility with other ORNL waste treatment facilities. Thus, emphasis was placed on the selection and evaluation of other resins. The investigation has shown that a weak-acid carboxylic-phenolic resin (Duolite CS100) is as effective as the sulfonic-phenolic resin in the loading cycle and can be regenerated with 0.5 M HNO_3 . The results of the study on the carboxylic-phenolic resin indicate a number of decided advantages: 1) no need for special hydrochloric acid handling equipment; 2) the small amount of acid regenerant required will eliminate the need to reclaim acid values; 3) the nitric acid regenerant waste can be combined with the intermediate-radioactivity-level waste stream for further treatment (evaporation in existing evaporator); 4) several tanks will be eliminated from the system, since the "split-elution" regeneration recommended with hydrochloric acid will not be needed; 5) the weak acid CS100 resin is more resistant to the oxidative effect of nitric acid in the 0.5-1 M range than is the strong acid C3 resin; and 6) the shrinking and swelling problem encountered previously with the CS100 resin in 1-2.5 M acid solutions was not serious in 0.5 M HNO_3 . The only remaining disadvantage is the present non-commercial status of the CS100 resin, available on special order at about \$50 per cubic foot. It is not an "experimental" resin, however, since it was formerly made commercially in large quantities.

Acknowledgment is made to W. E. Shockley for operational assistance in this study.



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2.0 FLOWSHEET

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 will not essentially alter the flowsheet proposed for the sulfonic-phenolic resin. The initial water treatment of precipitation, clarification and resin loading remain unchanged (Fig. 1). It is necessary to make the waste water about 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. 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. Thus, the increase in pH performs two functions, ionization of the phenolic groups and scavenging of some radioactivity. Fortunately, the activities in ORNL process water for which ion-exchange is not very effective (Ru, R.E.'s, Co, etc.) are scavenged and the activities that are only partly scavenged (Cs and Sr) are removed nicely by ion exchange, thus no great difficulty was encountered in reducing each of the major biological hazards to the order of 10% of MPC_w or less with the integrated precipitation-filtration-ion exchange steps.

After the pretreatment and loading steps, the ion-exchange resin, Duolite CS100, can be regenerated with ten resin bed volumes of 0.5 M HNO_3 . This elution step will remove greater than 99.9% of the radioactivity, primarily cesium and strontium, from the resin. The acid regenerant can then be combined with the intermediate or high level waste stream for further treatment. At ORNL, for example, it would be combined with tank farm wastes, neutralized and the supernatant solution evaporated in the stainless steel evaporator, the overheads or condensate being returned to the low-level waste treatment process. This is made possible by the use of the dilute nitric acid eluant and would not be feasible, because of high chloride ion concentration, with the Duolite C3 resin which requires 5 M HCl for regeneration.

3.0 EXPERIMENTAL

3.1 Effectiveness of the Carboxylic-Phenolic Resin in the Loading Cycle

Figure 2 shows the gross gamma breakthrough curves obtained during four separate batch loading runs with Duolite CS100, a carboxylic, phenol-formaldehyde-base ion-exchange resin. With this resin most of the total ion-exchange capacity is due to the carboxylic groups but the cesium capacity is controlled by the ionized phenolic groups because of their much greater cesium selectivity (a factor of 10-100 times greater than for sulfonic or carboxylic groups). The phenolic groups are also highly selective for strontium, but cesium is the end-point controlling activity since strontium is exchanged effectively on both the phenolic and carboxylic groups. Thus, when cesium exceeds the

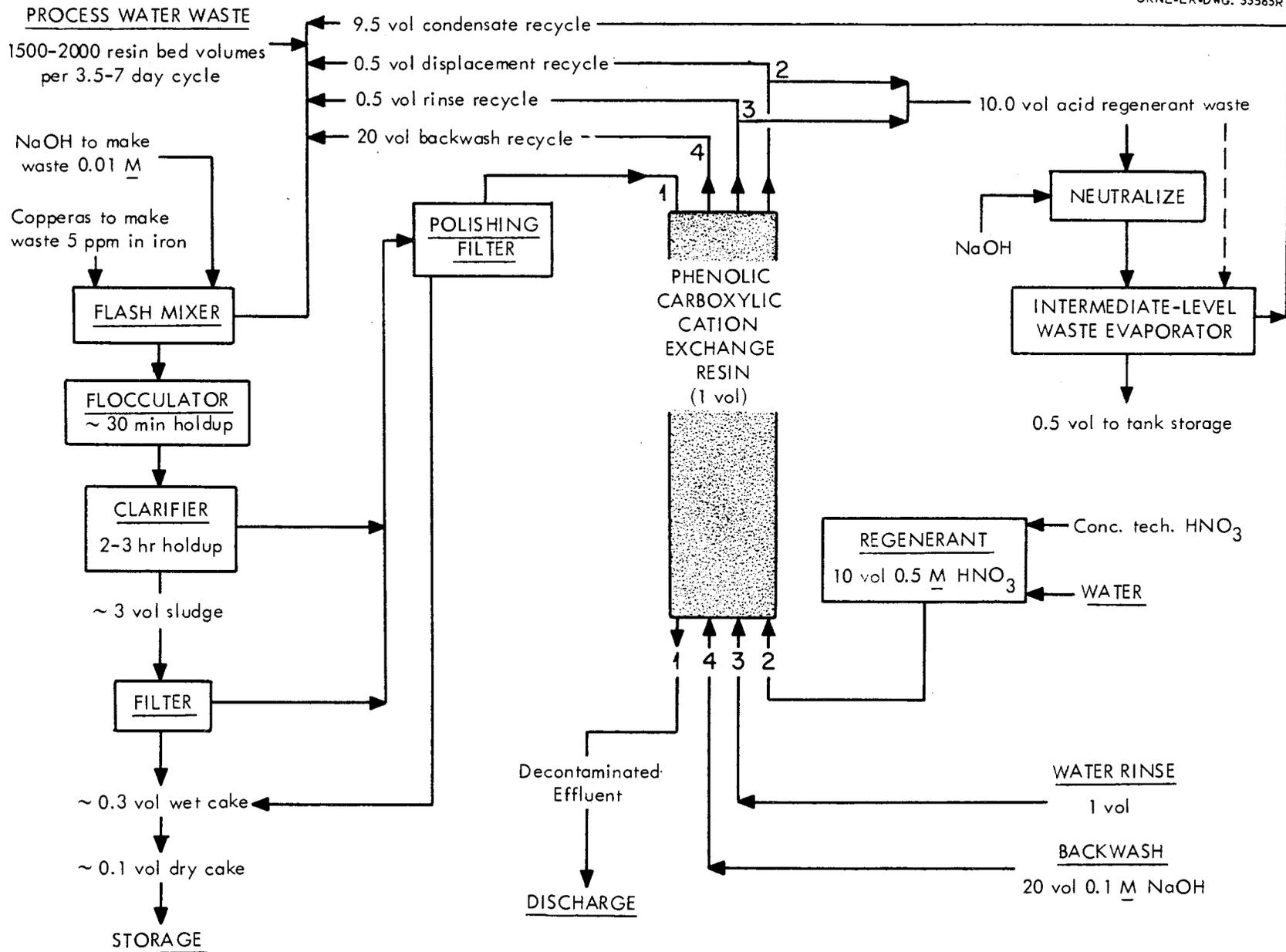


Fig. 1. Process Water Decontamination with Carboxylic-Phenolic Ion-Exchange Resin.

1% breakthrough level, the proposed end-point of a loading cycle in plant operation, strontium is still being effectively removed from solution ($D.F. > 10^3$) and cannot be detected in the column effluents with standard laboratory equipment.

The data plotted in Fig. 2 were obtained from fixed bed runs on 0.5-in.-dia columns, 6 in. long, containing 19.2 ml of Na^+ form resin at flow rates of ~ 625 bed volumes per day. Fifty liter samples of actual ORNL process water waste, except Run 27 which was made with tap water, taken at the present waste treatment plant inlet, were spiked with about 0.1 mc/liter each of Cs-137, Sr-85, and Ce-141 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 measurements. The breakthrough curves are based on gross gamma counts per minute per milliliter above 40 kev energy. Gamma energy scans of the effluent samples along 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, thus this portion of the curves was neglected and not plotted. This "background hash" (over and above actual counting background) consists primarily of anionic, non-ionic and colloidal activities initially in the waste and possibly present as impurities in the tracers used. Cesium broke through sharply when it finally appeared in the effluent, crossing the 1% breakthrough level after treatment of 1600 to 1900 resin bed volumes of waste. Extrapolation of the breakthrough curve to the 50% point indicated gross gamma distribution coefficients (volumetric) of 3200 to 3800. It should be noted that these K_d 's are primarily due to cesium and not at all due to strontium, since strontium was not present to detectable levels in any of the effluent samples. Although the distribution coefficients for strontium would be much higher, they are of little importance since cesium will control the loading cycle end-point. Cerium ion-exchange results in these runs is uncertain since there was not much left in the feed after pH adjustment and clarification, however, the overall process D.F. for cerium has been indicated to be approximately 10^3 .

3.2 Regeneration Characteristics of the Carboxylic-Phenolic Resin

After exhaustion of the resin capacity in the loading cycle, the next step in the process is to remove the activity or regenerate the resin without significantly decreasing the volume reduction factor achieved in the loading cycle. The regeneration step is necessary because of the cost of the resin, \$25-50 per cubic foot.

While the hydrochloric acid elution followed by evaporation scheme, reported previously, is entirely feasible and workable, the use of a nitric acid regenerant would be more desirable (Sect. 1.0). However, nitric acid in concentrations over 1 M vigorously attacks the phenolic resins, thus precluding the use of the sulfonic-phenolic resin, Duolite C3, which requires 10 resin bed volumes of 5 M acid to attain 99.9% regeneration. This regeneration level can be obtained with the same volume of 0.5-1.0 M acid if the weak acid carboxylic-phenolic resin, Duolite CS100, is employed in the process. Figure 3 shows the results of upflow regeneration of Duolite CS100 resin with 0.5 M HNO_3 , 1.0 M HCl and 2.5 M HCl . Upflow regeneration is used here to minimize leakage of radioactive ions in the subsequent downflow loading cycle. The fresh regenerant contacts the ions in

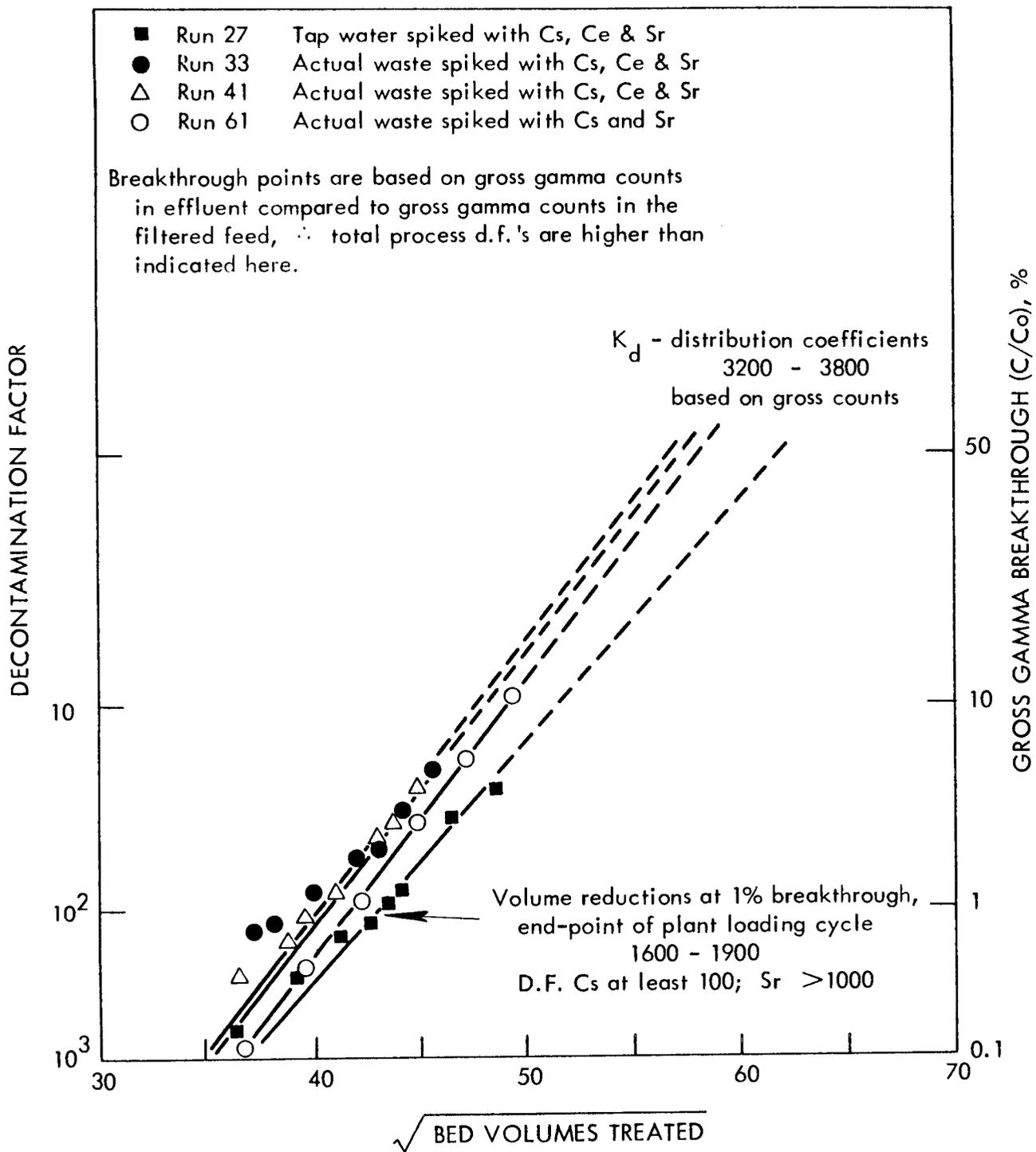


Fig. 2. Loading of Duolite CS100, Carboxylic-Phenolic Ion-exchange Resin.

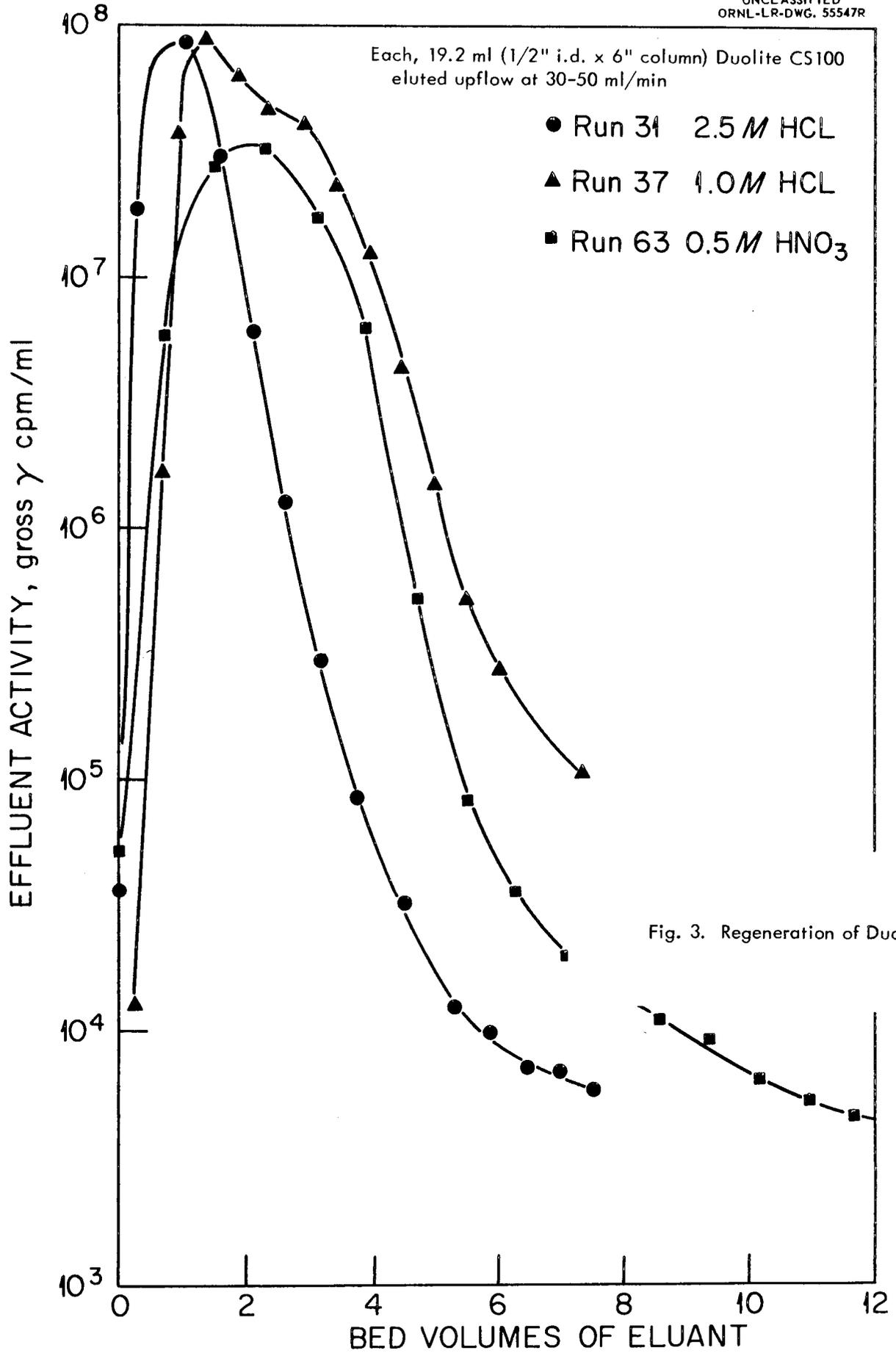


Fig. 3. Regeneration of Duolite CS10

the bottom of the bed first, displacing them upward. Thus, the most thoroughly regenerated portion of the bed is 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 and are best compared by relating regenerant effluent activity during a run with the peak regenerant effluent 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 in the three runs, Fig. 3, a 10^3 reduction in effluent activity, approximately a 99.9% regeneration level, was obtained with less than 10 resin bed volumes of regenerant.

In the regeneration of Duolite CS100 with 1.0 and 2.5 M acid, Runs 31 and 37, a shrinking and swelling between the acid and base forms of 30% was noted. However, with 0.5 M acid this was reduced to 10%, about the same as with Duolite C3 when 5 M acid regenerant was used.

As stated previously, nitric acid in concentrations over 1 M will attack phenolic resins, resulting in gassing, color throw, and loss of capacity in subsequent loading cycles. These same symptoms will appear if 0.5 M regenerant is allowed to remain in stagnant contact with the resin for over 72 hr. Figure 4 shows the loss in loading capacity resulting from a deliberately extreme test. The resin eluted in Run 63 (Fig. 3) was left in contact with the 0.5 M HNO_3 regenerant in a closed column for two months. The resin was then water washed, converted to the Na^+ form with 0.1 M NaOH, and reloaded under identical conditions to the previous loading. The problem indicated here can be eliminated completely if care is taken to assure that the phenolic resin is not allowed to contact concentrated nitric acid, or not allowed to remain in stagnant contact with the 0.5 M acid for long periods of time. The resin should be water washed immediately after elution with acid.

The ten resin bed volumes of eluant can be further volume reduced, thus adding to the overall volume reduction factor, by combining it with the intermediate-level radioactive wastes for evaporation. The overheads or condensate from this evaporation are recycled to the low-level treatment process, while the bottoms are treated as a high-level waste, possibly calcined to solids. The volume reduction factor from 1500 volumes of feed to 0.5 vol of evaporator bottoms is 3000. This is reduced to about 2000 by including the volume of filtered solids.

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2. Chemical Technology Division Annual Progress Report for Period Ending May 31, 1961, ORNL-3153 (in preparation).

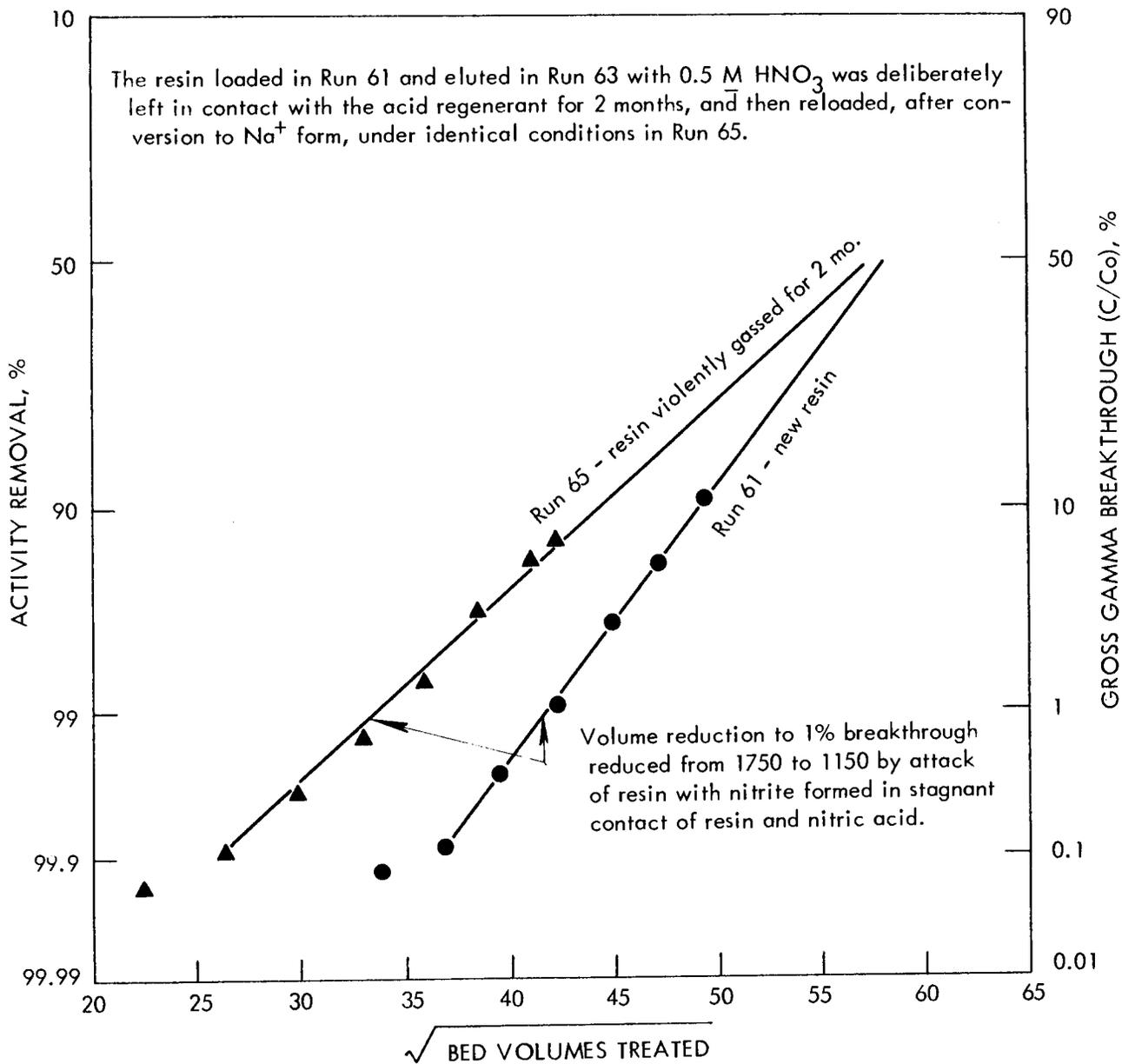


Fig. 4. Loss in Breakthrough Capacity Resulting from Nitric Acid Attack of Phenolic Resin.

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