RADWASTE ION-EXCHANGE OPTIMIZATION

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ABSTRACT

Increased volume reduction factors for radwaste liquid treatment and reduced costs for ion-exchange media replacement and disposal have been key driving forces for nuclear utilities to seek optimal performance from radwaste liquid ion-exchange treatment systems. This paper presents the methodology and the results of an EPRI/B&W project to identify optimal radwaste ion-exchange processing schemes that will provide cost savings for nuclear plant operators. The focus in this paper will be on the findings of both in-plant bench scale and prototype ion-exchange column tests using radwaste liquid generated at the Millstone Nuclear Station.

INTRODUCTION

Nuclear utilities are becoming increasingly interested in optimizing the performance of radwaste ion-exchange systems at operating plants. Extended service run lengths for radwaste ion-exchangers translate into reduced costs for ion-exchange media replacement and disposal. Improved removal of "colloidal" activity, e.g., cobalt and silver radionuclides, has also been a challenge for radwaste ion-exchange systems and is another item for optimization study.

This paper discusses the results of a major Electric Power Research Institute (EPRI)-sponsored project being conducted by Babcock & Wilcox to optimize radwaste ion-exchange performance in the nuclear power industry. The three main objectives of this work are (1) to identify ion-exchange materials, arrangements, and methods that will reduce the costs associated with purifying radwaste liquid streams, (2) to demonstrate through the prototype testing stage the effectiveness of the identified optimization alternatives, and (3) to document the results of the work with appropriate conclusions and recommendations in a manner that will be of benefit to the utilities.

To accomplish these objectives, a three-part approach is being implemented. This approach is comprised of the following major tasks: (1) Chemical and Radiochemical Characterization of Radwaste Liquid Streams, (2) In-Plant Bench Scale Column Testing, and (3) In-Plant Prototype Testing. This work is being performed at the Millstone Nuclear Station, which offers one operating 650 MWe BWR and one operating 830 MWe PWR for this study.

The results of the chemical and radiochemical characterization of radwaste liquid streams and of the equilibrium ion-exchange media selectivity screening tests have been presented at a previous Waste Management meeting (1). This paper will focus on the results obtained to date for bench scale column tests using BWR and PWR radwaste liquid, and on prototype testing, which is currently in progress at the Millstone Nuclear Station.

IN-PLANT BENCH SCALE TESTING: 13MM ID COLUMNS

The primary objective of these initial bench scale column tests was to identify, if possible, classes of commercially available ion-exchange and adsorbent media that offered enhanced selectivity for nuclide removal, with emphasis on key nuclides, i.e., cobalt-60, cesium-137, and iodine 131. Data acquired in the previously reported equilibrium selectivity testing was used as a basis for the selection of media to be evaluated in these column tests.

Two portable bench scale test systems were designed and constructed as part of the testing methodology established in this project. A single ion-exchange bench scale system, shown schematically in Fig. 1, consisted of a fifty liter feed tank, metering pump, and six panel-mounted, pressurized ion-exchange columns. Each column measured 13mm in ID by 300mm in length. With two such systems, up to twelve ion-exchange media could be evaluated simultaneously.

Each column contained 20cc of ion-exchange medium. One such column was established as a "standard" for performance comparison. Flowrates to each column were set at 60 column volumes/hour. Samples of the feed and liquid effluent were acquired at regular time intervals and gamma isotopically analyzed during the tests. The outlet stream of each column was passed through a conductivity cell to provide a rapid means of monitoring chemical conditions.

Table I summarizes the various classes of exchange media that were evaluated in these tests. These ion-exchange media were selected on the basis of screening tests conducted previously (1). Several exchange media not previously tested were included for completeness based on product information supplied by

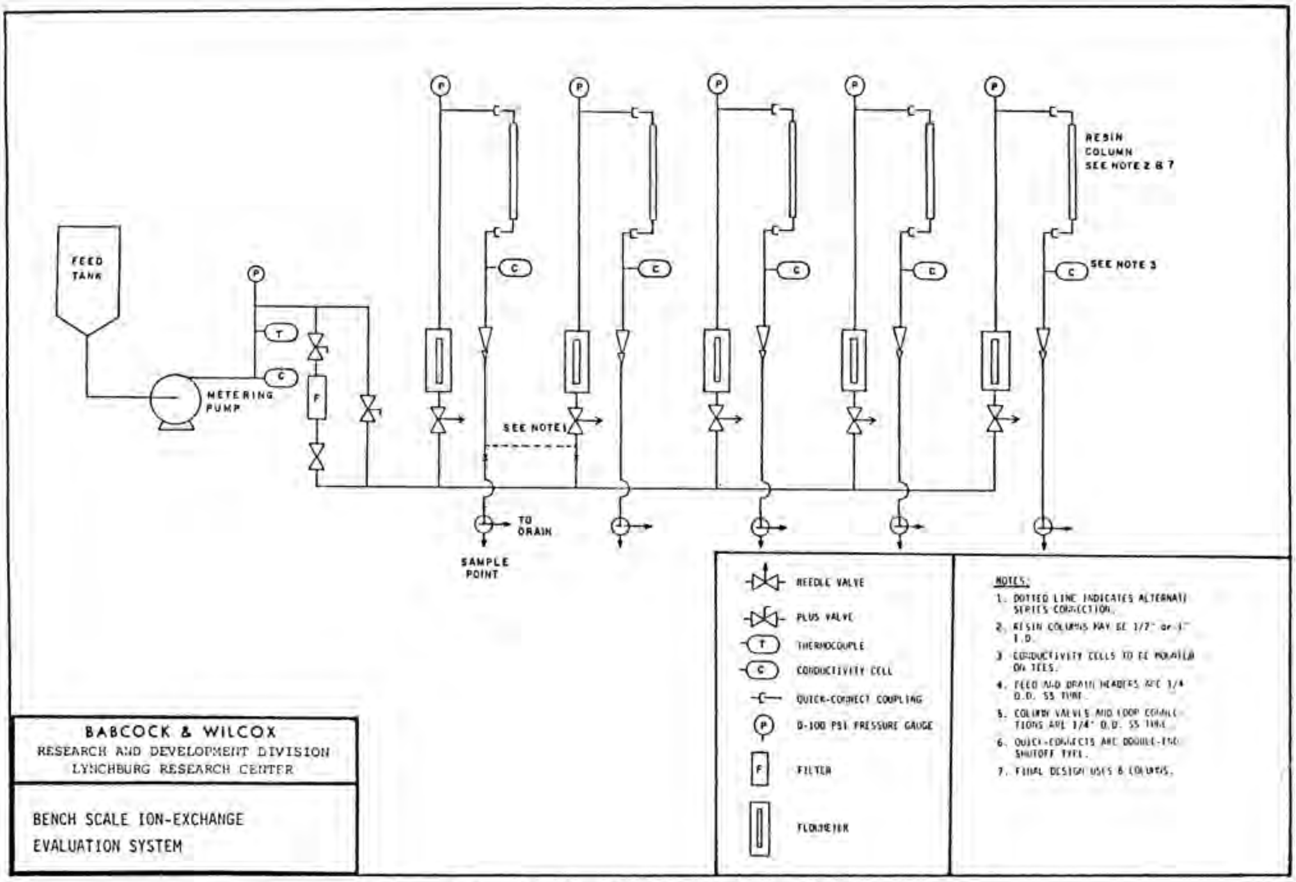

Fig. 1. Bench scale test system.

the various vendors. These new exchange and adsorbent media included spherical carbon, large-port mordenite, chelating resins, and both weak acid and weak base forms of exchangers. Over sixty ion-exchange and adsorbent media were evaluated during these tests.

TABLE I

Types of Exchange Media Evaluated

1) Strong Cation Resins
   (a) Gel
   (b) Macroporous/Macroreticular
   (c) Sodium ionic forms
   (d) Hydrogen ionic forms
   (e) Sulfonic functional groups
   (f) Methylene sulfonic functional groups
   (g) Styrene - DVB matrices
   (h) Phenolic matrices
   (i) Granular
   (j) Spherical
   (k) High crosslinking

2) Strong Anion Resins
   (a) Gel
   (b) Macroporous/Macroreticular
   (c) Hydroxide ionic forms
   (d) Chloride ionic forms
   (e) Type I - high basicity
   (f) Type II - lower basicity than Type I
   (g) Styrene - DVB matrices
   (h) Acrylic - DVB matrices
   (i) High porosity (for colloidal removal)

3) Chelating Resins

4) Zeolites
   (a) Chabazite
   (b) Large-port mordenite

5) Weak Acid Resins
   (a) Gel
   (b) Macro
   (c) Carboxylic functional groups
   (d) Phenolic functional groups
   (e) Condensate matrices
   (f) Styrene - DVB matrices
   (g) Acrylic - DVB matrices

6) Weak Base Resins
   (a) Gel
   (b) Macro
   (c) Condensate matrices
   (d) Epoxyamine matrices
   (e) Styrene - DVB matrices
   (f) Free base ionic forms
   (g) Hydrogen chloride ionic forms

7) Activated Carbons
   (a) Granular
   (b) Spherical

For the evaluation of data, the plotting of both column influent and effluent radionuclide activities for a key isotope for several media simultaneously was identified as a valid method to compare media performance. Examples of the graphical representation of the data are given in Fig. 2 for the BWR and Fig. 3 for the PWR. In general, the testing was terminated when the decontamination factor for the monitor

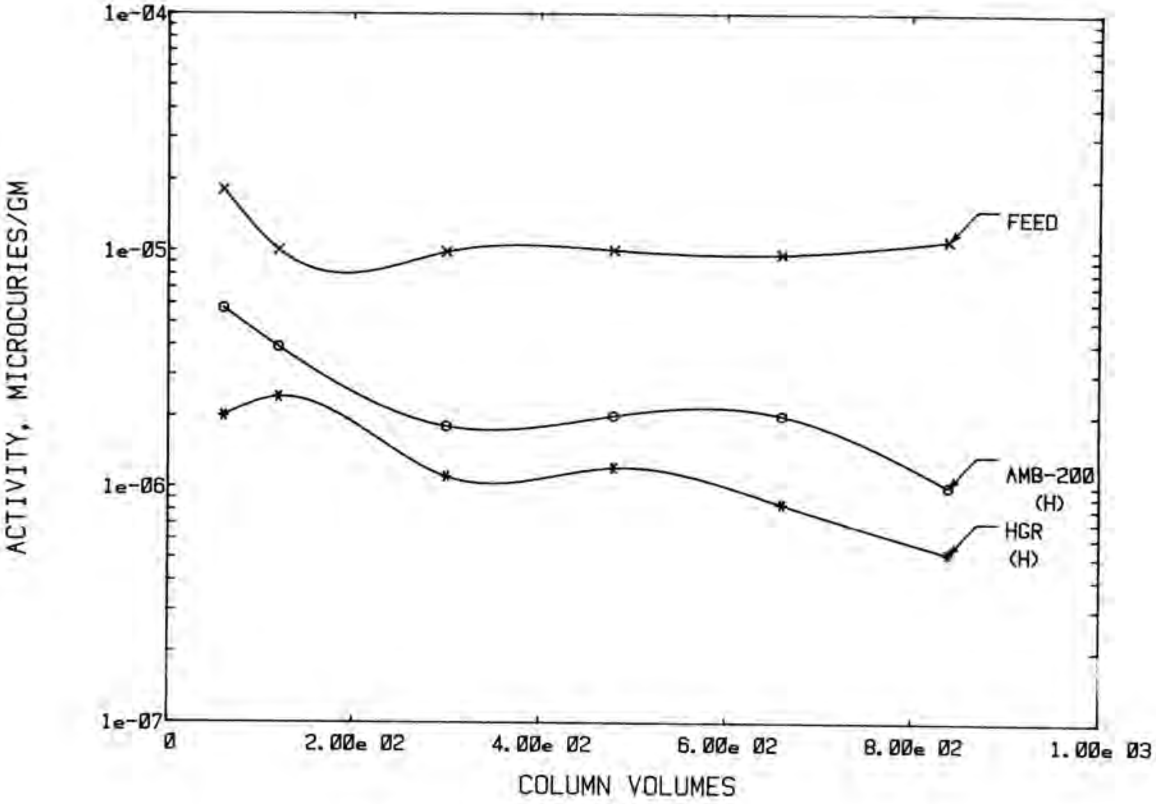

Fig. 2. Strong cation resin tests for BWR.

nuclide (Co-60, Cs-137, or I-131) reached a value of 10 or when the process liquid was depleted. At least 800 column volumes of data were obtained for each ion-exchange medium evaluated.

Correlations of performance with the type of ion-exchange medium were sought from the data represented by examples given in Fig. 2 and 3. While it is not possible to present the comprehensive data in this paper, a summary of the ion-exchange results under the conditions of the test may be presented for these in-plant tests:

BWR

1. Macroreticular/macroporous and gel type cation exchangers produced experimentally equal cobalt-60 decontamination factor performances.

2. A large-port mordenite and a chabazite, both of the zeolite class, reduced both cobalt-60 and cesium-137 effluent activities to less than minimum detectable levels, *demonstrating* feasibility for additional testing.

3. An anion exchanger of the acrylic-divinylbenzene matrix type produced improved cobalt-60 removal over similar media of the styrene-divinylbenzene type.

4. Macroreticular/macroporous and gel type anion exchangers produced experimentally equal iodine-131 decontamination factor performances.

5. Enhanced removal of cobalt-60 was not observed with the use of either complexing media or large-pored macroreticular/macroporous anion exchangers claimed to provide enhanced radiocolloid removal from waste liquid.

PWR

1. Macroreticular/macroporous and gel types of cation exchangers produced experimentally equal cobalt-60 decontamination factor performances.

2. Macroreticular/macroporous, gel, and zeolitic types of cation exchangers with an exchangeable sodium ion produced experimentally equal cobalt-60 decontamination factor performances. However, these were typically a factor of 10 lower than the cobalt-60 decontamination factors measured for media with an exchangeable hydrogen.

3. A large-port mordenite produced effluent cesium-137 activity at minimum detectable levels, indicating potential application for additional radwaste liquid testing.

4. Type II anion exchangers in the hydroxide form exhibited a factor of 3 improvement in cobalt-60 decontamination factor performance over the standard Type I anion exchanger.

5. Large-pore, macroreticular anion exchangers in the hydroxide form, often classified as effective radiocolloid adsorbers, indicated no significant improvement for cobalt-60 removal over the standard anion exchanger.

6. Macroreticular/macroporous and gel type exchangers produced experimentally equal iodine-131 decontamination factor performances.

7. Weak cation exchangers, at a waste feed pH = 11, exhibited improved cesium-137 decontamination factor performances and projected capacities over the standard cation exchanger.

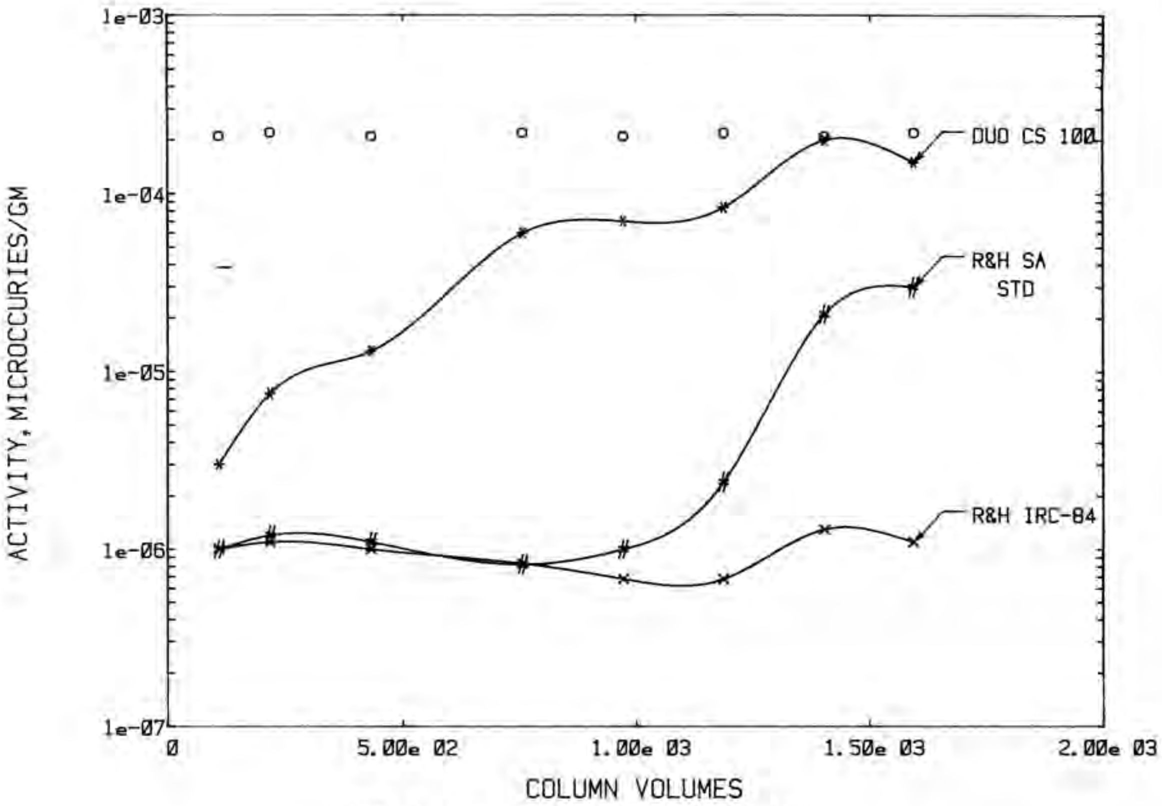

Fig. 3. Weak acid resin tests for PWR.

8. Weak anion exchangers, at a waste feed pH = 3.5, exhibited improved iodine-131 decontamination factor performances and projected capacities over the standard anion exchanger.

9. Spherical activated carbon provided Total Organic Carbon removal efficiencies near 92%, compared to a similar mesh granular carbon that produced a 60% efficiency.

The results from these tests were used to select individual component media for testing in the mixed bed form in 26mm ID columns. The next section presents the methodology and a summary of results for these larger column tests.

IN-PLANT BENCH SCALE TESTING: 26MM ID COLUMNS

The primary objective of these tests was to obtain comparative radwaste liquid "throughput" capacities on blends of the best ion-exchange media identified in the 13mm ID column tests. These media would be mixed or layered in various proportions in a column and tested in comparison for selectivity and capacity. Columns in this study were operated until radiochemical exhaustion for a monitor nuclide was achieved. Emphasis was placed on identifying maximum liquid volume reduction configurations of ion-exchange media.

In order to conduct these tests, the bench scale test units described previously were retrofitted with clear plastic columns of dimensions 26mm ID by 300mm in length. The columns could be pressurized to promote uniform fluid distribution within each column. Up to twelve columns could be operated simultaneously.

Each column contained 115cc of mixed or layered ion-exchange media. One such column was established as a standard. This standard was a mixed bed comprised of a 1:1 volume ratio of standard cation to standard anion exchanger. Flowrates to each column were 15 column volumes/hour. Samples of the feed and liquid effluent were acquired at regular time intervals and gamma isotopically analyzed during the tests. An automated data acquisition system recorded effluent conductivities every hour.

Twenty-three column tests were conducted using radwaste liquid at the Millstone Nuclear Station. Component media selected for these tests are summarized in Table II. Both layered and mixed media arrangements in various volume proportions were tested for nuclide capacity comparisons. Table III summarizes the radwaste liquid chemistry data obtained during these tests.

TABLE II

Ion-Exchange Media Summary

Cation Exchangers
Macroreticular Resin, 20% crosslinked
Macroporous Resin, 12% crosslinked
Large-port Mordenite
Weak Acid Resin

Anion Exchangers
Macroreticular, Styrene-DVB
Gel, Acrylic-DVB
Weak Base, Gel
Weak Base, High Capacity (3.5 meq/ml)
Weak Base, High Capacity (3.8 meq/ml)

Adsorbents
Beaded Carbon (BC)

TABLE III

Summary of Radwaste Liquid Chemistry

pH = 7.3 to 7.6 (25°C)
Conductivity = 400 to 800 μS/cm
Sodium = 50 to 100 ppm

Cobalt-60: 1×10^{-5} μCi/g to 4×10^{-3} μCi/g

Cesium-137: 8×10^{-5} μCi/g to 1×10^{-3} μCi/g

Iodine-131: 2×10^{-5} μCi/g to 2×10^{-4} μCi/g

Under the conditions of the test, a comparison of throughput capacities for the various column configurations indicated:

1. Layered versus mixed beds provided experimentally equal decontamination factor performances and capacities for cobalt-60.

2. The mordenite-bearing mixed and layered beds exhibited cobalt-60 capacities that were equal to those beds containing entirely organic exchangers, reinforcing the concept of cobalt removal by adsorption rather than exchange.

3. Weak base anion exchangers provided iodine-131 capacities that were, in the best cases, equal to that of the strong anion exchanger standard. As such, increased capacity for iodine-131 removal by the weak form of anion exchangers is not indicated.

4. The large-port mordenite had a capacity per unit volume for cesium-137 that was 20 to 26 times that for the standard cation exchanger.

Figure 4 illustrates the performance advantage of the large-port mordenite for radwaste liquid treatment compared to standard mixed bed treatment. The increase in the column effluent cesium that occurred halfway through the test can be correlated with the factor of 10 increase in the cesium-137 feed activity. Prior to that time, column effluent cesium-137 activities were at or below minimum detectible levels.

The large-port mordenite tested was available in 20/50 mesh at a price approximately 4 times that of standard cation exchange resin. In view of the performance for cesium removal, potential volume reduction and cost savings for radwaste liquid treatment at nuclear plants are indicated for zeolitic exchange media.

IN-PLANT PROTOTYPE TESTS

Prototype testing has been initiated at the Millstone Nuclear Station. The objective of these tests is to generate process data to perform a credible technical and economic assessment of the optimized ion-exchange system.

For these tests a miniature, pressurized vessel, ion-exchange test system complete with process instrumentation was designed and constructed. This system had two main components. One component was a portable skid containing three "quick-connect" ion-exchange pressure vessels with associated process pumps, piping, filters, and sampling ports. The other component was an automated data acquisition system that recorded process temperatures, differential pressures across the beds and filters, influent and effluent conductivities, effluent pH, flowrates, and total volume of radwaste liquid processed.

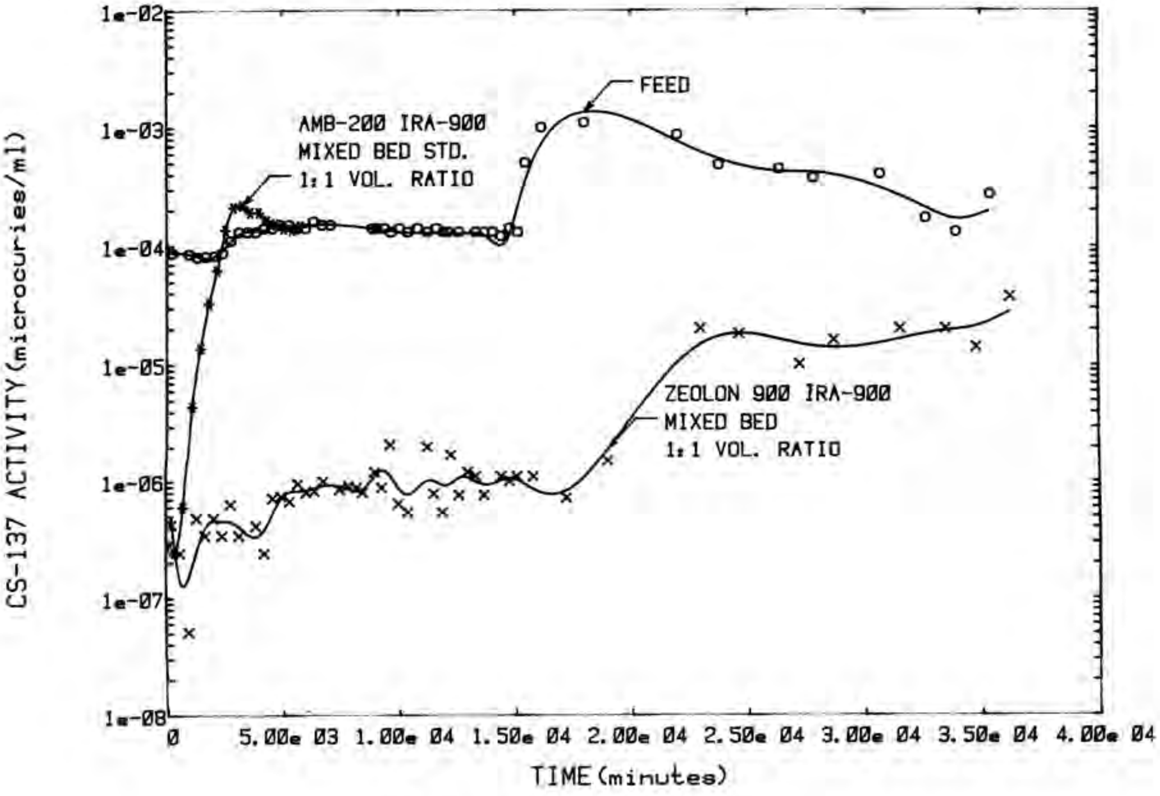

Fig. 4. Cs-137 activity vs. time.

In the first prototype test configuration, beds of activated carbon, large-port mordenite, and standard mesh mixed resin will be operated in series to evaluate the radionuclide decontamination factor and volume reduction performances. In the second configuration, a commercially available fine-mesh bead mixed bed resin will be substituted for the standard mesh bead resin to evaluate not only chemical and activity removal, but also differential pressure profile. This fine mesh bead has full-scale BWR application for chemical purification of radwaste streams if prototype differential pressure studies are successful.

Time permitting, an organic polymer will be added to the radwaste liquid to enhance cobalt-60 removal. This polymer addition will use results of an EPRI/Duke Power project to improve radwaste ion-exchange processing by chemical pretreatment.

SUMMARY

EPRI is addressing the need for improved radwaste liquid processing by sponsoring a major project in radwaste ion-exchange optimization. This study is currently in the prototype testing stage, with emphasis on volume reduction performance. An inorganic, commercially available radwaste medium that provides a twentyfold volume reduction improvement over standard organic cation exchangers for cesium removal has been identified and is currently undergoing prototype tests.

REFERENCES

1. N. P. Jacob, et al., "Optimization of Radwaste Ion-Exchange Processes at Nuclear Power Plants," Waste Management '84 Proceedings, Volume 2, 1984, p. 409.