

PWR WASTE LIQUID PROCESSING USING ZEOLITE AND ORGANIC RESINS

N. P. Jacob
Babcock and Wilcox
Lynchburg, Virginia 24506

J. R. Robertson
Millstone Nuclear Station
Waterford, Connecticut 06381

P. J. Robinson and C. S. Welty
Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

The Electric Power Research Institute (EPRI) has sponsored a technical program in radwaste ion-exchange processing through the pilot plant testing stage at the Millstone 2 PWR. The goal of this program was to reduce costs associated with radwaste liquid ion-exchange processing. This paper presents the results of the program's culmination, a full scale demonstration of the improved radwaste ion-exchange process. In this process, a single bed comprised of cesium-selective synthetic mordenite and organic ion-exchange materials was successfully used to remove nuclides from aerated waste generated at Millstone 2 PWR for discharge. This combination of ion-exchange materials demonstrated improved volume reduction and cost savings over the baseline system. This test verifies the technical approach used in prior EPRI waste characterization and column testing and provides credibility in the nuclear power industry for the improved ion-exchange process using ion-specific zeolite exchangers.

INTRODUCTION

Improving the performance of radwaste ion-exchange treatment systems is a vital part of the plant operator's effort to reduce the volume of nuclear waste. An increase in the volume of radwaste that can be treated by a unit volume of ion-exchange materials translates into reduced costs for waste disposal. Improved ion-exchange performance may produce additional operating costs savings by reducing the extent of waste reprocessing to achieve effluent criteria.

The Electric Power Research Institute (EPRI) has implemented in-plant test programs to address the nuclear power industry's needs for reducing waste liquid processing costs. EPRI studies for improving waste pre-treatment and establishing test methodologies for evaluating radwaste ion-exchange materials have been completed (1-5).

A recently completed study performed by Babcock & Wilcox at the Millstone 2 PWR focused on a methodology for analyzing waste streams and performing comparative column testing of ion-exchange materials using actual plant waste (2-5). Testing was completed through the pilot plant stage, using a combination of synthetic mordenite (zeolite) and organic ion-exchange materials to selectively remove nuclides from waste to be discharged. The results of the testing projected a fourfold reduction in solids waste and a 60 to 75% reduction of ion-exchange materials replacement and disposal costs using a zeolite/organic resins system versus a baseline all-organic system (5).

For the work to be reported here, the Electric Power Research Institute has completed the logical culmination of the Millstone PWR test program, a full-scale demonstration of the improved radwaste ion-exchange process. The objective of this work is to verify the technical approach and process economics evaluated during the comparative column testing phase. In addition, this full-scale demonstration would

provide credibility in the industry for the "new" process, which includes the use of a cesium-selective zeolite ion-exchange material.

This demonstration represents the first full-scale application of ion-selective zeolite and organic resin for processing low-level radwaste at an operating nuclear power plant in the United States.

ION-EXCHANGE MATERIALS

Three types of ion-exchange materials were selected to remove radionuclides from waste to be discharged. The selections were made on the basis of previous EPRI column testing at Millstone (5). The selected ion-exchange materials were in good supply and available at reasonable prices. Other ion-exchange materials utilization criteria invoked for this specific full-scale application included hardware compatibility, safety, and environmental issues.

A synthetic large port mordenite (zeolite) with a sodium-exchangeable cation was chosen for its demonstrated cesium selectivity in Millstone 2 radwaste liquid (5). The high silica-to-alumina ratio of synthetic mordenite (minimum 10/1) also offers the advantage over other classes of zeolites of superior resistance to matrix degradation by acid attack. This material has a rated 20/50 US Mesh particle size distribution, with an estimated maximum ion-exchange capacity of 1.7 to 1.8 meq/ml.

Two types of standard nuclear grade organic ion-exchange resins were selected. A sulfonated styrene-divinylbenzene gel (strong acid cation) with nominal 10% DVB crosslinking and a Type I quaternary on a styrene-divinylbenzene gel (strong base anion) were specified for use with the zeolite. Strong acid cation specifications included mesh size distribution, percentage of sites in the hydrogen form, percent water retention, and total capacity. Strong base anion specifications included mesh size distribution, percentage of sites in the hydroxide form, maximum

percent anionic contaminants, total capacity, and percent water capacity.

A mixed bed of these polymers was blended by the manufacturer in the specified ratio of 1.2 equivalents of OH⁻ to 1.0 equivalent of H⁺. This ratio was based on previous column testing that demonstrated superior removal of both iodine and cobalt from waste by anion-rich versus balanced mixed beds. The equivalence ratio was limited to 1.2/1 anion:cation so as not to exceed the pH effluent specification of 9.5.

For testing, a single bed would be used to treat plant waste to be discharged. This bed was to be comprised of 90% by volume mixed bed resin and 10% by volume zeolite. Normally, the single bed contains 40 ft³ of "proprietary" layered ion-exchange material. For this demonstration, a 30-ft³ bed was loaded to ensure that at least 500 bed volumes (BV) of waste would be processed prior to a scheduled refueling outage.

A summary of test performance criteria, ion-exchange bed dimensions, and operating conditions is given in Table I.

TABLE I

Test Performance Criteria and Operating Conditions

Objective: Selective Radionuclide Removal from Waste Liquid

Endpoint: Decontamination Factor = 2 or % of Feed Activity = 50%

Minimum Treated Waste Volume: 500 BV

Bed Dimensions:

Volume - Mordenite (top layer)	3 ft ³
Mixed Bed (bottom layer)	27 ft ³
TOTAL	30 ft ³
Height - Mordenite (top layer)	4 inches
Mixed Bed (bottom layer)	34 inches
TOTAL	38 inches

Diameter - 42 inches

Flowrates:

Volume = 30 gpm = 1₂ gpm/ft³
 Surface = 3.1 gpm/ft²

PROCEDURES

The synthetic mordenite was conditioned to remove fines prior to the full-scale radwaste ion-exchange test. The mordenite was backwashed with deionized water in a column to yield a 50% expansion for at least 10 minutes to a clear effluent. Effluent pH at the end of ten minutes was less than 7.

The PWR waste liquid processing system is illustrated in Fig. 1. Waste pretreatment is provided by a fiber-wound cartridge filter to remove particulate matter. This filter has a 3-micron nominal rating, but does not have an absolute pore size rating. The ion-exchange vessel contains 40ft³ of resin for treating waste. The effluent of the ion-exchange bed is stored in a monitor tank, sampled, analyzed, and released in compliance with chemical (boron and suspended solids) and radiochemical limits (as per 10 CFR 20, Appendix B, Table II).

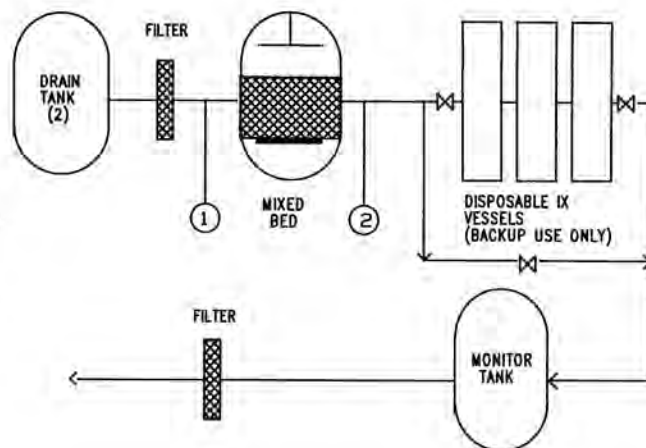


Fig. 1. Waste Processing System Schematic. (sample points indicated)

A total of 30 ft³ of ion-exchange material with a bed height of 38 inches was charged to the in-plant vessel. For the test, 27 ft³ of the previously specified mixed bed resin was added to the ion-exchange vessel. The 3 ft³ of synthetic large port mordenite was added as a layer (4 inches) on the mixed bed. This unit treated all of the aerated (also known as floor drain) waste generated at the plant.

Liquid samples of the waste feed (sample point 1 in Fig. 1) and effluent (sample point 2 in Fig. 1) were periodically taken during waste processing. Each sample was analyzed for pH and conductivity. In addition, periodic chemical analyses of the waste samples were performed. These chemical analyses included sodium, hardness, alkalinity, chloride, alkalinity, silica, boron, total organic carbon (TOC), and suspended solids.

Each feed and effluent sample were filtered through a 0.45-micron filter. Both the liquid (filtrate) and solid (retained on filter) phases of the waste samples were analyzed by gamma spectroscopy. Nuclide activities for cobalt-58, cobalt-60, iodine-131, and cesium-137 were monitored for this test.

WASTE CHEMISTRY RESULTS

The monitoring of waste feed chemistry was an important part of the test program. The chemical rather than the radiochemical constituents are the exhausting species for a radwaste ion-exchange system. It is for this reason that the system performance for removing radionuclides is sensitive to changes in waste feed chemistry.

The pH and conductivity data for this test are presented in Fig. 2. Both chemistry parameters varied widely throughout the test. The cycling between the feed and effluent pH measurements reflected changes in breakthrough of the different chemical species. The breakthrough of boric acid occurred at approximately 50 bed volumes. After breakthrough, the mixed bed began "dumping" boric acid to the processed waste, producing a slightly acidic effluent relative to the feed.

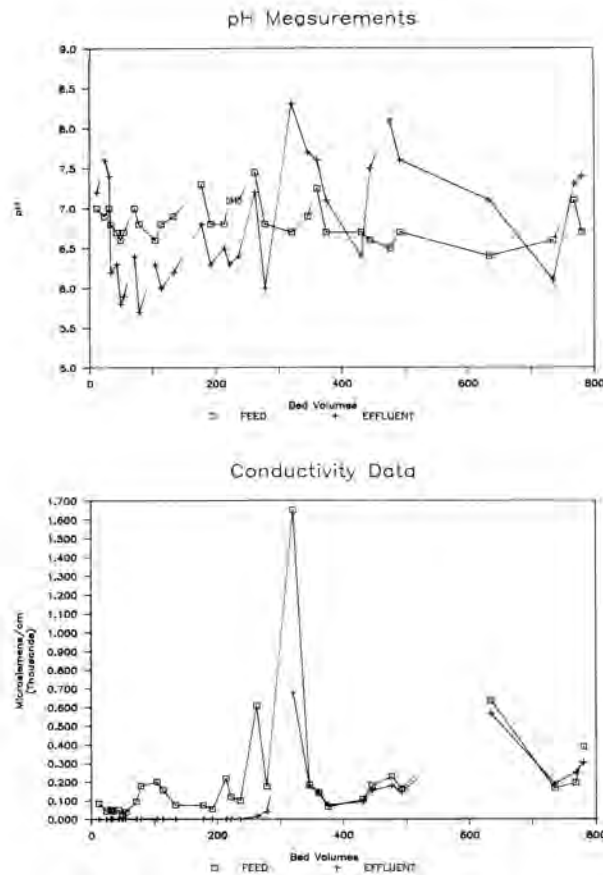


Fig. 2. pH and Conductivity versus Bed Volumes of Waste Processed.

The pH of the effluent paralleled that of the feed until the effluent conductivity breakthrough, which occurred at 300 bed volumes. At this point, a very significant increase of the conductivity of both the influent and effluent had been recorded and the pH trended up reflecting replacement of carbonate (alkalinity) by chloride. Thereafter, the effluent pH remained generally basic relative to the feed after the conductivity break. The two minimums in the effluent pH curve are potentially attributed to increases in the boric acid concentration of the effluent.

Conductivity measurements indicated that up to the 300-bed-volume mark, the ion-exchange bed effluent conductivity was consistently in the $<1 \mu\text{S}/\text{cm}$ range, with boric acid as the only major chemical species in the effluent. A sharp rise in effluent conductivity was observed at 300 bed volumes. This rise in effluent conductivity followed a tenfold increase in feed conductivity from $200 \mu\text{S}/\text{cm}$ to $2000 \mu\text{S}/\text{cm}$. The conductivity increase was ascribed to leakage of cooling water (seawater). One other major increase in feed conductivity occurred near the end of the run.

A summary of waste chemistry data is given in Table II.

WASTE RADIOCHEMISTRY RESULTS

Liquid Phase

The radiochemical data for the monitored liquid activities are presented in Fig. 3 as a function of bed volumes (BV) of waste processed. Each nuclide is represented by three curves. These are, from top to bottom: feed, effluent, and breakthrough (as a percent

TABLE II

Summary of Waste Feed Chemistry for Radwaste Ion-Exchange Demonstration

Parameter	Minimum	Average	Maximum
pH	6.4	6.8	7.5
Conductivity, $\mu\text{S}/\text{cm}$	28	210	1650
Boron, ppm	92	482	1547
TOC, ppm	3	5	12
<u>Cations, meq/L</u>			
Sodium	0.2	1.2	4.4
Hardness	0.1	0.9	4.3
<u>Anions, meq/L</u>			
Chloride	0.1	1.4	13.3
Alkalinity	0.2	0.5	1.1

of feed activity). As illustrated, wide variations in the waste feed radiochemistry were recorded. The observed difference between minimum and maximum feed activities measured during the test was three orders of magnitude.

In general, liquid effluent activities for the monitored nuclides remained in the $1 \text{E}(-6) \mu\text{Ci}/\text{g}$ range through the first 500 BV of processed waste. An increase in these activities was recorded following the intrusion of highly conductive cooling water into the radwaste system. Cobalt-58 and cobalt-60 activities in the waste feed and effluent increased toward the end of the run due to the release of reactor "crud" during power decreases leading to shutdown.

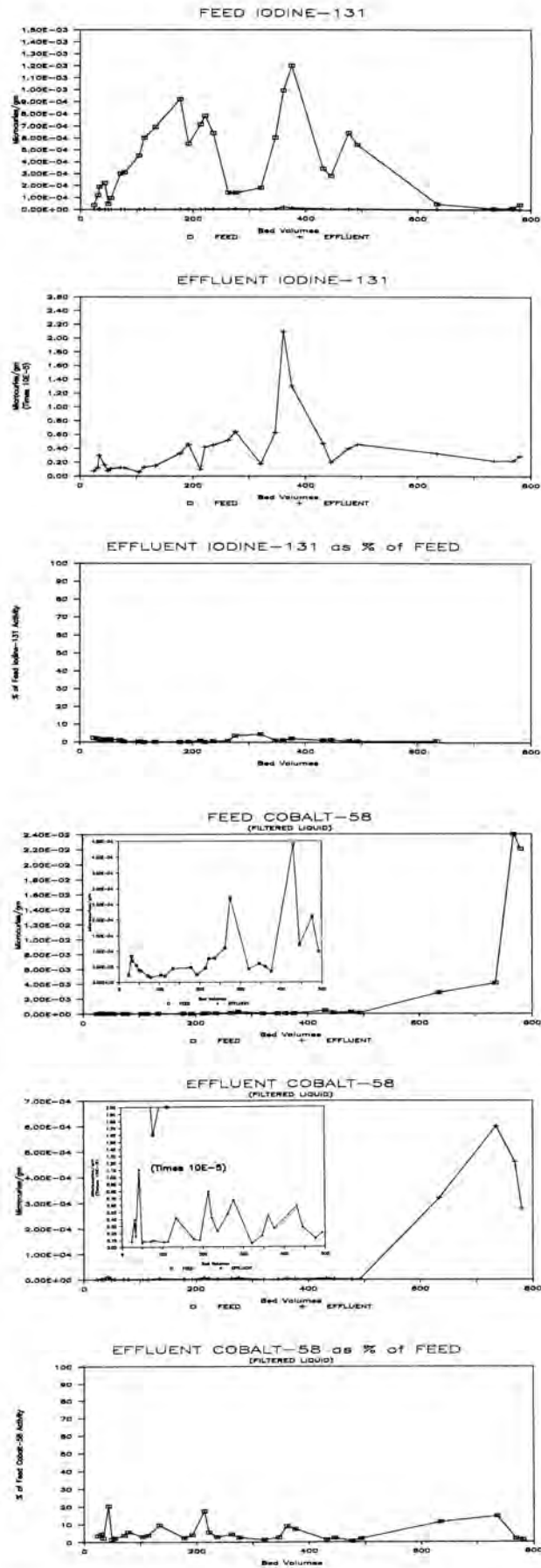


Fig. 3. Waste Radiochemistry Data for Four Monitored Nuclides.

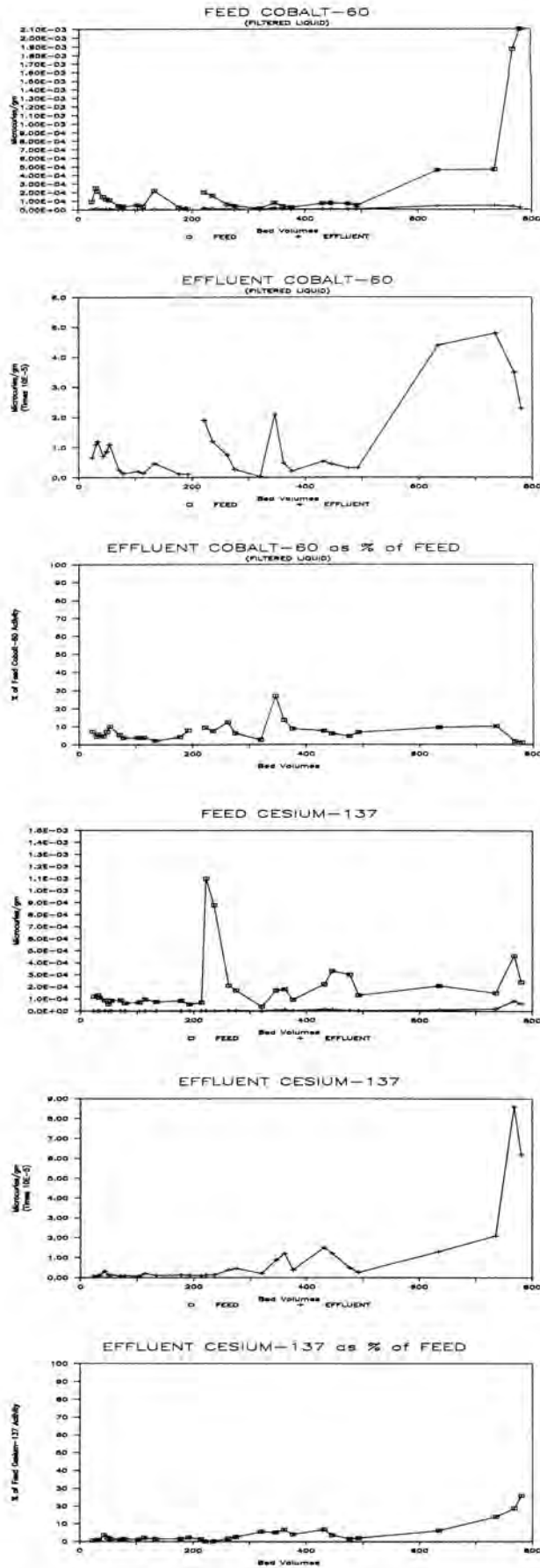


Fig. 3. (Con't.) Waste Radiochemistry Data for Four Monitored Nuclides.

Decontamination factor (DF) values are often used in the nuclear power industry to quantify radwaste ion-exchange process efficiency for removing nuclides. A summary of the maximum, minimum and average filtered liquid nuclide DF values measured for this test are presented in Table III.

TABLE III

Summary of Liquid Nuclide DF Values for Ion-Exchange Bed

Nuclide	Minimum	Average	Maximum
Cobalt-58	5	38	175
Cobalt-60	4	21	91
Iodine-131	4	192	763
Cesium-137	4	100	846

The ion-exchange bed processed 781 bed volumes of liquid to a 20% final leakage of cesium-137. The leakage of filtered cobalt-58, cobalt-60, and iodine-131 activities at 781 bed volumes was <1.5%. The test was terminated at 781 bed volumes due to the impending refueling outage and accompanying uncertainty of the waste chemistry during the outage.

Solids Phase

The percent of activity measured in the waste feed solids is illustrated for the nuclides in Fig. 4. The solids data represent the "non-exchangeable" fraction of the radionuclide in the waste feed (post-plant filter). The data indicate that the fraction of nuclide activity present in the waste solids was sensitive to both waste feed chemistry and

operating conditions. For example, the percent solids activity for all nuclides was high following the initial startup transient. Cesium-137 solids activity decreased to less than 1% for the balance of the test. The fraction of iodine-131 solids activity increased significantly during the pre-outage chemistry phase; conversely, the fraction of cobalt-58 and cobalt-60 activities in the solids decreased for this same time period of decreasing reactor power.

Filtration tests on the waste feed were performed to identify the size distribution of cobalt particulate activity following processing of waste containing spent bed sludge water. Samples of the waste feed were split and filtered through 0.45-, 3- and 8-micron filters. These data are summarized in Table IV. The data show that an 8-micron (absolute rated) filter removed a factor of 10 more cobalt from the plant-filtered waste liquid. These data indicate that a smaller pore size filter could have improved system efficiency for removing cobalt isotopes from waste.

TABLE IV

Filtration Experiment Results for Waste Using Varying Pore Size Filters

	<u>Micron Size</u>		
	<u>0.45</u>	<u>3.0</u>	<u>8.0</u>
Cobalt-60			
% Removed	99	96	92
DF	104	28	12
Cobalt-58			
% Removed	86	85	80
DF	7	7	5

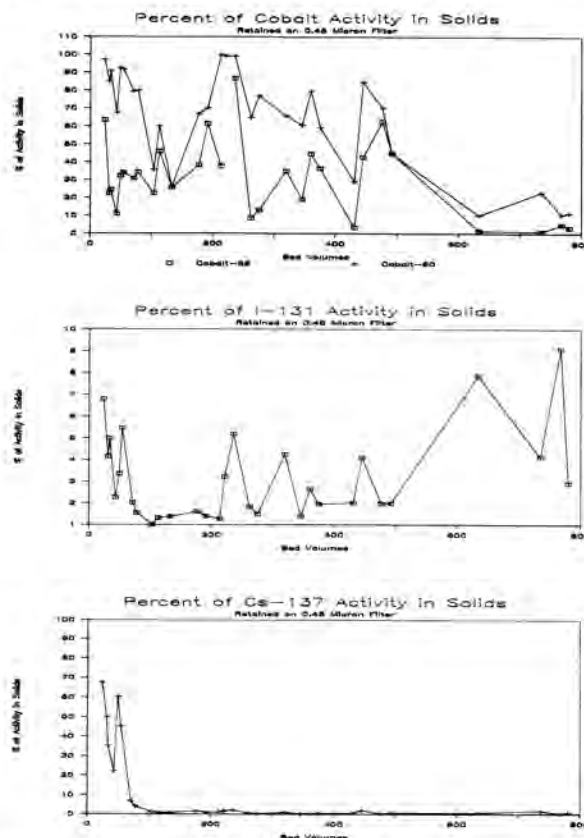


Fig. 4. Percent of Nuclide Activity in the Waste Feed Solids.

Process Economics

The replacement and disposal costs for the zeolite/organic ion-exchange system were calculated and compared to the baseline ion-exchange system, a layered organic polymeric bed. The assumptions for this cost analysis are summarized in Table V.

The costs (C) per 1000 gallons of waste processed as a function of bed volumes for the system were calculated by

$$C = 1000 \times \text{Total Costs/ft}^3 / (\text{BV} \times 7.5 \text{ gallons/ft}^3).$$

The relative costs per 1000 gallons of liquid processed for each system are:

Zeolite/Organics : \$60

Baseline : \$160

For treated waste to be discharged, the zeolite/organics system represents a factor of three improvement in volume reduction over the baseline system. The zeolite/organics system also produces a cost savings of 60% for replacing and disposing of ion-exchange materials over the baseline system. These figures are in good agreement with the estimated factor of four volume reduction improvement and the 60% to 75% costs savings reported previously (5).

TABLE V

Assumptions for Cost Analysis

	<u>Zeolite/Organic</u>	<u>Baseline</u>
Waste Processed, BV	781	266
Material Costs/ft ³		
Organic	\$146	\$125
Inorganic	225	
Bed	154	125
Labor/ft ³	25	20
Transportation/Disposal Costs/ft ³	175	175
TOTAL	\$354	\$320

CONCLUSIONS AND RECOMMENDATIONS

This paper has reported the first full-scale application of zeolite and organic resin for processing low-level waste liquids at an operating nuclear power plant in the USA. The treatment system used here is applicable to existing equipment containing mixtures in a single unit. No capital cost for equipment modification was involved.

As a minimum, pH and conductivity measurements of the feed and effluent for a radwaste ion-exchange system should accompany the radiochemistry analysis of the waste. These analyses may be useful in identifying the general changes in waste chemistry that influence system performance for removing nuclides. Other chemical analyses may be useful and should be performed on a periodic basis for the feed and effluent.

Specifications should accompany the purchase of organic radwaste ion-exchange materials. These specifications should be considered as part of a program to optimize radwaste ion-exchange performance. Examples of the types of specifications for strong

acid cation and strong base anion ion-exchange materials have been given previously in this paper.

Based on this study, inclusion of cesium-selective synthetic mordenites in the waste treatment system should increase the volume of waste that can be treated by a given volume of solids for plants with waste chemistry similar to that of Millstone 2. These ion-exchange materials may successfully be used as top layers in a radwaste ion-exchange bed. With proper pre-treatment, the synthetic mordenite does not appear to compromise the performance of the downstream organic ion-exchange materials for treating waste to be discharged. A minimum top layer depth of 4 to 6 inches is recommended.

Laboratory filtration tests should be performed on raw waste liquid. These tests will help to identify a range of pore size filters that may improve particulate activity removal.

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