# PILOT TESTING OF OPTIMIZED RADWASTE ION EXCHANGE AT MILLSTONE NUCLEAR STATION

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## ABSTRACT

EPRI sponsored a technical program directed at reducing costs associated with radwaste liquid ion-exchange media replacement and disposal. This paper presents the results of pilot tests performed by B&W to determine the technical and economic feasibility of an alternative treatment process. A combination of zeolite and organic exchange media were successfully used to treat aerated waste liquid at the Millstone Nuclear Station.

## INTRODUCTION

Nuclear utilities are interested in improving the volume reduction performance of radwaste liquid ion-exchange processes at operating plants. Reduced costs for waste liquid processing and the need to remain within annual waste allotments for burial are the driving forces for this interest. Extended operating time for radwaste ion-exchangers translates into reduced costs for ion-exchange media replacement and disposal. Greater efficiency for treatment of waste liquid may prevent costly reprocessing to achieve effluent criteria. In addition, the replacement or partial substitution of evaporators by ion-exchange processes may also reduce solidification and equipment maintenance costs.

The Electric Power Research Institute (EPRI) has addressed the nuclear industry's need for reducing waste liquid processing costs by funding this program. The three main objectives of the program are to (1) identify ion-exchange materials, arrangements, and methods that will reduce the costs associated with purifying radwaste liquid streams, (2) demonstrate through field testing the effectiveness of the identified optimization alternatives, and (3) document the results of the work with appropriate recommendations in a manner that will benefit radwaste operators.

Babcock & Wilcox conducted performance testing of ion-exchange media at the Millstone Nuclear Station. Emphasis was given to selecting non-proprietary, commercially available ion-exchange media in good supply and at reasonable cost. The testing included (1) Definition of Cleanup Criteria and Waste Liquid Operating Conditions, (2) Chemical and Radiochemical Characterization of Waste Liquid Streams, (3) Selection of Ion-Exchange Media, (4) Bench Scale Testing, (5) Pilot Testing, and (6) Process Evaluation.

The first four tasks of the program have been completed and have been reported previously. Intensive waste liquid characterization and field testing campaigns were conducted at the Millstone Nuclear Station. This paper documents the ion-change pilot testing results for treatment of aerated waste liquid at the Millstone PWR.

## REVIEW OF CLEANUP CRITERIA AND WASTE CHEMISTRY

PWR waste liquid is normally processed to meet the effluent concentration limits on suspended solids, radionuclides, and boron for non-recyclable liquids. For this program, the primary emphasis focuses on the removal of the radiochemical species from waste liquid. To accomplish this objective, the waste liquid feed is filtered and subsequently processed by ion-exchange. The ion-exchanger vessel has a resin volume of 40 cubic feet. It contains a proprietary "layered" configuration. The plant has the option of using a secondary portable ion-exchange system which provides additional capacity. Processed liquid waste is stored in a monitor tank and assayed for radionuclides. The contents of this tank are released in accordance with the limits established in Table II, 10 CFR 20.

Extensive PWR chemical and radiochemical analyses on the aerated waste liquid have been reported previously as part of this program.[1-3] Summaries of waste chemistry and radiochemistry analyses are given in Tables I and II, respectively.

TABLE I

Summary of Waste Liquid Chemistry

| | Minimum | Median | Maximum |
|---|---|---|---|
| pH | 5.9 | 6.8 | 7.0 |
| Conductivity, μS/cm | 77 | 166 | 415 |
| Suspended Solids,ppm | 7 | 8 | 17 |
| Cations, meq/l | | | |
| Lithium | 0.009 | 0.009 | 0.014 |
| Sodium | 0.17 | 0.65 | 2.6 |
| Calcium | 0.13 | 0.36 | 0.49 |
| Magnesium | 0.03 | 0.17 | 0.55 |
| Iron | 0.01 | 0.03 | 0.06 |
| Copper | 0.001 | 0.005 | 0.006 |
| Nickel | <0.003 | <0.003 | <0.003 |
| Chromium | <0.0004 | <0.0004 | <0.0004 |

Table I, continued.

| | Minimum | Median | Maximum |
|---|---|---|---|
| Anions, meq/ml | | | |
| Chloride | 0.23 | 0.39 | 2.3 |
| M-Alkalinity | 0.66 | | 0.70 |
| Sulfate | 0.03 | 0.23 | 0.42 |
| Nitrate | 0.01 | 0.06 | 0.07 |
| Fluoride | 0.006 | 0.009 | 0.01 |
| Sulfite | <0.003 | 0.003 | 0.007 |
| Nitrite | <0.002 | | 0.007 |
| Other,ppm | | | |
| Boron | 5 | 41 | 64 |
| Silica | 3.7 | 3.8 | 5.9 |
| TOC | 3.2 | 3.7 | 4.6 |
| Acetate | <0.1 | <0.1 | <0.1 |

TABLE II

Summary of Waste Liquid Radiochemistry

Microcuries/gm

| Nuclide | Minimum | Median | Maximum |
|---|---|---|---|
| Chromium-51 | 3.0E(-6) | 1.4E(-4) | 9.6E(-4) |
| Manganese-54 | 2.1E(-6) | 1.8E(-5) | 8.6E(-5) |
| Cobalt-58 | 1.1E(-4) | 8.0E(-4) | 6.0E(-3) |
| Cobalt-60 | 6.6E(-5) | 2.5E(-4) | 4.1E(-3) |
| Iodine-131 | 6.2E(-5) | 1.8E(-4) | 4.2E(-4) |
| Cesium-134 | 2.3E(-4) | 1.0E(-3) | 2.5E(-3) |
| Cesium-137 | 3.4E(-4) | 1.5E(-3) | 3.6E(-3) |

In general, potassium and ammonium ions were not measured in appreciable concentrations (<0.1 ppm) in the PWR waste liquid.

## TESTING

The pilot plant testing of the PWR radwaste ion-exchange system is the culmination of a two-year program. A detailed bench scale test program identified the best ion-exchange/adsorber combination for use in the Millstone system.[2,3] The objective of the pilot plant tests is to develop process technical and economic data that can be used to assess the optimized system performance. The pilot plant was designed to maintain process operating conditions, record pertinent data, and operate with only minimum attention of plant personnel.

The ion-exchange pilot test system was designed and constructed at the B&W Lynchburg Research Center. The system has two main components. One component is a portable skid containing three "quick-connect" ion-exchange columns with associated process pumps, piping, pre-filters (10 micron), and sampling ports. The columns were 76 millimeter I.D. by 700 millimeter in length, with a resin bed depth of 550 to 600 mm. The physical length of the column assembly permitted convenient storage in a shielded 55-gallon drum. The second component is an automated data acquisition system that recorded process temperatures, differential pressures across filters and beds, influent and effluent conductivities, effluent pH, flowrates, and total volume of radwaste liquid processed.

Two tests were performed using the basic configuration in Figure 1.

A summary of the ion-exchange and adsorbent media selected for pilot testing is given in Table III.

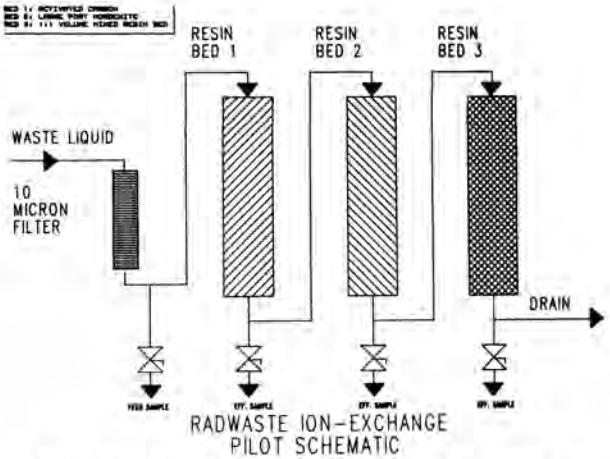



Fig. 1. Schematic of Pilot Plant Test Columns.

TABLE III

Ion-Exchange Media Selected for Pilot Testing

| Cation Exchangers | Anion Exchangers | Adsorbent |
|---|---|---|
| Large port mordenite<br>Granular<br>Sodium form<br>20/50 mesh | Type I Gel A<br>Styrene DVB Bead<br>Hydroxide form<br>16/40 mesh | Activated Carbon |
| Strong Cation A<br>Sulfonic<br>Macroporous<br>Bead<br>Hydrogen form<br>12% crosslinked<br>16/40 mesh | Type I Gel B<br>Styrene DVB Bead<br>Hydroxide form<br>30/60 mesh | |
| Strong Cation B<br>Sulfonic<br>Gel<br>Bead<br>Hydrogen form<br>8% crosslinked<br>30/60 mesh | | |

The first test consisted of three beds of activated carbon, large-port mordenite, and standard mesh mixed resin (1:1 by volume cation to anion) in series. Each bed contained approximately 0.09 cubic feet of medium. In the second test, a commercially available fine-mesh (30/60) mixed bed (1:1 by volume) resin was substituted for the standard resin. This particular fine-mesh resin was not available for bench scale column testing. It was included in the pilot testing so that its performance could be evaluated in the program.

The radwaste liquid feed flowrate was established at 2 gpm/cu. ft. and 4 gpm/sq. ft. for these tests. Samples of the feed and effluent were taken and analyzed by gamma spectroscopy.

## RESULTS

### Test Using Activated Carbon, Zeolite, 16/40 Mesh Mixed Bed

Approximately 3700 gallons (equivalent to 5700 individual column volumes) were processed to complete the first pilot plant test. The nuclides cobalt-60, cesium-137 and iodine-131 were trended during these tests.

The waste feed stream pH was 6.1. Conductivity measurements made during the test are summarized in Fig. 2.

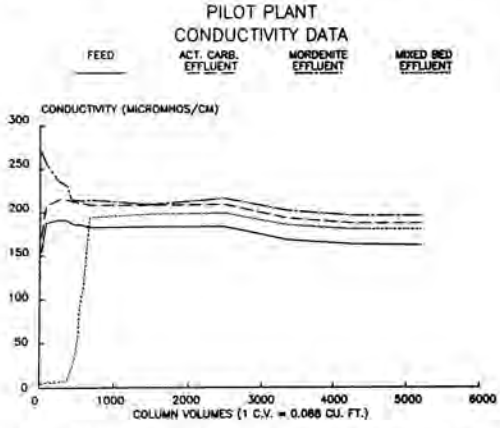



Fig. 2. Conductivity Trends for Pilot Plant Test.

The electrical conductivity of the feed remained relatively constant at 170 micromhos/cm. The initial conductivity excursion in the zeolite effluent may be ascribed to residual sodium transported from the bed to the processed water.

Figure 3 summarizes the feed and activity effluent measurements and decontamination factor (DF) for cobalt-60. Cobalt-60 in the waste feed was removed in part on each of the three beds. Initial system decontamination factor (defined as the ratio of feed activity to effluent activity) was about 300.

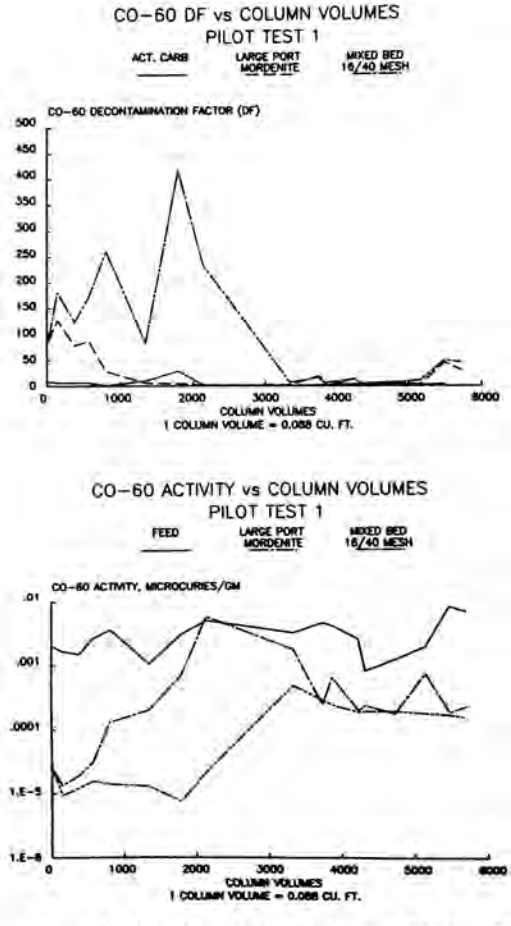



Fig. 3. Cobalt-60 Activity and DF for Pilot Plant Test 1.

The activated carbon bed displayed variable cobalt-60 DF and exhibited very limited loading capacity for cobalt-60. This bed became exhausted after 2300 column volumes of operation. Cobalt-60 in the effluent of the large port mordenite bed increased to equal that in the feed (DF = 1) at 2300 column volumes. The mordenite effluent subsequently showed a decreasing level of cobalt-60 activity, continuing to improve in DF through the end of the test. The mordenite and mixed bed effluents achieved equal cobalt-60 effluent activity at 3400 column volumes and remained at this level until the end of the test. Final overall system DF was 50 after 5700 column volumes.

Figure 4 shows that cesium-137 activity in the large port mordenite effluent remained less than minimum detectable activity (MDA) throughout this first test. This MDA was 1.7 E(-6) microcuries/gm after 5700 column volumes for a minimum DF = 675. The original volume of mordenite was left in service after the completion of the first test.

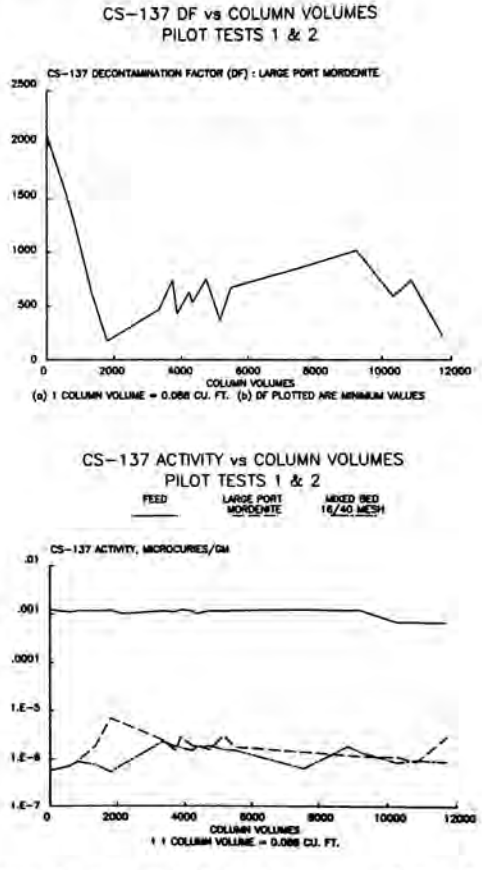



Fig. 4. Cesium-137 Activity and DF for Pilot Plant Test.

Figure 5 compares the iodine-131 activity in the feed, activated carbon effluent, and mixed bed effluent. The decontamination factor is also plotted as a function of column volumes. Significant iodine-131 loading of the activated carbon bed occurred only during the first 150 column volumes. Thereafter, iodine-131 removal was achieved by the strong anion gel resin in the mixed bed. The initial iodine-131 DF across cross the mixed bed exceeded 100. The iodine-131 activity in the effluent of the mixed bed was MDA

< 4.7 E(-7) microcuries/gm at 2140 column volumes and MDA < 1.3 E(-6) microcuries/gm at 3878 column volumes. The iodine-131 DF was 15 at the end of the test.

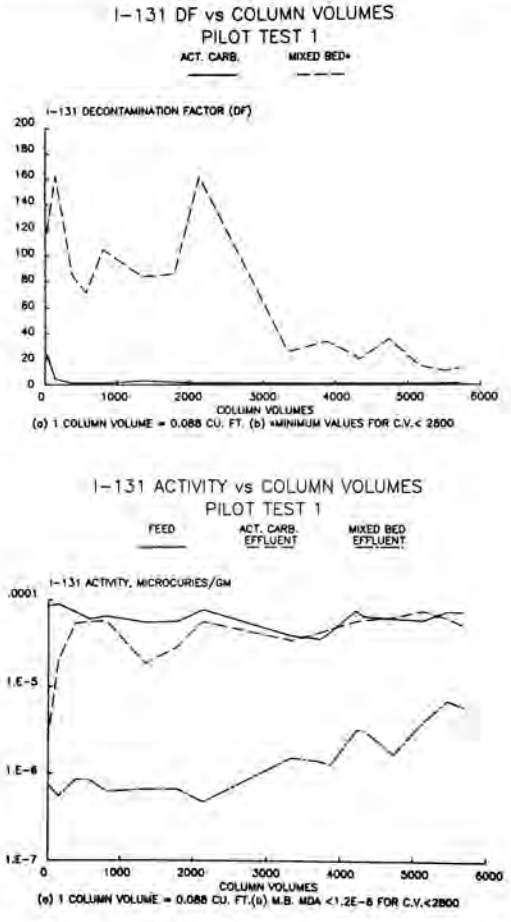



Fig. 5. Iodine-131 Activity and DF for Pilot Plant Test 1.

## Test Using Activated Carbon, Zeolite, and 30/60 Mixed Resin

The activated carbon and standard mesh mixed bed resin columns were replaced when the decontamination factors for iodine-131 and cobalt-60 were equal to 15 and 50, respectively. Another 5700 column volumes of waste feed were processed by this pilot plant.

The performance of the pilot plant for cobalt-60 removal is given in Fig. 6. Initial system decontamination factors were about 300, with a final system decontamination factor of about 10. Cobalt-60 removal trends for this system are similar to those encountered for the first pilot system tested. However, cobalt-60 feed activities for this test were 3 to 10 times lower than those for the first pilot test.

The large port mordenite column was never replaced during these tests. As indicated by Fig. 4, the effluent from this column maintained a MDA cesium-137 activity of < 2.9 E(-6) microcuries/gm after 11700 column volumes of operation. This corresponds to a minimum cesium-137 loading of approximately 11 microcuries/cc of large port mordenite. The decontamination factor for cesium-137 produced by the mordenite remained consistently in a minimum range of 500 to 1000 throughout the testing.

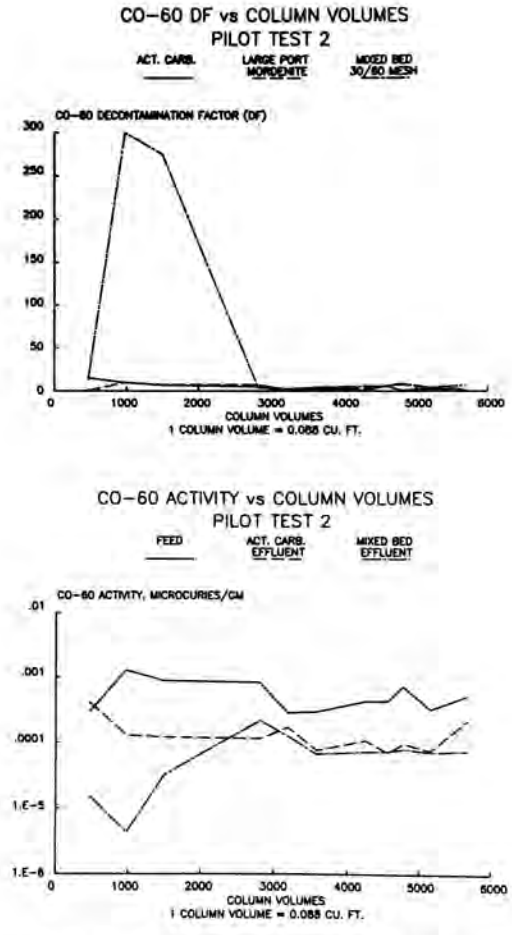



Fig. 6. Cobalt-60 Activity and DF for Pilot Plant Test 2.

Figure 7 compares the iodine-131 activity in the feed with that in the mixed bed column effluent. Iodine-131 feed activities were a factor of 3 to 10 lower for these fine mesh resin tests than for the conventional mesh resin tests. The iodine-131 effluent activity remained less than or equal to the MDA limit of 1E(-6) microcuries/gm throughout this second test.

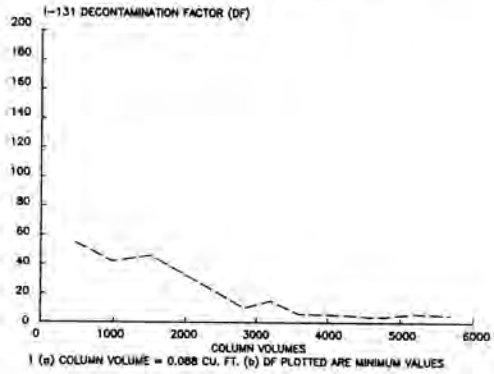
A summary of pilot plant test results is given in Table IV.

## PROCESS EVALUATION

Using the process data from the pilot plant tests, an evaluation of media replacement and disposal costs was performed. Cost comparisons between a reference and proposed system were made.

Tables V and VI present the assumptions and estimated costs for radwaste ion-exchange media replacement and disposal. These costs have been updated from those presented previously.[3] Two cation media capacities for cesium removal were assumed at 5000 and 10,000 gallons per cubic foot. Costs for the purchase of ion-exchange media and for resin transportation and burial were calculated based on actual operating plant experience. Curie loadings for the various beds were based on the pilot plant influent radiochemistry analyses and media capacities (defined to a nuclide DF endpoint).

I-131 DF vs COLUMN VOLUMES
PILOT TEST 2




I-131 ACTIVITY vs COLUMN VOLUMES
PILOT TEST 2

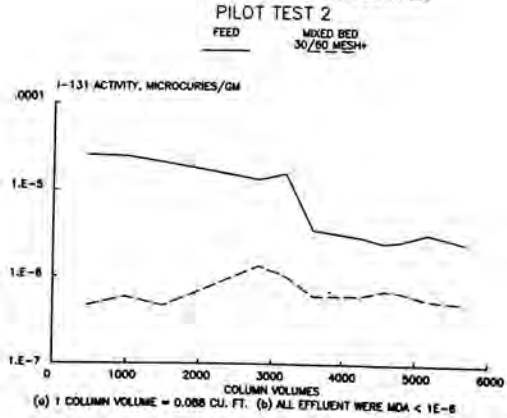



Fig. 7. Iodine-131 Activity and DF for Pilot Plant Test 2.

TABLE IV

Summary of Radwaste Ion-Exchange Pilot Tests

| Nuclide | Exchanger | Column Volumes | DF Init./Final | Final Act. µCi/gm |
|---|---|---|---|---|
| Co-60 | System, Std. Mesh | 5,700 | 300/50 | 1.5E(-4) |
| | System, Fine Mesh | 5,700 | 300/10 | 7.6E(-5) |
| I-131 | Mixed Bed Resin 16/40 (1:1 C:A) | 5,700 | >150/10 | 3.0E(-6) |
| | Mixed Bed Resin 30/60 (1:1 C:A) | 5,700 | >40 | <1.0E(-6) |
| Cs-137 | Synthetic Mordenite | >11,500 | >1000/>300 | <2.9E(-6) |

The costs per 1000 gallons of radwaste liquid treated are estimated to be:

Reference System: $44 to $64

Proposed System: $17

Table V

Assumptions for Optimized Radwaste Ion-Exchange

| | Reference System | Proposed System |
|---|---|---|
| Liquid Processed, gal | 3,000,000 | 3,000,000 |
| Capacity, gal./cu. ft. | | |
| Carbon (Mixed Bed Changeout) | 40,000 | 40,000 |
| Cation Media (Cesium DF = 10) | 5,000 (10,000) | 100,000 |
| Mixed Bed (Iodine DF = 10) (Cobalt DF = 10) | 40,000 | 40,000 |
| Resin Costs, $/cu. ft. | | |
| Carbon | 50 | 50 |
| Cation Media | 60 (resin) | 270 (mordenite) |
| Mixed Bed (1:1) | 100 | 100 |
| Trans./Disposal, $K/190 cu. ft. cask | | |
| (150-180 cu. ft. media ) | 28 | 31* |

* Includes increased surcharge for curie content per shipment.

TABLE VI

Comparison of Media Replacement and Disposal Costs

| | Reference System (cf) | Cost $K | Proposed System (cf) | Cost $K |
|---|---|---|---|---|
| 1) Activated Carbon | 75 | 3.8 | 75 | 3.8 |
| 2) Cation Media | 300-600 | 18-36 | 30 | 8.1 |
| 3) Mixed Bed | 75 | 7.5 | 75 | 7.5 |
| 4) TOTAL MEDIA | 450-750 | 29.3-47.3 | 180 | 19.4 |
| 5) Shipments | 3-4 | 104-144 | 1 | 31 |
| 6) TOTAL (4+5) | | 133-192 | | 50 |

This scoping cost analysis indicates that the costs for ion-exchange media replacement and disposal using the proposed ion-exchange system may be reduced by 60% to 75% for this plant.

Cost savings for ion-exchange media replacement and disposal are anticipated to be plant specific due to differences in waste chemistry. In addition, the costs generated above may be conservative due to the relatively large quantities of activated carbon included for disposal. The activated carbon does not contribute significantly to the volume reduction and increases the transportation/burial costs.

SUMMARY

EPRI is addressing the need for improved radwaste liquid ion-exchange processing. Babcock and Wilcox has completed a study of radwaste ion-exchange through the pilot plant phase at the Millstone Nuclear Station. The focus in this work was on the use of non-proprietary, commercially available ion-exchange and adsorbent media in good supply and at reasonable cost.

A methodology demonstrated in the EPRI program is recommended to utilities to assist in the selection of ion-exchange media for radwaste liquid processing. This methodology includes definition of waste cleanup criteria, chemical and radiochemical characterization of waste streams, ion-exchange media selection, performance verification of media, process evaluation, and implementation.

A radwaste ion-exchange configuration that incorporated a large port mordenite and organic polymers with two different mesh size distributions was successfully demonstrated on the pilot plant scale. This work suggests that the selectivity of certain zeolites for cesium may increase volume reduction factors and reduce costs for the treatment of radwaste liquids. The use of this approach for identifying optimal radwaste ion-exchange processing resulted in a projected 60% savings for media replacement and disposal costs at the Millstone site.

ACKNOWLEDGEMENTS

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2. N. P. Jacob, et al., "Radwaste Ion Exchange Optimization," Waste Management '85 Proceedings, Volume 2, 1985, p.573.

3. N. P. Jacob, et al., "Radwaste Ion Exchange Optimization," Proceedings of the 1985 International Water Conference, Pittsburgh, PA, 1985.