

OPTIMIZATION OF RADWASTE ION-EXCHANGE PROCESSES
AT NUCLEAR POWER PLANTS

N. P. Jacob, E. Morgan, J. M. Storton, J. F. Kramer
Babcock & Wilcox
(a McDermott company)
Lynchburg, Virginia 24505

J. P. Kangley
Millstone Nuclear Station
Wakeford, Connecticut 06385

M. D. Naughton
Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

Considerable emphasis is being given by nuclear utilities to optimizing the performance of radwaste ion-exchange processes. Extension of ion-exchange capacity and increased efficiency for removal of chemical and radiochemical species means reduced costs for resin purchase and disposal. Mixed radwaste liquid presents a challenge for ion-exchange processes due to the presence of species that are deleterious to ion-exchange resin. This paper presents current results of the project sponsored by the Electric Power Research Institute to improve BWR and PWR radwaste ion-exchange performance.

INTRODUCTION

Ion-exchange is a flexible process that offers significant advantages for the purification of both pressurized water reactor (PWR) and boiling water reactor (BWR) radwaste liquid. Ion-exchange is efficient, offers relatively simple processing schemes, requires minimal capital investment, provides excellent volume reduction capability, and can now be acquired as a vendor service. In addition, ion-exchange may be tailored to treat specific waste streams according to chemical characteristics. This particular advantage is important in view of the differences between PWR and BWR liquid waste chemistry.

Ion-exchange resin systems, however, exhibit limited total capacity for removal of chemical and radiochemical species from liquid radwaste systems. The renewal of this capacity requires either chemical regeneration or replacement of the ion-exchange resin.

The current trend in the nuclear power industry is to remove the exhausted, radioactive resin from service, followed by dewatering and expeditious disposal of these resins in vessels appropriate for long-term burial. Unfortunately, these ion-exchangers are often discharged well before the maximum available operating capacity of the resin is achieved. Reasons for decreased ion-exchange capacity are numerous, and can include fouling of resin by organics and suspended matter, gas bubble occlusion of ion-exchange sites,

and improper flow distribution effects. This decreased capacity manifests itself in increased costs for resin disposal.

Nuclear utilities are now emphasizing the optimization of the operating performance of ion-exchange systems with regard to chemical and radiochemical species removal and capacity utilization efficiency. Efficient utilization of ion-exchange capacity will extend average "once-through" lifetime of the bed and thus reduce the removal and replacement frequency of resin changes. Increased service run lengths for ion-exchangers in the radwaste system can significantly reduce costs for resin investment and disposal. Another requirement for superior resin purification efficiency is continued compliance with radioiodine and radiocesium liquid effluent limits as defined by regulation. Efficient radiocobalt removal from radwaste liquid has also proved to be challenging for nuclear plants.

Improving Ion-Exchange Performance

Within the last two years, work has been initiated within the nuclear power industry to improve the ion-exchange performance for the processing of mixed liquid radwaste. Emphasis has been given to liquid waste characterizations and comparisons of various resin types for performance. At least two of the service companies and a major nuclear utility have current programs to improve ion-exchange performance in radwaste systems.

"Advanced Low Level Radwaste Treatment Systems Technology" is a major program sponsored by the Engineering and Operations Department of the Electric Power Research Institute (EPRI). To address the growing need in the commercial nuclear power industry for improved radwaste ion-exchange performance, a project within this EPRI-sponsored program is being conducted by Babcock & Wilcox. The three main objectives of this work are (1) to identify ion-exchange materials, arrangements, and methods that will reduce costs associated with purifying radwaste liquid streams, (2) to demonstrate, through the prototype testing stage, the effects of the identified optimization method, and (3) to document the results of this work with appropriate conclusions and recommendations that will be of benefit to nuclear utilities.

To accomplish these objectives, a three-part approach is being implemented: (1) chemical and radiochemical characterization of radwaste liquid streams, (2) in-plant bench scale column testing, (3) in-plant prototype column testing. This work is currently being performed at the Millstone Nuclear Station, which conveniently offers both an operating 650 MWe BWR and an operating 830 MWe PWR for this study.

This paper presents the results obtained to date on this very important project and discusses future plans for additional in-plant ion-exchange testing.

Millstone Radwaste Liquid Streams

Radwaste treatment systems were reviewed prior to performing the intensive sampling and ion-exchange testing campaigns. Only those liquid streams that were currently being treated by ion-exchange or that appeared to be viable candidates for ion-exchange were selected for sampling characterizations and future resin testing. Preference was given to the floor drains processing system at the BWR and the aerated drains processing system at the PWR due to the challenge that these waters presented to ion-exchangers.

The portion of the BWR liquid radwaste system of interest to this project is illustrated in Figure 1. Points within the system where liquid samples were routinely taken during the study are indicated. During sampling, important operating parameters were also noted. These parameters included processing flowrates, stream temperatures, in-line conductivity readings, tank levels during processing, and filter/ion-exchanger differential pressure.

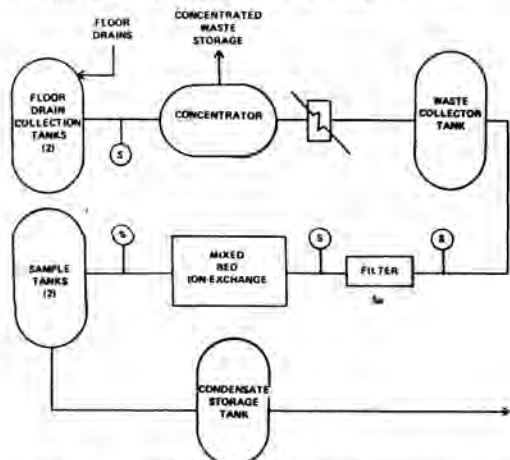


Fig. 1. BWR Radwaste Liquid Processing System.

The BWR system is designed for purification and recycle of liquid wastes generated during plant operations. Various high conductivity (>50 $\mu\text{S}/\text{cm}$) floor drains and sump waters are pumped to storage tanks and processed without filtration by a simple concentrator. Distillate from the concentrator is sent to the waste collection tank, containing low conductivity (<50 $\mu\text{S}/\text{cm}$) water. Waste collector tank liquid is filtered and ion-exchanged through a 4.5m³ (160 ft³) mixed bed. The effluent of this mixed bed is stored in sample tanks, and may ultimately be transferred to condensate storage. At Millstone, the mixed bed ion-exchanger used in the treatment of waste collector liquid is simply a single charge of "spent" condensate polisher resin. The waste collector ion-exchange resin is discharged from service when the conductivity of the effluent water reaches 1 $\mu\text{S}/\text{cm}$.

The portion of the PWR aerated liquid waste treatment system of interest to this study is illustrated in Figure 2. Points within the system where liquid samples were obtained for chemical and radiochemical analyses are indicated. Aerated waste first undergoes filtration (3-micron filter pore size) and subsequently is processed by ion-exchange. The ion-exchanger bed is 1.1m³ (40 ft³) in size and consists of a proprietary "layered bed" configuration. An option exists, as shown, for utilization of secondary ion-exchangers provided by a service company. Liquid waste processed in this fashion is stored in a monitor tank and filtered prior to discharge.

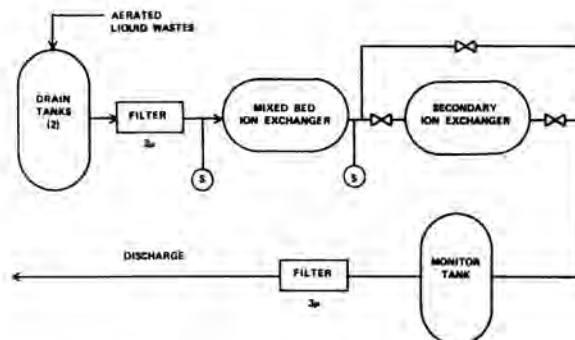


Fig. 2. PWR Radwaste Liquid Processing System.

Waste Stream Characterization

Exhaustive chemical and radiochemical analyses were performed by B&W on all liquid radwaste samples obtained during three intensive sampling campaigns conducted over a five-month interval. Considerable emphasis must be placed on the chemical definition of liquid radwaste streams prior to the formulation and operation of a well-balanced, optimized ion-exchange system. The endorsement of liquid waste stream characterization is due to the fact that the chemical rather than radiochemical constituents in the treated waters utilize the major fraction of the ion-exchange capacity.

Major results of the chemical analyses for the Millstone BWR and PWR liquid waste streams are summarized in Table 1. A brief yet useful radiochemical characterization of liquid radwaste is given in Table 2. These tables present ranges of chemical and radiochemical parameters measured over the time interval indicated previously.

TABLE I

Summary of Chemical Analyses of
Millstone Radwaste Liquid

	BWR Floor Drains	PWR Aerated Waste
pH	6.6-8.2	5.9-7.0
K (μ S/cm)	250-2700	77-415
SS (ppm)	10-2200	7-17
Lithium (ppm)	<0.01	0.06-0.10
Sodium (ppm)	20-510	4-60
Calcium (ppm)	4-11	4-10
Magnesium (ppm)	2-30	0.4-7
Iron (ppm)	0.8-11	0.3-2
Nickel (ppm)	0.3-1.1	0.1
Chromium (ppm)	0.02-0.04	0.01
Copper (ppm)	1.2-2.3	0.04-0.22
M-Alkalinity (ppm)	0.6-2.2	0.6-0.7
Chloride (ppm)	55-650	8-82
Fluoride (ppm)	0.07-0.10	0.1-0.2
Boron (ppm)	N/A	45-64
Sulfate (ppm)	4-190	1-11
Sulfite (ppm)	0.4-0.9	0.1-0.2
Nitrate (ppm)	0.1-1.0	0.6-4
Silica (R, ppm)	0.1-1.1	4-7
Acetate (ppm)	0.1	0.1
Total Organic Carbon (ppm)	0.6-4	3-5
Detergents (ppm)	<1	<1

Before ion-exchange

TABLE II

Summary of Millstone Waste Liquid Radiochemistry

	BWR	PWR
Activity Levels	10^{-6} to 10^{-3} μ Ci/g	10^{-7} to 10^{-3} μ Ci/g
Predominant Nuclide	Co-60	Cs-134/137
Activity in Crud	~20%: Cs-134/137, I-131/133, Tc-99 >70%: Mn-54, Co-58/60	<5%: Cs-134/137, I-131/133 >40%: Co-58/60, Mn-54, Cr-51

In addition to the BWR floor drain liquid analyses, a chemical characterization was also performed on waste collection liquid both before and after ion-exchange processing. These results are not presented.

The chemical measurements summarized in Table 1 and the general radiochemical characterization of radwaste waters given in Table 2 can be used to indicate for radwaste ion-exchange systems:

- o Types of Pretreatment
- o Types of Resins/Absorbents
- o Sizing of Beds for Maximum Run Length
- o Applicable Resin Configurations and Loading Sequence
- o Excessive Concentrations of Chemicals that Foul Ion-Exchangers

Ion-Exchange Testing

The testing evaluation of many potential ion-exchange materials and resins dictates a developmental approach. In order to provide an initial screening of many such materials in an expeditious fashion, batch equilibrium tests for 50 ion-exchangers were performed using composite radwaste liquid samples derived from Millstone. For these tests, a small quantity of the resin was weighed and placed in a flask with 100 ml of filtered BWR or PWR liquid waste. These flasks were capped and placed in a constant temperature bath. Up to 15 tests could be conducted simultaneously. The entire bath was agitated for a period of 72 hours. Following this time period, both liquid and resin were gamma isotopically analyzed. Both decontamination factors (DF) and equilibrium distribution coefficients were calculated from these data for each resin candidate using a computer program. The program classified DF and distribution coefficients values in decreasing order for each class of ion-exchange material (cation, anion, etc.), while identifying each type of resin and associated vendor. While this series of tests is not meant to be exhaustive, it served to provide a useful initial screen of many candidate ion-exchange materials for selectivity. Over 700 data points were generated for use in calculating equilibrium coefficients.

Samples of the preliminary resin rankings from these screening tests are given in Table III and IV. Duplicate equilibrium tests are currently being performed in our laboratories to confirm select data points. Supplementary tests are being conducted to examine the influence of chemical additions on ion-exchange performance.

TABLE III

Summary of Preliminary BWR Equilibrium
Resin Test Results
(Listed by Descending Distribution Coefficient)

Hydrogen Forms	
Cobalt	Cesium
R&H IR-122	Ionac CFP-110 (M)*
Dowex HCR-S	R&H AMB-200 (M)
R&H IR-120	Dowex HGR
Duolite ARC-9359 (M)	R&H IR-122
Ionac NC-11	Ionac NC-11
Ionac CFP-110 (M)	R&H IR-120
Ionac NC-10	Duolite ARC-9359 (M)
Duolite EX-467 (WA-M)	Dowex HCR-S
Dowex HGR	Ionac NC-10
R&H AMB-200 (M)	
Sodium Form	
Dowex HCR-S	Linde IE-96
Linde IE-96	R&H IR-120
R&H IR-120	Duolite ARC-9359
Duolite ARC-9359 (M)	Duolite CS-100 (WA-M)
Duolite CS-100 (WA-M)	Dowex HCR-S
R&H IRA-938 (SB-M)	R&H IRA-938 (SB-M)

* M = macroreticular

TABLE IV

Summary of Preliminary PWR Equilibrium
Resin Test Results
(Listed by Descending Distribution Coefficient)

Hydrogen Form	
Cobalt	Cesium
R&H AMB-200 (M)	R&H AMB-200 (M)
Ionac NC-11	Ionac CFP-110 (M)
Ionac CFP-110 (M)	Ionac NC-11
Duolite ARC-9359 (M)	Dowex HCR-S
Dowex CCR-2 (WA)	R&H IR-120
Duolite C-20	Duolite ARC-9359 (M)
Ionac NC-10	Duolite C-20
Dowex HCR-S	
R&H IR-120	
Sodium Form	
Ionac CFP-110 (M)	Duolite ARC-9359 (M)
Dowex HGR	R&H AMB-200 (M)
R&H IR-122	Ionac CFP-110 (M)
R&H AMB-252	Dowex HGR
R&H AMB-200 (M)	R&H IR-122
R&H IR-120	R&H IR-120
Dowex HCR-S	R&H AMB-252

Future Testing

The two phases of work planned for this study are bench scale and prototype column evaluation. These tests will be conducted at the plant using radwaste liquid streams. The most selective ion-exchange resins identified in the equilibrium test will be selected for bench scale column testing. The purpose of this bench scale testing is to identify the most optional materials to use in an ion-exchange system. Advanced bench scale tests will study the performance and capacity utilization as a function of resin configurations, ratios of cation-to-anion, types of resins, flowrates, types of pretreatment, and pressure.

The best arrangement identified in the bench scale column tests will then be examined in a prototype for optimal utilization and for chemical and radiochemical species removal efficiency. Prototype tests are expected to be seen at both the BWR and PWR. Then prototype tests will provide sufficient on-stream process data necessary to make a technical assessment of the process. This process information will provide a basis for developing engineering cost estimates for full scale system, including capital and operating costs. These cost estimates will be compared to costs associated with the existing treatment system. Such a comparison will be needed to demonstrate the cost effectiveness of the new ion-exchange system.

Summary

Considerable attention is now being given by nuclear utilities to improve the performance of radwaste ion-exchange systems. This challenge is currently being addressed by EPRI as well as by the nuclear utilities themselves. Waste steam characterization conducted over a five-month interval at the Millstone Station shows significant chemical and radiochemical differences not only between BWR and PWR, but also significant fluctuation in such measure-

ments at each unit. Screening equilibrium tests have identified several ion-exchange materials for future bench scale column testing. Future tests will be focused on evaluation of the best resin systems in a prototype phase.