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# EPICOR-II Resin Degradation Results From Second Samples of PF-8 and PF-20

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Prepared by R. D. Sanders, Sr., J. W. McConnell, Jr.

EG&G Idaho, Inc.

Prepared for  
U.S. Nuclear Regulatory  
Commission



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Manuscript Completed: September 1986  
Date Published: October 1986

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Prepared for  
Division of Waste Management  
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U.S. Nuclear Regulatory Commission  
Washington, DC 20555  
NRC FIN A6188

PREVIOUS REPORT IN SERIES

NUREG/CR-4150, "EPICOR-II Resin Degradation Results from First Resin Samples of PF-8 and PF-20, EG&G Idaho, Inc., July 1985.

## **ABSTRACT**

The 28 March 1979 accident at Three Mile Island Unit 2 released approximately 560,000 gallons of contaminated water to the Auxiliary and Fuel Handling Buildings. The water was decontaminated using a demineralization system called EPICOR-II developed by Epicor, Inc. The Low-Level Waste Data Base Development—EPICOR-II Resin/Liner Investigation Project, funded by the U.S. Nuclear Regulatory Commission (NRC), is studying the chemical and physical conditions of the synthetic ion exchange resins found in several EPICOR-II prefilters. The work is being done by EG&G Idaho, Inc., at the Idaho National Engineering Laboratory (INEL). This report summarizes results and analyses of the second sampling of ion exchange resins from EPICOR-II prefilters PF-8 and -20. Results are compared with baseline data from tests performed on unirradiated Epicor, Inc., resins to determine if degradation is continuing due to the high internal radiation dose received by the EPICOR-II resins. Results also are compared with results from the first sampling of the resins from EPICOR-II prefilters PF-8 and PF-20, and with those of other researchers.



## SUMMARY

The 28 March 1979 accident at Three Mile Island Unit 2 released approximately 560,000 gallons of contaminated water to the Auxiliary and Fuel Handling Buildings. The water was decontaminated using a three-stage demineralization system called EPICOR-II containing organic and inorganic ion exchange media. The first stage of the system was designated the prefilter, and the second and third stages were called demineralizers. Fifty EPICOR-II prefilters with high concentrations of radionuclides were transported to the Idaho National Engineering Laboratory (INEL) for interim storage before final disposal at the commercial disposal facility in the State of Washington. During the interim storage period at INEL, research was conducted on materials from those EPICOR-II prefilters. This study addresses the condition of the ion exchange resins in those prefilters.

Resin cores were obtained from prefilters PF-8 and -20 during a first and second sampling using special tools developed for that purpose. Removal of samples from the cores and cleaning and preparation of those samples are discussed. A series of characterization tests was performed on the resins to determine if degradation due to radiation had occurred during interim storage. Those tests included American Society for Testing Materials (ASTM) procedures, infrared spectroscopy, gas chromatography, high performance liquid chromatography, scanning electron microscopy, and barium chloride precipitation. Details of test methodology and results are described.

Analyses comparing test results of the first and second samplings of resins from EPICOR-II prefilters PF-8 and -20 and unirradiated resins obtained from Epicor, Inc., show that resin degradation is continuing in the EPICOR-II resins examined. The mechanism of degradation in those EPICOR-II prefilters is compared with earlier work and found to be consistent with those findings. The strong acid cation resins (divinylbenzene, styrene base structure) are losing effective cross-linking and functional groups, as well as experiencing first an increase and eventually a decrease in total exchange capacity as the absorbed radiation dose increases. The phenolic cation resins (phenol-formaldehyde base structure) show a loss of effective cross-linking and oxidation of the polymer chain. Analyses of resins removed from EPICOR-II prefilters PF-8 and -20 over the next several years should show a further increase in degradation.





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# EPICOR-II RESIN DEGRADATION—RESULTS FROM SECOND SAMPLES OF PF-8 AND PF-20

## INTRODUCTION

The 28 March 1979 accident at Three Mile Island Unit 2 released approximately 560,000 gallons of contaminated water to the Auxiliary and Fuel Handling Buildings. That water was decontaminated using a demineralization system called EPICOR-II developed by Epicor, Inc. The contaminated water was cycled through three stages of organic and inorganic ion exchange media. The first stage of the system was designated the prefilter, and the second and third stages were called demineralizers. After the filtration process, the ion exchange media in 50 of the prefilters contained radionuclides in concentrations greater than those established for disposal of similar materials as low-level wastes. Those prefilters were transported to the Idaho National Engineering Laboratory (INEL) for interim storage before final disposal. A special overpack, or high-integrity container, was developed during that storage period for use in disposing of the prefilters at the commercial disposal facility in the State of Washington.

During the interim storage period at INEL, continuing research was conducted by EG&G Idaho, Inc., on materials from those EPICOR-II prefilters, under the EPICOR and Waste Research and Disposition Program funded by the U.S. Department of Energy (DOE). That work now is directed by the U.S. Nuclear Regulatory Commission (NRC) as part of the Low-Level Waste Data Base Development—EPICOR-II Resin/Liner Investigation Project. Studies are being conducted on

(a) organic ion exchange resins from selected prefilters and (b) corrosion-resistant behavior of the phenolic-coated steel walls of the prefilter liners.<sup>1</sup> The resins are being examined to measure degradation, and tests are being performed to characterize solidified ion exchange media.

Degradation studies traditionally have been conducted using resins irradiated by external sources, such as a reactor core or Co-60.<sup>2</sup> The gamma dose provided by an external source simulates that received from radionuclides retained on the resin matrix by ion exchange. Modes of degradation do not differ between external and internal radiation; but Reference 1 states that internal radiation causes more extensive damage than external radiation, presumably from such sources as short-range, high-energy beta radiation. The organic resin of EPICOR-II prefilters had been contained in liners for approximately 6 years and experienced internal radiation doses of up to  $10^8$  rad.

This report discusses the resin degradation studies conducted on the second samples of organic ion exchange resins removed from two EPICOR-II prefilters (PF-8 and -20) and compares results with findings from studies of the first sampling, as described in Reference 3. As part of the EPICOR and Waste Research and Disposition Program, 46 prefilters were disposed of at a commercial disposal facility.<sup>4,5</sup> Four prefilters used in the NRC studies will be stored in temporary storage casks outside the Hot Shop of Test Area North Building 607 (TAN-607) at INEL.



## MATERIALS AND METHODS

### EPICOR-II Prefilters

EPICOR-II prefilter liners are 4-ft-dia by 4-ft-high cylinders with 1/4-in.-thick walls and tops and 1/2- to 5/8-in.-thick bottoms (Figure 1). The liners are of welded construction using ASTM Type A-36 carbon steel. Thin internal and external surfaces are painted with Phenoline<sup>a</sup> 368 coating. Each liner contains about 30 ft<sup>3</sup> of ion exchange media. Several types of media (i.e., cation, anion, mixed bed, and/or zeolite) were placed in each liner in layers. Of the prefilters received at INEL, 39 contained both organic ion exchange resins and inorganic zeolite; 11 contained organic resins only. During the filtration process, a perforated, four-branch influent manifold distributed contaminated water over the ion exchange media, while the effluent was drawn off from the bottom of the prefilter through a porous, multibranched return manifold. Both manifolds are piped to a manifold plate on top of the liner. A vent port and adapters for liquid-level detectors also are located on the manifold plate. A manway is located beside the manifold plate on the top of the liner, through which ion exchange media were loaded into the liner. Removal of resins from the prefilter also was accomplished through that manway, using coring tools.

Throughout this report, the following nomenclature applies to various sizes and configurations of materials removed from EPICOR-II prefilters for examination:

- **Resin Core**—one core removed from each prefilter PF-8 and -20 using coring tools
- **Resin Samples**—100-mL volumes of resin removed from the cores [three samples from PF-8 (designated PF-8#1, PF-8#2, and PF-8#3) and one from PF-20 (designated PF-20)]
- **Aliquots**—small quantities obtained from the resin samples.

To develop baseline data for resin degradation studies, unirradiated ion exchange resins representative of those in the prefilters were obtained from

Epicor, Inc. The unirradiated resins were identified by functional group, exchangeable species, and matrix (e.g., sulfonic acid, strong acid cation, and styrene). They were characterized for comparison with the resins from PF-8 and -20. Both the irradiated and unirradiated resins were examined using similar techniques. The resins were pretreated to permit weighing and drying of samples without problems caused by contamination or decomposition. Then, ASTM tests were used to determine exchange capacity, density, and moisture content.<sup>6</sup> Infrared spectroscopy (IR) was used to identify functional groups (e.g., sulfonic acid, phenolic, and quaternary ammonium) and matrix material (styrene and phenol). Vapor phase chromatography was used to analyze the rinse, soak, and acid rinse solutions from the ASTM tests quantitatively for styrene, divinylbenzene, or other soluble organic species. High-performance liquid chromatography was used to look for other possible soluble organic products.

### Coring

Resin cores were removed remotely from prefilters PF-8 and -20 during the second coring in 1985, using coring equipment based on a design developed at Battelle Columbus Laboratories (BCL) and modified for use at INEL.<sup>7</sup> PF-8 (containing organic resins) and PF-20 (containing organic resins and zeolite) were selected for the resin degradation studies because they are highly loaded representatives (1400 and 2000 Ci, respectively) of the two types of EPICOR-II prefilters. The coring equipment was described in Reference 3.

The resin core contained layers of ion exchange media in the same relative positions as in the prefilter bed. The void in the coring tool above the upper level of the resin was filled with unirradiated zeolite before lowering the tool to the horizontal position. The zeolite filler prevented shifting of the resin during transport. The coring tools were placed horizontally in separate casks and transported from the TAN-607 Hot Shop to a hot cell at the Test Reactor Area (TRA) for gamma-scanning and removal of resin samples.

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a. Trade name of the Carboline Company.

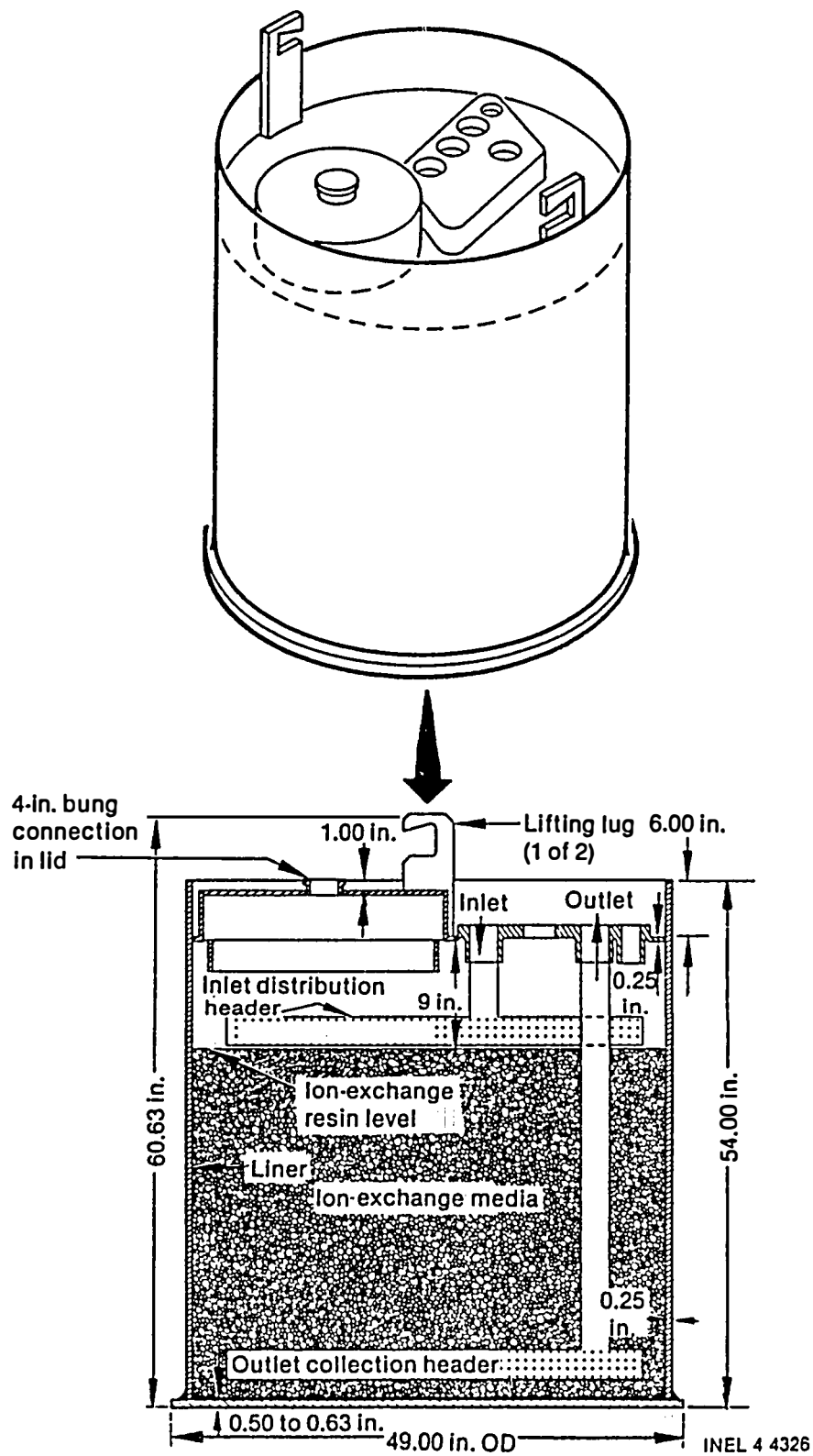


Figure 1. Schematic (isometric and full section) of an EPICOR-II prefilter.

## Measuring Radiation Doses in the Resin Beds

Full-depth gross gamma scans were made in the prefilter resin beds after removing the cores. Those scans were used to estimate the total integrated radiation dose absorbed by the resins. Measurements were made with a Victoreen Model 510 roentgen rate meter which used an air-equivalent ionization chamber radiation detector (Model 607) and associated current measuring electrometer. The task was accomplished by remotely lowering the radiation detector down the 2-by-3-in. holes created in the resin beds during the coring process. The averages of the actual gamma scan measurements made during insertion and retraction of the detector at each location are given in Figures 2 and 3. Radiation measurements made at the elevations of interest were used with the calculations of maximum cumulative doses of Reference 8 to estimate the total integrated beta dose. The beta dose and the measured gamma dose for each resin sample location are listed in Table 1. As would be expected, the doses are increasing with time.

## Gamma Scanning of Resin Cores

The full-length resin cores from PF-8 and -20 were scanned in the coring tool using a Ge(Li) gamma-ray detector (with associated electronics and a 0.5-in.-wide by 1.0-in.-high collimator) to determine axial gross gamma activity versus length of the core.<sup>9</sup> The axial locations of highest radionuclide activity for the resin cores were determined using those scans. Then, isotopic spectral measurements were made at the locations of highest activity during the first sampling from PF-20, as shown in Figure 4. There were two radionuclides having measurable concentrations detected by the gamma spectral scans, Cs-134 and Cs-137. Based on that information from the first sampling, isotopic gamma-ray intensities for Cs-134 and Cs-137 were measured as a function of distance along the resin cores. The results for Cs-137 are shown in Figures 5 and 6 for PF-8 and -20, respectively. The resin samples were collected from or near those regions of highest radionuclide loading. However, it is noted that the PF-20 sample was not collected from the region in the organic resin of highest radionuclide

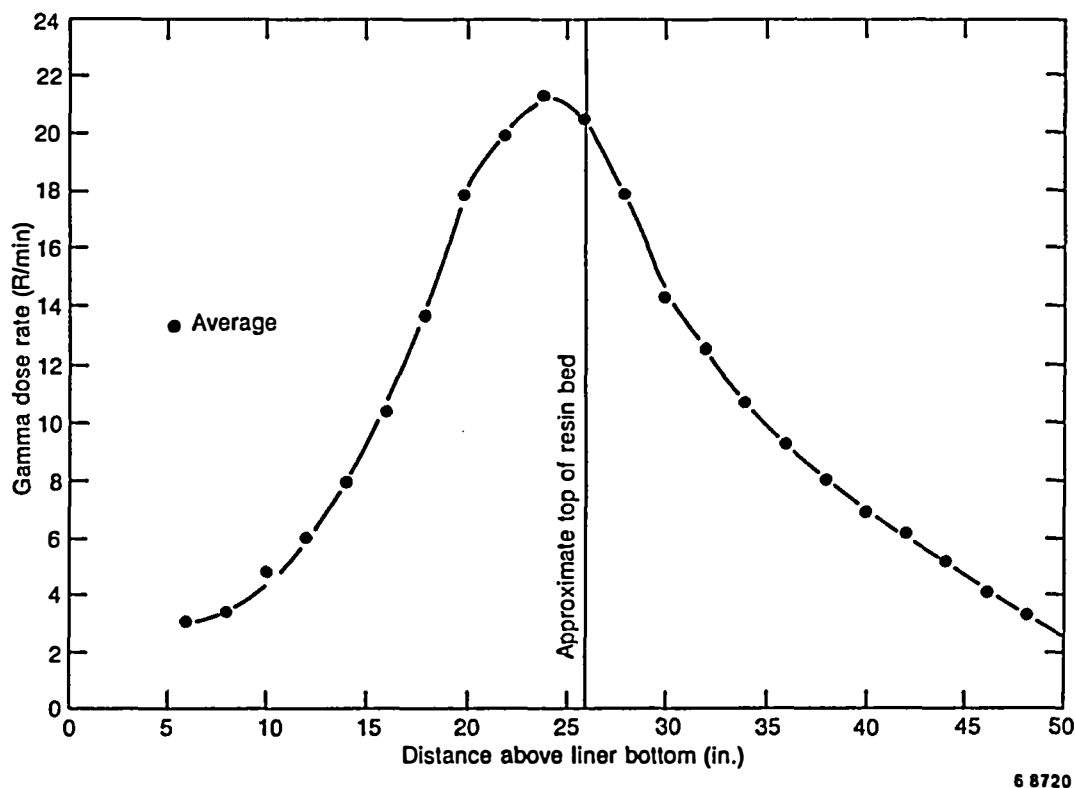


Figure 2. Results of full-depth gross gamma measurements taken inside the hole created in the resin bed by the coring of EPICOR-II prefilter PF-8.

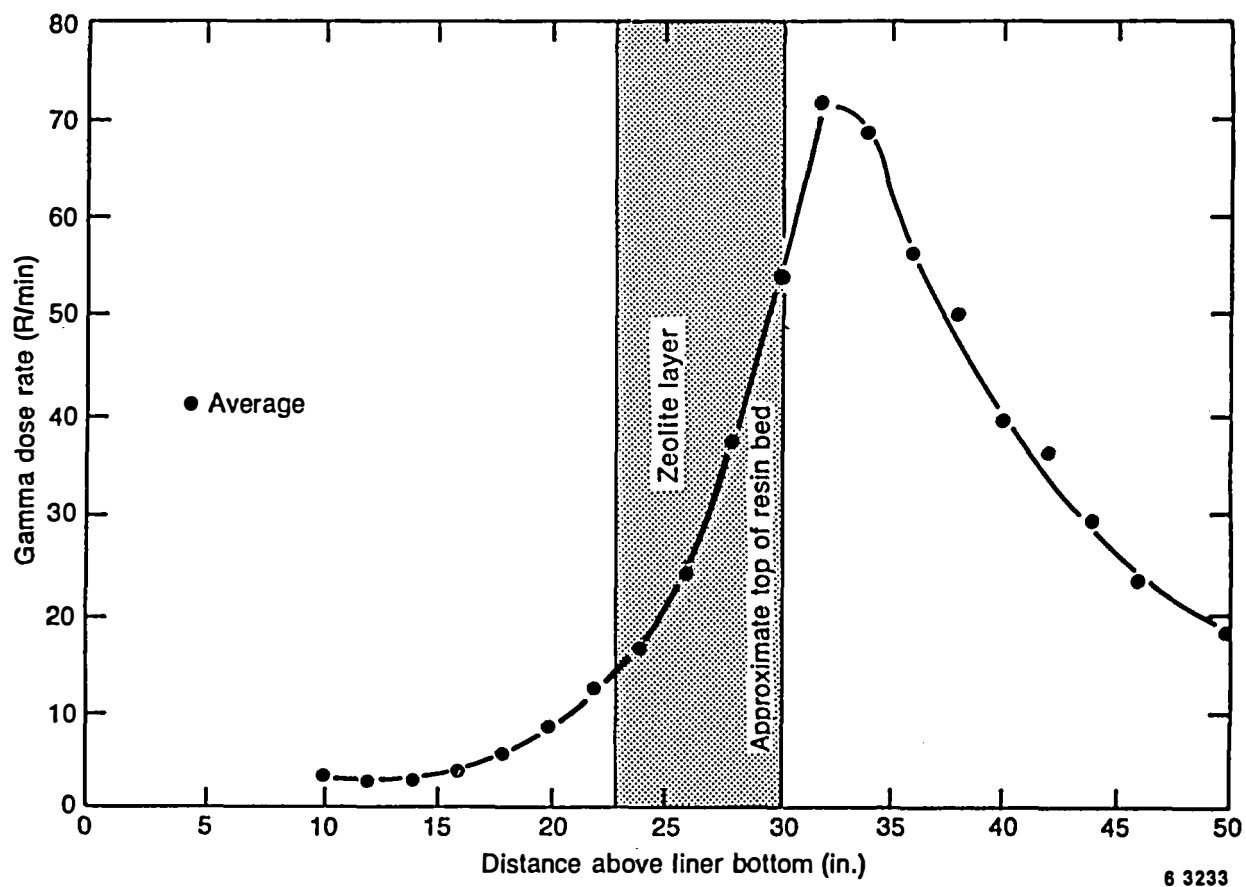


Figure 3. Results of full-depth gross gamma measurements taken inside the hole created in the resin bed by the coring of EPICOR-II prefilter PF-20.

Table 1. Calculated radiation doses to resins from EPICOR-II prefilters PF-8 and -20

Sample	Date Prefilter Removed from Service at TMI-2	Date Resin Cored	Measured $\gamma$ Activity at Location of Sample in Prefilter (R/min)	Total $\gamma$ Radiation Dose (rad)	Total $\beta$ Radiation Dose (rad)	Total Radiation Dose (rad)
PF-8#1	18 Dec 79	4 Oct 83	23.8	$4.9 \times 10^7$	$1.9 \times 10^7$	$6.8 \times 10^7$
PF-8#2	18 Dec 79	4 Oct 83	14.3	$2.9 \times 10^7$	$1.1 \times 10^7$	$4.0 \times 10^7$
PF-20	13 March 80	11 Oct 83	14.3	$2.7 \times 10^7$	$1.0 \times 10^7$	$3.7 \times 10^7$
PF-8#1	18 Dec 79	10 Oct 85	20.0	$7.6 \times 10^7$	$2.9 \times 10^7$	$10.6 \times 10^7$
PF-8#2	18 Dec 79	10 Oct 85	10.0	$4.7 \times 10^7$	$1.8 \times 10^7$	$6.6 \times 10^7$
PF-8#3	18 Dec 79	10 Oct 85	21.3	$7.9 \times 10^7$	$3.1 \times 10^7$	$11.0 \times 10^7$
PF-20	13 March 80	14 Oct 85	10.0	$4.7 \times 10^7$	$1.7 \times 10^7$	$6.4 \times 10^7$

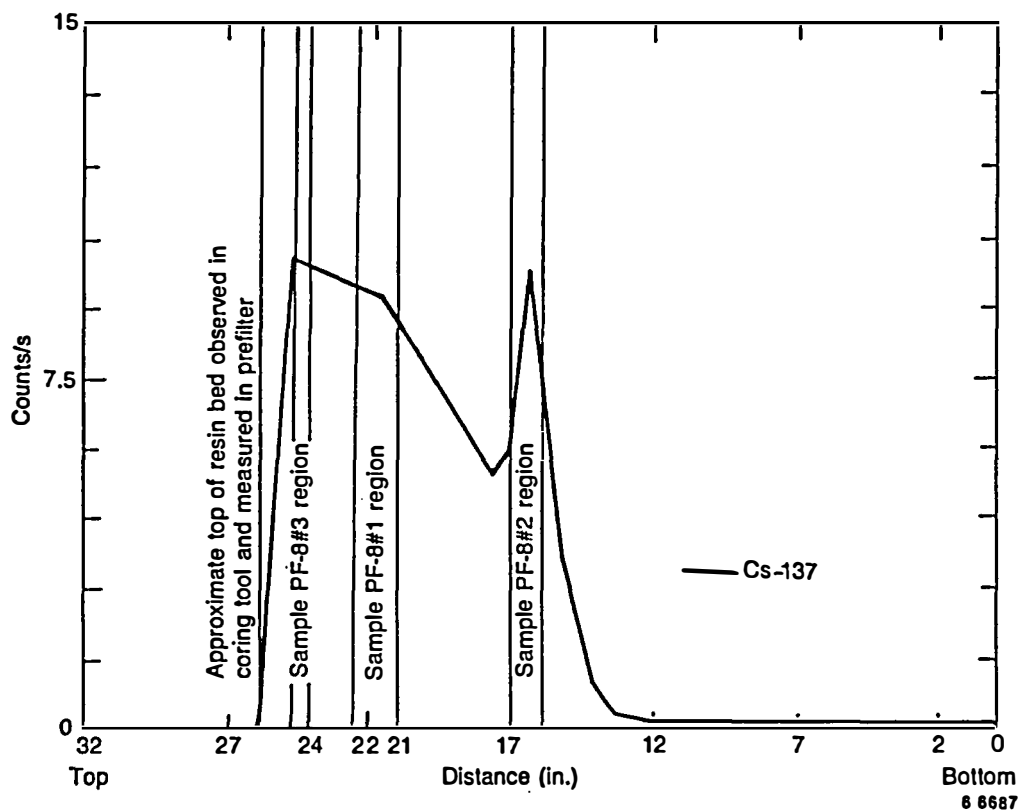


Figure 4. Results of isotopic spectral measurements of the resin core from EPICOR-II prefilter PF-20 at an elevation of 29.25 in. (location of highest radioactivity).

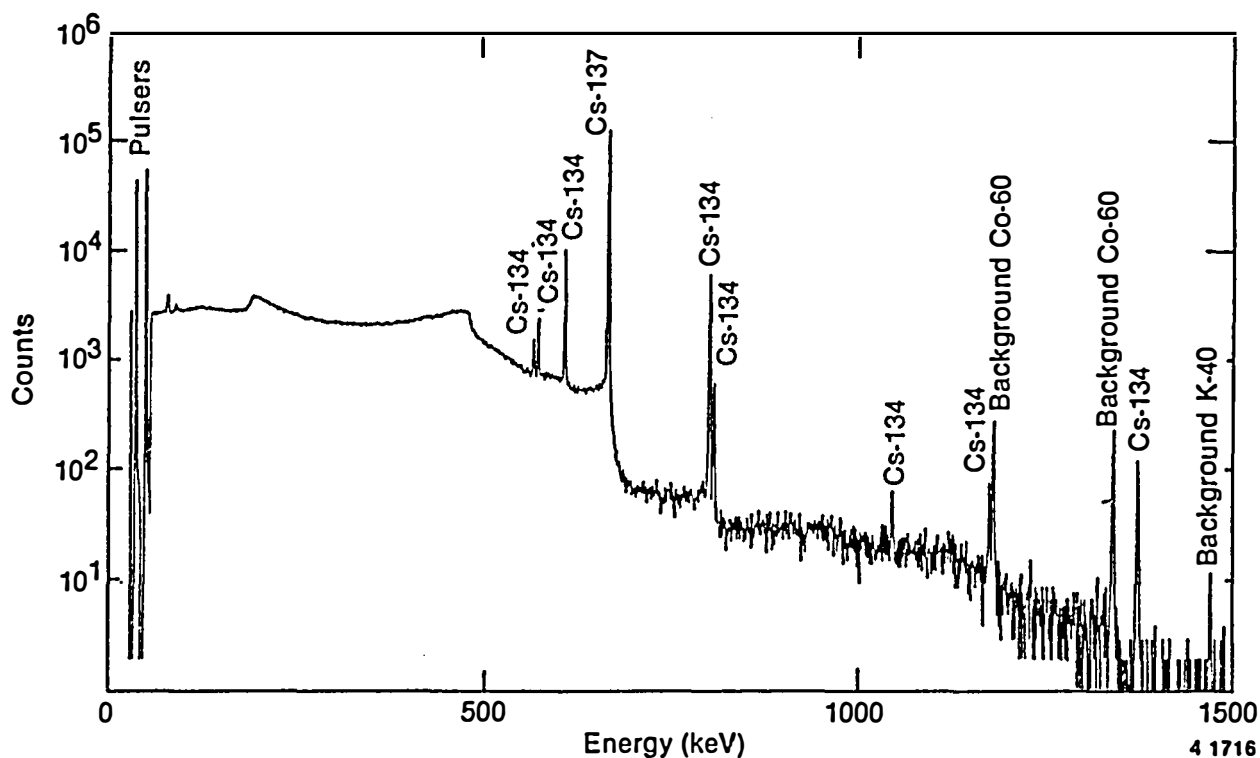


Figure 5. Isotopic (Cs-137) gamma-scan over the length of the resin core from EPICOR-II prefilter PF-8, showing locations where the resin samples were removed.



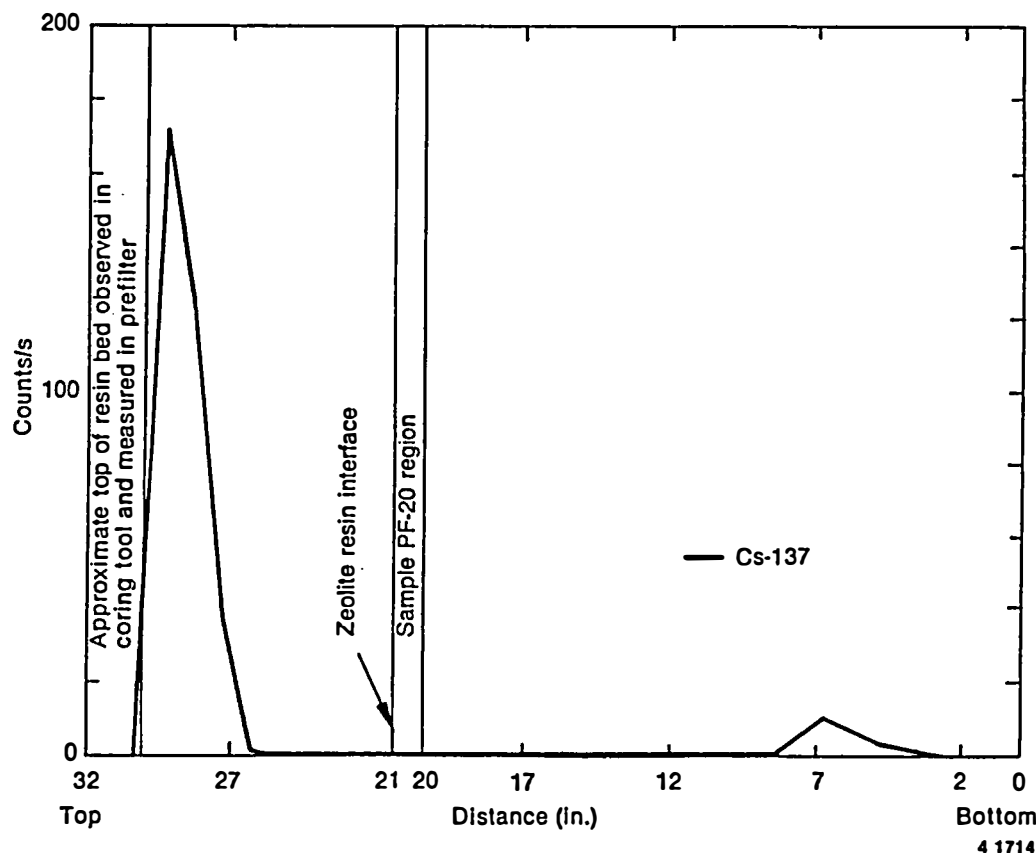


Figure 6. Isotopic (Cs-137) gamma-scan over the length of the resin core from EPICOR-II prefilter PF-20, showing locations where the resin samples were removed.

loading (near the bottom of the core), but rather the sample was removed from the resin adjacent to the zeolite. In that prefilter, the zeolite contained by far the highest concentration of radionuclides and thus produced an integrated dose much higher than that seen at the bottom of the resin core (see Figure 3). Because zeolites have not been used in routine ion exchange service at commercial nuclear power plants, the scope of this study has been limited to the degradation of organic ion exchange resins; therefore, only organic resin samples were removed from the cores.

## Sampling

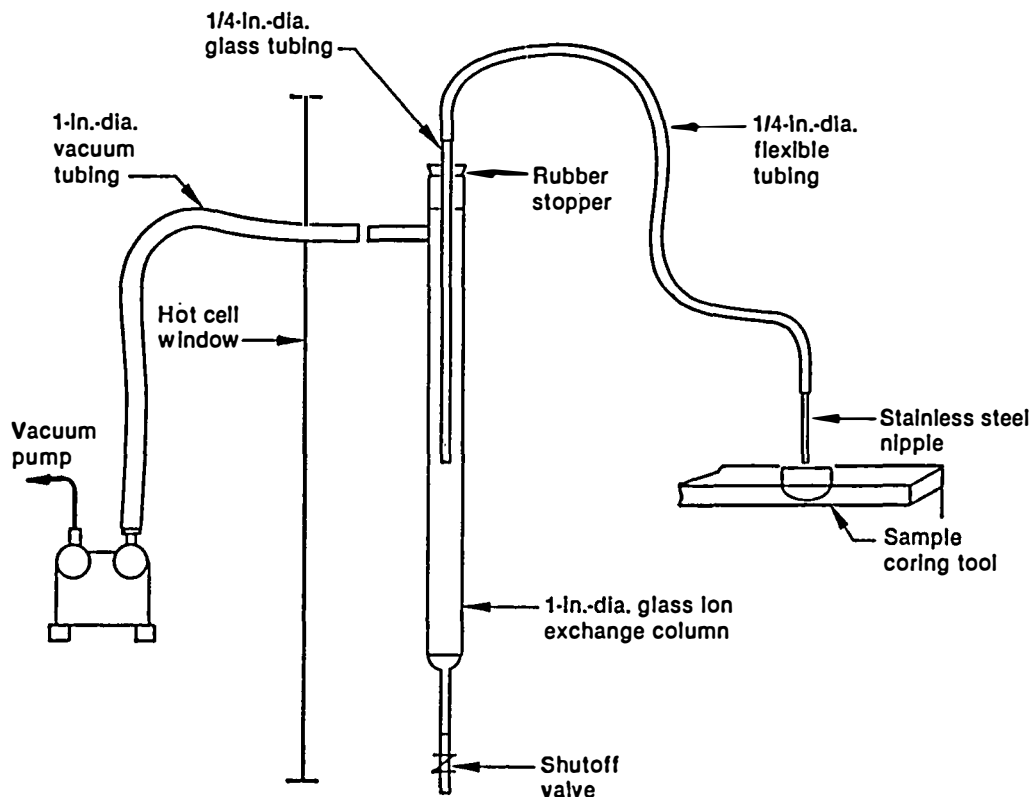
At TRA, each resin-filled coring tool was transferred from its cask into the hot cell for remote removal of resin samples. The shutter of the coring tool was withdrawn to expose the ion exchange media (resin). The cores of PF-8 and -20 (with shutters removed) are pictured in Figure 7. Composite figures of the cores showing ion exchange media layers were shown in Reference 3. [It should be

noted that some smearing of material from one layer into another occurred when the shutter was inserted and withdrawn. That smearing required careful removal of the mixed surface material to expose unmixed resin near the center of the core, for the unmixed material was the target for collection.]

The resin samples were obtained from the cores using a vacuum pump and water-filled, graduated glass column (Figure 8). One end of a flexible rubber tube was attached near the top of the glass column, and the other end was connected to a vacuum pump outside the hot cell. A segment of rubber tubing was attached from the top of the glass column to a stainless steel tube to form a wand (see Figure 8). With the vacuum pump operating, the wand was positioned with a master-slave manipulator over the target resin in such a way that the resin was drawn into the wand, thence into the water-filled column. Sample sizes of 100 mL were collected. Three samples were collected from the PF-8 core, two styrene cation resin (PF-8#1 and PF-8#3) and one phenolic cation resin (PF-8#2). A



Figure 7. Photograph of resin cores with shutters removed from EPICOR-II prefilters PF-20 (upper sample) and PF-8 (lower sample).



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Figure 8. Schematic of apparatus used to collect resin samples from the coring tools.

sample of styrene cation resin was collected from PF-20. No anion resin sample was collected from either core because of the much lower radionuclide content of the anion exchange resin and accompanying low radiation dose (resulting in much less degradation than in the cation exchange resins). However, consideration will be given to the possibility of examining anion resin in the future as accumulated dose increases.

## Sample Preparation

The radiation levels in the PF-8 and -20 samples were of such intensity that work performed on those resins would have had to have been done within a hot cell environment. That type of environment would have made the characterization and analysis of the resin samples very costly and time consuming. It had been shown by tests performed at INEL on unirradiated resins that an Epicor, Inc., resin could be stripped of 99% of its cations using a 10% hydrochloric acid solution.<sup>10</sup> Based on that information, the radionuclides (cations) were

eluted from the PF-8 and -20 resin samples. [This technique is based on normal resin industry regeneration procedures and will not contribute to degradation of the ion exchange resins.]

Samples were removed from the coring tools, drawn into a 1-in.-dia. by 18-in.-high ion exchange column filled with distilled water (see Figure 8), and allowed to stand 24 h in the water-filled column. The ion exchange column then was reconfigured, as shown in Figure 9. The distilled water soak was removed through the shutoff valve at the bottom of the column and retained for gas chromatographic (GC) analysis. [GC was used for determining the presence of any soluble organic resin degradation products.] The distilled water soak was analyzed for the presence of any functional group components, such as sulfonic acid, which had been dissociated from the resin. All resin samples were rinsed two times with distilled water which was added by the pump through the tubing at the top of the column. The distilled water rinse also was saved for GC analysis and functional group tests.

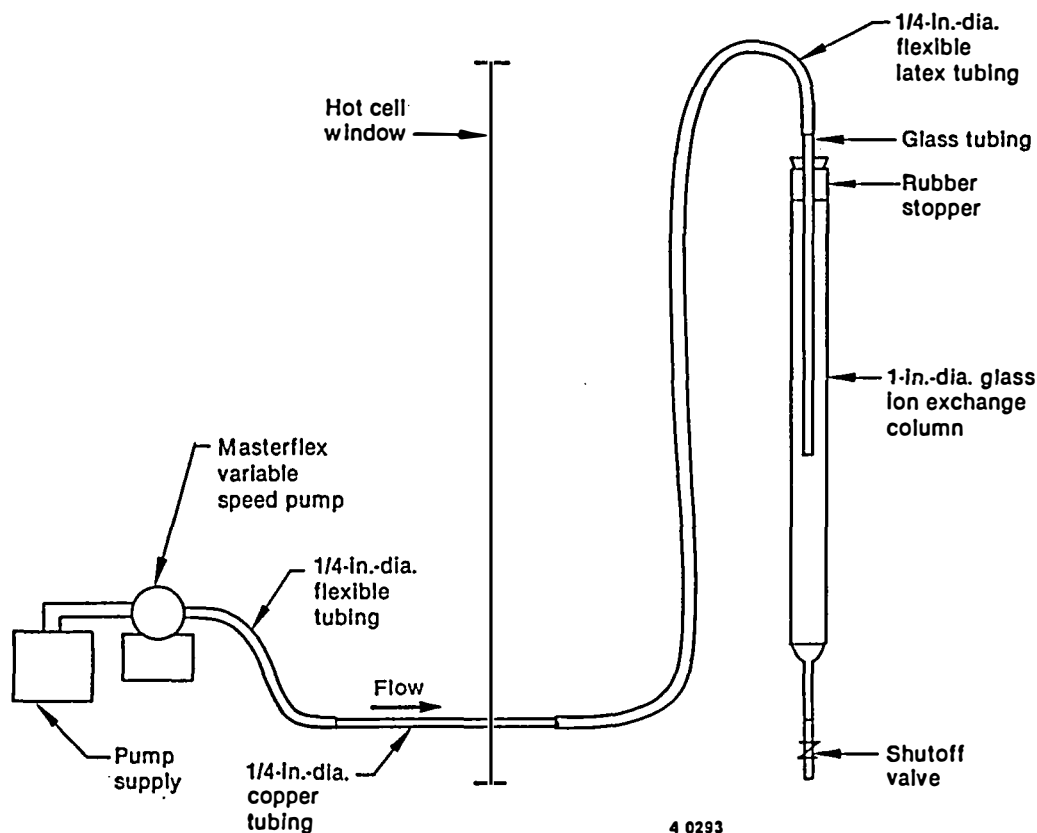


Figure 9. Schematic of apparatus used to elute radionuclides from the resin samples.

A solution of 10% hydrochloric acid was pumped through each resin sample at a rate of 100 mL/min, using the configuration shown in Figure 9. That procedure continued until 55 sample volumes (the amount determined to remove 99% of the cations) or 5.5 L of acid were pumped through the resins. Representative quantities of that acid rinse were collected for later GC and functional group analyses.

The distilled water soak, distilled water rinse, and hydrochloric acid rinse reduced the radionuclide content of the resins and made it possible to remove the samples from the hot cell and perform the analyses in a Type II fume hood equipped with a high-efficiency particulate air filter on the outlet duct.

Each of the liquid samples was monitored for radioactivity upon removal from the hot cell. Those measurements were used to maintain radiological control and also as an indication of resin degradation.

## Characterization of Unirradiated and Irradiated Resins

Several analytical methods are needed to characterize a specific ion exchange resin. Those methods include the following:

- ASTM Procedures for the Physical and Chemical Properties of Particulate Ion Exchange Resins<sup>11</sup>
- Infrared spectroscopy
- Gas chromatography
- Liquid chromatography
- Barium chloride precipitation for determination of sulfonic acid groups

- Scanning electron microscopy.

All of the above analytical methods were used to characterize the samples from PF-8 (strong acid cations and phenolic cation) and PF-20 (strong acid cation) and unirradiated Epicor, Inc., resins (strong acid cation and phenolic cation).

**ASTM Tests.** ASTM procedures were used to determine the chemical and physical conditions of the ion exchange resins. Results from analysis of irradiated resins (from both the first and second sampling) were compared with results from unirradiated resins to determine if degradation had occurred. The following ASTM tests<sup>a</sup> were used for the strong acid cation and phenolic cation exchange resins:

- Pretreatment (ASTM D2187-77 Method A)
- Water retention capacity (ASTM D2187-77 Method B)
- Backwashed and settled density (ASTM D2187-77 Method C)
- Salt splitting capacity (ASTM D2187-77 Method E)
- Total exchange capacity (ASTM D2187-77 Method F)

**Pretreatment.** The pretreatment phase of the ASTM procedure was used to convert ion exchange resins to one standard form (usually the sodium form for cation resins). The standard form provides a baseline from which the other ASTM tests can be performed. An ion exchange column apparatus (Figure 10) was set up, and the resin sample added to the column. The resin was backwashed with distilled water to remove any extraneous particles. The resin was rinsed with a 10% hydrochloric acid solution to remove any existing cations, converting the resin to the hydrogen form. From the hydrogen form, the resin was converted to the sodium form by rinsing with a solution of 100 g of sodium chlo-

ride per liter of distilled water at a rate of 31 mL/min for 1 h. The resin was then in a standard form for analysis.

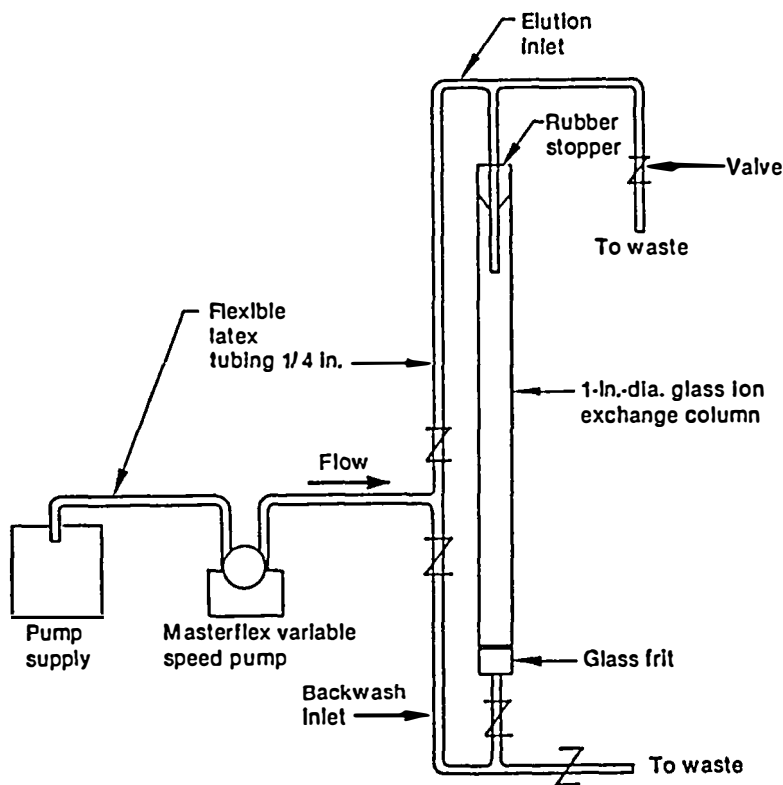
**Water Retention Capacity.** Testing of ion exchange resins for water retention capacity indicates the porosity of the resin. The porosity of a resin is dependent on the amount of effective cross-linking. The higher the water retention capacity, the lower the effective cross-linking. In the case of the PF-8 and -20 resins, the water retention capacity is an indication of the amount of divinylbenzene cross-linking. That relationship cannot be quantified because of the proprietary nature of the EPICOR-II resins. Some loss of effective cross-linking occurs before the release of radionuclides.<sup>12</sup> The test consisted of drying known amounts of pretreated PF-8 and -20 styrene and phenolic cation resins in an oven at  $110 \pm 5^\circ\text{C}$  for a minimum of  $18 \pm 2$  h. The differences in weights before and after drying were used to calculate the water retention capacity. The test was performed in triplicate, and the average was calculated.

**Backwashed and Settled Density.** The backwashed and settled density test was developed to determine changes in effective cross-linking between new and used resins. The density is directly proportional to the amount of effective cross-linking in the resin. As previously noted, some loss of effective cross-linking occurs before radionuclides are released (Reference 12). The test consisted of backwashing a known amount of resin with distilled water for 10 min. The resin was allowed to settle, and the volume was recorded. Then, the density was calculated based on a known weight of resin in grams to a known volume of water in milliliters. The test was performed in triplicate, and the average was calculated.

**Salt Splitting Capacity.** The salt splitting capacity test is designed to show only the number of sulfonic acid groups contained in a cation ion exchange resin. A decrease in salt splitting capacity would show a loss of functional sulfonic acid groups. The loss of sulfonic acid groups would allow the release of those radionuclides tied to those functional groups. Phenolic, carboxylic acid, and phosphonic acid functional groups also will exhibit, to some degree, salt splitting capacity. The test assembly apparatus is depicted in Figure 11. The resin was converted to the hydrogen form by flowing 10% hydrochloric acid solution over the resin at a rate of

a. The tests were performed in accordance with ASTM standards, and deviations are within allowable limits of those standards.





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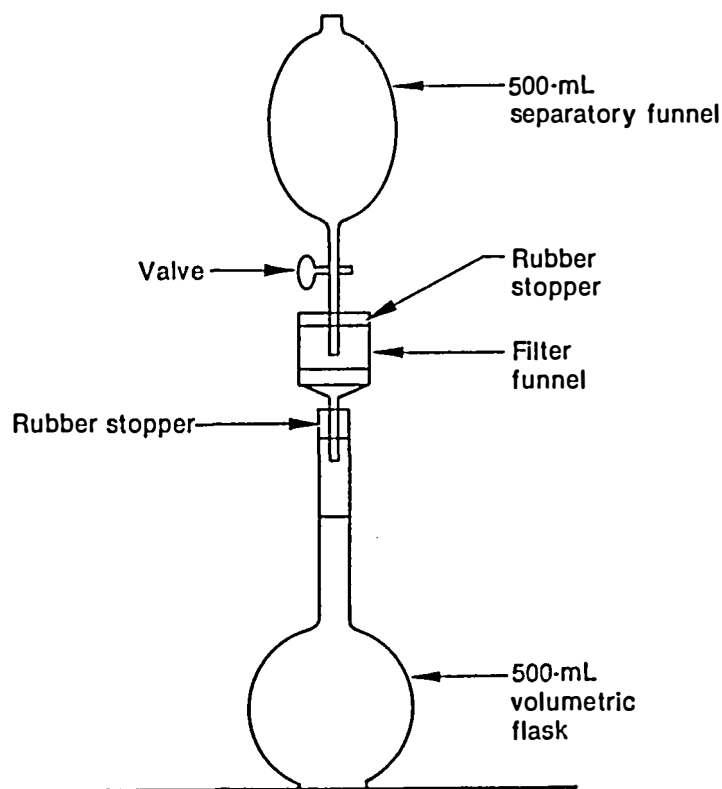
Figure 10. Schematic of standard ASTM apparatus used for pretreatment of resins and backwashed and settled density test.

31 mL/min. The hydrogen form cation resin was eluted with a 50 g/L sodium chloride solution at a rate of 31 mL/min. The eluted sodium chloride solution was titrated with standard 0.10 *N* sodium hydroxide solution to determine the amount of hydrogen exchanged in the elution process. The test was performed in triplicate, and the average was calculated.

**Total Exchange Capacity.** The total exchange capacity test is used to determine exchange capacity of cation ion exchange resins that contain functional groups in addition to, or different from, sulfonic acid functional groups. A decrease in total exchange capacity indicates the loss of functional groups and subsequent loss of radionuclides. Different functional groups include phenolic, carboxylic acid, and phosphonic acid. The apparatus shown in Figure 11 was assembled, and a 10% hydrochloric acid solution was eluted through the resin to convert it to the hydrogen form. The resin was transferred to a separate flask containing 200 mL of standard 0.10 *N* sodium hydroxide solution. The solution also contained 50 g of sodium

chloride per liter. The resin was allowed to equilibrate in the solution for a minimum of 16 h. An aliquot of the solution was collected and titrated with standard 0.10 *N* hydrochloric acid solution. The adsorption of hydroxide ion by the resin in the presence of sodium chloride is proportional to the total exchange capacity. The test was performed in triplicate, and the average was calculated.

**Infrared Spectroscopy.** Infrared spectroscopy involves identifying the rotational and vibrational motion of atoms in a molecule induced by infrared radiation. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum. The spectrum is uniquely characteristic of the functional groups comprising the molecules and the overall configuration of the atoms within the molecule. Infrared spectroscopy can therefore be used to positively identify a pure organic molecule. IR was used to determine if the styrene and phenolic cation resins in PF-8 and -20 were the same as the unirradiated styrene cation and phenolic cation resins obtained from Epicor, Inc. IR spectra of the unirradiated Epicor, Inc.,



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Figure 11. Schematic of standard ASTM apparatus for determining salt splitting and total exchange capabilities.

resins were compared with IR spectra from PF-8 and -20 resins to determine if any changes in molecular structure of the PF-8 and -20 resins had occurred because of the high internal radiation dose. [Changes can be seen by a shift in peak location or a major decrease in intensity.] A change in molecular structure would indicate scission of the polymer backbone and eventual release of radionuclides.

The resin samples were dried at a temperature of 110°C to remove excess moisture and ground in a porcelain mortar and pestle to a size of less than 80 mesh. Then, 10 mg of the resin were added to 100 mg of dried potassium bromide (KBr) and placed in a pellet press. A compressive force was applied to the pellet press, and a pellet containing the resin was obtained for IR scanning. The KBr pellet was placed into the sample beam of a Perkin Elmer Model 1430 infrared spectrophotometer, and an IR spectrum was obtained.

**Gas Chromatography.** Gas chromatography is the technique by which a liquid sample is vaporized and separated into components by means of a GC

column containing a mobile phase and a stationary phase. In the case of the EPICOR-II resin samples, a 1/8-in.-O.D. by 6-ft-long GC column containing 0.34% tetranitrofluorenone as the mobile phase and Carbowax C as the stationary phase was chosen for the GC analysis. In addition, a column containing 1.0% SP-1240DA as the mobile phase and Supelcoport as the stationary phase was also used.

The aliquots chosen for GC analysis were the distilled water soak and rinse solutions from the resin samples. All solutions from resin samples were prepared for analysis using Environmental Protection Agency Method 612, "Test for Chlorinated Hydrocarbons in Municipal and Industrial Waste Water," as follows:

1. A 100-mL aliquot of the sample solution was placed in a separatory funnel for solvent extraction. The solvent chosen for extraction was dichloromethane. Styrene and divinylbenzene are soluble in dichloromethane and not in distilled water; therefore, any styrene or divinylbenzene in the aliquot will be extracted into the dichloromethane.

2. 20 mL of dichloromethane were added to the separatory funnel. The funnel was inverted several times to allow for complete mixing.
3. The aliquot/solvent mixture in the separatory funnel was allowed to stand until the phases separated. The dichloromethane phase was drawn off and placed in an Erlenmeyer flask.
4. The aliquot in the separatory funnel was extracted two more times with 20 mL of dichloromethane each time.
5. The combined dichloromethane extracts were evaporated by means of a Kuderna-Danish Concentrator to a total volume of 10 mL.

The solution then was ready for GC analysis. Any soluble organic products (divinylbenzene, styrene, or other organic fractions) in the original sample would be concentrated in the dichloromethane, indicating polymer breakdown and eventual release of radionuclides.

Five microliters of the dichloromethane extracts were analyzed using a Perkin Elmer Sigma IB Flame Ionization Detector gas chromatograph. Five microliters of the standard divinylbenzene/acetone solution and five microliters of the standard styrene/dichloromethane solution also were analyzed for proper peak identification and confirmation. The GC conditions were as follows:

- Injection temperature = 250°C
- Detector temperature = 300°C
- Oven temperature program = 120°C for 2 min, then increase to 180°C at an 8°C/min rate, then hold at 180°C for 20 min.

**Liquid Chromatography.** High-performance liquid chromatography (HPLC) is the technique by which a liquid is separated into its components by means of liquid solid chromatography, partition chromatography, ion-exchange chromatography, or exclusion chromatography. This study relied on the technique of partition chromatography, an HPLC technique in which the solute is partitioned between two immiscible solvents, one fixed and the other mobile. The fixed phase was a HPLC ODS C-

18 column,<sup>a</sup> and the mobile phase was acetonitrile. Aliquots of the dichloromethane extracts of the soak-and-rinse solutions from PF-8 and -20 were injected into a Kratos HPLC using a UV-VISIBLE Detector, and HPLC chromatograms were obtained.

**Barium Chloride Precipitation for Determination of Sulfonic Acid Groups.** It has been shown that the EPICOR-II cation resins are sulfonic acid, divinylbenzene, styrene type resins (Reference 6). The high internal radiation dose received by those resins could cause loss of the functional groups (sulfonic acid) and release of the radionuclides tied to the lost functional groups. The loss of functional groups would cause an increase in the sulfate concentration of the distilled water soak and rinse solutions taken from the samples of PF-8 and -20 strong acid cation resins.

A 25-mL aliquot was removed from each solution and transferred to a graduated cylinder. Enough barium chloride was added to the solution in the graduated cylinder to ensure an excess amount. The contents of the cylinder were agitated and allowed to stand a minimum of three minutes. A portion of the solution from the graduated cylinder was transferred to a 1-cm (path length) polyethylene sample cell and placed into a visible spectrophotometer set a wavelength of 420 nm. The absorption values of the solution was obtained and compared with adsorption values of standard sulfate solutions. Results of those tests are reported in the "Results and Interpretation" section of this report.

**Scanning Electron Microscopy.** In order to determine the physical conditions of the resin samples from PF-8 and -20, scanning electron microscope (SEM) photomicrographs were obtained of the resins at different magnification levels. The photomicrographs allowed examination of the resins for cracks, bead breakage, bead softening, agglomeration, and so forth. Most types of physical damage of the resins would not allow the release of radionuclides.

The irradiated resin samples from the second sampling of PF-8 and -20 were attached to an SEM planchet by means of double-sided sticky tape. The resins were spattered with gold to make them conductive. SEM photomicrographs were obtained of the resins.

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a. Product distributed by Waters Chromatography.

## RESULTS AND INTERPRETATION

The unirradiated resins showed no apparent change from previous analyses (References 3 and 6). Because of the age (4 years old) of the unirradiated resins, they might be expected to show some degradation due to aging. The irradiated resins from PF-8 and -20 also would be expected to show some degradation due to age (almost 6 years old).<sup>2,12</sup> The unirradiated resins showed no degradation because of age; therefore, in this study, any degradation of the irradiated resins was presumably from radiation damage and not from age.

Other causes of degradation would be handling/mechanical damage and freezing. A review of the history of prefilters PF-8 and -20 shows that the ion exchange media were exposed to subfreezing temperatures while stored at INEL between the first and second samplings. However, examinations using the unirradiated resins to determine freezing damage have shown that none has occurred. Also, handling was held to a minimum; as a result, damage should have been minimal.

During sample preparation, the resins were soaked and then rinsed in distilled water. The soak water from each of the samples was brown in color, indicating the presence of sulfates. Samples PF-8#1, PF-8#3, and PF-20 exhibited restrictions to flow during the initial elution process using distilled water, indicating the onset of degradation. Further indication of degradation is shown by the release of radionuclides to the soak and rinse water, as shown in Table 2. The more highly nuclide loaded samples from PF-8 show significant radioactivity in the soak and rinse waters. That would not have occurred with undegraded resins. Some differences are noted between the first and second sampling measurements; these differences were caused by different elution and measurement techniques.

### ASTM Tests

Table 3 presents results of the following ASTM tests performed on unirradiated and irradiated resins from the second sampling: (a) water retention capacity, (b) backwashed and settled density, (c) salt splitting capacity, and (d) total exchange capacity.

The differences between ASTM tests performed on unirradiated Epicor, Inc., strong acid cation resin and PF-8#1, PF-8#3 and PF-20 strong acid cation resins from the second sampling are presented in Table 4. The differences were calculated

using the measured data shown in Table 3. The results show that the resin samples receiving more radiation dose exhibit greater changes in measured properties. Water retention capacities increased with dose; while backwashed and settled density, salt splitting capacity, and total exchange capacity decreased. (No change was observed for the PF-20 exchange capacity.) Increase in water retention capacity indicates a loss in effective cross-linking, the amount of loss being dependent on radiation dose (Reference 12). A decrease in backwash and settled density also is an indirect indication of loss of effective cross-linking, which can lead to eventual loss of radionuclides (Reference 6). The decrease in salt splitting capacity of the irradiated resins is an indication of loss of functional groups, sulfonic acid, and accompanying loss of radionuclides (Reference 6). The lack of difference between the PF-20 total exchange capacity for the second sampling and the unirradiated value, however, is a decrease from the value found during the analysis of the first samples. [It was found in the research of Reference 2 that oxidation of the polymer chain will cause an initial increase in total exchange capacity followed by a decrease as the radiation damage exceeds that contribution]. This would indicate that PF-20 has reached the threshold needed for degradation to begin.<sup>2,12</sup> Furthermore, the higher radiation dose to the PF-8#1 and PF-8#3 resins explains the decrease in total exchange capacity as the radiation damage exceeds the contribution from oxidation (Reference 2). The decrease in total exchange capacity may result in a loss of radionuclides.

Table 5 shows the differences between ASTM test parameters for the PF-8 phenolic cation resin from the second sampling and the Epicor, Inc., unirradiated phenolic cation resin. The differences between the PF-8 phenolic cation resin and the unirradiated phenolic cation resin are increasing, similar to the changes observed in the strong acid cation resins. The results (shown in Tables 3 and 5) for the PF-8#2 phenolic cation resin show an increase in water retention capacity and a decrease in backwashed and settled density, indicating a loss in effective cross-linking which will lead to the eventual loss of radionuclides. However, the increase in salt splitting capacity indicates oxidation of the polymer (formation of carboxylic acid

**Table 2. Radioactivity of resin soak, rinse, and acid composite samples**

Sample	First Sampling Measurement at Contact (mR)	Second Sampling Measurement at Contact (mR)
PF-8#3—24-h soak <sup>a</sup>	No resin sample	50
PF-8#3—Rinse <sup>b</sup>	No resin sample	30
PF-8#3—Acid composite <sup>c</sup>	No resin sample	500
PF-8#1—24-h soak <sup>a</sup>	100 <sup>d</sup>	40
PF-8#1—Rinse <sup>b</sup>	35 <sup>d</sup>	30
PF-8#1—Acid composite <sup>c</sup>	800 <sup>d</sup>	500
PF-8#2—24-h soak <sup>a</sup>	45	5
PF-8#2—Rinse <sup>b</sup>	100	6
PF-8#2—Acid composite <sup>c</sup>	80	35
PF-20—24-h soak <sup>a</sup>	2 <sup>d</sup>	25
PF-20—Rinse <sup>b</sup>	No sample	15
PF-20—Acid composite <sup>c</sup>	80 <sup>d</sup>	35

a. 24-h soak used a total of 100 mL demineralized water. All 100 mL were counted.

b. Rinse used a total of 100 mL demineralized water. All 100 mL were counted.

c. Acid composite used a total of 5 L of 10 percent hydrochloric acid. 200 mL were counted in the first sampling, and 500 mL were counted in the second sampling.

d. The resin sample was agitated to promote flow of liquid through the sample.

**Table 3. Results of ASTM tests on irradiated resins from the second sampling and unirradiated ion exchange resins**

ASTM Test Parameter	Resin Sample					
	PF-8#1 Strong Acid Cation	PF-8#3 Strong Acid Cation	PF-20 Strong Acid Cation	PF-8#2 Phenolic Cation	Unirradiated Strong Acid Cation	Unirradiated Phenolic Cation Resin
Water retention capacity (%)	54.50 ± 0.22	56.70 ± 0.23	52.00 ± 0.21	56.50 ± 0.22	48.40 ± 0.19	52.06 ± 0.21
Backwashed and settled density (g/mL)	0.73 ± 0.004	0.68 ± 0.004	0.76 ± 0.004	0.62 ± 0.003	0.84 ± 0.004	0.64 ± 0.003
Salt splitting capacity (meq/g <sup>a</sup> )	5.01 ± 0.08	4.91 ± 0.08	5.25 ± 0.08	3.81 ± 0.08	5.28 ± 0.080	3.09 ± 0.080
Total exchange capacity (meq/g <sup>a</sup> )	5.33 ± 0.05	5.50 ± 0.05	5.58 ± 0.06	6.38 ± 0.070	5.60 ± 0.060	6.78 ± 0.07

a. Measured in milliequivalents per gram of dry resin.

**Table 4. ASTM test parameter changes of PF-8 and -20 strong acid cation resins (second sampling) versus unirradiated Epicor, Inc., strong acid cation resin**

ASTM Test Parameter	Resin Sample		
	PF-8#1	PF-8#3	PF-20
Water retention capacity	13% increase	17% increase	7% increase
Backwashed and settled density	13% decrease	19% decrease	10% decrease
Salt-splitting capacity	5% decrease	7% decrease	1% decrease
Total exchange capacity	5% decrease	2% decrease	No change

groups), which reduces the tendency to release radionuclides by increasing exchange capacity (Reference 6). The total exchange capacity of the PF-8#2 phenolic cation resin has decreased (Table 5), indicating that PF-8#2 has reached and passed the threshold limit where degradation begins and the loss of effective cross-linking has overcome the polymer oxidation.<sup>2,12</sup>

## Infrared Spectroscopy

The IR scans of the unirradiated and irradiated resins from PF-8 and -20 were presented in Reference 3. The IR scans from the second sampling of the PF-8 and -20 resins (Figures 12, 13, 14 and 15) are identical to the IR scans of Reference 3, indicating that any changes in polymer structures observed with other techniques have not altered the

**Table 5. ASTM test parameter changes of PF-8 phenolic cation resin (second sampling) versus unirradiated Epicor, Inc., phenolic cation resin**

ASTM Test Parameter	PF-8#2
Water retention capacity	9% increase
Backwashed and settled density	3% decrease
Salt splitting capacity	23% increase
Total change capacity	6% decrease

IR scans of the resins between the first and second sampling. Figures 12, 13, and 14 show a comparison between the PF-8 and PF-20 strong acid cation resin and the Epicor unirradiated strong acid cation resin. Figure 15 is a comparison between the phenolic cation resin from PF-8 and the unirradiated phenolic cation resin obtained from Epicor, Inc.

## Gas Chromatography

Characteristic gas chromatograms were presented in Reference 3. The dichloromethane extracts from the second sampling of PF-8 and -20 run on the 0.34% tetranitrofluorenone/Carbopack C column were identical to those in Reference 3. For comparison, the chromatograms from the second sampling 24-h soak samples from PF-8#1, #2, #3, and PF-20 (Figures 16, 17, 18 and 19) are presented.

It was determined through further study (Reference 13) that other soluble products, i.e., benzoic acid, might be present. Gas chromatography was performed on the extracts using a column (1% SP-1240DA/ Supelcoport) specific to other possible components. The results of that analysis also showed no soluble organic products in the dichloromethane extracts of the 24-h soak and rinse solutions and are therefore not shown here.

## Liquid Chromatography

Twenty microliters of a standard containing 10  $\mu$ L of styrene and 10  $\mu$ L of divinylbenzene were injected into the Kratos HPLC. The results of this

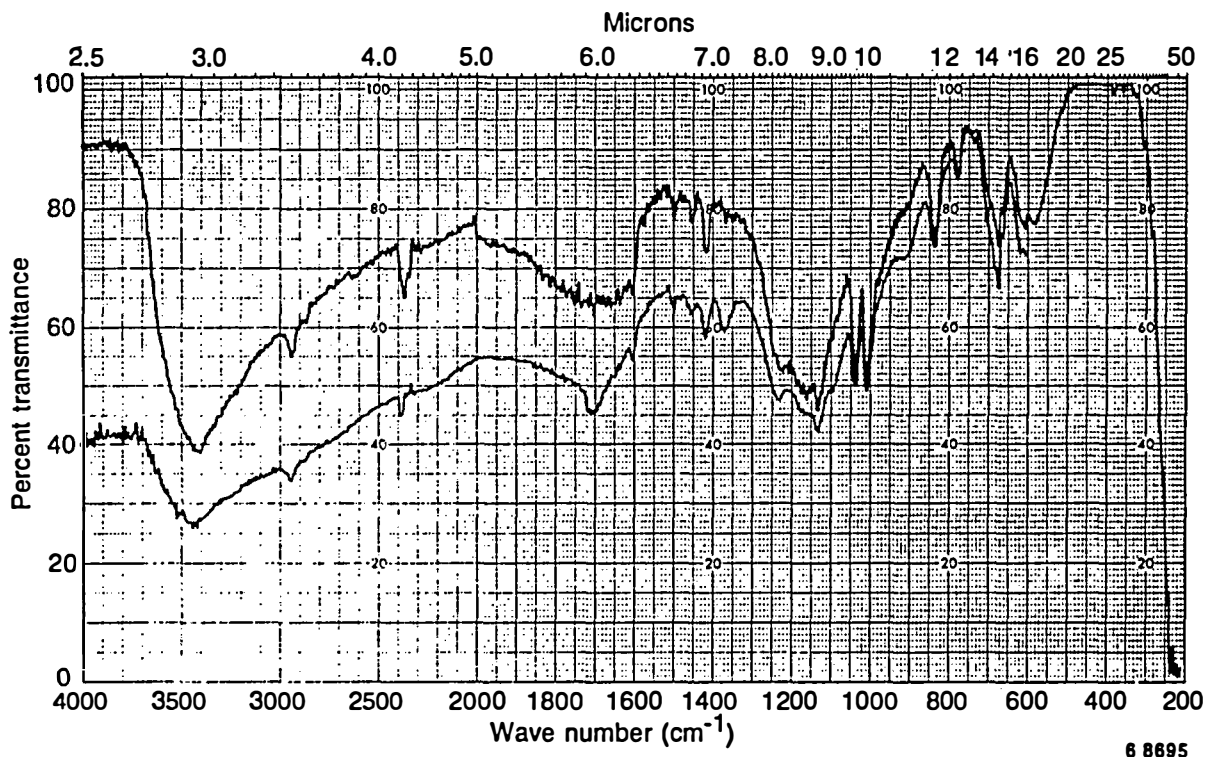


Figure 12. Comparison of Epicor unirradiated strong acid cation resin (top spectrum) with that of the strong acid cation resin from PF-20 (bottom spectrum).

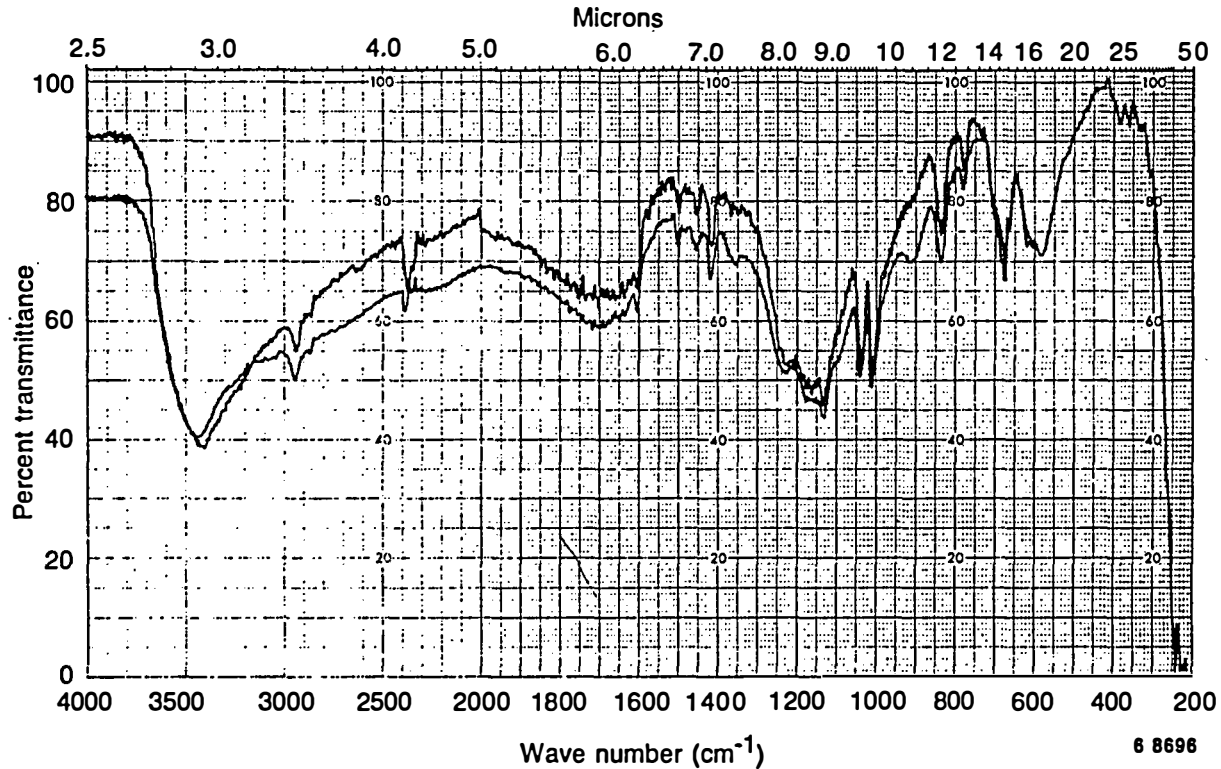


Figure 13. Comparison of Epicor unirradiated strong acid cation resin (top spectrum) with that of the strong acid cation resin from PF-8#1 (bottom spectrum).



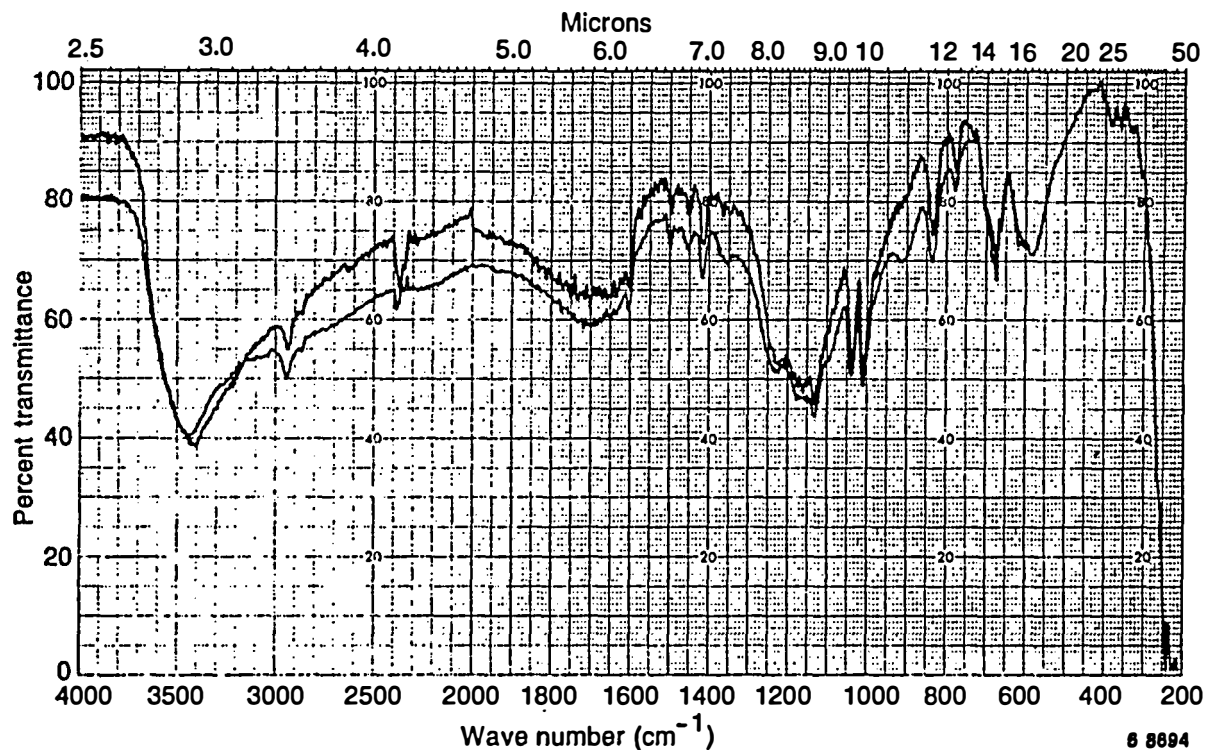


Figure 14. Comparison of Epicor unirradiated strong acid cation resin (top spectrum) with that of the strong acid cation resin from PF-8#3 (bottom spectrum).

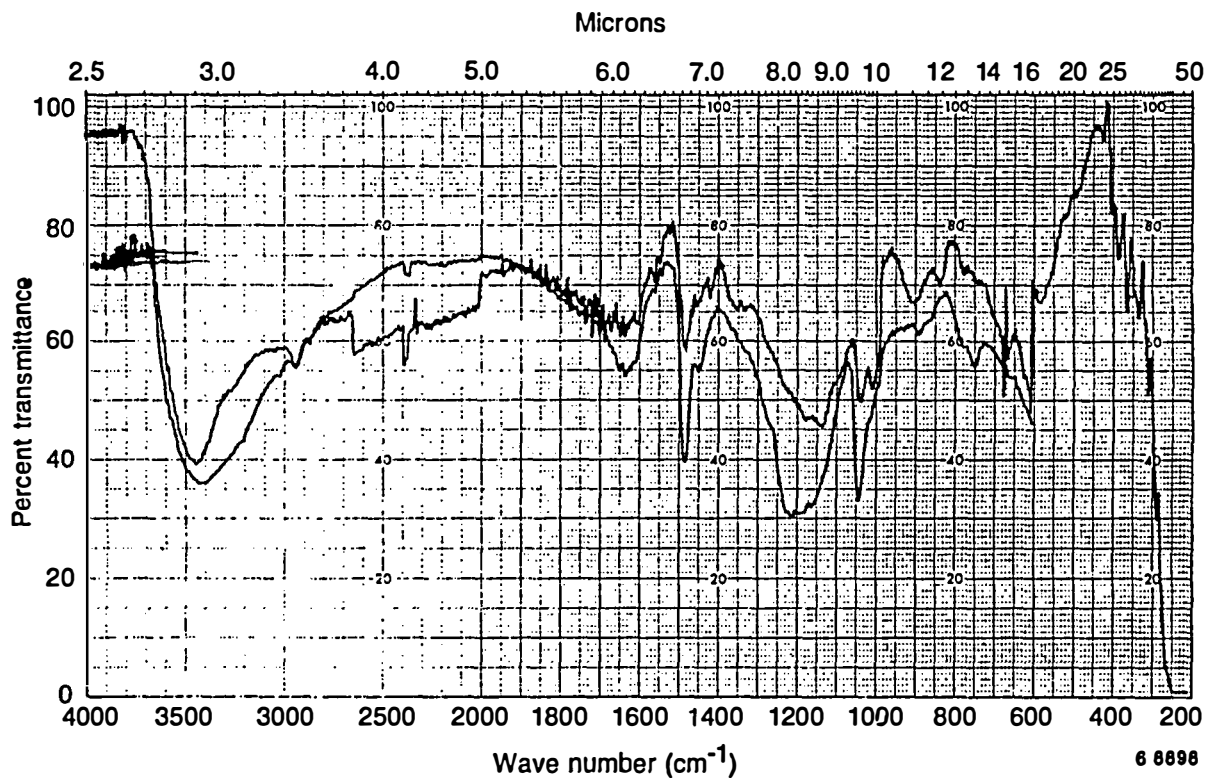


Figure 15. Comparison of Epicor unirradiated phenolic cation resin (top spectrum) with that of the phenolic cation resin from PF-8#2 (bottom spectrum).

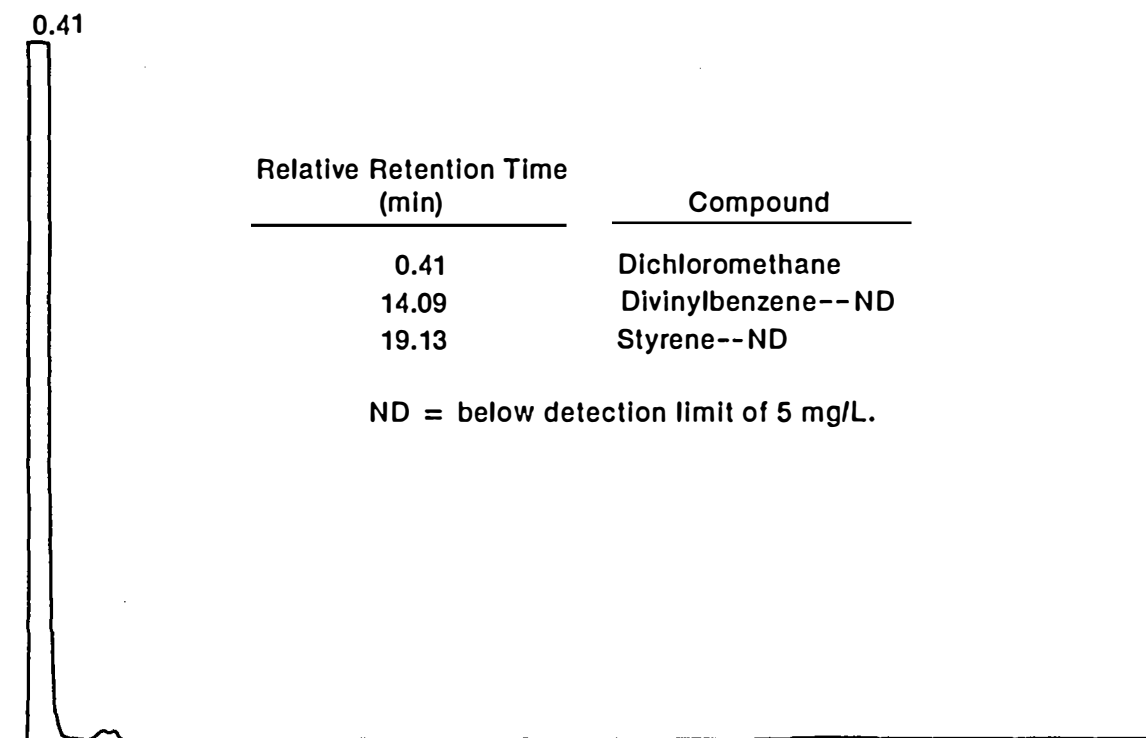


Figure 16. Chromatogram of 24-h distilled water soak solution from PF-8#1 strong acid cation resin sample.

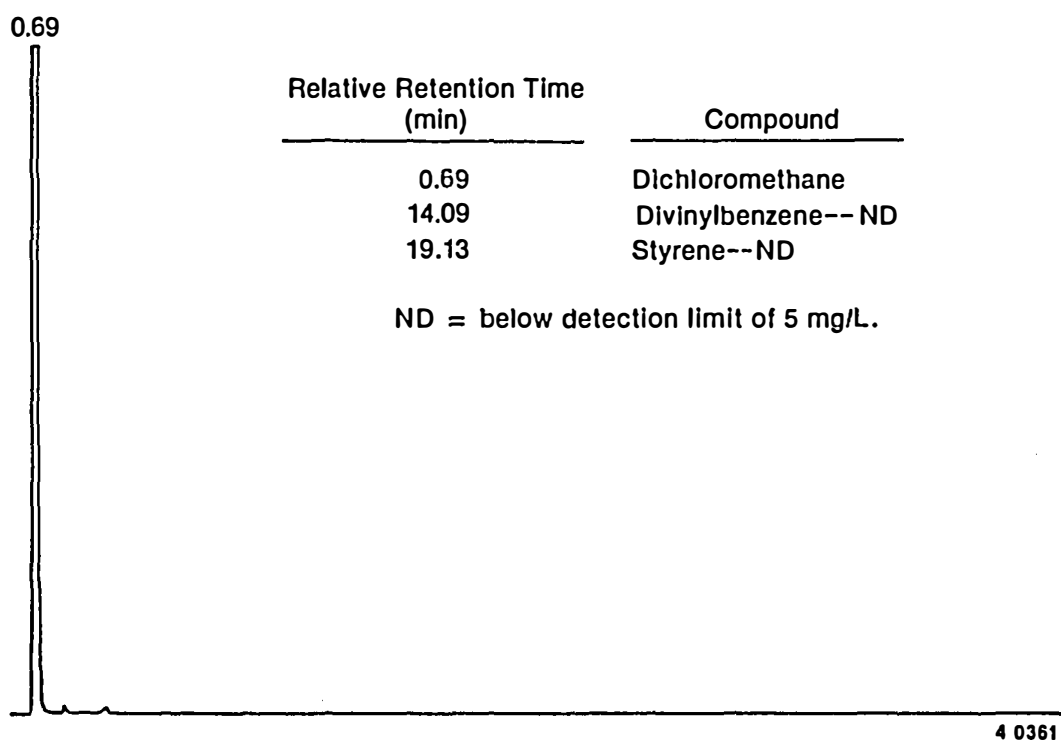


Figure 17. Chromatogram of 24-h distilled water soak solution from PF-8#2 phenolic cation resin sample.

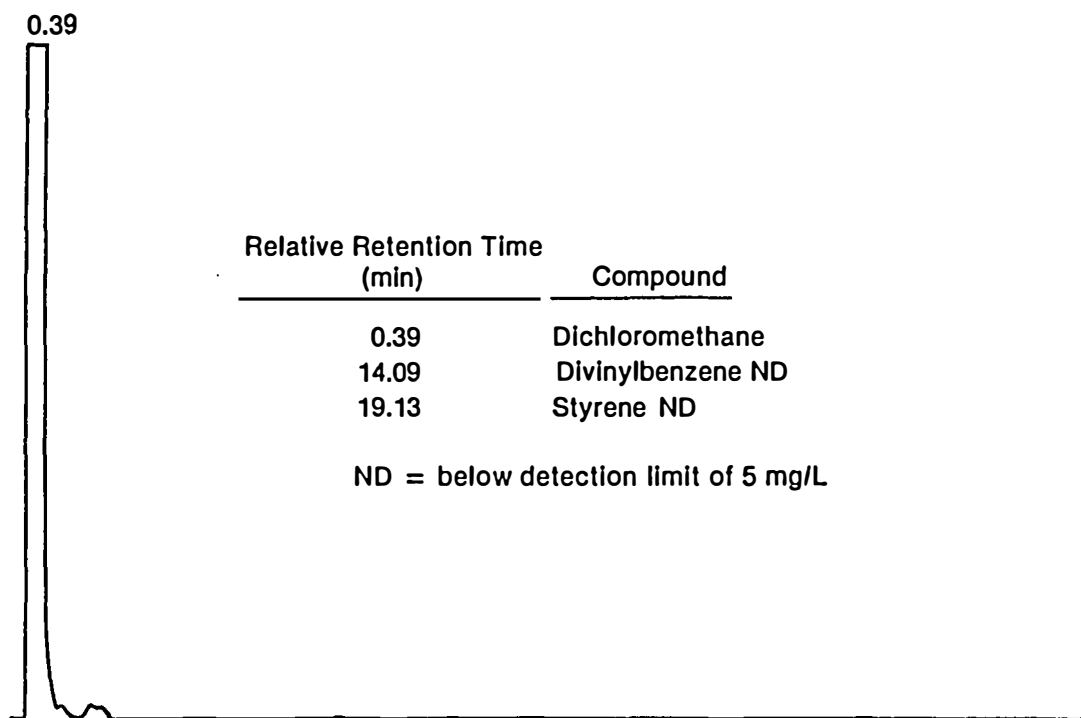


Figure 18. Chromatogram of 24-h distilled water soak solution from PF-8#3 strong acid cation resin sample.

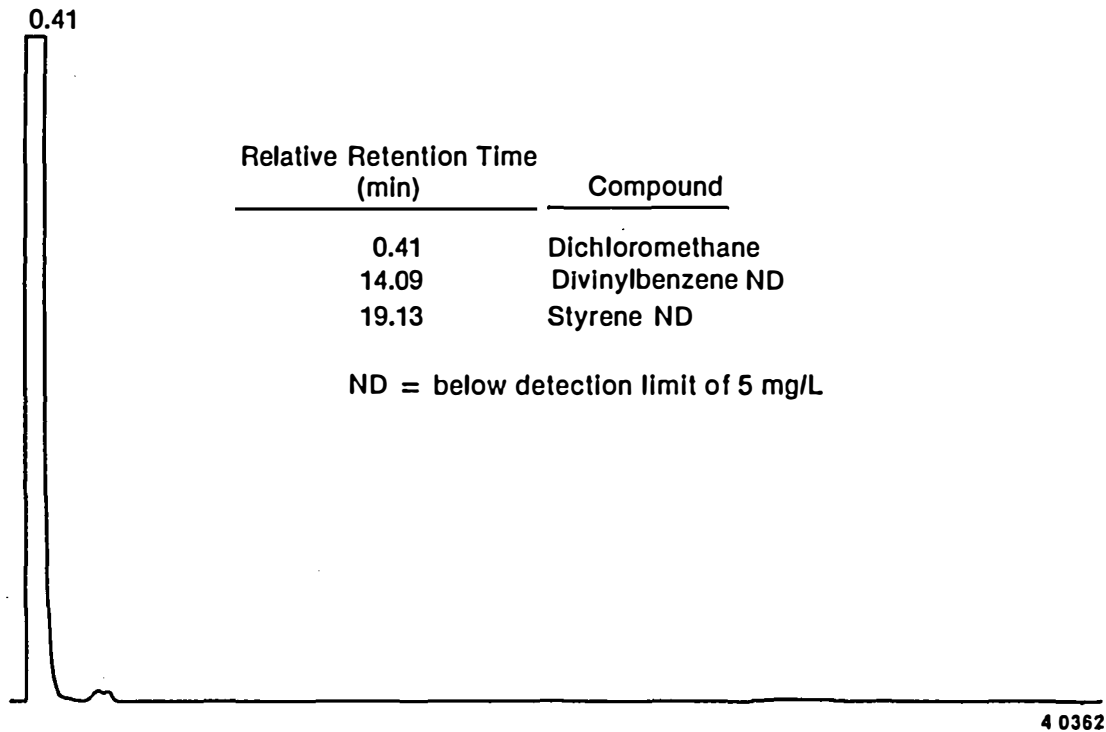


Figure 19. Chromatogram of 24-h distilled water soak solution from PF-20 strong acid cation resin sample.

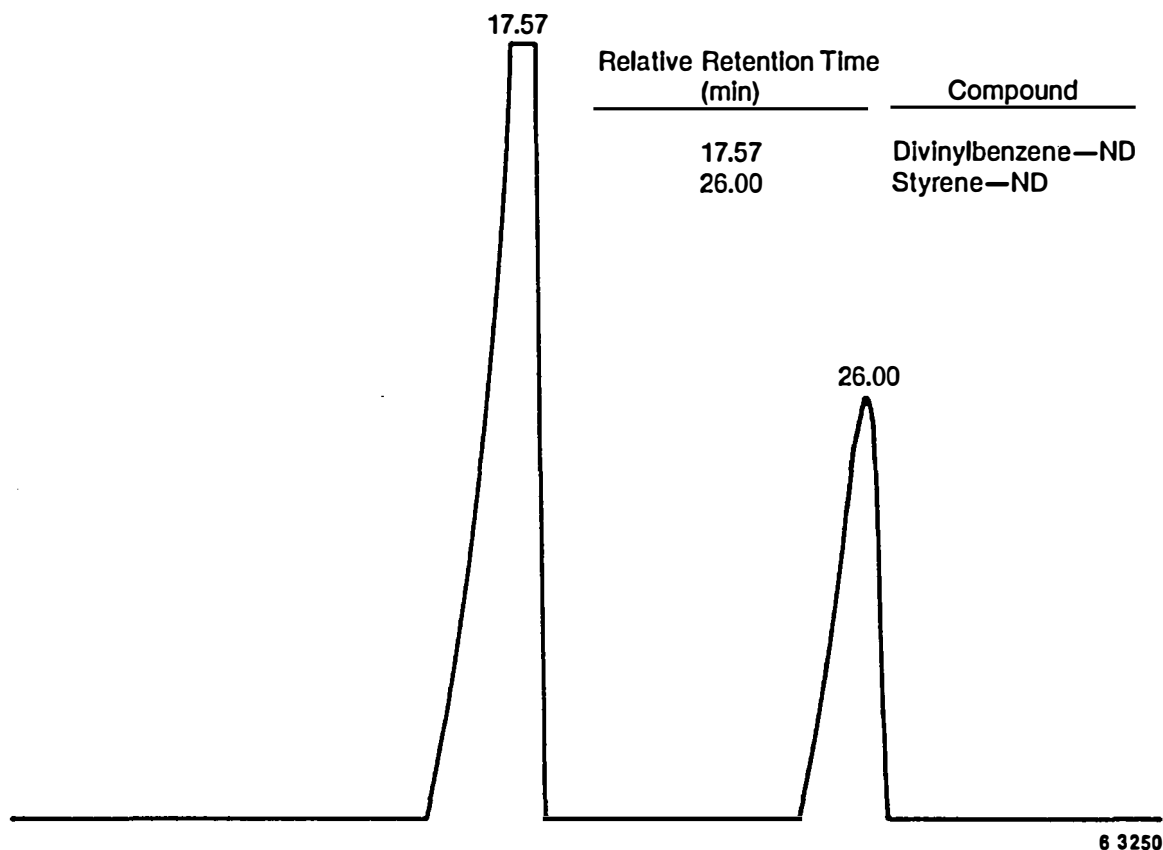


Figure 20. HPLC chromatogram of 10  $\mu$ L of styrene and 10  $\mu$ L of divinylbenzene in 20 mL of dichloromethane.

HPLC chromatogram are presented in Figure 20. Twenty microliters of the dichloromethane extracts of the distilled water 24-h soak samples from PF-8#1, PF-8#2, PF-8#3, and PF-20 strong acid cation resins were also analyzed as separate samples in the Kratos HPLC. These resulting chromatograms showed that any soluble organic products in the 24-h soak samples were below the detectable levels of the HPLC (0.05 mg/L for both styrene and divinylbenzene). The HPLC chromatogram from the PF8#3 sample is presented as Figure 21. This chromatogram is typical of all samples and shows no styrene or divinylbenzene.

### Barium Chloride Precipitation for Determination of Sulfonic Acid Groups

Results of the barium chloride precipitation tests from the second sampling are shown in Table 6. The results show large sulfate concentrations in the PF-8#1, PF-8#3, and PF-20 cation resin distilled water soak solutions. Those large concentrations indicate a loss of functional groups, with subse-

quent loss of radionuclides attached to those groups. The bond energies of the carbon-sulfur bonds are lower than energies of the carbon-carbon bonds within the polymer (66 kcal/mol versus 84 kcal/mol).<sup>14</sup> High-energy radiation, such as that received by the EPICOR-II resins, would damage the weaker bonds of the resin first. This can be seen by the high sulfate concentrations and the low pH values (<3) of the distilled water soak and rinse solutions from the strong acid cation resin samples. As the accumulated dose becomes high enough, the high-energy carbon-carbon bonds will also be broken; however, that point has not been reached.

The phenolic resins contain no sulfonic acid groups; therefore, the distilled water soak samples showed no sulfate (Reference 6).

### Scanning Electron Microscopy

The SEM photomicrograph of the unirradiated strong acid cation resin from Epicor, Inc., is presented in Figure 22. Figures 23 and 24 are photomicrographs of strong acid cation resin from the second sampling of

Relative Retention Time (min)	Compound
17.57	Divinylbenzene
26.00	Styrene

ND = below detection limit of .05 mg/L

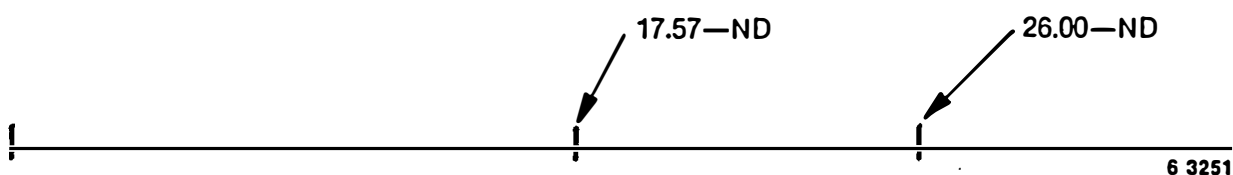


Figure 21. HPLC chromatogram of distilled water 24-h soak solution from PF-8#3 strong acid cation resin.

**Table 6. Results of barium chloride precipitation tests (from the second sampling) for determining sulfonic acid groups**

Sample Solution	Sulfate Concentration (mg/L)	pH
DI water <sup>a</sup>	ND <sup>b</sup>	—
PF-8#1 DI water, 24-h soak	3400	1.8
PF-8#3 DI water, 24-h soak	460	2.0
PF-20 DI water, 24-h soak	200	2.2
Unirradiated EPICOR, Inc., strong acid cation resin 24-h soak	ND	4.5

a. DI = distilled.

b. ND = none determined.

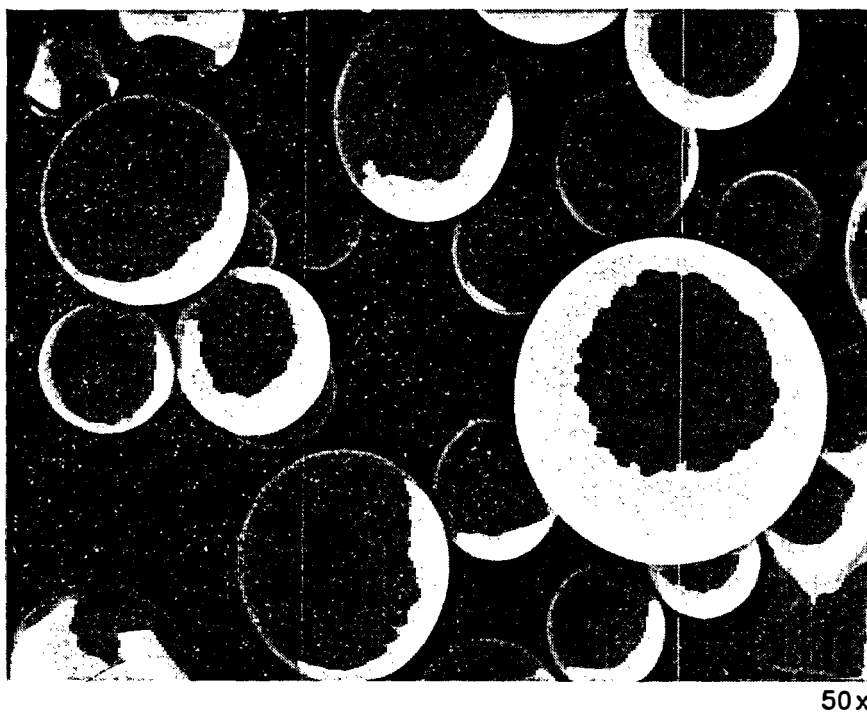


Figure 22. SEM photomicrograph of unirradiated Epicor, Inc. strong acid cation resin at 50 magnification.

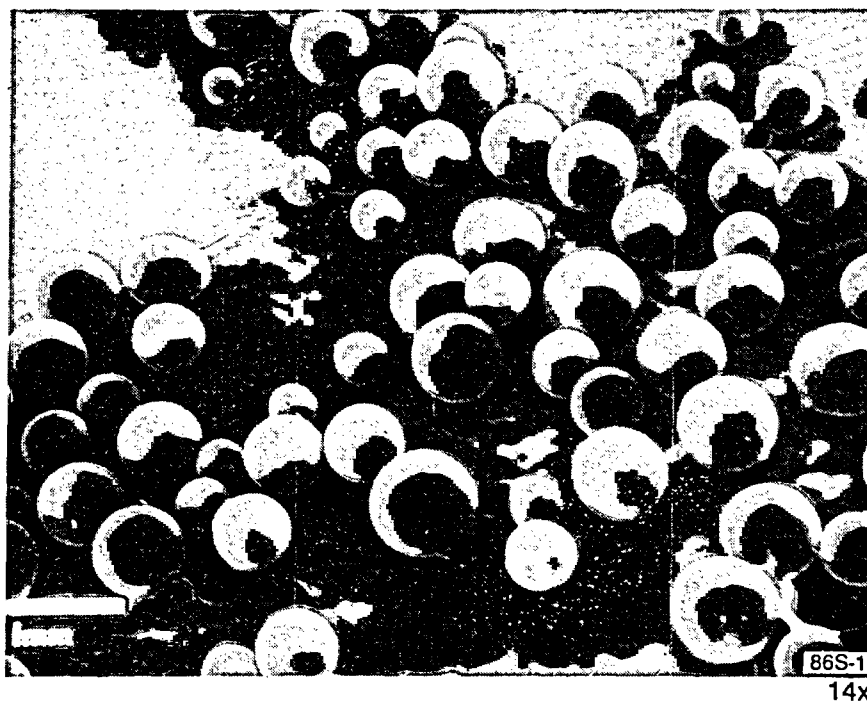


Figure 23 SEM photomicrograph of Epicor-II strong acid cation resin sample PF-20 at 14 magnification.

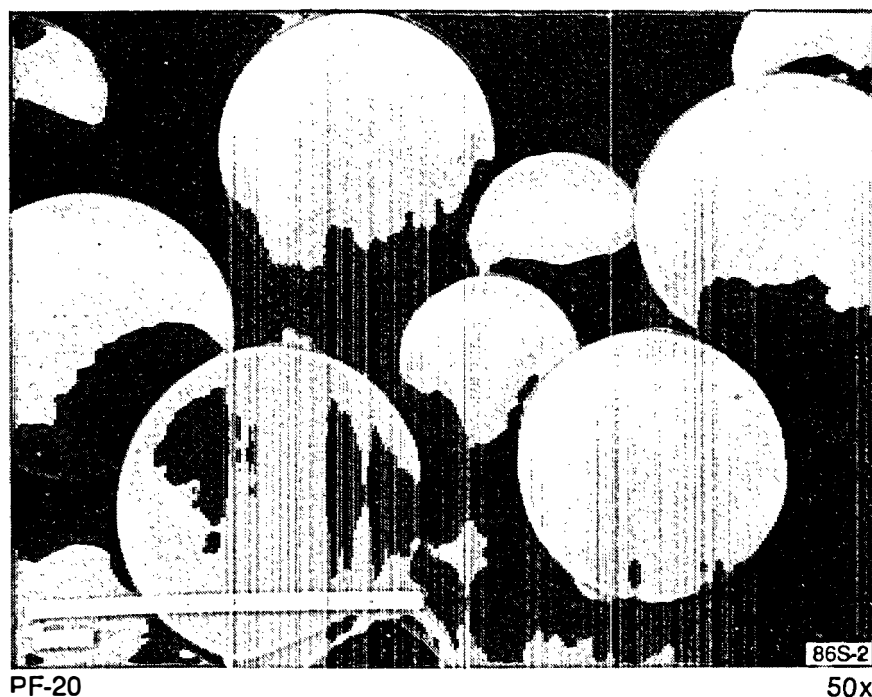


Figure 24. SEM photomicrograph of Epicor-II strong acid cation resin sample PF-20, showing a closeup of several resin beads at 50 magnification.

PF-20. Figures 25 and 26 are photomicrographs of strong acid cation resin from PF-8#1. Figures 27 and 28 are photomicrographs of strong acid cation resin from PF-8#3.

Comparing the photomicrographs of the unirradiated EPICOR-II strong acid cation resin presented in Figure 22 with photomicrographs of the second sampling of PF-20 (Figures 23 and 24) shows little or no difference between the unirradiated and irradiated resins and, therefore, no physical damage due to the radiation dose received (i.e., no cracking, breaking, etc.). Comparing the photomicrograph in Figure 22 with photomicrographs of PF-8#1 strong acid cation resin from the second sampling (Figures 25 and 26) shows considerable physical damage to the PF-8#1 resin in both cases. The photomicrographs in Figures 25 and 26 show resin bead damage similar to that observed during the first sampling, and as the radiation dose increases that type of damage will increase.

Comparing photomicrographs of unirradiated strong acid cation resins from Figure 22 with those

of PF-8#3 (Figures 27 and 28) shows damage that is different than that observed in PF-8#1. The resin bead appears to have cracked similar to those seen in the PF-8#1 sample and then fallen apart. The damage to the resin leaves it with a shattered (ragged) appearance. PF-8#3 received a higher radiation dose than other samples and showed more damage.

The photomicrograph of the unirradiated Epicor, Inc., phenolic cation resin is presented in Figure 29. Comparing the PF-8#2 phenolic cation resin (from the second sampling) in Figures 30 and 31 with the unirradiated phenolic cation resin of Figure 29 indicates less damage than that observed during the first sampling, which is attributed to the lower dose received by the PF-8#2 resin sample. The spheres that appear in Figure 30 are the contamination of PF-8#1 strong acid cation resin that was intermixed with PF-8#2 phenolic cation resin during coring operations. The contamination during the second sampling is less than observed during the first sampling and is considered insignificant.



Figure 25. SEM photomicrograph of Epicor-II strong acid cation resin sample PF-8#1 at 14 magnification. The elastic-like substance on the left is adhesive from the mounting tape used to retain resin.

## Synopsis of Results

Results from the various analytical tests performed on EPICOR-II strong acid cation resin samples PF-8#1, PF-8#3, and PF-20 and phenolic

cation resin sample PF-8#2 from the first and second sampling are listed in Table 7. Values in the table are expressed in terms of changes in results obtained from tests on the irradiated EPICOR-II resins versus the unirradiated resins furnished by Epicor, Inc.



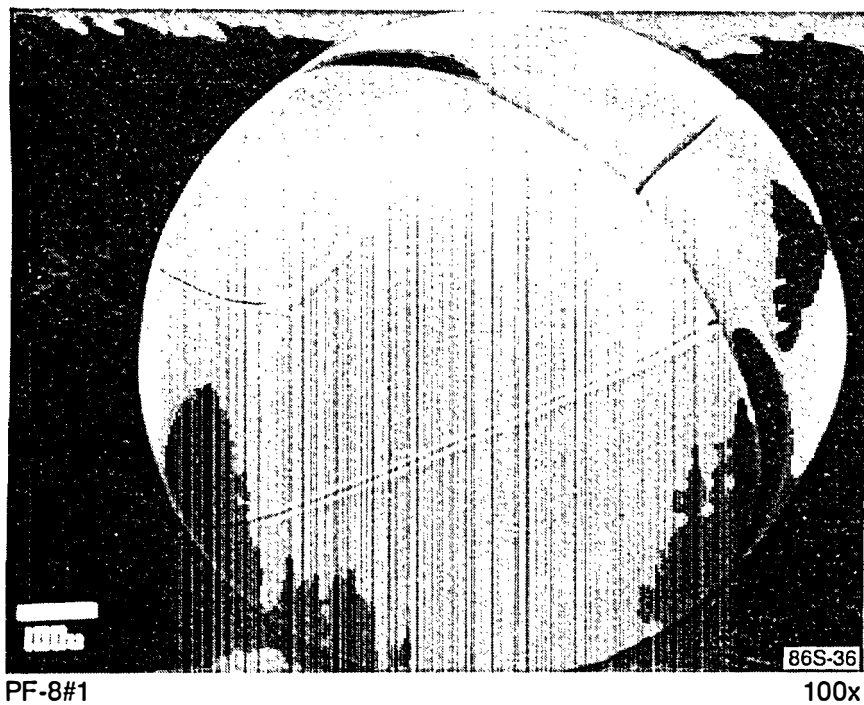


Figure 26. SEM photomicrograph of Epicor-II strong acid cation resin sample PF-8#1, showing a closeup of one resin bead at 100 magnification.

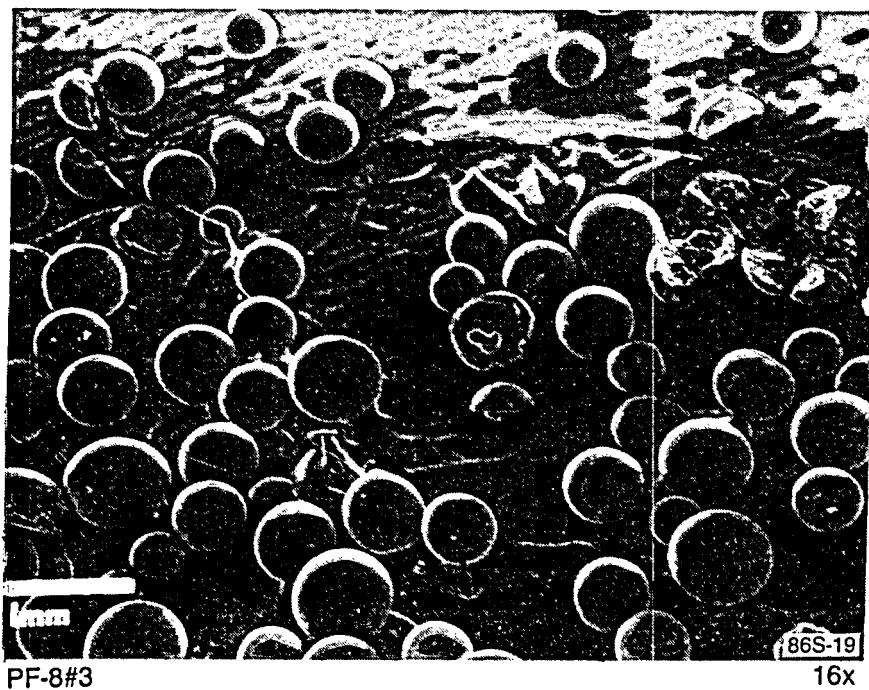


Figure 27. SEM photomicrograph of Epicor-II strong acid cation resin sample PF-8#3 at 16 magnification.



Figure 28. SEM photomicrograph of Epicor-II strong acid cation resin sample PF8#3, showing one resin bead at 500 magnification.



Figure 29. SEM photomicrograph of unirradiated Epicor, Inc. phenolic cation resin at 50 magnification.

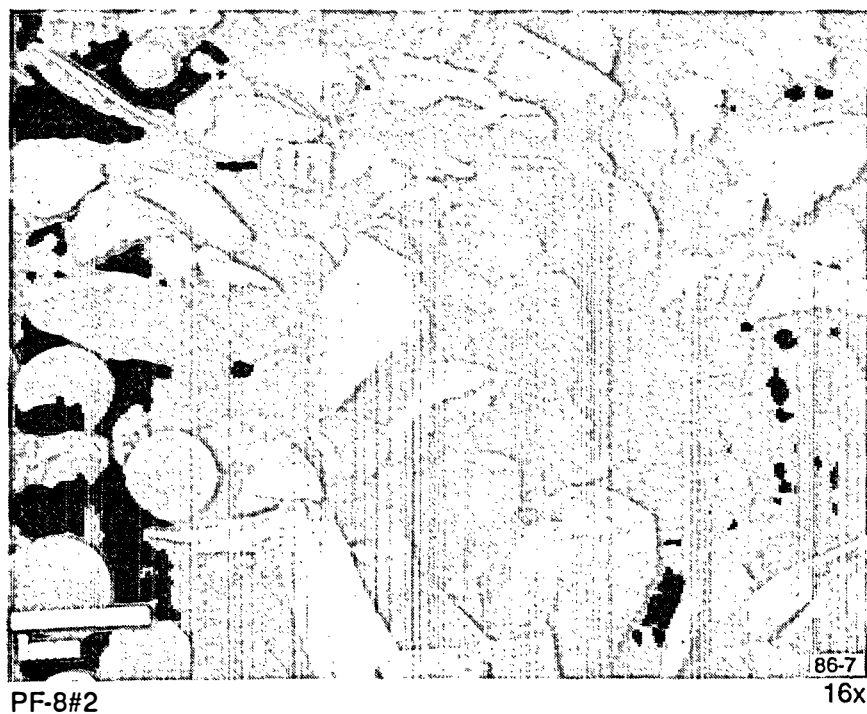


Figure 30. SEM photomicrographs of Epicor-II, phenolic cation resin sample PF8#2 at 16 magnification.



Figure 31. SEM photomicrograph of Epicor-II, phenolic cation resin sample PF8#2, showing a closeup of one resin particle at 50 magnification.

**Table 7. Synopsis of results from analysis of EPICOR-II irradiated resin samples PF-8#1, PF-8#2, PF-8#3, and PF-20 from the first and second samplings<sup>a</sup>**

Analytical Technique	Resin Sample				
	Sampling	PF-8#1 Strong Acid Cation	PF-8#2 Phenolic Cation	PF-8#3 Strong Acid Cation	PF-20 Strong Acid Cation
<b>ASTM Tests</b>					
• Water retention capacity	1, 2	Increase/increase	Increase/increase	No sample/increase	Increase/increase
• Backwashed and settled density	1, 2	Decrease/decrease	Decrease/decrease	No sample/decrease	Decrease/decrease
• Salt splitting capacity	1, 2	Decrease/decrease	Increase/increase	No sample/decrease	Decrease/no change
• Total exchange capacity	1, 2	Decrease/decrease	No change/decrease	No sample/decrease	Increase/no change
Infrared spectroscopy	1	No apparent changes in structure	No apparent changes in structure	No sample	No apparent changes in structure
	2	No apparent changes in structure	No apparent changes in structure	No apparent changes in structure	No apparent changes in structure
Gas chromatography	1	No soluble products determined	No soluble products determined	No sample	No soluble products determined
	2	No soluble products determined	No soluble products determined	No soluble products determined	No soluble products determined
BaCl <sub>2</sub> precipitation for sulfonic acid groups	1	Sulfonic acid groups are being lost	This resin contains no sulfonic acid groups	No sample	Sulfonic acid groups are being lost
	2	Sulfonic acid groups are being lost	This resin contains no sulfonic acid groups	Sulfonic acid groups are being lost	Sulfonic acid groups are being lost
High-performance liquid chromatography	2	No soluble products determined	No soluble products determined	No soluble products determined	No soluble products determined
Scanning electron microscopy	1	Resin bead cracking observed	Damage observed on a few particles	No sample	No damage noted
	2	Resin bead cracking observed	No damage noted	Resin bead cracking observed	No damage noted
Visual observations	1	Nothing unusual	Contamination with PF-8#1 resin observed	No sample	Nothing unusual
	2	Rinse and soak solutions showed a brown color	Rinse and soak solutions showed a brown color	Rinse and soak solutions showed a brown color	Rinse and soak solutions showed a brown color
Physical observations	1	Lack of flow during elution	Nothing unusual	No sample	Nothing unusual
	2	Lack of flow during elution	Nothing unusual	Lack of flow during elution	Lack of flow during elution

a. Results are expressed and differences in values observed for irradiated EPICOR-II resins versus unirradiated resins supplied by Epicor, Inc.

## DISCUSSION AND CONCLUSIONS

Several important studies of ion exchange resins have been conducted, including research by Battelle Columbus Laboratory (BCL),<sup>15,16</sup> Brookhaven National Laboratory (BNL),<sup>2,12,17,18</sup> and the Idaho National Engineering Laboratory (INEL).<sup>3</sup> The BCL work covered characterization of EPICOR-II prefilters PF-3 and -16; the BNL research included radiation effects on ion exchange resins. A complete discussion of the findings of those researchers is presented in Reference 3, and a discussion comparing BCL and BNL results with those obtained at INEL is given below. This section also compares the results from the first sampling of EPICOR resins PF-8 and -20 with the results from the second sampling.

The results obtained by BNL and BCL agree with the findings of the INEL research of EPICOR-II prefilters during the 1st and 2nd sampling. The following items were found during the BNL and BCL research which specifically relate to the INEL work:

- Most cation resins show significant degradation only after they have received a [radiation] dose greater than  $10^8$  rad.
- The primary effects of radiation on ion exchange resins are degradation [by loss of effective cross-linking] of the macromolecular structure, along with scission of ion exchange functional groups.
- The exchange capacity of ion exchange resins, in general, decreases with increasing radiation dose.
- In cation ion exchangers, initially there is an increase in functional groups capable of exchange, as a result of radiation in the presence of air or moisture. Those are phenolic and carboxyl groups produced as a result of oxidation.
- The initial increase in exchange sites tends to increase the total exchange capacity (TEC) of the resin. However, the accompanying scission of existing exchange groups often results in a net decrease in TEC values.
- In general, the salt forms of ion exchange resins are more resistant to radiation than the  $H^+$  or  $OH^-$  forms.
- Prolonged exposure of ion exchange resins to radiation inflowing (dynamic) systems

causes more drastic changes in their physical and chemical properties than ion exchange resins irradiated to static system.

- Radiation [caused] chemical changes in ion exchange resins are a direct function of the total [radiation] dose absorbed by the resin.

INEL findings thus far correlate with findings of other researchers;<sup>2,12</sup> however, degradation has been identified in the EPICOR-II resins at a lower total integrated radiation dose than observed previously ( $4 \times 10^7$  rad versus  $10^8$  rad).<sup>2,3</sup>

The first and second samplings confirm that degradation in the PF-8 and -20 strong acid cation resins has occurred. The onset of degradation has also been confirmed in the phenolic cation resin of PF-8. The INEL study has shown that degradation is occurring at a lower total dose than was reported in earlier studies.<sup>2,12</sup> The physical observations noted during the second sampling of the cores are comparable with those observed during the first sampling (i.e., lack of flow during initial elution of the strong acid cation resins). The soak and rinse solutions from the initial elution of the second sampling had a brown discoloration (indicating a loss of sulfonic acid groups and subsequent oxidation to sulfates), whereas the same solutions during the first sampling were colorless. It has been found (Reference 19) that the color of the soak solution changes from pale yellow to deep amber as the radiation dose increases. That change is consistent with the analytical results from the first and second sampling. Both the first and second samplings showed 24-h soak samples having a pH of less than 3.0.

It is concluded from analysis of the first and second samplings that the following mechanisms of degradation are occurring within the EPICOR-II strong acid cation resins:

- Loss of effective cross-linking (which could lead to eventual release of radionuclides if degradation progressed to the total failure of the polymer structure), as shown by the increase in water retention capacity, decrease in salt splitting capacity, and decrease in backwashed and settled density.
- Loss of functional groups (with accompanying loss of radionuclides), as indicated by the increase in sulfate concentrations in

the soak and rinse solutions and loss in salt splitting capacity.

- Resins from PF-20 showed an initial increase in total exchange capacity (TEC) during the first sampling due to oxidation of the polymer chain before onset of degradation.<sup>2</sup> The TEC then decreased to no change caused by loss of effective cross-linking. This is evidence that degradation has begun in PF-20. The resins from PF-8 are showing a decrease in total exchange capacity with increasing radiation dose. The decrease in exchange capacity exhibited by PF-8 and -20 will lead to an eventual release of radionuclides.

It is also concluded from analysis of the first and second samplings that the following mechanisms of degradation are occurring within the EPICOR-II phenolic cation resins:

- Loss of effective cross-linking (which could lead to eventual release of radionuclides), as shown by the increase in water retention capacity and decrease in back-washed and settled density
- Oxidation of the polymer chain (which would reduce the tendency to release radionuclides), as indicated by the increase in salt splitting capacity.

Previous resin studies show that degradation caused by internal radiation doses will be more severe than degradation caused by external irradiation, because of introduction of the radiation into the polymer structure (References 2, 12, 17, and 18). The internal dose received by the organic ion exchange resins in EPICOR-II prefilterers PF-8 and -20 has been sufficient to initiate degradation. The degradation at the time of the first sampling was measurable. The equilibrium of the polymer structure has been shifted towards polymer breakdown; this is substantiated by results of the second analysis. Further increases in degradation are expected to be seen in the third coring of the EPICOR-II prefilter ion exchange resins, planned for October 1987.

One important indicator of the capability of ion exchange media to retain radionuclides is the total exchange capacity. The four samples examined in the INEL study exhibited different reactions to radiation. Samples PF-8#1 and PF-8#3, the strong acid cation resins with the highest radiation dose,

showed reduced total exchange capacity. Sample PF-8#2, the phenolic cation with a similar low dose, showed decreased capacity. That indicates that the PF-8#1 and PF-8#3 resins have reached a dose high enough to cause the exchange capacity to decrease, while the PF-8#2 phenolic cation sample went from no change at the first sampling lower dose to a decreased exchange capacity at the second sampling higher dose. PF-20, the strong acid cation with the lowest radiation dose, showed no change in total exchange capacity. The PF-20 resin had increased capacity at the first sampling and had returned to no change at the second sampling, indicating onset of degradation. Those changes agree with the findings of Reference 12. The results of the INEL study indicate that the threshold dose for the onset of degradation due to internal radiation in EPICOR-II resins is between  $3.7 \times 10^7$  and  $4.0 \times 10^7$  rads.

The mechanisms of radiation identified in the second sampling of this study indicate a further reduction in resin ion exchange capacity in the upper locations of the prefilterers, which were subjected to high radiation doses. That reduction will result in the release of radionuclides. The radionuclide release was seen as the loss of sulfonic acid groups in PF-8#1, PF-8#3, and PF-20 resin samples. The release of radionuclides from the resins would allow migration of the radionuclides within the EPICOR-II prefilterers, and the sulfonic acid groups would lower the pH of the liquid in the prefilterers. The low-pH liquid should be neutralized by the remaining unused ion exchange material in the prefilterers. That is supported by the measurement of residual waste pH from the 50 prefilterers which were stored at INEL. (Forty-six of those prefilterers have been disposed at the commercial disposal facility near Hanford, WA). The pH measurements of residual water obtained more than three years after the prefilterers were used were in the range of about 5 to 8. Those pH readings indicate that the acidic solution is being modified as it passes through the anion and mixed bed resins in the lower regions of the prefilterers.

A threshold dose for degradation in EPICOR-II ion exchange resins has been identified by this work to be about  $4 \times 10^7$  rads. That value is somewhat less than the  $10^8$ -rad accumulated dose limit recommended in the Technical Position on Waste Form.<sup>20</sup> The resin properties which have changed due to degradation, such as those examined by the ASTM methods, exhibit small changes (10% or less, as seen in Tables 4 and 5) at the threshold dose; while higher doses (above  $10^8$  rad) have

produced more pronounced property changes.<sup>2,17,18</sup> It can also be seen from the information in those tables that different resins react differently at a similar dose (comparing styrene to phenolic base resin).

While the results produced thus far in this study show that the EPICOR resins definitely began losing radionuclides below  $10^8$  rads, it is premature to reduce the recommended dose limit. First, the release of a nuclide by an exchange site does not assure that the nuclide will be released by the exchanger to the environment; rather, it could be picked up on another site. This would be a temporary condition (until a higher dose is reached) but does delay the ultimate release of the nuclide. It is just such a process that is occurring within the EPICOR-II prefilters; the process is made possible by the fact that ion exchangers are operated only to or near the point where a predetermined level of radionuclides begins appearing in the effluent (exchanger breakthrough). That results in a number of free sites in the exchangers being available for recapture of any loose radionuclides. Second, this study has examined only two types of resin. Examination of a third resin type, the strong base anion, would result in a cost-effective way of expanding the data base. Third, it would be pru-

dent to more closely examine the effects of threshold dose over the planned life of this study (three more samplings).

It has been concluded by the authors that it is too early in the study to discuss a reduction in the present NRC-recommended threshold dose of  $10^8$  rad based on only two samplings of two resin types. This opinion takes into account the built-in exchange capacity of commercial ion exchange systems noted previously, along with the relatively small amount of data produced thus far by the study. However, as degradation continues in the EPICOR-II prefilters, continued sampling and analysis will provide a clearer picture of the threshold dose. The addition of radiation content information from soak and rinse waters and acid rinse, along with GC and HPLC analysis of those waters over the remaining study period, should identify the onset of structural damage to the resin bead.

Three more examinations are planned for PF-8 and -20 resins. These future corings and analyses will assist in determining the rate at which organic ion exchangers are degraded by internal radiation under conditions representative of actual use and storage. Relating degradation of the resins to total integrated radiation dose will aid in identifying the effects of degradation on release of radionuclides from the ion exchange media.

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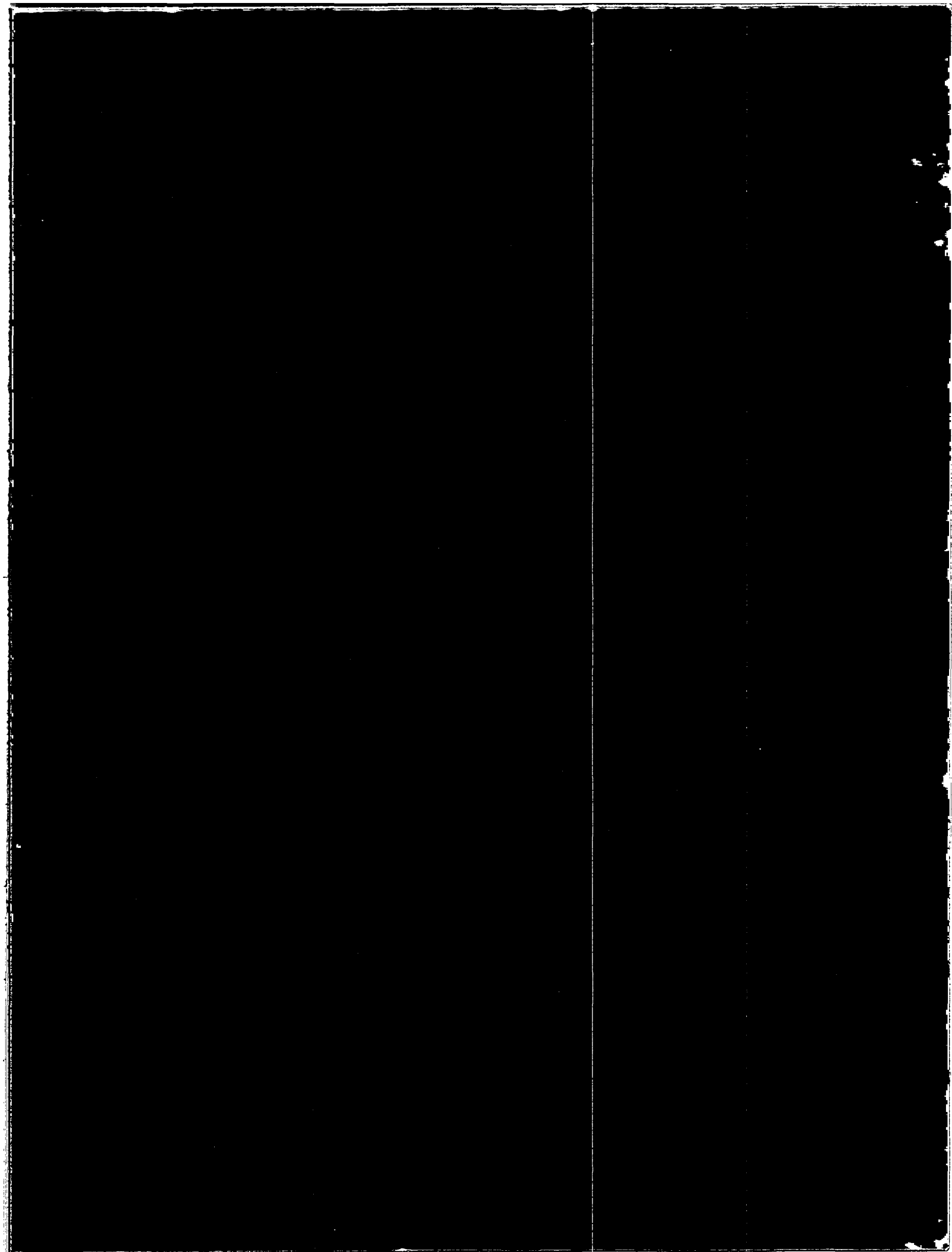


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NRC FORM 335 (2-84) NRCM 1102, 3201, 3202 <b>BIBLIOGRAPHIC DATA SHEET</b> SEE INSTRUCTIONS ON THE REVERSE		U.S. NUCLEAR REGULATORY COMMISSION 1 REPORT NUMBER (Assigned by TIDC, add Vol. No., if any) NUREG/CR-4608 EGG-2452	
2 TITLE AND SUBTITLE EPICOR-II Resin Degradation--Results From Second Samples of PF-8 and PF-20		3 LEAVE BLANK	
5 AUTHOR(S) Robert D. Sanders, Sr. John W. McConnell, Jr.		4 DATE REPORT COMPLETED MONTH   YEAR September   1986	
7 PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) EG&G Idaho, Inc. Idaho Falls, Idaho 83415		6 DATE REPORT ISSUED MONTH   YEAR October   1986	
10 SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Waste Management Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Washington, DC 20555		8 PROJECT/TASK/WORK UNIT NUMBER  9 FUND OR GRANT NUMBER A6188	
11a TYPE OF REPORT Technical		b PERIOD COVERED (Inclusive Dates)	
12 SUPPLEMENTARY NOTES			
13 ABSTRACT (200 words or less)  <p>The 28 March 1979 accident at Three Mile Island Unit 2 released approximately 560,000 gallons of contaminated water to the Auxiliary and Fuel Handling Buildings. The water was decontaminated using a demineralization system called EPICOR-II developed by Epicor, Inc. The Low-Level Waste Data Base Development—EPICOR-II Resin/Liner Investigation Project, funded by the U.S. Nuclear Regulatory Commission (NRC), is studying the chemical and physical conditions of the synthetic ion exchange resins found in several EPICOR-II prefilters. The work is being done by EG&amp;G Idaho, Inc., at the Idaho National Engineering Laboratory (INEL). This report summarizes results and analyses of the second sampling of ion exchange resins from EPICOR-II prefilters PF-8 and -20. Results are compared with baseline data from tests performed on unirradiated Epicor, Inc., resins to determine if degradation is continuing due to the high internal radiation dose received by the EPICOR-II resins. Results also are compared with results from the first sampling of the resins from EPICOR-II prefilters PF-8 and PF-20, and with those of other researchers.</p>			
14 DOCUMENT ANALYSIS & KEYWORDS/DESCRIPTORS  EPICOR-II, resin degradation		15 AVAILABILITY STATEMENT  Unlimited	
16 IDENTIFIERS/OPEN ENDED TERMS		16 SECURITY CLASSIFICATION (This page) Unclassified (This report) Unclassified	
		17 NUMBER OF PAGES	
		18 PRICE	





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OCTOBER 1980