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EPICOR-II Resin Degradation Results from First Resin Samples of PF-8 and PF-20

**John W. McConnell, Jr.
Robert D. Sanders, Sr.**

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RESULTS FROM FIRST RESIN SAMPLES
OF PF-8 AND PF-20**

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Idaho Falls, Idaho 83415

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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, 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. This report summarizes results and analyses of the first 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 has occurred due to the high internal radiation dose received by the EPICOR-II resins. Results also are compared with recent findings on resin degradation by Battelle Columbus Laboratories and Brookhaven National Laboratory.

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 using special tools developed for that purpose. A description of how those tools were used is given herein. Removal of samples from the cores, along with cleaning and preparation of those samples, is discussed. A series of characterization tests

were performed on the resins to determine if degradation due to radiation had occurred during interim storage. Those tests included American Society for Testing Materials procedures, infrared spectroscopy, gas chromatography, scanning electron microscopy, and barium chloride precipitation. Details of test methodology and results are described.

Analyses comparing test results of resins from EPICOR-II prefilters PF-8 and -20 with unirradiated resins obtained from Epicor, Inc. show resin degradation has occurred in some of the EPICOR-II resins examined. The mechanism of degradation is compared with work of other researchers and is consistent with their findings. The strong acid cation resins (divinylbenzene, styrene base structure) are losing effective cross-linking along with a scission of functional groups and are 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 FIRST RESIN 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. That work has been transferred to 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.¹ 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 an external source, such as a reactor core or Co-60 source.² 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 the literature notes that internal radi-

ation 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 4 years and experienced internal radiation doses of about 10^7 rad.

This report discusses the resin degradation studies conducted on organic ion exchange resins removed from two EPICOR-II prefilters (PF-8 and -20). As part of the EPICOR and Waste Research and Disposition Program, 46 prefilters are being disposed at a commercial disposal facility.^{3,4} 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. 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 [two samples from PF-8 (designated PF-8#1 and PF-8#2) and one from 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, American Society for Testing Materials (ASTM) tests were used to determine exchange capacity, density, and moisture content.⁵ 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 and divinylbenzene.

MATERIALS AND METHODS

EPICOR-II Prefilters

EPICOR-II prefilter liners are 4-ft-diameter 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. The internal and external surfaces are painted with Phenoline^a 368 coating. Each liner contains about 30 ft³ 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, and 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, multibranch 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. Ion exchange media were loaded into the liner through the manway. Removal of resins from the prefilter was accomplished through that manway, using coring tools.

Coring

Resin cores were removed remotely from prefilters PF-8 and -20 in 1983, using coring equipment based on a design developed at Battelle Columbus Laboratories (BCL) and modified for use at INEL.⁶ 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 consisted of the following: (a) coring tool guide, which locates the coring tool over the prefilter resin bed; (b) spacer, which aligns and guides the coring tool into the bed; (c) coring tool and shutter, used for collecting, transporting, and storing the resin core; (d) casing and

shutter, used for retaining the void space in the bed and preventing collapse of the resin bed after removing the coring tool; and (e) vibrator tool, which drives the coring tool, casing, and shutters into the resin bed. Figure 2 shows a research EPICOR-II prefilter with coring equipment setup. Figures 3 through 7 show the process of obtaining a resin core.

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.

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 taken 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-in. by 3-in. holes created in the resin beds during the coring process. The averages of the actual gamma scan measurements taken during insertion and retraction of the detector at each location are given in Figures 8 and 9. Measurements taken at the elevations of interest were used with the calculations of maximum cumulative doses of Reference 7 to estimate the total integrated beta and gamma radiation dose for each resin sample (Table 1).

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)

a. Trade name of the Carboline Company

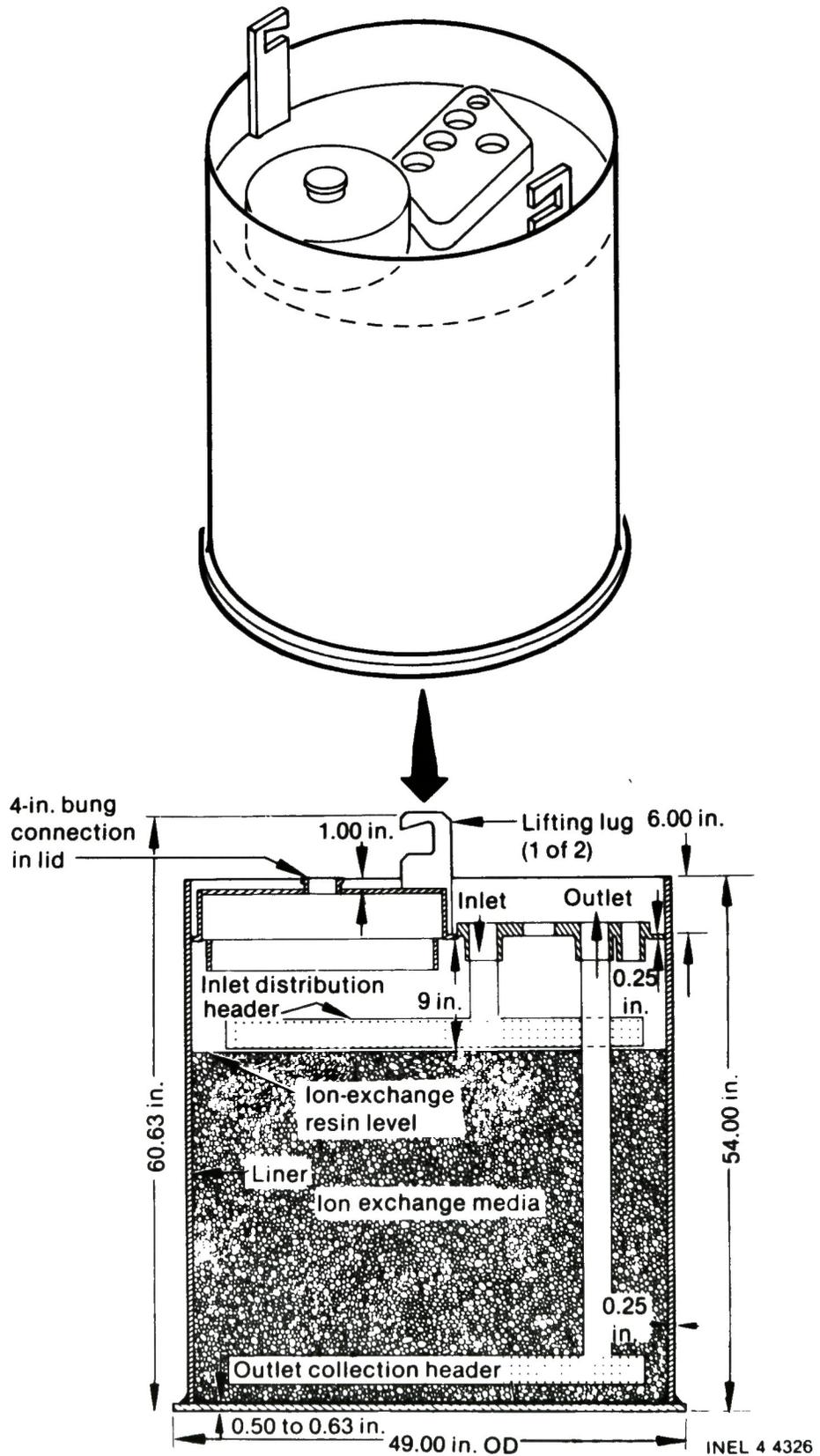


Figure 1. Schematic (isometric and full section) of an EPICOR-II prefilter.

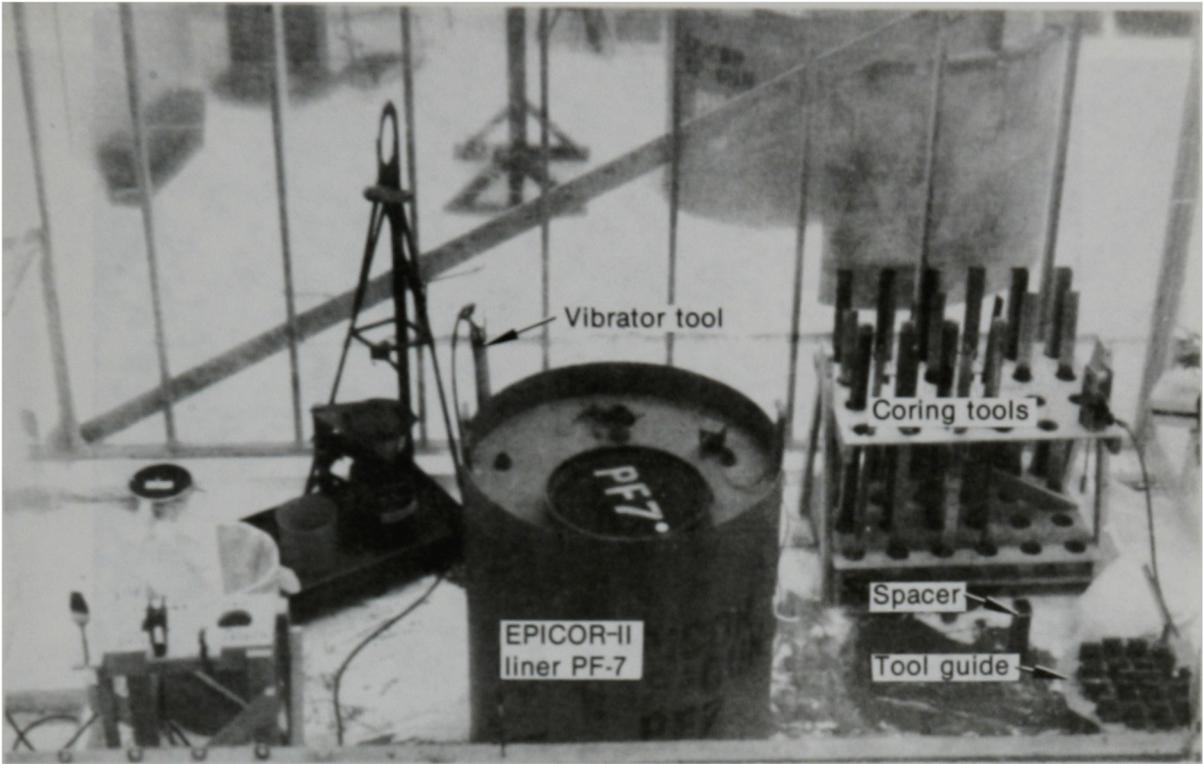


Figure 2. Coring equipment setup in the TAN-607 Hot Shop, used to remotely collect resin cores from EPICOR-II prefilters.

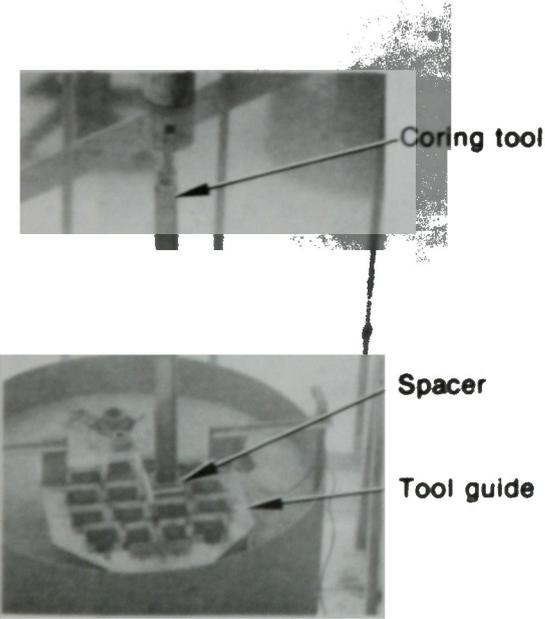


Figure 3. The coring tool being lowered remotely into the resin bed during the coring process of an EPICOR-II prefilter.

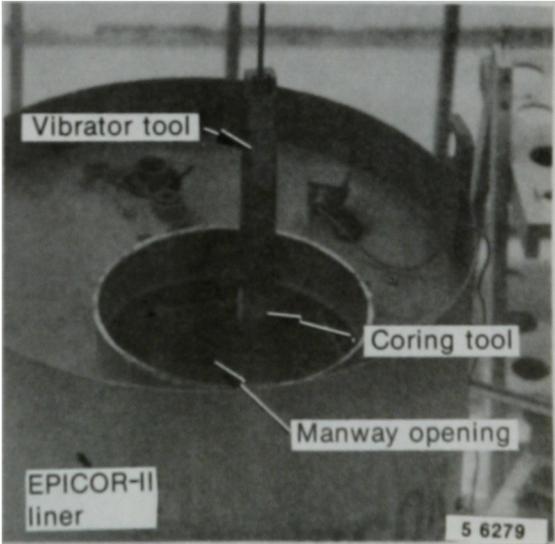


Figure 4. The vibrator tool driving the coring tool into the resin bed during the coring process of an EPICOR-II prefilter.

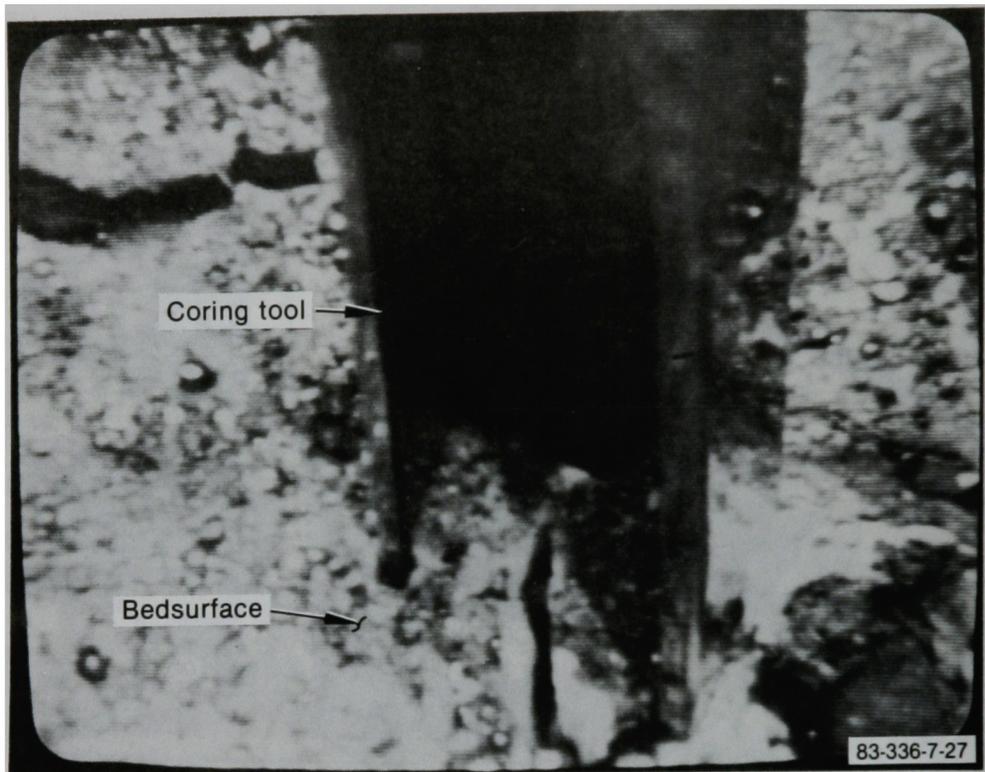


Figure 5. The coring tool/resin bed interface (before insertion of the shutter) during coring of an EPICOR-II prefilter.

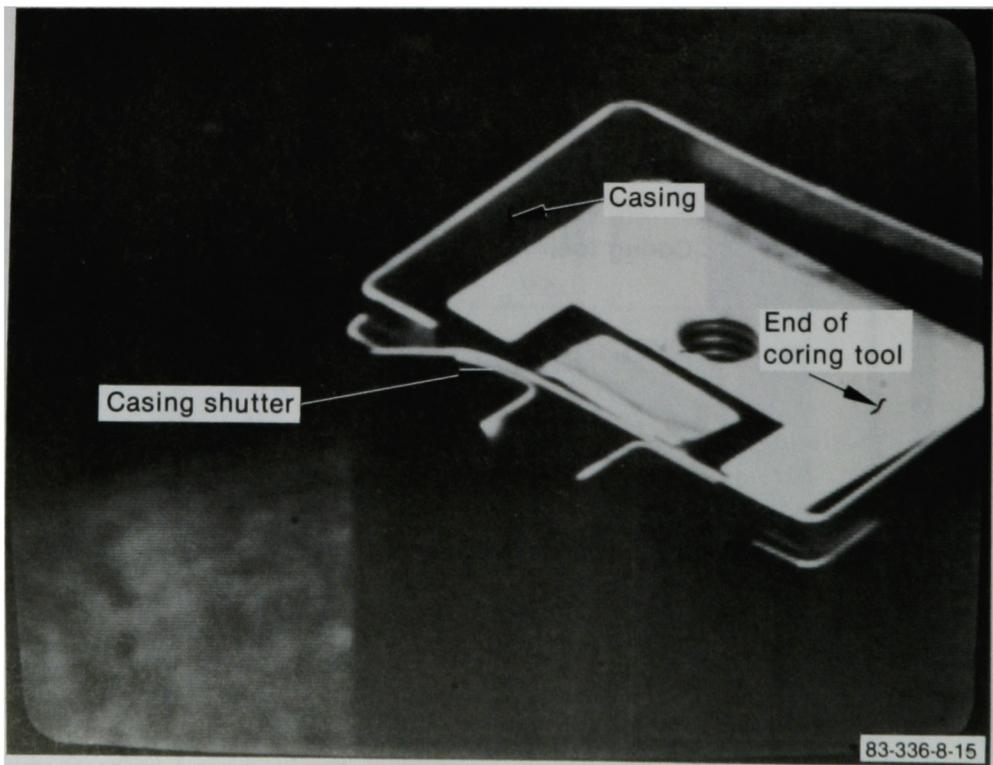


Figure 6. The upper end of a coring tool, casing, and shutters after insertion into the resin bed of an EPICOR-II prefilter.

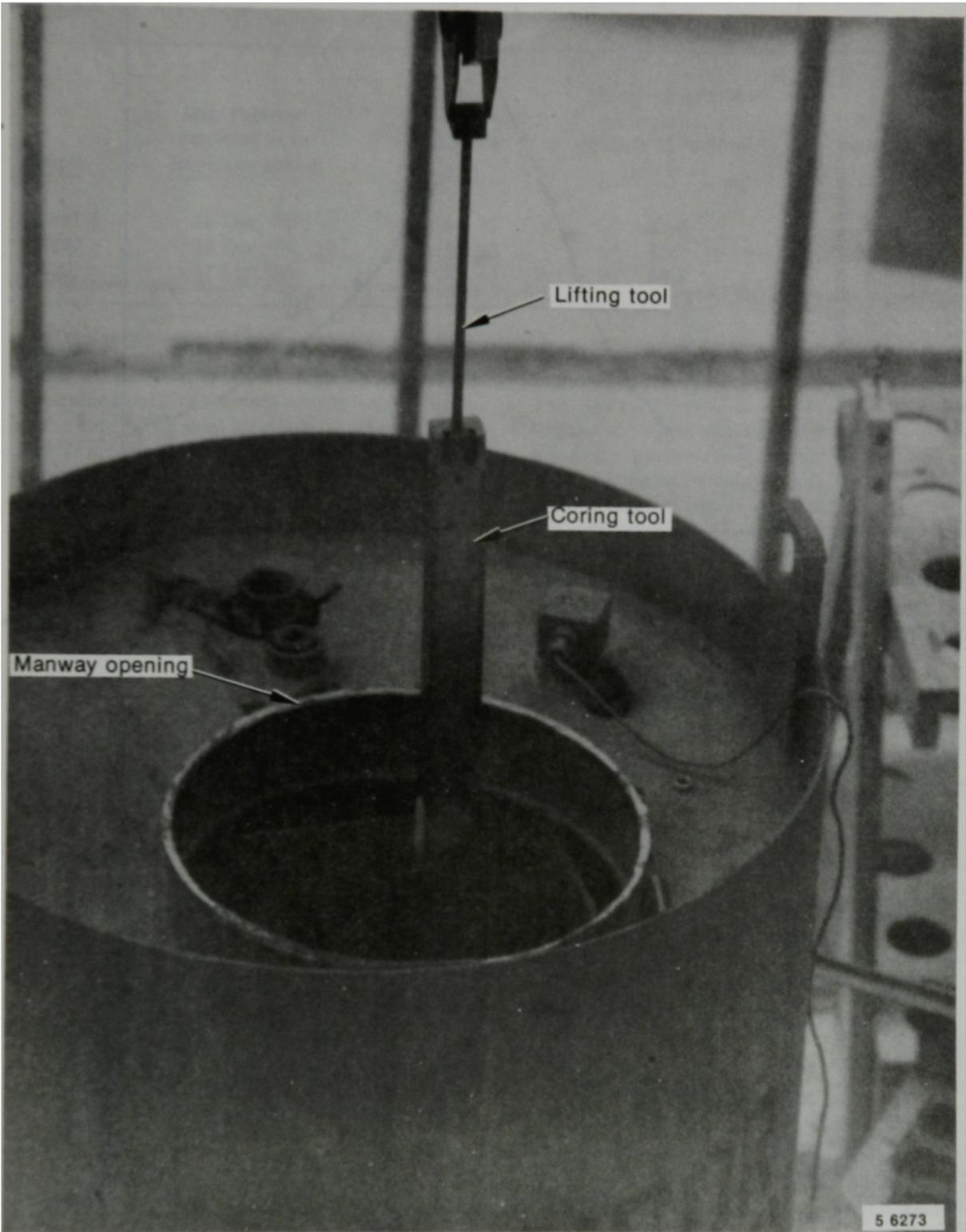


Figure 7. The coring tool (containing a resin core) being removed from an EPICOR-II prefilter

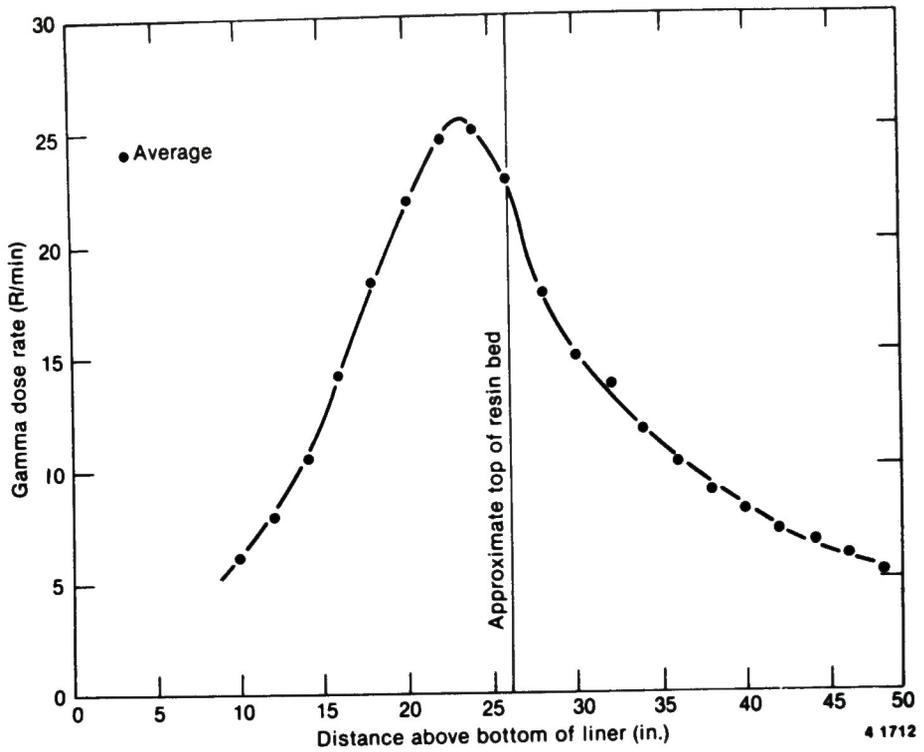


Figure 8. Results of full-depth gross gamma measurements taken inside the hole created in the resin bed by the coring of EPICOR-II prefilter PF-8.

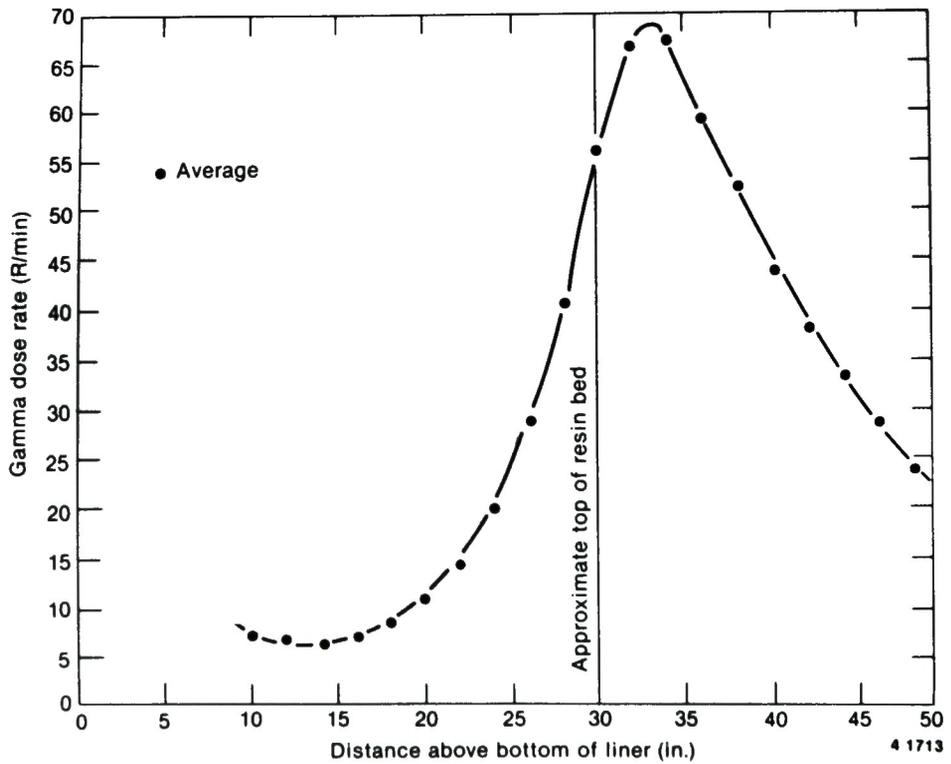


Figure 9. Results of the full-depth gross gamma measurements taken inside the hole created in the resin bed by the coring of EPICOR-II prefilter PF-20.

Table 1. Estimated 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 Activity at Location of Sample in Prefilter (R/min)	Total β and γ Radiation Dose (rad)
PF-8#1	18 Dec. 79	4 Oct. 83	23.4	6.8×10^7
PF-8#2	18 Dec. 79	4 Oct. 83	15.3	4.0×10^7
PF-20	13 Mar. 80	11 Oct. 83	14.3	3.7×10^7

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.⁸ The axial locations of highest radionuclide activity for the resin cores were determined using those scans. Then, isotopic spectral measurements were taken at the locations of highest activity, as shown in Figure 10 for PF-20. There were two radionuclides having measurable concentrations detected by the gamma spectral scans, Cs-134 and -137. Isotopic gamma-ray intensities for Cs-134 and -137 were measured versus distance along

the resin cores. The results for Cs-137 are shown in Figures 11 and 12 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 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

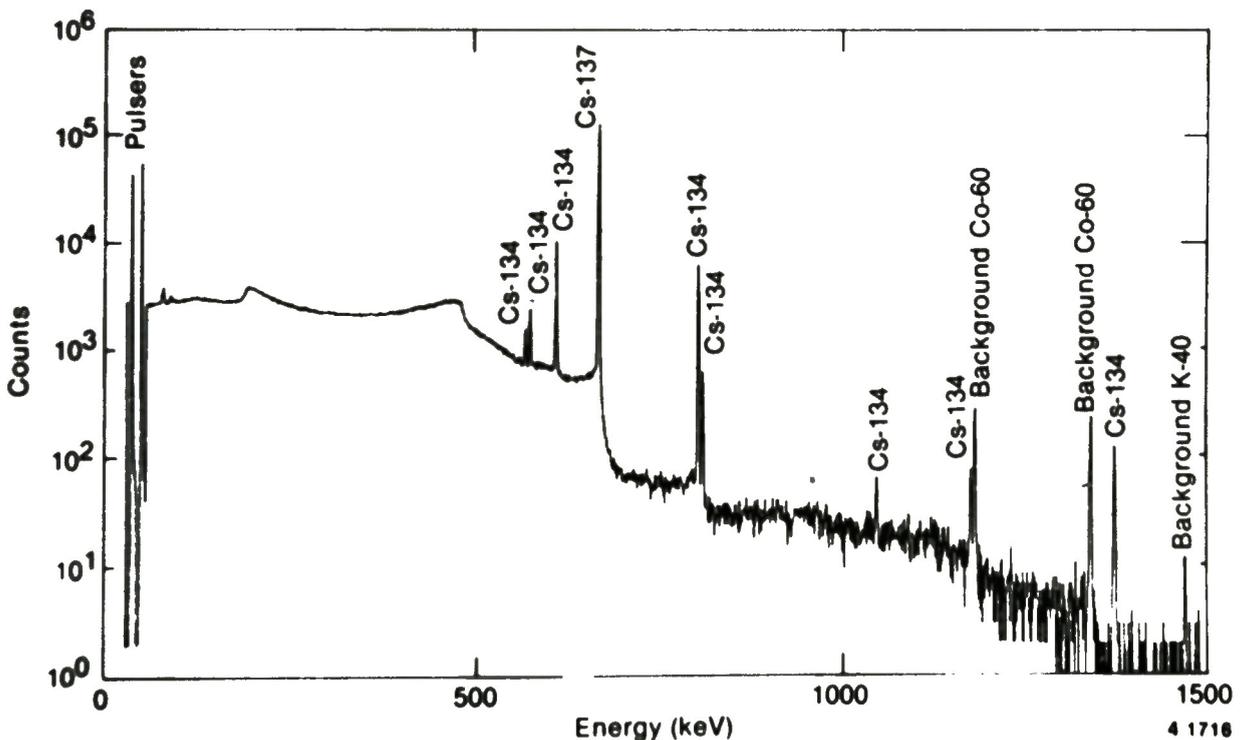


Figure 10. Results of isotopic spectral measurements of the resin core from EPICOR-II prefilter PF-20 at an elevation of 29.25 in. (location of highest radioactivity).

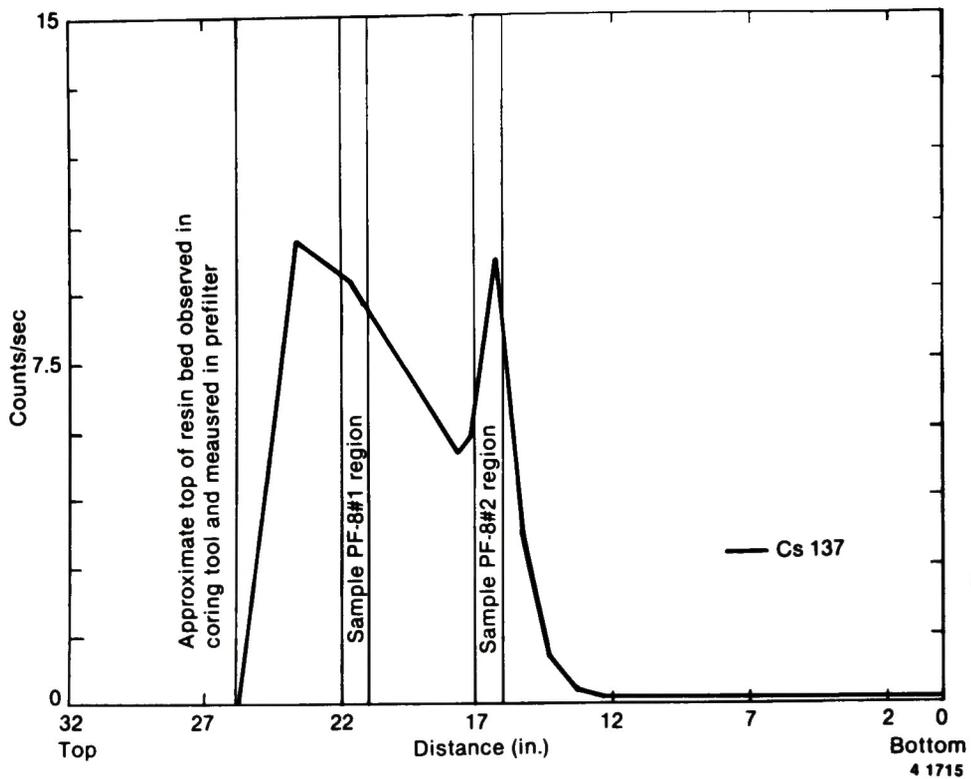


Figure 11. Isotopic (Cs-137) gamma scan over the length of the resin core from EPICOR-II prefilter PF-8, showing locations where the resin samples were removed.

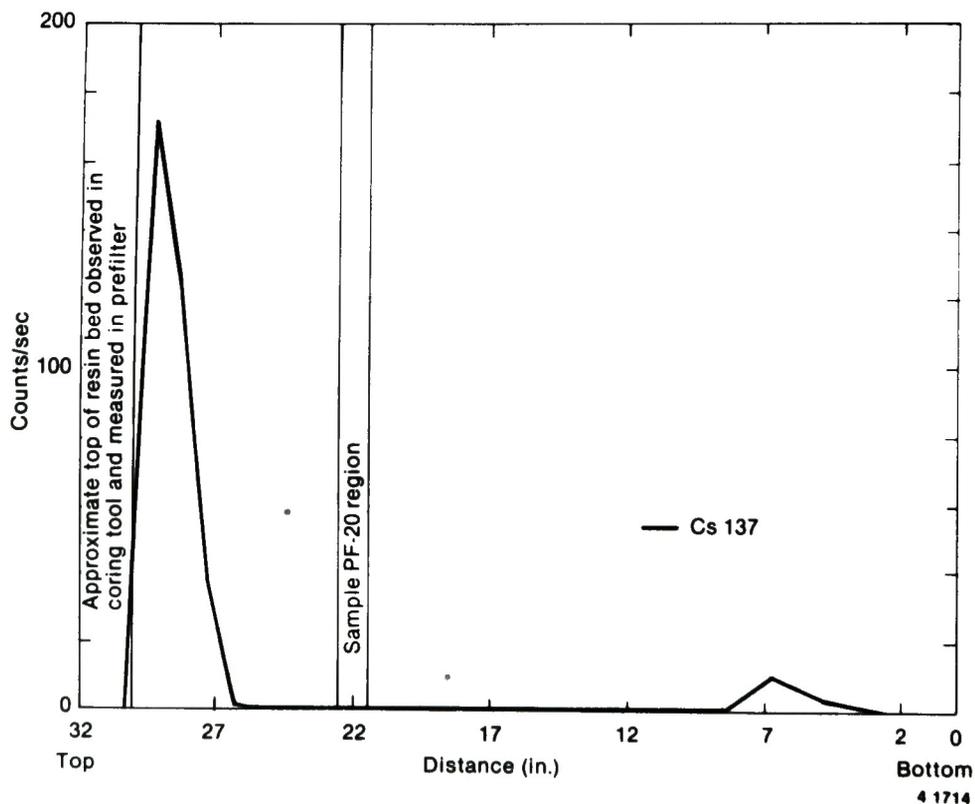


Figure 12. Isotopic (Cs-137) gamma scan over the length of the resin core from EPICOR-II prefilter PF-20, showing location where the resin sample was removed.

resin core (see Figure 9). This study is concerned with 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 coring tool shutter was withdrawn to expose the ion exchange media (resin). The cores of PF-8 and -20 with shutters removed are shown in Figures 13 and 14, respectively. Those figures are composites of photographs taken through the hot cell periscope and show the layers of different ion exchange media in the cores. It is noted that some smearing of material from one layer into another occurred when the shutter was inserted and withdrawn. That smearing of one layer into another required careful removal of the mixed surface material to expose unmixed resin near the center of the core. The unmixed material was the target for collection. The locations where the resin samples were removed from the coring tool are shown in Figures 15, 16, and 17.

The resin samples were obtained from the cores using a vacuum pump and water-filled, graduated glass column (Figure 18). One end of a flexible rubber tube was attached near the top of the glass column, and the other end to a vacuum pump outside the 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 18). With the vacuum pump operating, the wand was positioned over the target resin with a master-slave manipulator in such a way that the resin was drawn into the wand and thence the water-filled column. Sample sizes of 100 mL were collected. Two samples were obtained from the PF-8 core, one styrene cation resin (PF-8#1) and one phenolic cation resin (PF-8#2). A single styrene cation resin sample was obtained 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).

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 be 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.⁹ Based on that information, it was decided to elute the radionuclides (cations) from the PF-8 and -20 resin samples.

As described in the previous section, samples were removed from the coring tools and drawn into a 1-in.-diameter by 18-in.-high ion exchange column filled with distilled water (see Figure 18). The samples were allowed to stand 24 hours in the water-filled column. The ion exchange column then was reconfigured as shown in Figure 19. The distilled water was removed through the shutoff valve of the column and retained for gas chromatography (GC) analysis. [GC was used for determining the presence of any soluble organic resin degradation products.] Resin samples PF-8#1 and PF-20 showed restriction to flow during this initial elution procedure. The distilled water also was analyzed for the presence of any functional group components, such as sulfonic acid, which had been dissociated from the resin. Resin sample PF-8#1 then was rinsed two times with distilled water which was added by the pump through the tubing at the top of the column. Resin sample PF-8#2 was rinsed once, and sample PF-20 was not rinsed with distilled water. The distilled water rinse also was saved for GC analysis and functional group tests.

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 19. That procedure was continued until 55 sample volumes (the amount determined to remove 99% of the cations) or 5.5 L of acid was 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 containing a high-efficiency particulate air filter on the outlet duct.

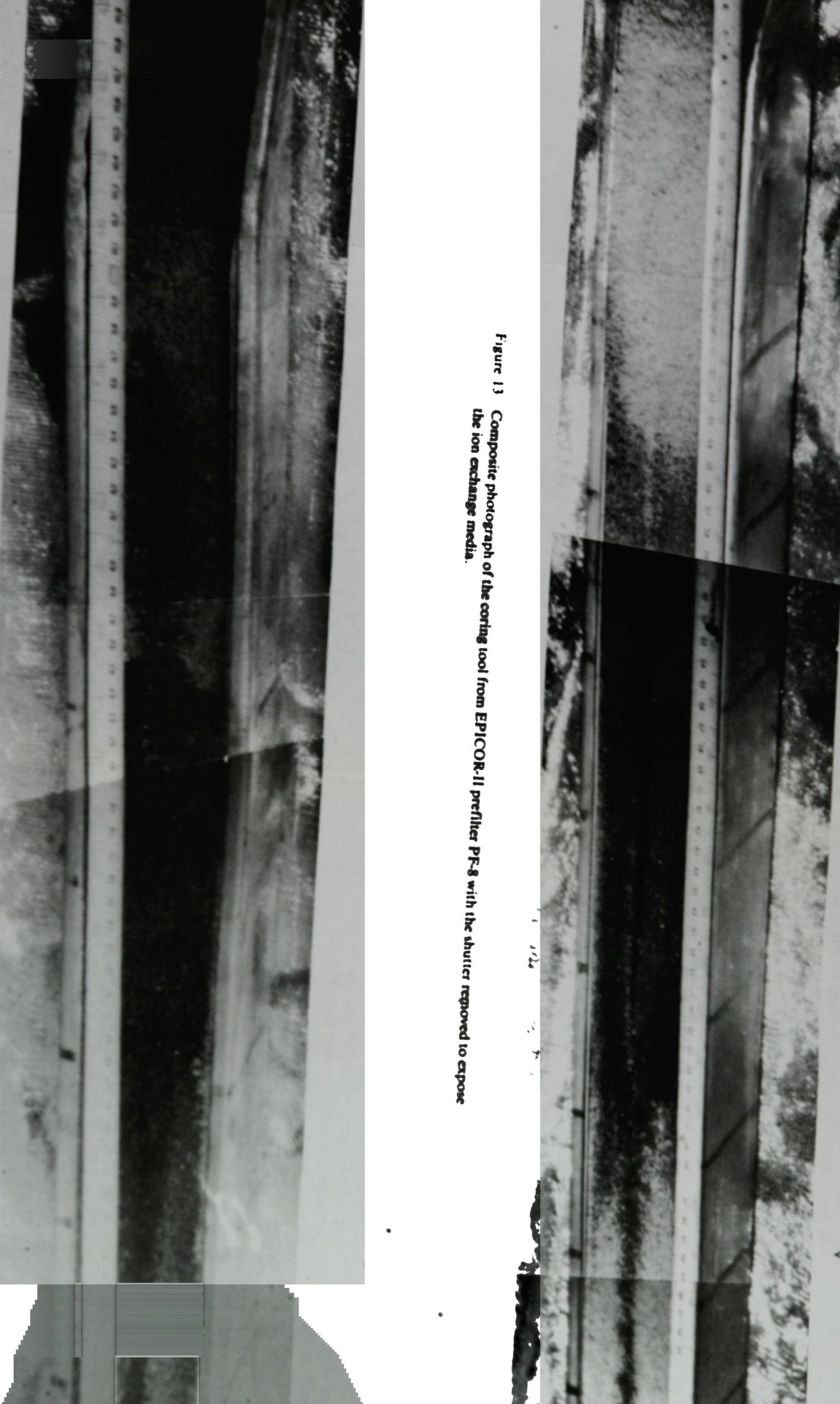


Figure 13 Composite photograph of the coring tool from EPICOR-II prefilter PF-8 with the shutter removed to expose the ion exchange media.

Anion or mixed bed resin

Phenolic cation resin

Strong acid cation resin

Figure 14 Composite photograph of the coring tool from EPICOR-II prefilter PF-8 with the shutter removed to expose the ion exchange media.

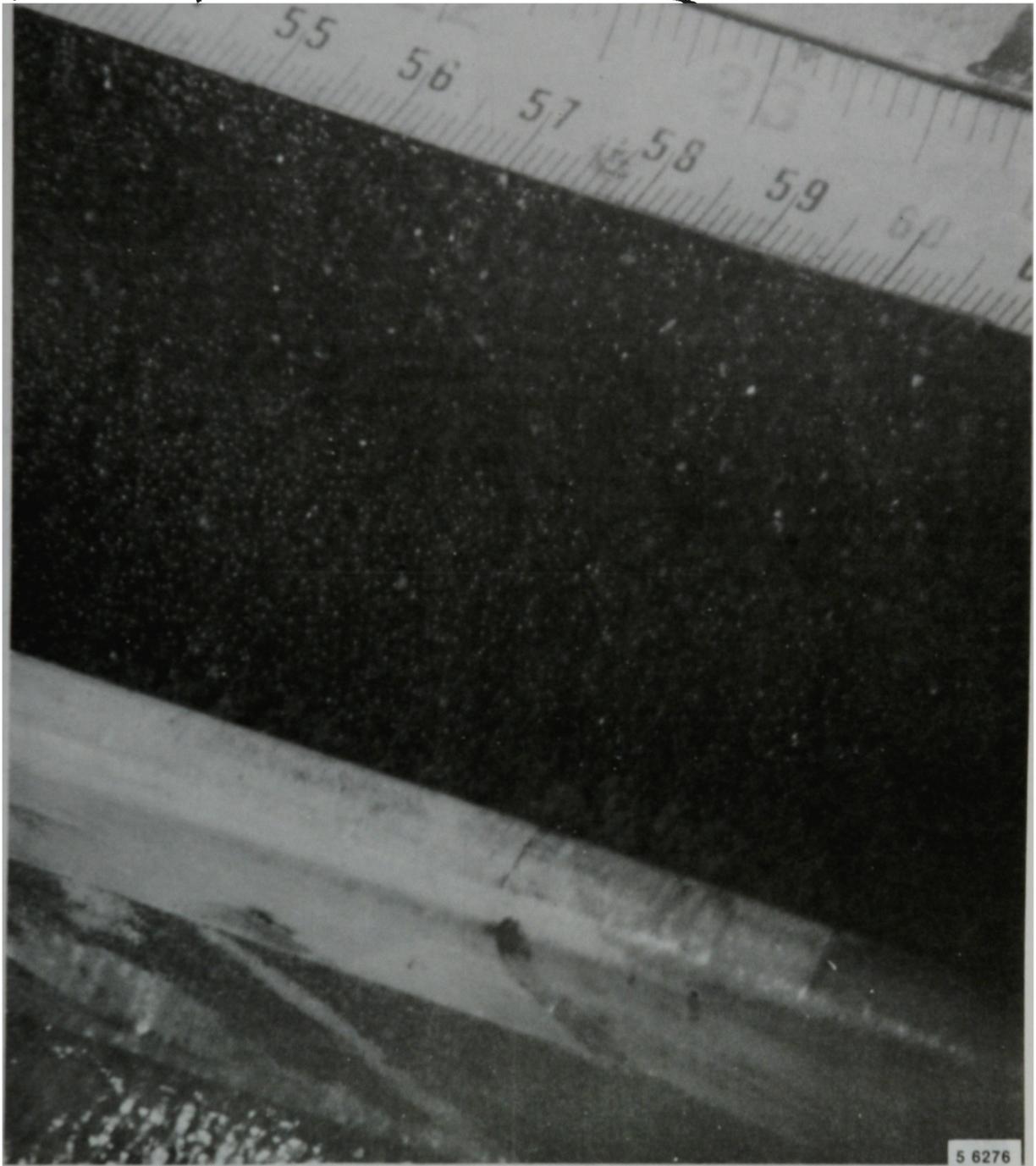


Figure 15. Location where resin sample PF-8#1 was removed from the coring tool.

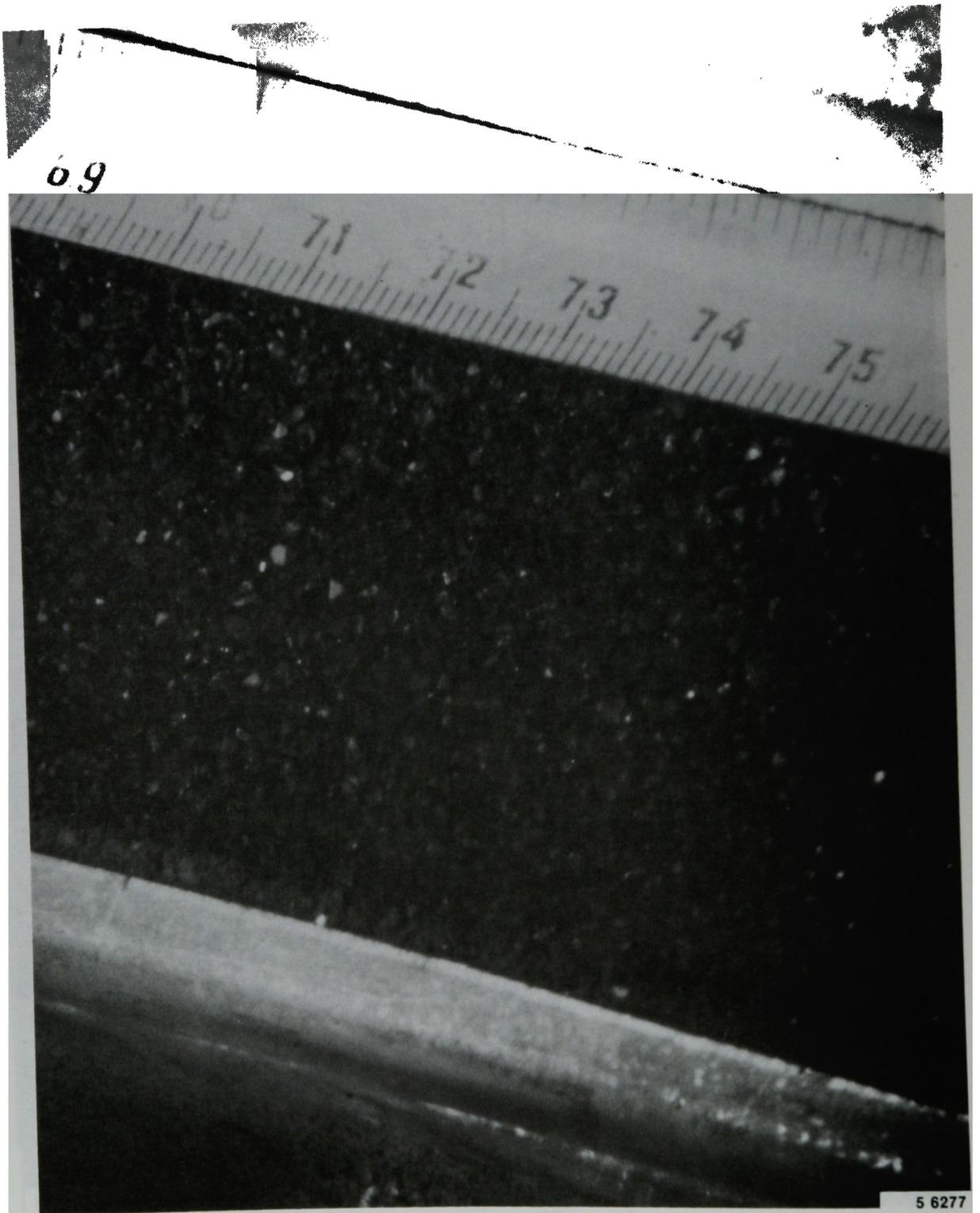
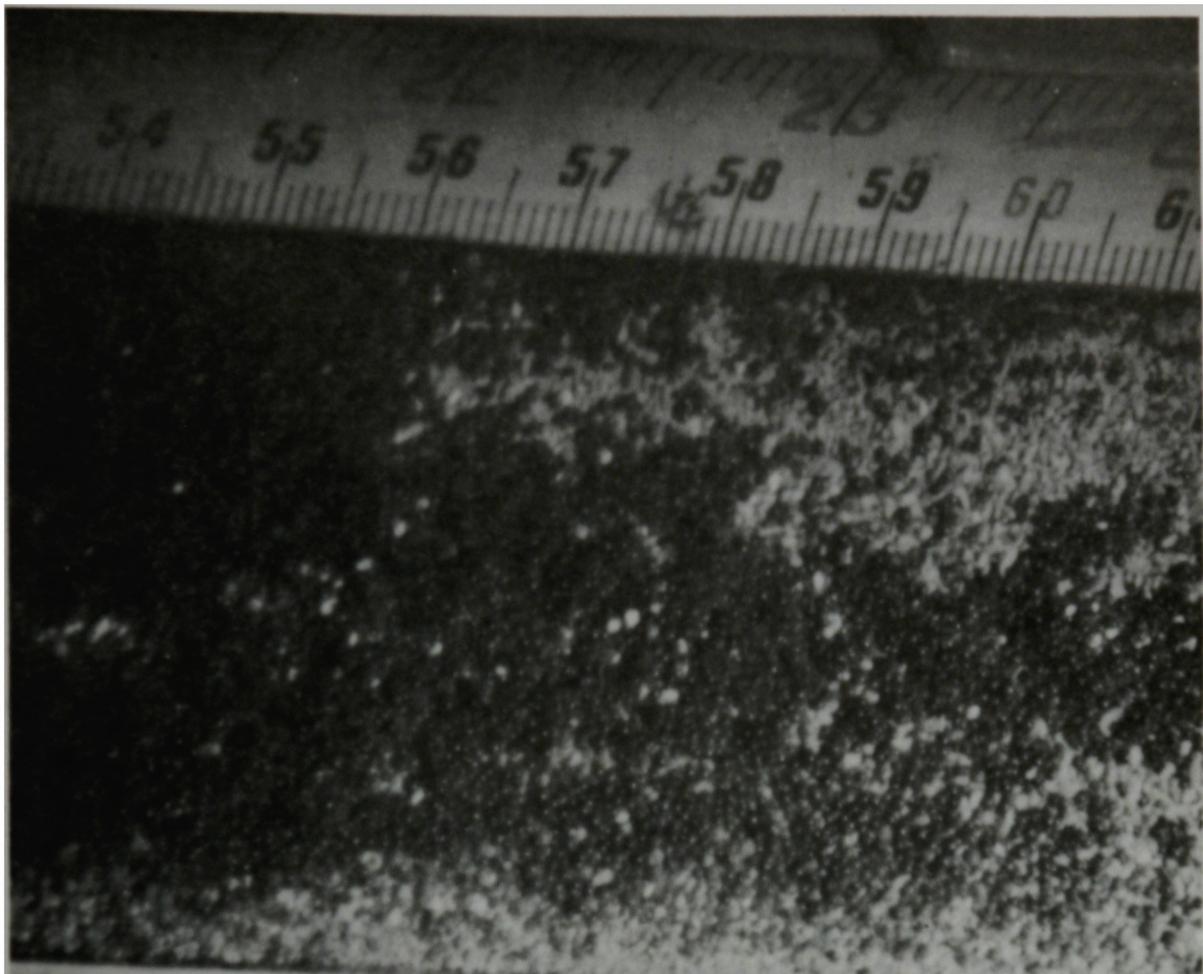
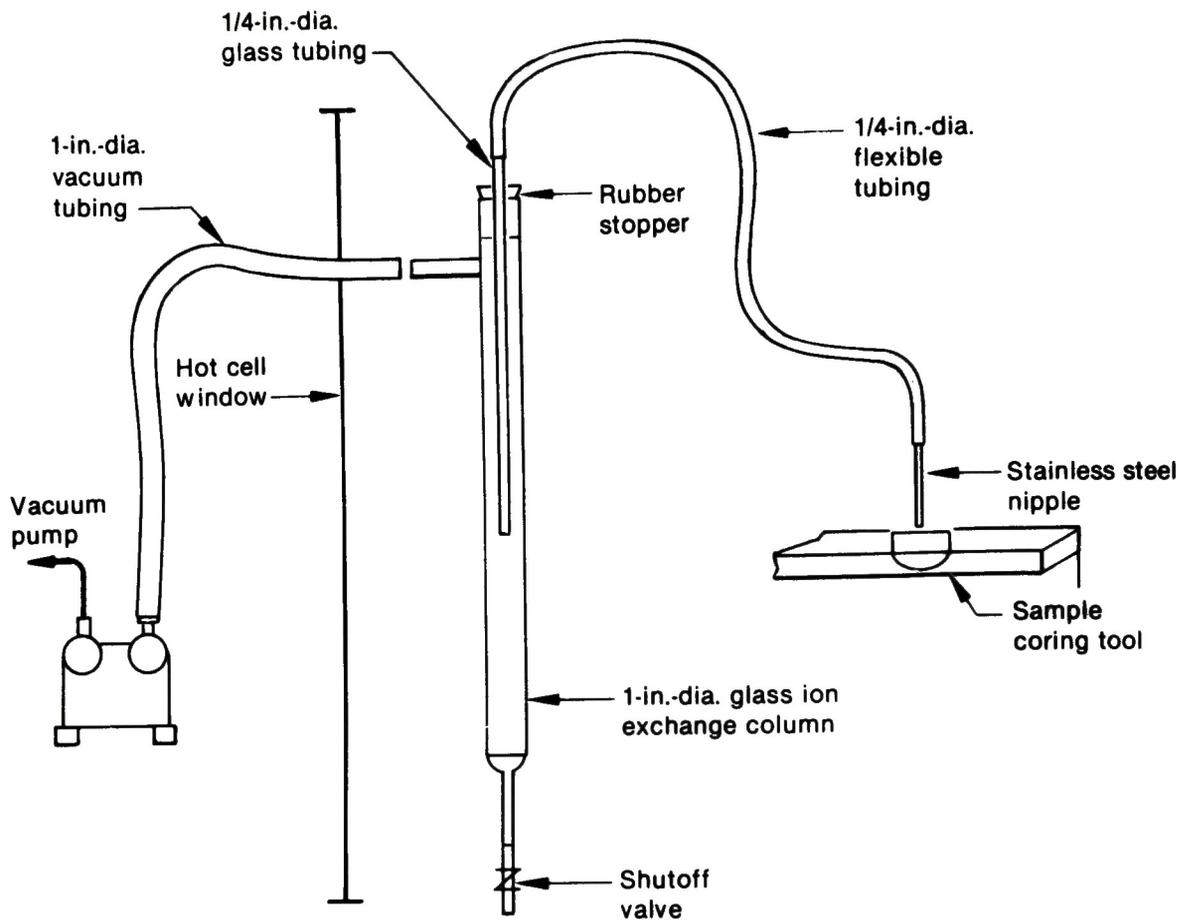


Figure 16. Location where resin sample PF-8#2 was removed from the coring tool.



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Figure 17. Location where resin sample PF 20 was removed from the coring tool.



4 0292

Figure 18. Schematic of apparatus used to collect resin samples from the coring tools.

Characterization of Unirradiated and Irradiated Resins

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

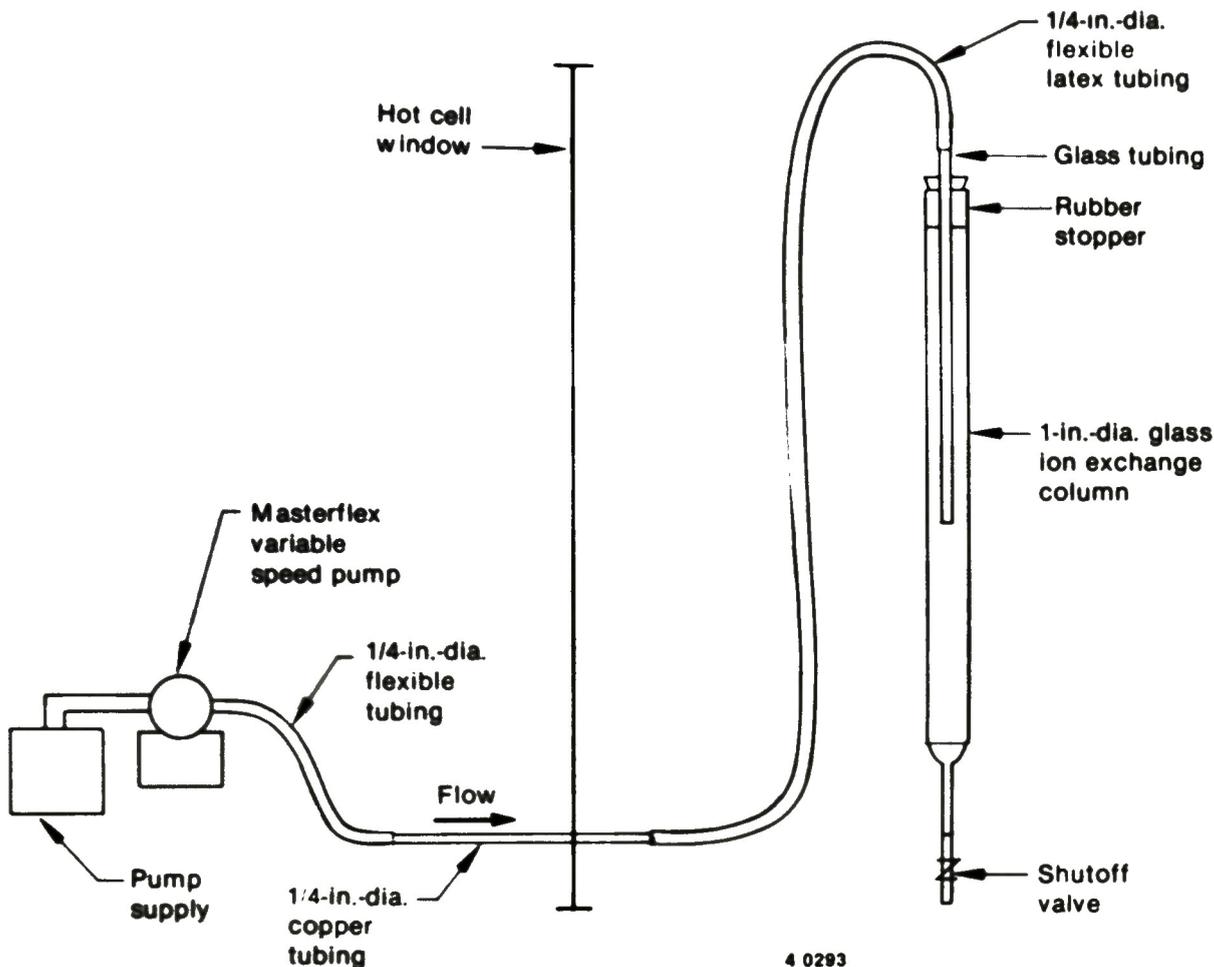
- ASTM Procedures for the Physical and Chemical Properties of Particulate Ion Exchange Resins¹⁰
- Infrared spectroscopy
- Gas chromatography
- Barium chloride precipitation for determination of sulfonic acid groups
- Scanning electron microscopy.

All of the above analytical methods were used to characterize the samples from PF-8 (strong acid cation 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 (such as those from EPICOR-II prefilters) were compared with results from unirradiated resins to determine if degradation had occurred. The following ASTM tests^a were used for the strong acid cation and phenolic cation exchange resins:

- Pretreatment (ASTM D2187-77 MethodA)

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



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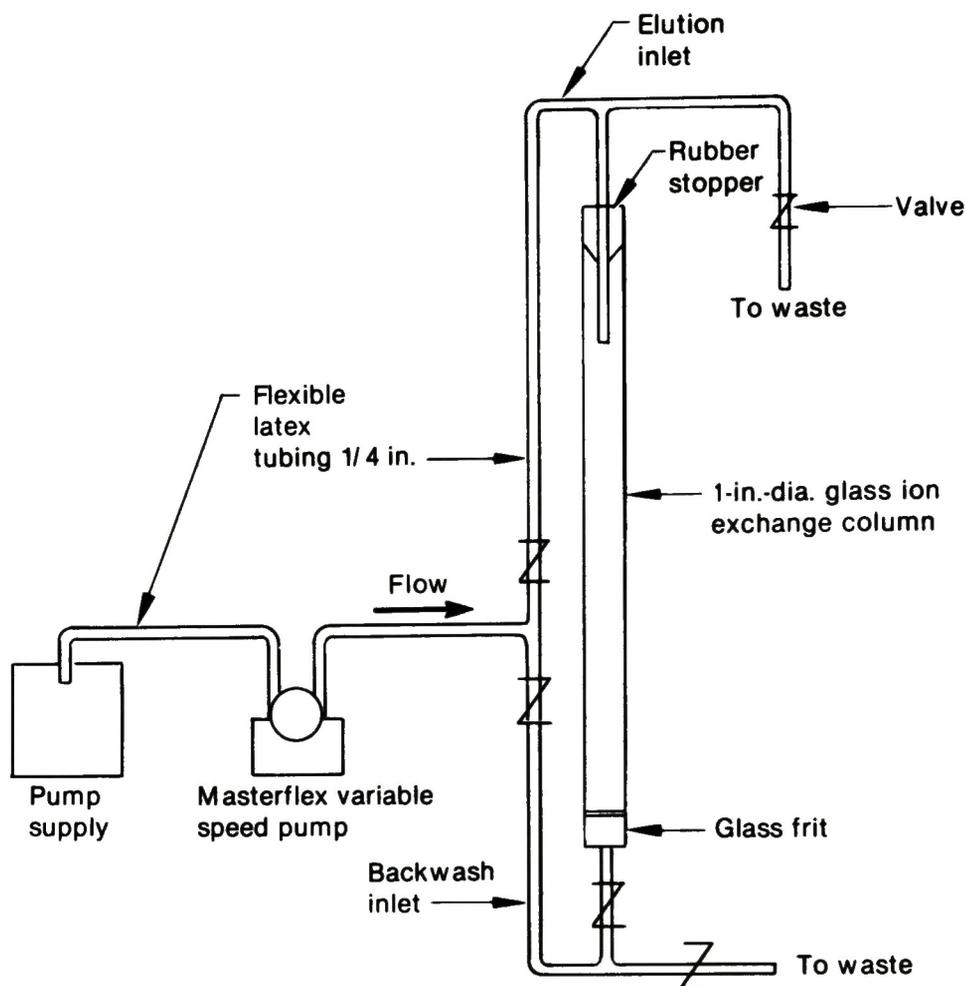
Figure 19. Schematic of apparatus used to elute radionuclides from the resin samples.

- 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 20) 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 grams of sodium chloride per liter of distilled water at a rate of 32 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



4 0290

Figure 20. Schematic of standard ASTM apparatus used for pretreatment of resins and backwashed and settled density test.

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.¹¹ 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 ± 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 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 11). 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 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 calculated.

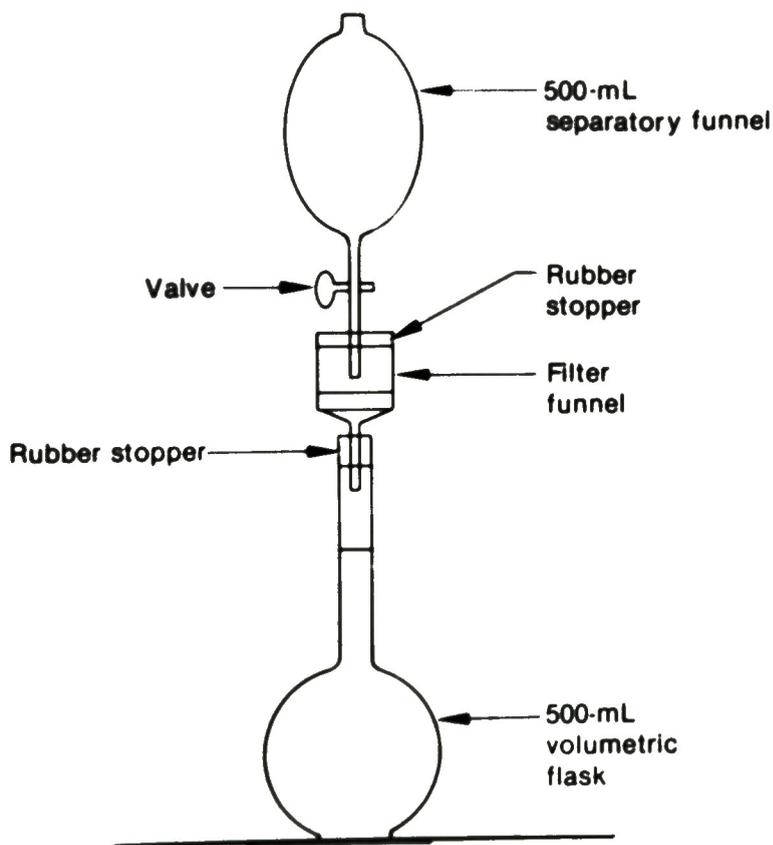
Salt Splitting Capacity. The salt splitting capacity test is designed to show only the number of sulfonic acid groups contained in a cation ion exchange resin. A decrease in salt splitting capacity would show a loss of functional sulfonic acid groups. The loss of sulfonic acid groups would allow the 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 21. The resin was converted to the hydrogen form by flowing 10% hydrochloric acid solution over the resin at a rate of 32 mL/min. The hydrogen form cation resin was eluted with a 50 grams per liter sodium chloride solution at a rate of 32 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 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 21 was assembled, and a 10% hydrochloric acid solution 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 grams 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 calculated.

Infrared Spectroscopy. Infrared spectroscopy involves identifying the rotational and vibrational motion of atoms in a molecule induced by infrared



4 0291

Figure 21. Schematic of standard ASTM apparatus for determining salt splitting and total exchange capacities.

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 of 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. 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 was 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 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 Carboxpack C as the stationary phase was chosen for the GC analysis.

The aliquots chosen for GC analysis were the distilled water soak and rinse solutions from the resin samples, and also the hydrochloric acid rinse solutions from the resin samples. All of the solutions from the resin samples were prepared for analysis using the 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 sol-

vent extraction. The solvent chosen for extraction was methylene chloride. Styrene and divinylbenzene are soluble in methylene chloride and not in distilled water; therefore, any styrene or divinylbenzene in the aliquot will be extracted into the methylene chloride.

2. 20 mL of methylene chloride 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 methylene chloride 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 methylene chloride each time.
5. The combined methylene chloride extracts in the Erlenmeyer flask were dried using sodium sulfate to remove any extraneous water.
6. The dried methylene chloride 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 or styrene) in the original sample would be concentrated in the methylene chloride. The presence of any of those soluble products would indicate polymer breakdown and eventual release of radionuclides.

Five microliters of the methylene chloride 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/methylene chloride (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.

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 5). 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 resin 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) polyeth-

ylene sample cell and placed into a visible spectrophotometer set at a wavelength of 420 nm. The absorption value of the solution was obtained and compared with absorption 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 to the resins would not allow the release of radionuclides.

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

RESULTS AND INTERPRETATION

Results of analysis of the unirradiated Epicor, Inc. resins and irradiated resin samples from EPICOR-II prefilters PF-8 and -20 are given in this section.

The unirradiated resins showed no apparent change from previous analyses (Reference 5). Because of the age (2 years old) of the unirradiated resins they might be expected to show some degradation. The irradiated resins from PF-8 and -20 also would be expected to show some degradation due to age (almost 4 years old).^{2,11} The unirradiated resins showed no degradation because of age; therefore, in this study, any degradation of the irradiated resins was assumed to be from radiation damage and not from age.

Other causes of degradation could be handling/mechanical damage and freezing. A review of the history of prefilters PF-8 and -20 indicates that the ion exchange media were not exposed to subfreezing temperatures. Also, handling was held to a minimum, and, as a result, damage should have been minimal.

ASTM Tests

Results of the following ASTM tests performed on unirradiated and irradiated resins are listed in Table 2: (a) water retention capacity, (b) backwashed and settled density, (c) salt splitting capacity, and (d) total exchange capacity.

Presented in Table 3 are the differences between ASTM tests performed on unirradiated Epicor, Inc. strong acid cation resin, and PF-8#1 and PF-20 strong acid cation resins. The differences were calculated using the data shown in Table 2 and applying the uncertainty values in the most conservative manner (i.e., to show the least changes). The increases in water retention capacities shown in Table 3 for the irradiated resins indicate a loss in effective cross-linking. The amount of loss is dependent on radiation dose (Reference 11); that is, the PF-8 sample received more radiation dose than the PF-20 sample and exhibits an increase in water retention capacity, or a loss in effective cross-linking. Table 3 also shows a decrease in the backwashed and settled density of the PF-8 and -20

Table 2. Results of ASTM tests on irradiated and unirradiated ion exchange resins

ASTM Test Parameter	Resin Sample				
	PF-8#1 Strong Acid Cation	PF-20 Strong Acid Cation	PF-8#2 Phenolic Cation ^a	Unirradiated Strong Acid Cation	Unirradiated Phenolic Cation Resin
Water retention capacity (%)	53.61 ± 0.21	48.93 ± 0.20	53.22 ± 0.21	48.40 ± 0.19	52.06 ± 0.21
Backwashed and settled density (g/mL)	0.75 ± 0.004	0.73 ± 0.004	0.60 ± 0.003	0.84 ± 0.004	0.64 ± 0.003
Salt splitting capacity (meq/g ^b)	4.85 ± 0.080	4.89 ± 0.075	3.85 ± 0.080	5.28 ± 0.080	3.09 ± 0.080
Total exchange capacity (meq/g ^b)	5.43 ± 0.05	5.78 ± 0.060	6.73 ± 0.070	5.60 ± 0.060	6.78 ± 0.07

a. Sample PF-8#2 was contaminated with 18.5% strong acid cation resin.

b. Measured in milliequivalents per gram of dry resin.

Table 3. ASTM test parameter changes of PF-8 and -20 strong acid cation resins versus unirradiated EPICOR, Inc. strong acid cation resin^a

ASTM Test Parameter	Resin Sample	
	PF-831	PF-20
Water retention capacity	4.81% increase	0.14% increase
Backwashed and settled density	0.09 g/mL decrease	0.11 g/mL decrease
Salt splitting capacity	0.28 meq/g decrease	0.25 meq/g decrease
Total exchange capacity	0.06 meq/g decrease	0.06 meq/g increase

a. Results reflect the most conservative values calculated from the reported uncertainty values presented in Table 2.

samples. That also is an indication of loss of effective cross-linking, which can lead to eventual loss of radionuclides (Reference 5). 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 5). The total exchange capacity shows a slight decrease for the PF-8#1 resin and a slight increase for the PF-20 resin. The increase in the total exchange capacity of PF-20 is due to oxidation of the polymer chain before radiation damage begins to degrade the resin. Furthermore, the higher radiation dose to the PF-8#1 resin explains the decrease in total exchange capacity as the radiation damage

exceeds the contribution from oxidation. The decrease in total exchange capacity may result in a loss of radionuclides.

Table 4 shows the differences between ASTM test parameters for the PF-8 phenolic cation resin and the Epicor, Inc. unirradiated phenolic cation resin. The differences between the PF-8 phenolic cation resin and the unirradiated phenolic cation resin are not as great as were observed in the strong acid cation resins. The PF-8#2 phenolic cation resin sample was contaminated with about 18.5% PF-8 strong acid cation resin. The contamination could have contributed to the differences in the test

Table 4. ASTM test parameter changes of PF-8 phenolic cation resins versus unirradiated EPICOR, Inc. phenolic cation resin^a

ASTM Test Parameter	Change
Water retention capacity	0.74% increase
Backwashed and settled density	0.04 g/mL decrease
Salt splitting capacity	0.61 meq/g increase
Total exchange capacity	No change

a. Results reflect the most conservative values calculated from the reported uncertainty values presented in Table 2.

results between the irradiated and unirradiated phenolic resins. The results (shown in Tables 2 and 4) for the PF-8#2 phenolic cation resin, however, show a slight increase in water retention capacity and a decrease in backwashed and settled density, indicating a loss in effective cross-linking, which can lead to the eventual loss of radionuclides. The increase in salt splitting capacity indicates oxidation of the polymer; that is, formation of carboxylic acid groups, which would reduce the tendency to release radionuclides by increasing exchange capacity (Reference 5). There was no change in the total exchange capacity of the PF-8#2 phenolic cation resin.

Infrared Spectroscopy

Shown in Figures 22 through 26 are the IR scans of the KBr pellets containing the resin samples PF-20, PF-8#1, PF-8#2, and the unirradiated strong acid cation and phenolic resins from Epicor, Inc. The spectrum shown in Figure 22 is typical of a

sulfonic acid divinylbenzene styrene strong acid cation resin (Reference 5). Shown in Figure 23 is the IR spectrum of the unirradiated Epicor, Inc. phenolic cation resin, a typical IR scan for that type of resin (Reference 5). Figures 24 and 25 show spectra of the strong acid cation resins from PF-8#1 and PF-20. The IR spectrum shown in Figure 26 is from the phenolic cation resin sample PF-8#2.

Figure 27 compares the spectrum from PF-8#1 with that of the unirradiated strong acid cation resin. Figure 28 compares the spectrum of PF-20 with that of the unirradiated strong acid cation resin. The spectra from PF-8#1 and PF-20 show that (a) the resins are the same as the strong acid cation resin received from Epicor, Inc. and (b) no significant changes in polymer structure are apparent in the irradiated resins from the two EPICOR-II prefilters.

Figure 29 compares the PF-8#2 phenolic cation resin with the unirradiated Epicor, Inc. phenolic cation resin. The spectra show no differences,

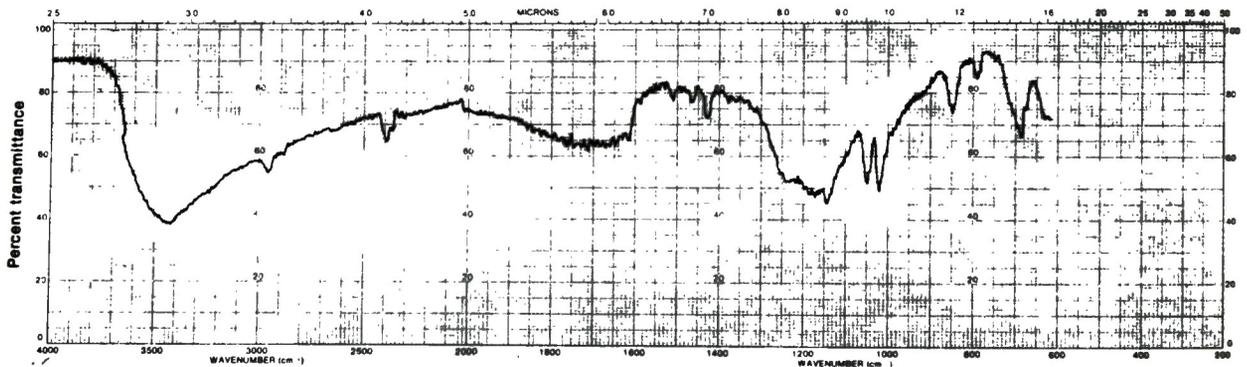


Figure 22. IR spectrum of unirradiated Epicor, Inc. strong acid cation resin.

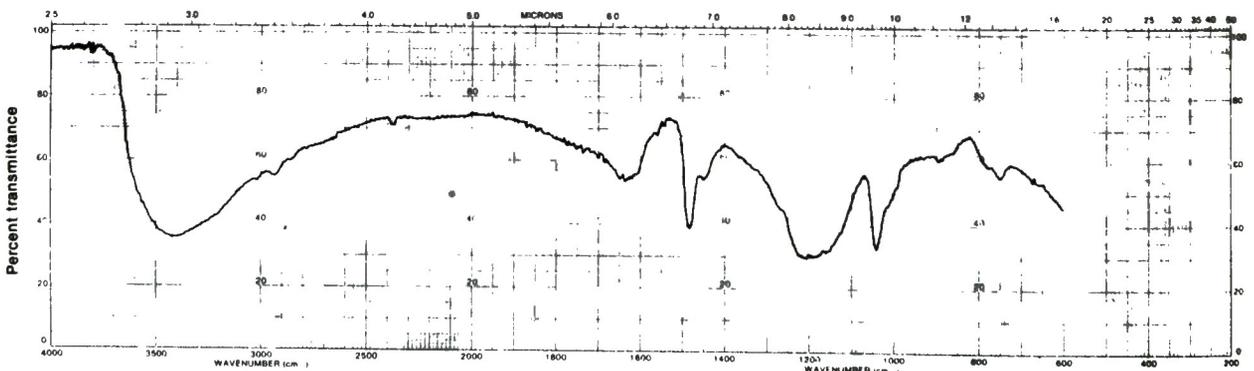


Figure 23. IR spectrum of unirradiated Epicor, Inc. phenolic cation resin.

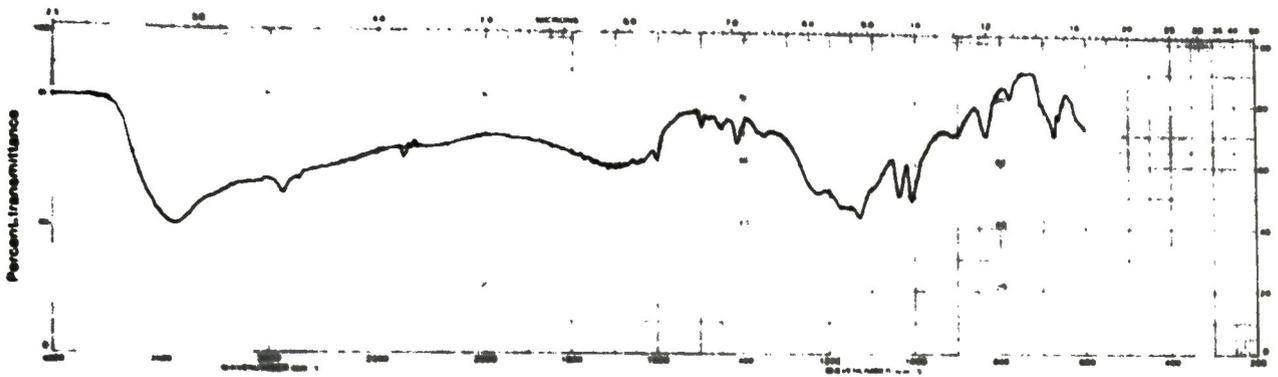


Figure 24. IR spectrum of EPICOR-II strong acid cation resin sample PF-8#1.

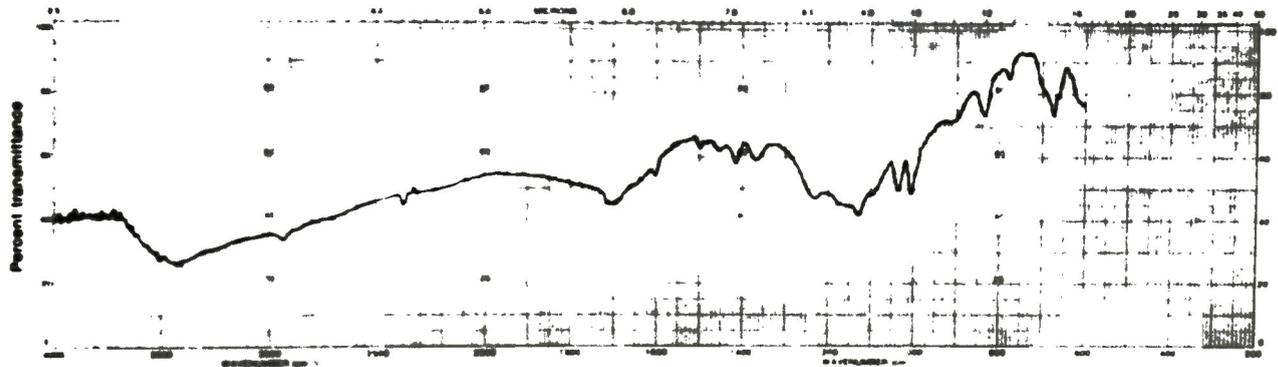


Figure 25. IR spectrum of EPICOR-II strong acid cation resin sample PF-20.

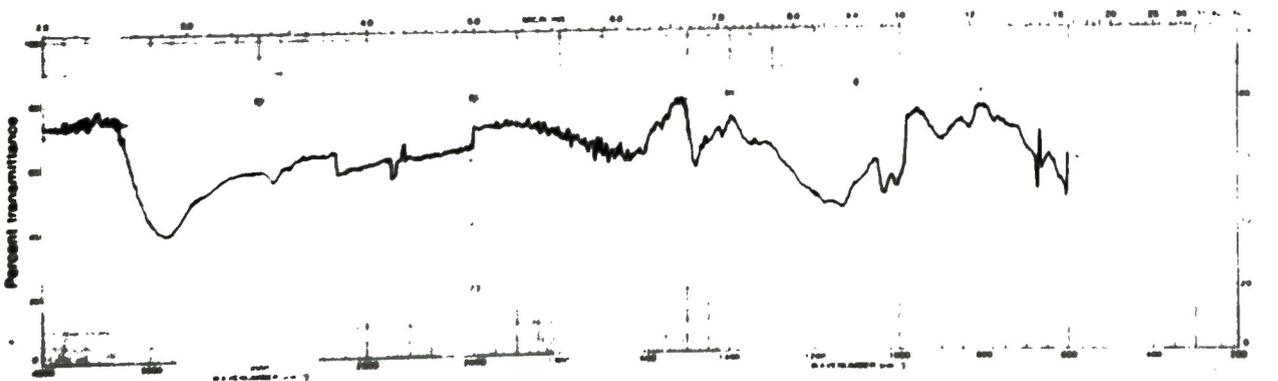


Figure 26. IR spectrum of EPICOR-II phenolic cation resin sample PF-8#2.

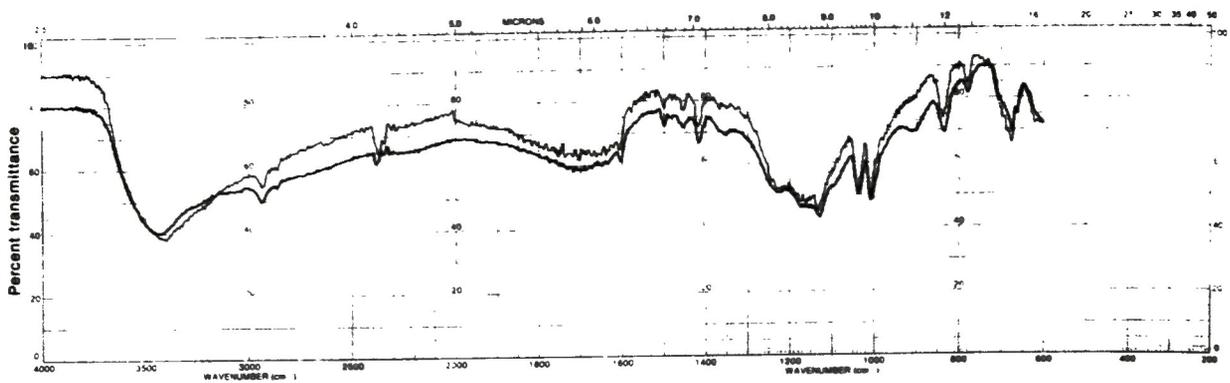
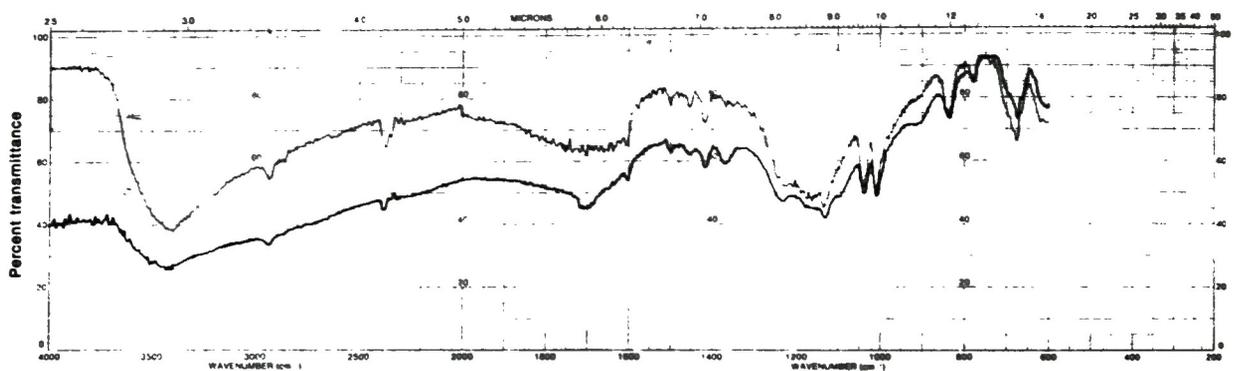


Figure 27. Comparison of the IR spectrum from unirradiated Epicor, Inc. strong acid cation resin (top spectrum) with that of sample PF-8#1 strong acid cation resin (bottom spectrum).



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Figure 28. Comparison of the IR spectrum from unirradiated Epicor, Inc. strong acid cation resin (top spectrum) with that of sample PF-20 strong acid cation resin (bottom spectrum).

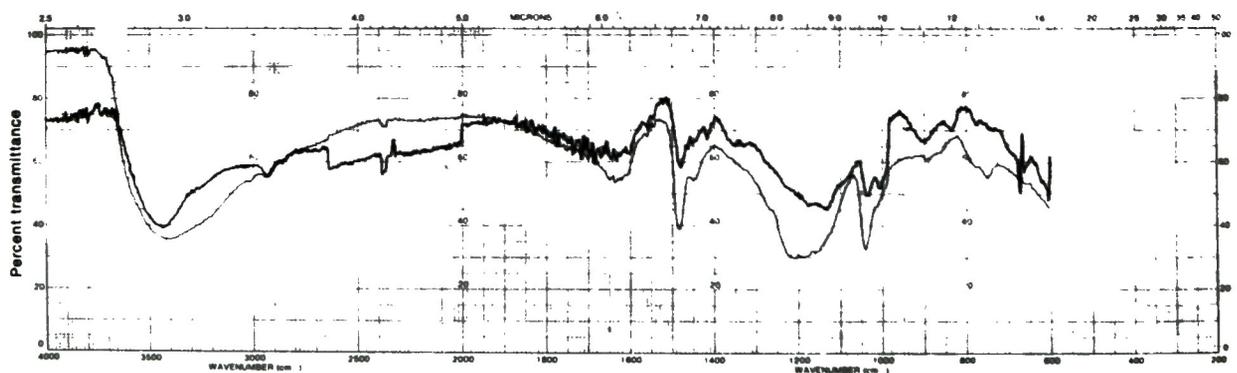


Figure 29. Comparison of the IR spectrum from unirradiated Epicor, Inc. phenolic cation resin (top spectrum) with that of sample PF-8#2 phenolic cation resin (bottom spectrum).

which indicates (a) the phenolic resin from PF-8#2 and the phenolic resin from Epicor, Inc. are the same and (b) no significant changes in polymer structure have occurred in the irradiated resins from the EPICOR-II prefilters.

Gas Chromatography

Shown in Figures 30 and 31 are the chromatograms of standard amounts of styrene and divinylbenzene. Those chromatograms are used as retention time standards (i.e., the time it takes to elute a chemical from a GC column) for comparison with other chromatograms. Figures 32 through 35 are chromatograms of the various distilled water soak and rinse solutions from strong acid cation resin samples PF-20 and PF-8#1, and from phenolic cation resin sample PF-8#2.

Comparing chromatograms of Figures 32, 33, and 34 with Figures 30 and 31 shows no soluble organic products such as divinylbenzene or styrene are present in the soak and rinse solutions taken from the PF-8 and -20 strong acid cation resin samples.

Comparing the chromatogram of Figure 35 with the chromatograms of Figures 30 and 31 shows no

soluble organic products such as divinylbenzene or styrene are present in the soak solution taken from the PF-8#2 phenolic cation resin. The phenolic cation resin contains no styrene and, therefore, should show no styrene.

Barium Chloride Precipitation for Determination of Sulfonic Acid Groups

Results of the barium chloride precipitation tests are shown in Table 5. The results show large sulfate concentrations in the PF-8#1 and PF-20 cation resin distilled water soak and rinse solutions. Those large concentrations indicate a loss of functional groups, with subsequent 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 85 kcal/mol).¹² 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.

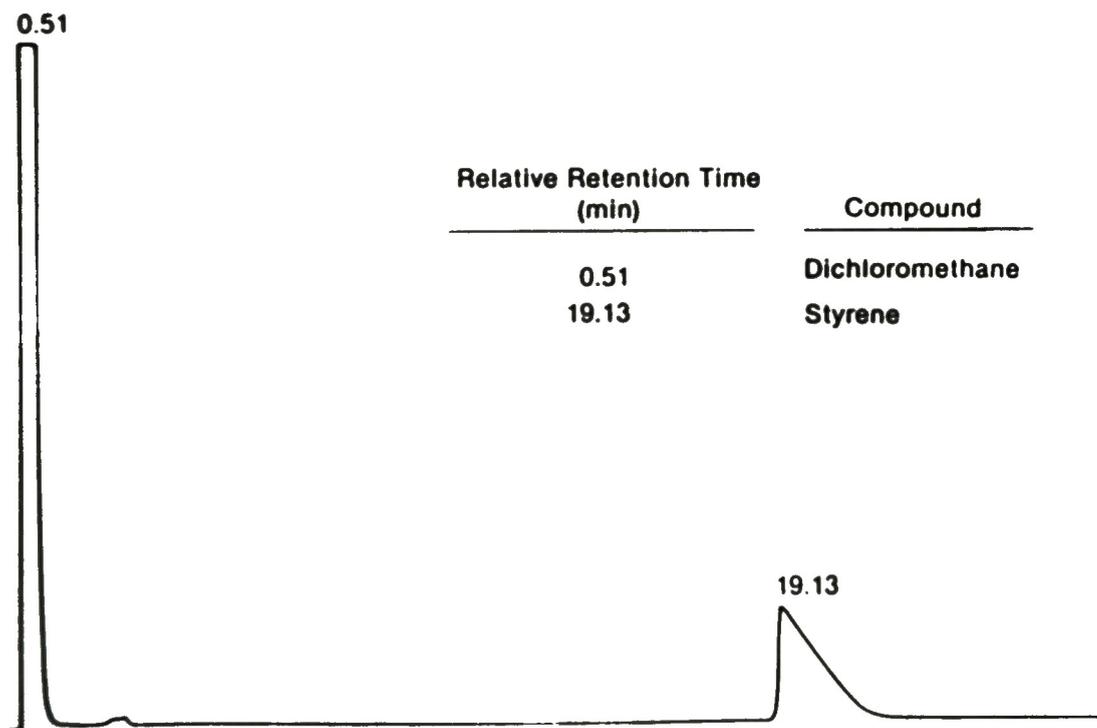


Figure 30. Chromatogram of 1 mL of styrene in 100 mL of dichloromethane.

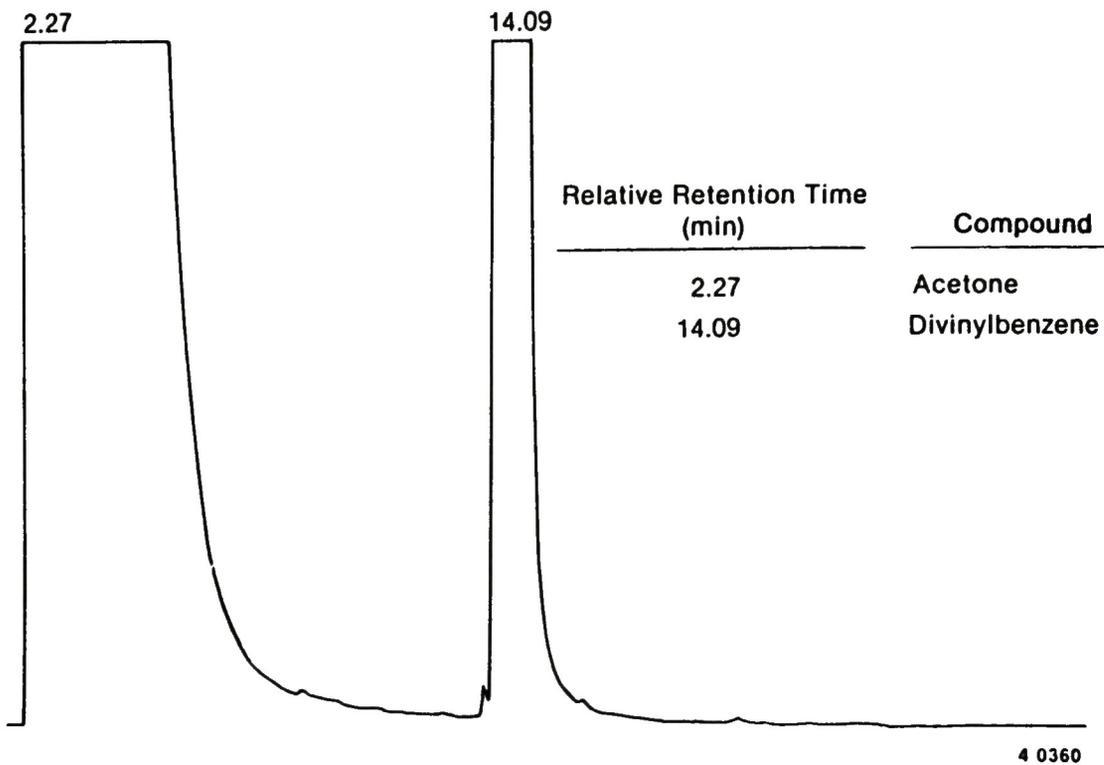


Figure 31. Chromatogram of 1 mL of divinylbenzene in 100 mL of acetone.

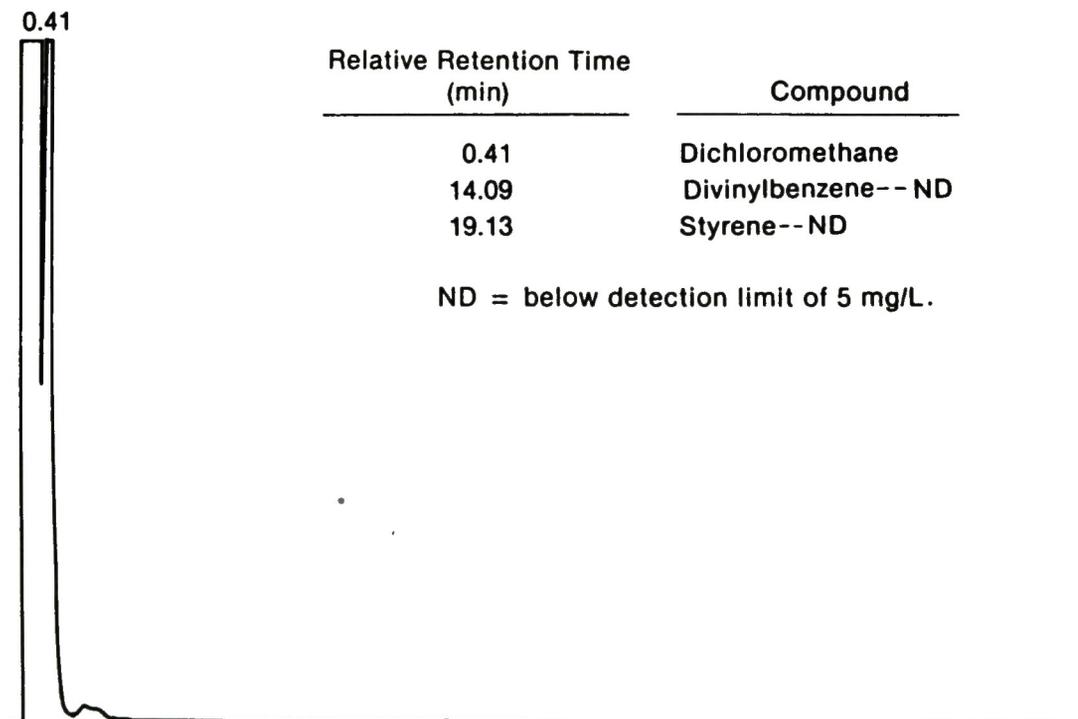


Figure 32. Chromatogram of distilled water 24-h soak solution from PF-8#1 strong acid cation resin sample.

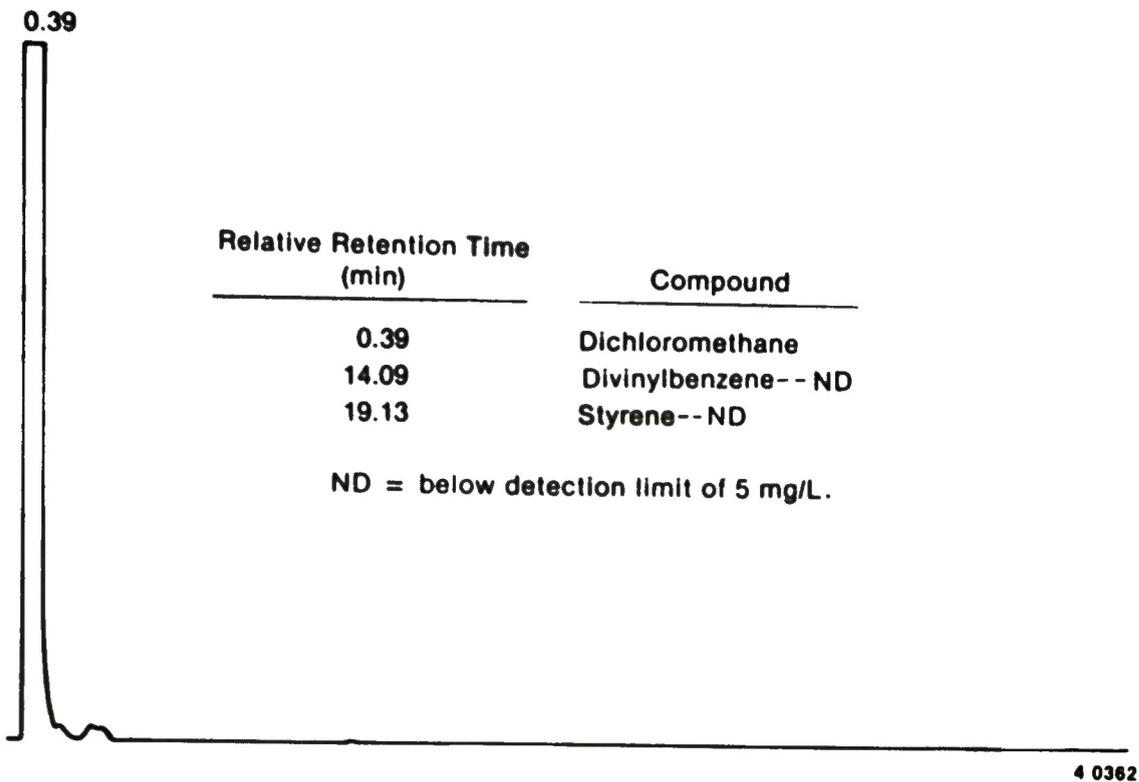


Figure 33. Chromatogram of distilled water rinse solution from PF-8#1 strong acid cation resin sample.

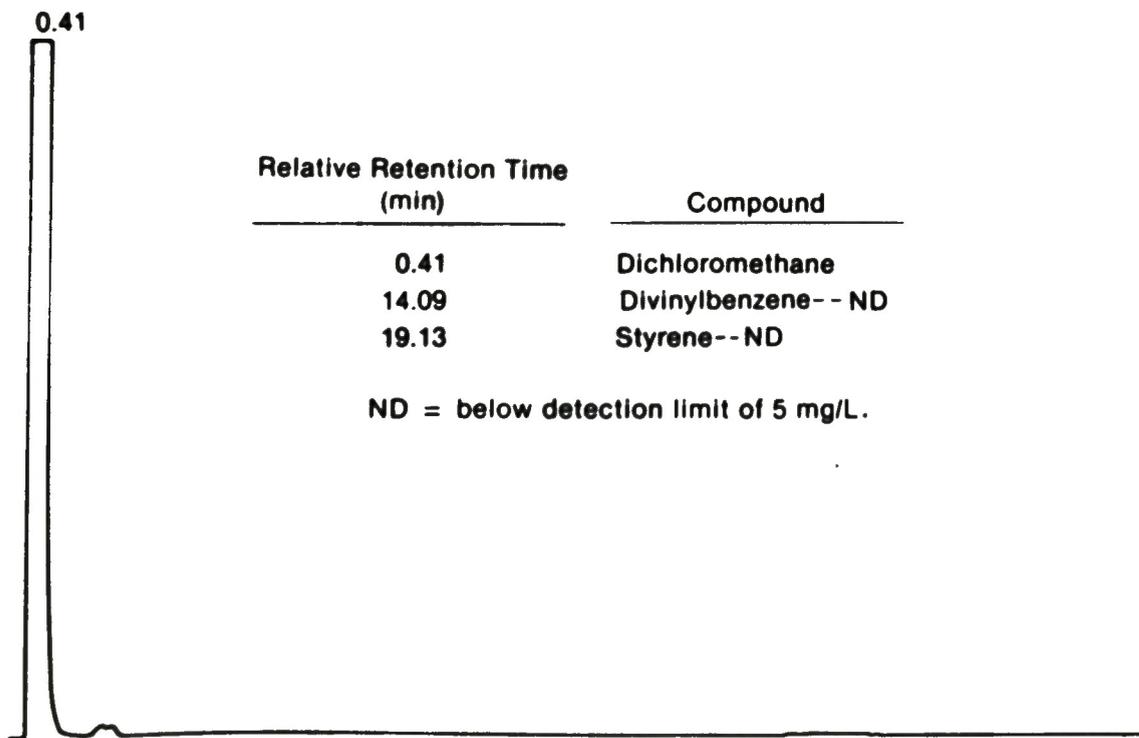


Figure 34. Chromatogram of 24-h distilled water soak solution from PF-20 strong acid cation resin sample.

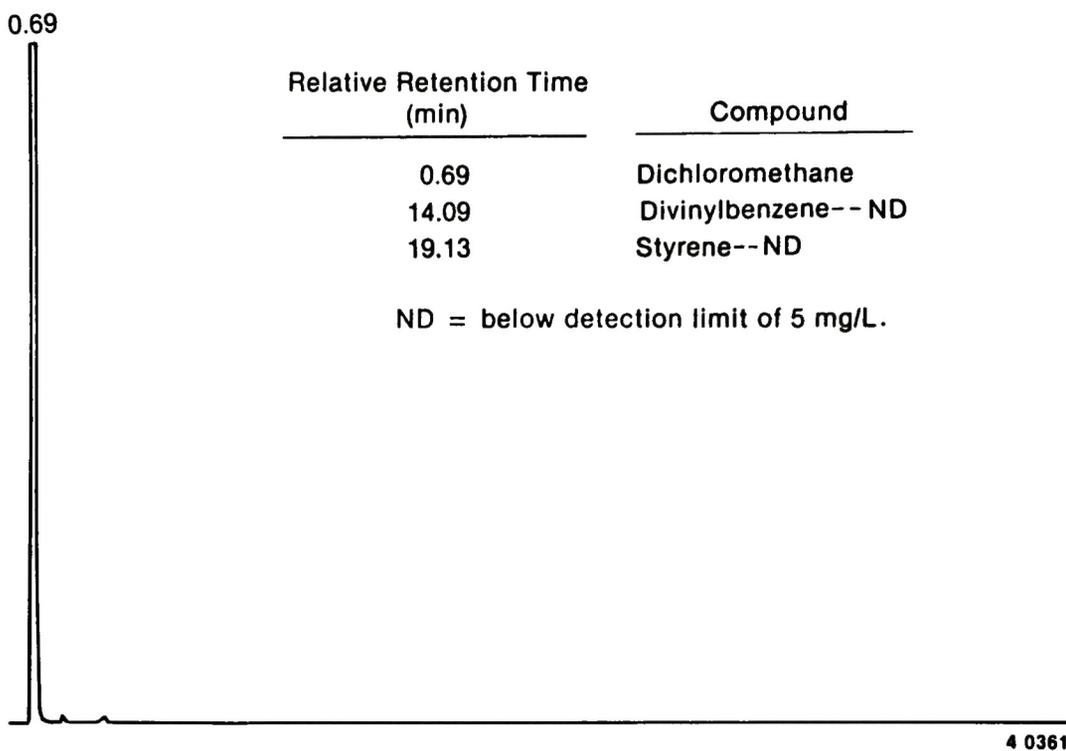


Figure 35. Chromatogram of 24-h distilled water soak solution from PF-8#2 phenolic cation resin sample.

Table 5. Results of barium chloride precipitation tests for determining sulfonic acid groups

Sample Solution	Sulfate Concentration (mg/L)	pH
DI water ^a	ND ^b	—
PF-8#1 DI water, 24-h soak	1750	2.4
PF-8#1 DI water, first rinse	2000	2.3
PF-8#1 DI water, second rinse	60	2.9
PF-20 DI water, 24-h soak	434	2.8
Unirradiated Epicor, Inc. strong acid cation resin 24-h soak	ND	4.5

a. DI = distilled.

b. ND = none determined.

The phenolic resins contain no sulfonic acid groups; therefore, the distilled water soak and rinse samples showed no sulfate (Reference 5).

Scanning Electron Microscopy

The SEM photomicrographs in Figures 36 and 37 show the unirradiated strong acid cation resin from Epicor, Inc. Figures 38 and 39 are photomicrographs of strong acid cation resin from PF-20. Figures 40 and 41 are photomicrographs of strong acid cation resin from PF-8#1.

Comparing Figures 36 and 37 with photomicrographs of PF-20 (Figures 38 and 39) shows little or no difference between the unirradiated and irradiated resins and, therefore, no damage to the PF-20 resin (i.e., no cracking, breaking, etc.). Comparing Figures 36 and 37 with photomicrographs of PF-8#1 strong acid cation resin (Figures 40 and 41) shows considerable damage to the PF-8#1 resin. The photomicrographs in Figures 40 and 41 show resin bead damage that is more extensive and of a different fracture type than what had been observed by BCI

in resins from EPICOR-II prefilters PF-3 and -16.^{13,14} It is believed that the differences were caused by the higher radiation dose received by the PF-8#1 strong acid cation resin. That type of damage, however, should not lead to release of radionuclides.

The photomicrographs in Figures 42 and 43 show the unirradiated Epicor, Inc. phenolic cation resin. Comparing the PF-8#2 phenolic cation resin in Figures 44, 45, and 46 with the unirradiated phenolic cation resin in Figures 42 and 43 indicates some damage to the irradiated resin. The particles in the photomicrographs of the unirradiated phenolic cation resin are smooth, and any breaks or cracks in the particles are uniform. On the other hand, several particles in the phenolic cation resin sample from PF-8#2 are ragged, sponge-like, and porous. Several nonuniform cracks have appeared in the PF-8#2 resin particles. The spheres that appear in Figure 44 are the contamination from the PF-8#1 strong acid cation resin sample that was intermixed with PF-8#2 phenolic cation resin during coring operations. As stated previously, the type of physical damage observed should not cause release of radionuclides.

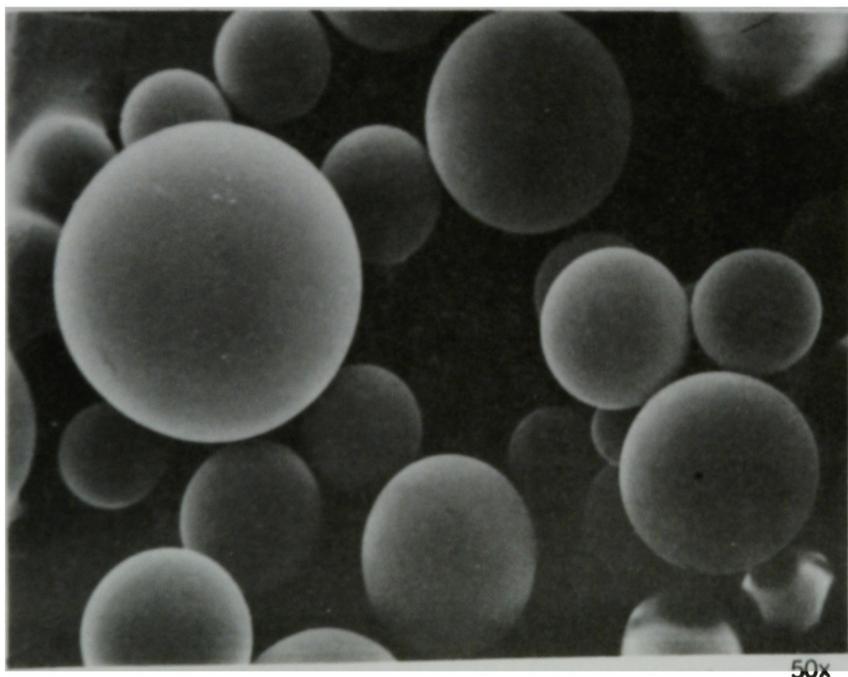
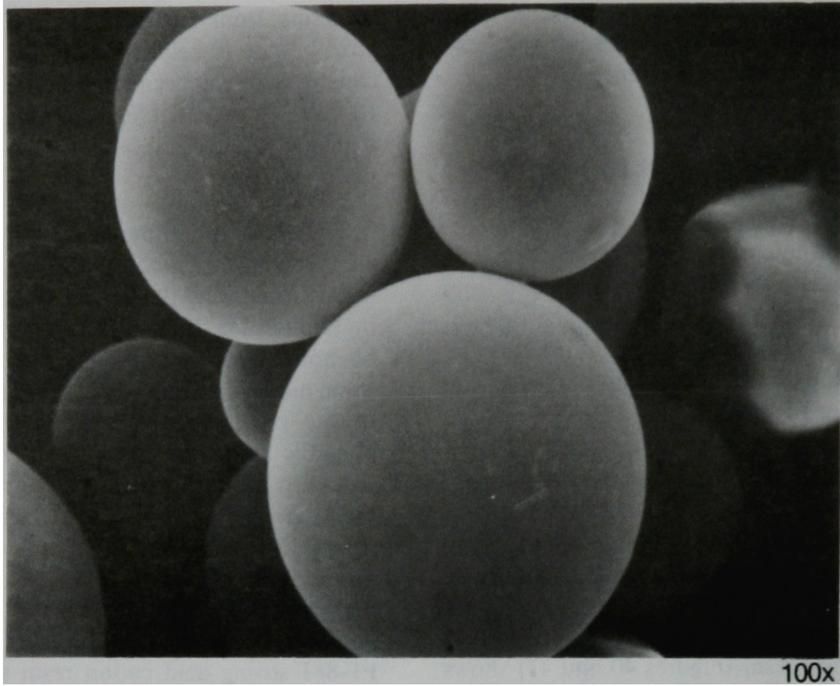


Figure 36. SEM photomicrograph of unirradiated Epicor, Inc. strong acid cation resin at 50 magnification.



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Figure 37. SEM photomicrograph of unirradiated Epicor, Inc. strong acid cation resin at 100 magnification.

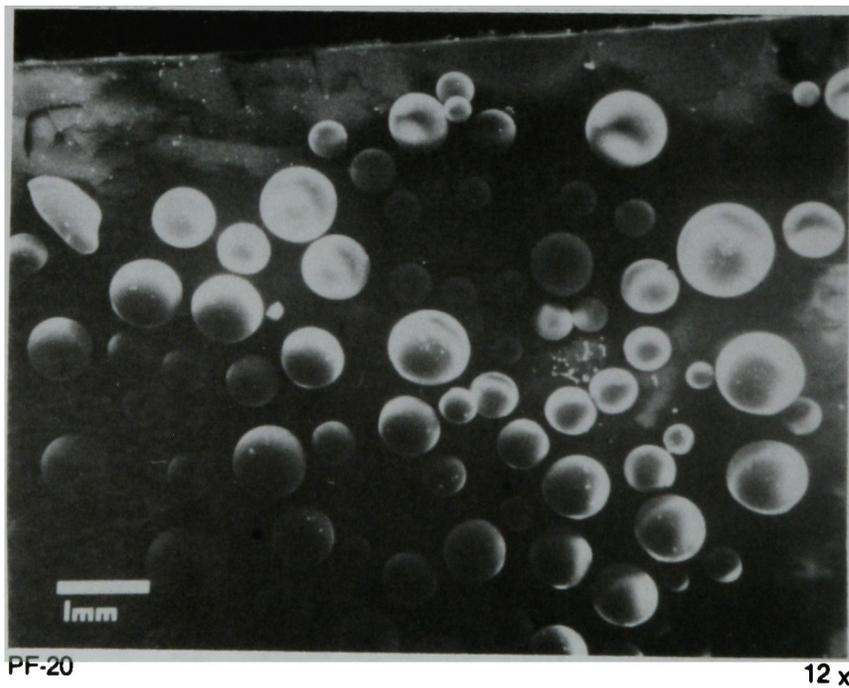
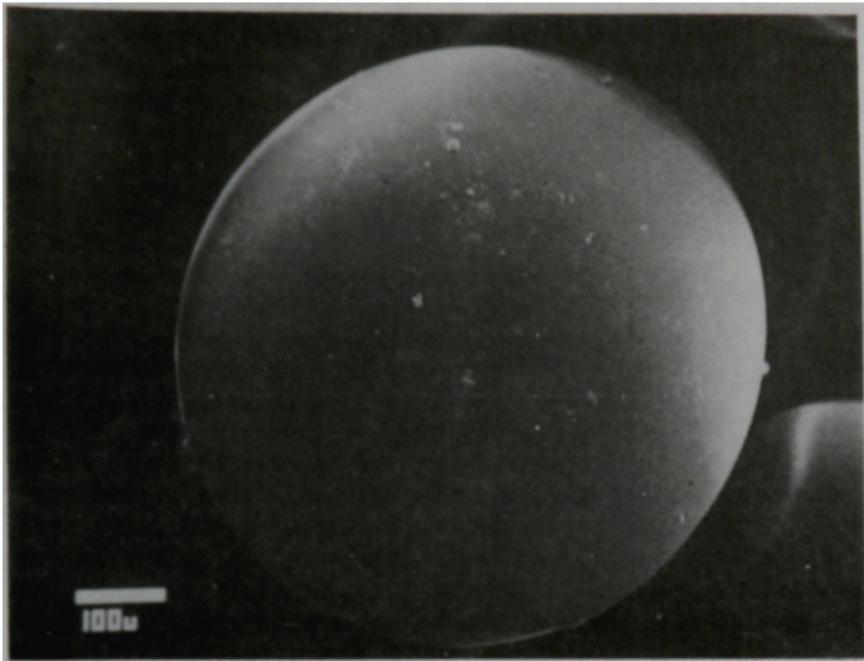


Figure 38. SEM photomicrograph of EPICOR-II strong acid cation resin sample PF-20.

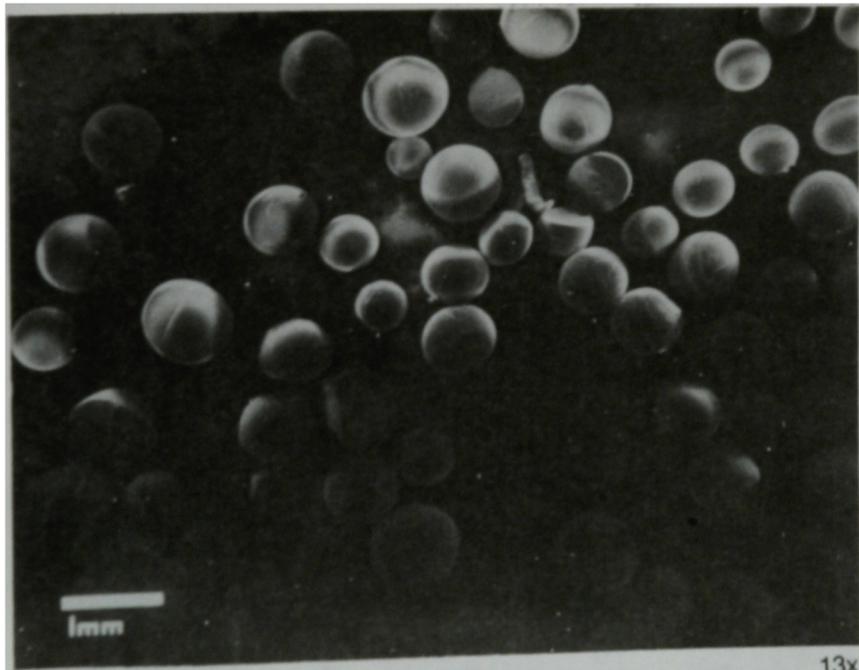


PF-20

120x

5 6283

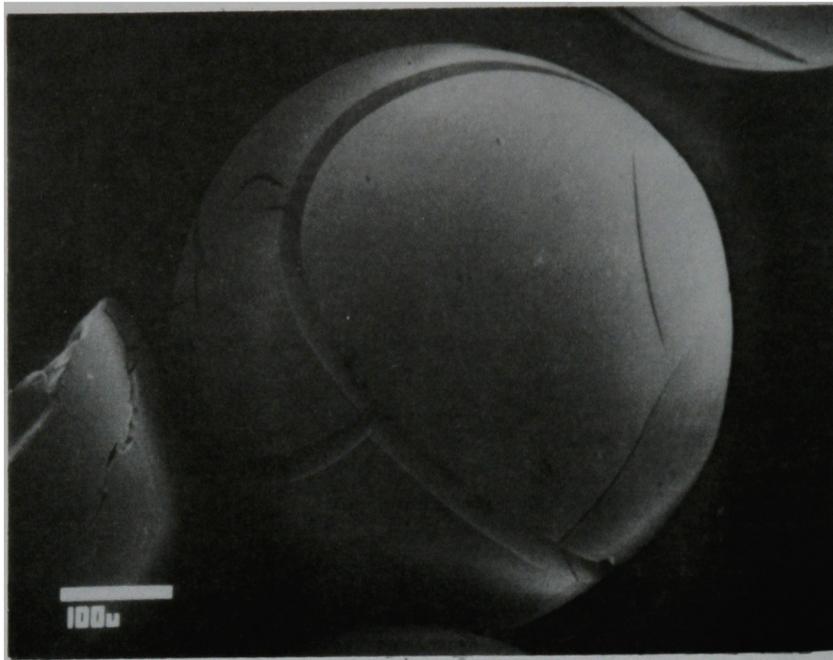
Figure 39. SEM photomicrograph of EPICOR-II strong acid cation resin sample PF-20 showing a closeup of one resin bead at 120 magnification.



PF-8#1

13x

Figure 40. SEM photomicrograph of EPICOR-II strong acid cation resin sample PF-8#1 at 13 magnification.



PF-8#1

150x

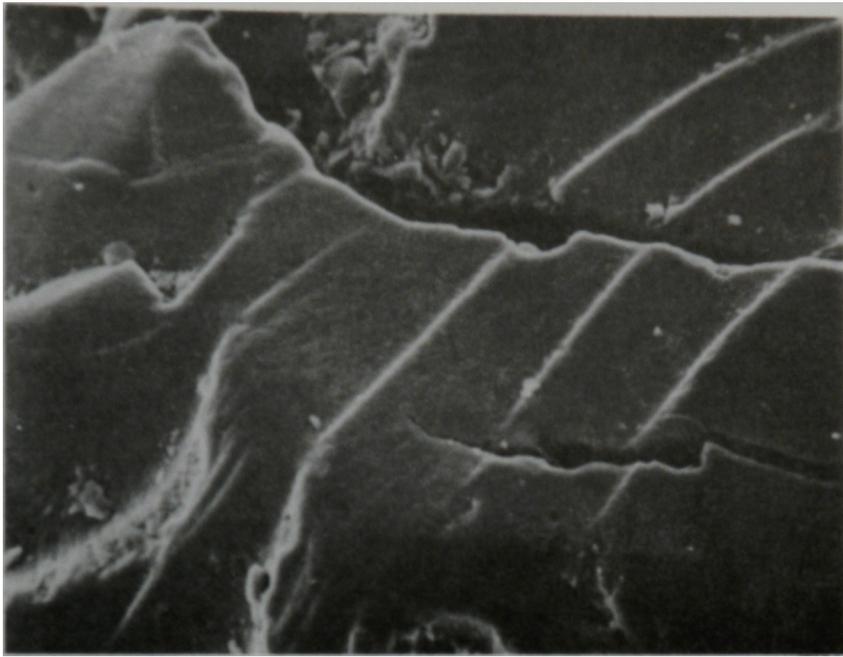
5 6280

Figure 41. SEM photomicrograph of EPICOR-II strong acid cation resin Sample PF-8#1 showing a closeup of one resin bead at 150 magnification.



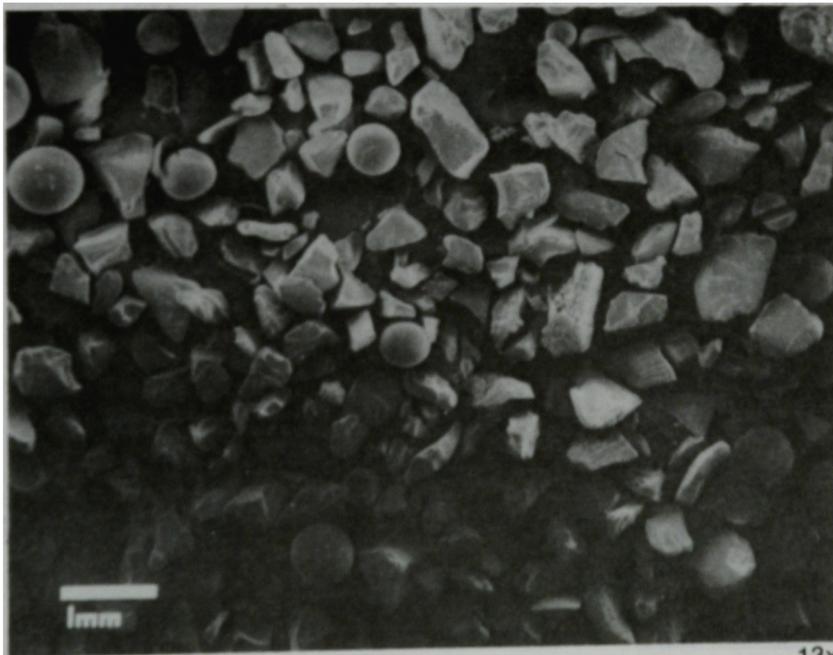
50x

Figure 42. SEM photomicrograph of unirradiated Epicor, Inc. phenolic cation resin at 50 magnification.



500x
5 8281

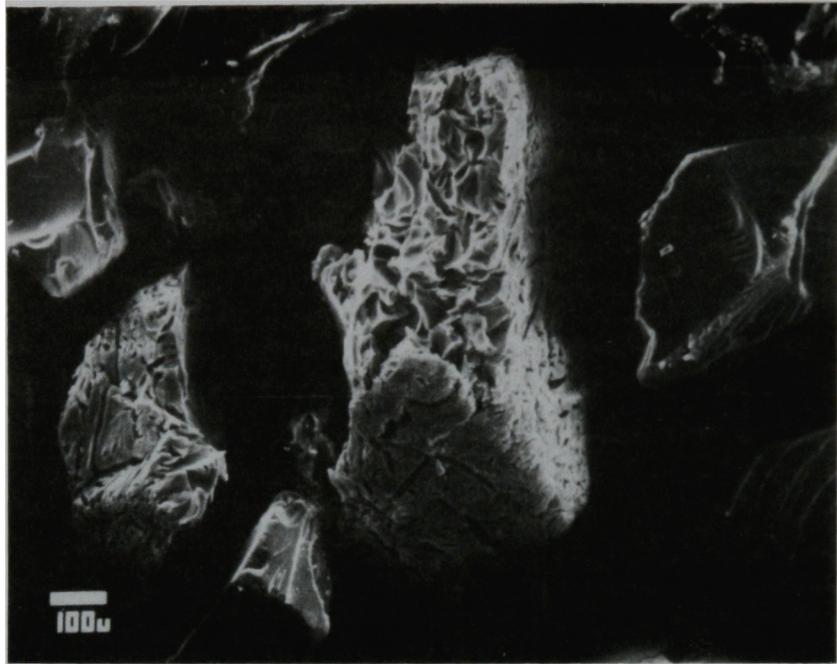
Figure 43. SEM photomicrograph of unirradiated Epicor, Inc. phenolic cation resin showing a closeup of one resin particle at 500 magnification.



PF-8#2

13x

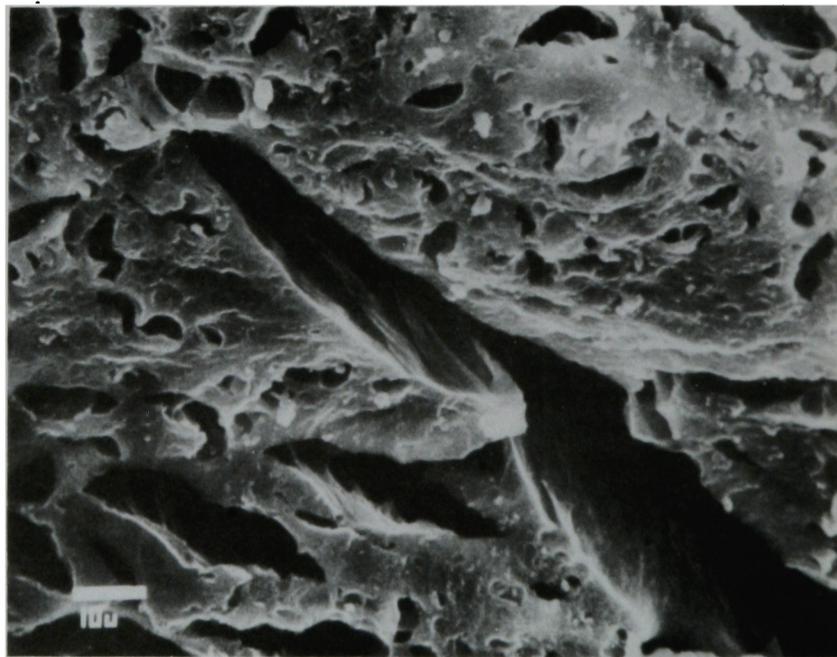
Figure 44. SEM photomicrograph of EPICOR-II phenolic cation resin sample PF-8#2 at 13 magnification.



PF-8#2

80x
5 6284

Figure 45. SEM photomicrograph of EPICOR-II phenolic cation resin sample PF-8#2, showing a closeup of one resin particle at 80 magnification.



PF-8#2

1000x
5 6285

Figure 46. SEM photomicrograph of EPICOR-II phenolic cation resin sample PF-8#2, showing a closeup of one resin particle at 1000 magnification .

Summary of Results

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

resin sample PF-8#2 are summarized in Table 6. Values in the table are expressed in terms of changes in results obtained from tests on the irradiated EPICOR-II resins versus the unirradiated Epicor, Inc. resins.

Table 6. Summary of results from analysis of EPICOR-II irradiated resin samples PF-8#1, PF-20, and PF-8#2^a

Analytical Technique	Resin Sample		
	PF-8#1 Strong Acid Cation	PF-20 Strong Acid Cation	PF-8#2 Phenolic Cation
ASTM Tests			
<ul style="list-style-type: none"> • Water retention capacity • Backwashed and settled density • Salt splitting capacity • Total exchange capacity 	Increase Decrease Decrease Decrease	Increase Decrease Decrease Increase	Increase Decrease Increase No change
Infrared spectroscopy	No apparent changes in structure	No apparent changes in structure	No apparent changes in structure
Gas chromatography	No soluble products determined	No soluble products determined	No soluble products determined
BaCl₂ precipitation for determination of sulfonic acid groups	Sulfonic acid groups are being lost	Sulfonic acid groups are being lost	This resin contains no sulfonic acid groups
Scanning electron microscopy	Resin bead cracking observed	No damage noted	Damage observed on a few particles
Visual observations	Nothing unusual observed	Nothing unusual observed	Contamination with PF-8#1 resin observed
Physical observations	Lack of flow during elution observed	Lack of flow during elution observed	Nothing unusual observed

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

DISCUSSION

Several important studies of ion exchange resins have been conducted, including research by Brookhaven National Laboratory (BNL)^{2,11,15,16} and BCL.^{13,14} The BNL research included radiation effects on ion exchange resins. The BCL work covered characterization of EPICOR-II prefilters PF-3 and -16. This section compares those results with results of the study of PF-8 and -20 resins at INEL.

Brookhaven National Laboratory Research

The study conducted at BNL (Reference 11) was directed at compiling information concerning damage to synthetic organic ion exchange resins by radiation. The following material contains excerpts from that study applicable to the research done at INEL:

- 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 in flowing (dynamic) systems causes more drastic changes in their physical and chemical properties than ion exchange resins irradiated to static systems.
 - Radiation [caused] chemical changes in ion exchange resins are a direct function of the total [radiation] dose absorbed by the resin.

The EG&G Idaho research at INEL on prefilters PF-8 and -20 has shown that the above generalizations are applicable to the EPICOR-II resins. However, it must be pointed out that the above generalizations might not apply in every case (i.e., resins having different structures than the EPICOR-II resins may not exhibit the same properties).

Additional work conducted by BNL on irradiation of ion exchangers was reported in References 15, and 16. That research was concerned with gas generation, agglomeration, and pH changes within the resin environment as a result of degradation caused by external radiation. The BNL work^{11,15,16} notes that soak and rinse water from irradiated resins showed low pH. References 15 and 16 report agglomeration of various organic resins at external radiation doses greater than 10^9 rad, although EPICOR D-mix resin showed no agglomeration even at 10^9 rad.

Battelle Columbus Laboratories Research

The BCL research was conducted on EPICOR-II prefilters PF-3 and -16 (References 13 and 14). The investigation of PF-16 showed little or no degradation of resins. The research on PF-3 was a more in-depth study of the EPICOR-II liners and their contents. The resin was sampled, and visual observations were made, including scanning electron microscopy. The following material contains excerpts from Reference 13 concerning observations from the characterization of PF-3:

- Degradation of the ion exchange media because of radiation appeared to be minimal, if any. The only evidence of cracking

and fragmentation of the media particles was found, not in the top region of the resin bed where most of the gamma-emitting radionuclides were deposited, but in the bottom of the resin bed. In the bottom region, the resin particles showed significantly more cracking, spalling, and fragmenting than in PF-16. This would indicate damage had occurred from the loading of resin into the prefilter.

- The pH determinations showed that the ion exchange media was acidic in nature, with the pH decreasing from the top to the bottom of the resin bed.
- The top region of the resin bed was very effective in removing both cesium and strontium from the contaminated water; plutonium and uranium, however, were uniformly distributed throughout the resin.

Idaho National Engineering Laboratory Research

The study at INEL of resins from EPICOR-II prefilters PF-8 and -20 and unirradiated Epicor, Inc. resins has shown that degradation caused by radiation of the strong acid cation and phenolic cation resins has occurred, as predicted by other researchers. The research done at INEL was concerned with chemical and physical measurement of degradation of organic ion exchangers. That study, however, has shown that the pH of soak and rinse water from EPICOR-II resins is low (3.0), as also was noted in References 11, 15, and 16. Agglomeration of the strong acid cation and phenolic cation resins was not seen, as such, during the INEL study, although a restriction to flow was observed during initial in-column elution of the PF-8#1 and PF-20 strong acid cation samples. References 15 and 16 reported agglomeration of various organic resins at external radiation doses greater than 10^9 rad, while the PF-8 and PF-20 strong acid cation samples experienced doses slightly over 10^7 rad. Reference 16 reported no agglomeration of the EPICOR D-mix resin, even at 10^9 rad. The INEL

study was not directed at gas generation; therefore, no comparison with that parameter is made.

Based on the INEL study and research at BNL and BCL, the following mechanisms of degradation are thought to be occurring within the EPICOR-II strong acid cation resins:

- The resins are losing 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 their increase in water retention capacity, decrease in salt splitting capacity, and decrease in backwashed and settled density.
- The resins are losing functional groups (with accompanying loss of radionuclides), as indicated by their increase in sulfate concentrations in the distilled water soak and rinse solutions and loss in salt splitting capacity.
- The resins from PF-20 are showing an initial increase in total exchange capacity as a result of oxidation of the polymer chain. The resins from PF-8 are showing a decrease in total exchange capacity because of increasing radiation dose. This decrease will lead to an eventual release of radionuclides.

Based on the INEL study and research at BNL and BCL, the following mechanisms of degradation are thought to be 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 backwashed and settled density
- Oxidation of the polymer chain (which would reduce the tendency to release radionuclides), as indicated by the increased salt splitting capacity.

CONCLUSIONS

Results found thus far at INEL in the study of degradation of EPICOR-II organic ion exchange resins correlate with findings of other researchers. Degradation has been identified in the EPICOR-II resins at a lower total integrated radiation dose than observed previously (10^7 rad versus 10^8 rad).²

Research on degradation of ion exchange resins has been done on externally irradiated ion exchangers (References 2, 11, 15, and 16). Those 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. The internal dose received by the organic ion exchange resins in EPICOR-II prefilters PF-8 and -20 was sufficient to initiate degradation. The degradation at the time of this analysis was measurable. The equilibrium of the polymer structure had been shifted towards polymer breakdown; and the polymer breakdown will progress (Reference 11). Any increases in degradation will be seen in the second or third corings of the EPICOR-II prefilter ion exchange resins, which are planned over the next four years.

One important indicator of the capability of ion exchange media to retain radionuclides is the total exchange capacity. The three samples examined in the INEL study exhibited different reactions to radiation. Sample PF-8#1, the strong acid cation with the highest radiation dose, showed reduced total exchange capacity. PF-20, the strong acid cation with the lowest radiation dose, showed increased total exchange capacity. Sample PF-8#2, the phenolic cation with a similar low dose, showed no change. The resin sample PF-8#1 had reached a radiation dose high enough to cause the exchange capacity to decrease, while the PF-20 sample reached a lower dose, where exchange capacity increased. Based on the results of this research, the PF-8#2 phenolic cation resin had not reached the threshold of degradation. The above differences

agree with findings of Reference 11. It would be expected that the phenolic resin would be more radiation resistant than the styrene divinylbenzene resin (Reference 11).

The mechanisms of degradation discussed in this study indicate a reduction in resin ion exchange capacity in the upper locations of the prefilters, 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 and PF-20 resin samples. The release of radionuclides from the resins would allow migration of the radionuclides within the EPICOR-II prefilters, and the sulfonic acid groups would lower the pH of the liquid in the prefilters. The low pH liquid should be neutralized by the remaining unused ion exchange material in the prefilters. That is supported by the measurement of residual water pH from the 50 prefilters which were stored at INEL (46 of those prefilters have been disposed at the commercial disposal facility near Hanford, WA). The pH measurements of residual water obtained more than three years after the prefilters were used were in the range of about 5 to 8. Those pH readings indicate that the acidic solution is being neutralized as it passes through the anion and mixed bed resins in the lower regions of the prefilters.

In order to further relate degradation to total radiation dose and determine if the degradation rate is exponential or linear, a minimum of two more examinations are required for PF-8 and -20 resins. Those 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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