

DEGRADATION OF RESINS IN EPICOR-II PREFILTERS
FROM THREE MILE ISLAND

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ABSTRACT

The Low-Level Waste Data Base Development--EPICOR-II Resin/Liner Investigation Project funded by the U.S. Nuclear Regulatory Commission examining the chemical and physical conditions of the synthetic ion exchange resins found in several EPICOR-II prefilterers. This paper summarizes results and analyses of the first sampling of ion exchange resins from EPICOR-II prefilterers PF-8 and -20. Results are compared with baseline data from tests performed on unirradiated EPICOR resins to determine if degradation has occurred due to the high internal dose received by the resins.

INTRODUCTION

This paper discusses the resin degradation study conducted on organic ion exchange resins removed from two EPICOR-II prefilterers from Three Mile Island, Unit 2. Further description of those prefilterers and the research being conducted on those prefilterers can be found in Ref. 1, 2, and 3.

Resin degradation studies traditionally have been conducted using resins irradiated by an external source, such as a reactor core or Co-60 source. The gamma dose provided by an external source simulates the one received from radionuclides retained on the resin matrix by ion exchange. Modes of degradation do not differ between external and internal radiation; however, the literature notes that internal radiation causes more extensive damage than external radiation, presumably from short-range, high-energy beta radiation. The organic resin of EPICOR-II prefilterers had been contained in liners for approximately four years and experienced internal radiation doses of about 10^7 rad.

As part of the EPICOR and Waste Research and Disposition Program sponsored by the Department of Energy (DOE) at the Idaho National Engineering Laboratory (INEL), 46 prefilterers are being disposed at a commercial disposal facility.^{4,5} Four prefilterers used in the Nuclear Regulatory Commission's (NRC's) studies will be stored in temporary storage casks outside the Hot Shop of Test Area North Building 607 (TAN-607) at the INEL.

MATERIALS AND METHODS

Nomenclature

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

- Resin Core--one removed from each prefilter PF-8 and -20 using coring tools
- Resin Samples--100-mL volumes removed from the cores [2 from PF-8(PF-8#1 and PF-8#2) and 1 from PF-20 (no sample number)]
- 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 prefilterers were provided by 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. Then, ASTM tests were used to determine exchange capacity, density, and moisture content.⁶ 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 ASTM rinse, soak, and acid rinse solutions quantitatively for styrene and divinylbenzene.

Coring

Resin cores were removed remotely from EPICOR-II prefilterers 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.⁷ 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 prefilterers. Full-length isotopic gamma scans were made of each resin core to produce an axial profile of radionuclide distribution.

Those profiles were used to determine the regions of highest radionuclide loading in the resin core. Then, isotopic spectral gamma measurements were taken at locations of highest radionuclide concentration.⁸ The two radionuclides having measurable concentrations detected by gamma spectroscopy were Cs-134 and Cs-137. Full-depth gross gamma scans also were made in the prefilterer resin beds after removal of the cores. Those scans were used to estimate the total integrated dose absorbed by the resins.

The coring equipment consisted of the following: (a) coring tool guide, which locates the coring tool over the prefilterer 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 removal of the coring tool; and (e) vibrator tool, which drives

the coring tool, casing, and shutters into the resin bed, and Ref. 2 further describes the coring equipment.

Measuring Radiation Doses in the Resin Beds

Total radiation doses were estimated for the resin samples using measurements taken during full-depth gross gamma scans within the prefilter resin beds.² Measurements taken at the elevations of interest were used with the graph in Reference 9 to estimate the total integrated radiation dose for each resin sample. Those dose estimates were PF-8 #1 (3×10^7 rad), PF-8 #2 (1.8×10^7 rad), and PF-20 (1.7×10^7 rad).

Sampling

At the Test Reactor Area (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 layers of different ion exchange media could be seen with the shutter withdrawn. It was 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. It was the unmixed material that was the target for collection.

The collection of resin samples was accomplished using a vacuum pump and water-filled, graduated glass column. 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. From the top of the column was run a rubber tubing attached to a stainless steel wand tube. With the vacuum pump running, 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 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. The resin samples were collected from or near those regions of highest radionuclide loading. This study is concerned with degradation of organic ion exchange resins; therefore, only organic resin samples were removed from the cores. No anion 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 level in the samples was of such intensity that work performed on resins loaded with radionuclides would have had to be done within a hot cell environment. This type of environment would make the characterization and analysis of the resin samples very costly and time-consuming. It had been shown by tests performed at the INEL on unirradiated samples, that an EPICOR resin could be stripped of 99% of its cations.¹⁰ Based on that information, it was decided to strip the radioactivity from the PF-8 and -20 resin samples using a 10% hydrochloric acid solution.

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. The samples were allowed to stand 24 hours in the water-filled column. The ion exchange column then was reconfigured and the distilled water was removed through the shutoff valve of the

column and retained for gas chromatography (GC) analysis. The resin samples from PF-8#1, #2, and -20 were then rinsed three times each with distilled water which was added by the pump through the tubing at the top of the column. Resin sample PF-8#1 showed a restriction to flow during this initial elution procedure. That distilled water also was saved for GC analysis and functional group tests.

A solution of 10% hydrochloric acid was pumped through the resin samples at a rate of 100 mL/min. That was continued until 55 sample volumes (the amount determined to remove 99% of the cations) or 5.5 L of acid flowed over the resins. Representative quantities of that acid rinse were collected.

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.

Characterization of Unirradiated and Irradiated Resins

All of the following 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. furnished resins (strong acid cation and phenolic cation).

- o ASTM Procedures for the Physical and Chemical Properties of Particulate Ion Exchange Resins¹¹
- o Infrared spectroscopy
- o Gas chromatography
- o Barium chloride precipitation for determination of sulfonic acid groups
- o Scanning electron microscopy.

ASTM Tests. ASTM procedures were used to determine the chemical and physical conditions of the ion exchange resins. For details of those procedures see Ref. 2 and 11. Results from analysis of loaded 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.

1. 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). This standard form provides a baseline from which the other ASTM tests can be performed.
2. Water retention capacity testing of ion exchange resins 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.

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

3. The backwashed and settled density test was used to determine changes in effective cross-linking between new resins and used. The density is proportional to the amount of effective cross-linking in the resin.
4. 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. Phenolic, carboxylic acid, and phosphonic acid functional groups also will exhibit, to some degree, salt-splitting capacity.
5. 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.

Infrared Spectroscopy. Infrared Spectroscopy (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 traces of those unirradiated resins were compared with IR traces 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 dose of radiation.

Gas Chromatography. Gas chromatography (GC) 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. Any organic products (divinylbenzene or styrene) in the original sample were concentrated in methylene chloride.

Barium Chloride Precipitation for the Determination of Sulfonic Acid Groups. It has been shown that the EPICOR-II cation resins are sulfonic acid, divinylbenzene, styrene type resins (Ref. 6). The high internal radiation dose received by those resins could cause loss of the functional groups (sulfonic acid). This loss 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. Results of those tests are reported in the "Results" section of this report.

Scanning Electron Microscopy. 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, and so forth.

RESULTS

The unirradiated resins showed no apparent change from previous analyses (Ref. 6). Because of the age of the unirradiated resins (2 years old) they might be expected to show some degradation. The irradiated resins of PF-8 and -20 (4 years old) also would be expected to show some degradation due to age.^{12,13} The unirradiated resins showed no degradation because of age, and therefore in this study, any degradation of the irradiated resins was assumed to be from radiation damage and not from age.

ASTM Tests

Results of the following ASTM tests performed on unirradiated and irradiated resins are listed in Table I.

Infrared Spectroscopy

Figure 1 compares the spectrum from PF-8#1 with that of the unirradiated strong acid cation resin. Figure 2 compares the spectrum of PF-20 with that of the unirradiated strong acid cation resin. The spectra from PF-8#1 and -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 3 compares the PF-8#2 phenolic cation resin with the EPICOR unirradiated phenolic cation resin. The spectra show no differences, which indicates (a) the phenolic from PF-8#2 and the phenolic from EPICOR are the same, and (b) no significant changes in polymer structure have occurred in the irradiated resins from the EPICOR-II prefilters.

Gas Chromatography

Comparing chromatograms for PF-8#1 and PF-20 cation showed² 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 chromatograms for PF-8#2 phenolic with the standard showed² no soluble organic products such as divinylbenzene or styrene are present in the soak and rinse solutions taken from the PF-8 phenolic cation resin samples, as would be expected.

Barium Chloride Precipitation for Determination of Sulfonic Acid Groups

Results of the barium chloride precipitation tests showed large sulfate concentrations and low pH (less than 3) in the PF-8#1 and -20 strong acid cation resin distilled water soak and rinse solutions. Those large concentrations indicate a loss of functional groups resulting from degradation. The phenolic resins contain no sulfonic acid groups; therefore, those samples showed no sulfate (Ref. 6).

Scanning Electron Microscopy

Comparing the photomicrograph of the unirradiated strong acid cation resin from EPICOR, Inc. (Fig. 4) with photomicrographs of PF-8#1 strong acid cation resin (Fig. 5) shows considerable damage to the PF-8#1 resin. The photomicrograph in Fig. 5 shows resin bead damage that is more extensive and of a different fracture type than what had been observed by BCL in resins from EPICOR-II prefilters PF-3 and -16.^{14,15} It is believed that the difference in that damage was caused by the higher radiation dose received by the PF-8#1 strong acid cation resin.

Comparing the PF-8#2 phenolic cation resin in Fig. 6, with the photomicrograph of unirradiated phenolic cation resins from EPICOR, Inc. in Fig. 7 indicates some damage. The particles in the photomicrographs of the unirradiated phenolic cation resin are smooth, and any breaks or cracks within the resins are uniform. On the otherhand, several particles in the phenolic cation resin sample from PF-8#2 are ragged, sponge-like, and porous. Several nonuniform cracks have appeared within the PF-8#2 resin.

TABLE I

Results of ASTM Tests on Irradiated and Unirradiated ION Exchange Resins

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

a. The PF-8#2 sample was contaminated with 18.5% strong acid cation resin from the PF-8#1 sample.

b. Measured in milliequivalents per gram of dry resin.

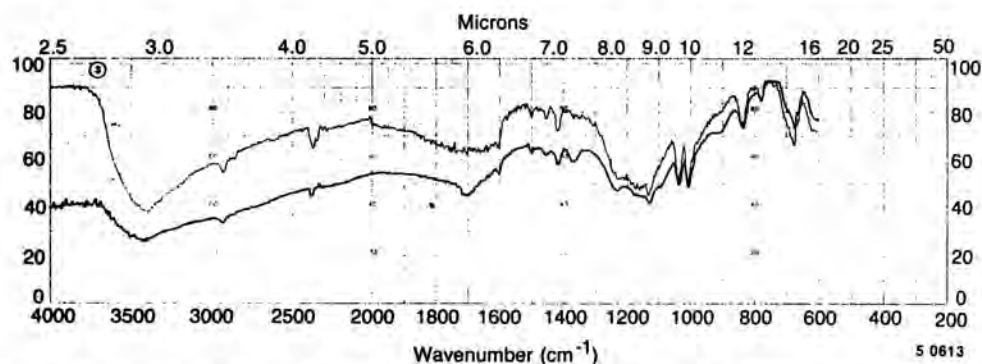


Fig. 1. Comparison of the IR spectrum from Epicor unirradiated strong acid cation resin (top spectrum) with that of sample PF-8#1 strong acid cation resin (bottom spectrum).

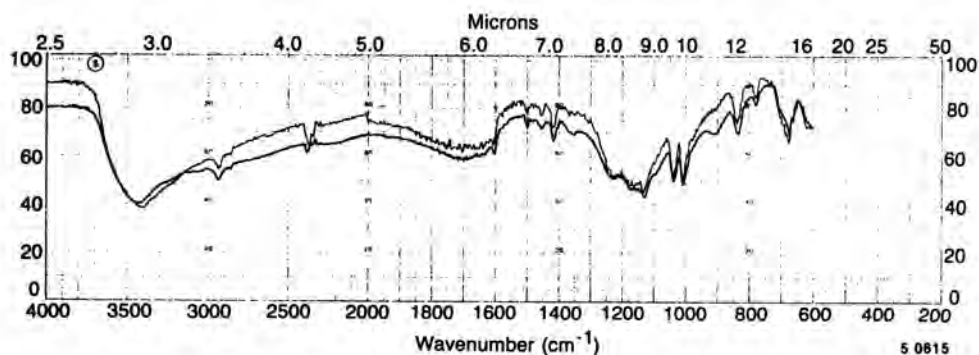


Fig. 2. Comparison of the IR spectrum from Epicor unirradiated strong acid cation resin (top spectrum) with that of sample PF-20 strong acid cation resin (bottom spectrum).

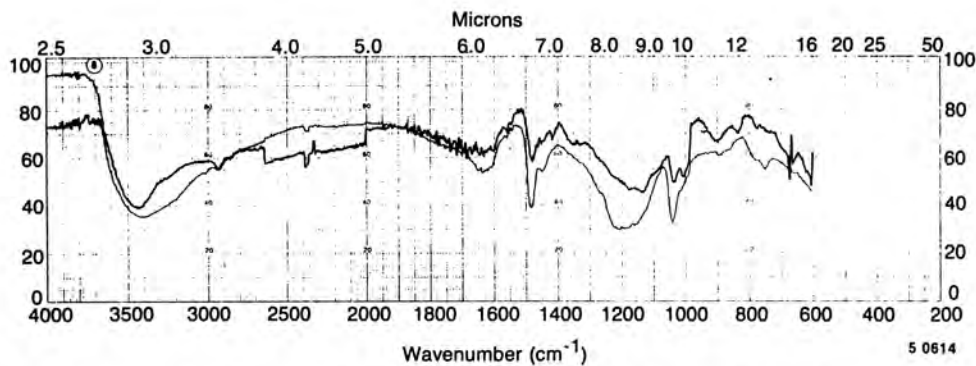
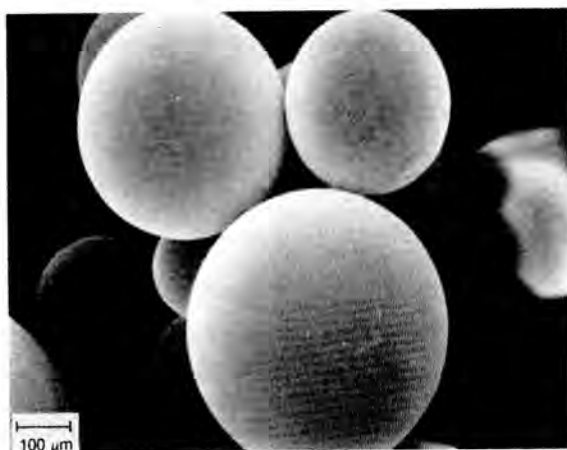
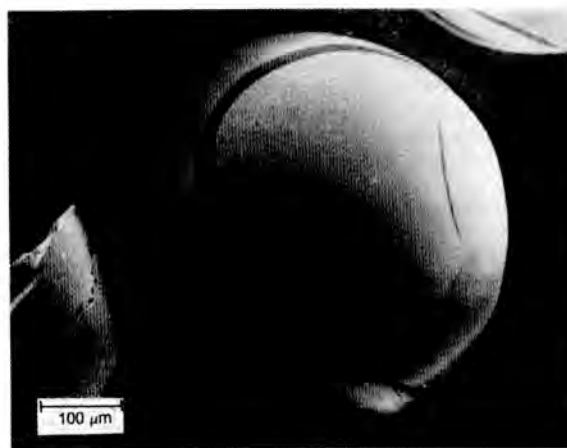


Fig. 3. Comparison of the IR spectrum from Epicor unirradiated phenolic cation resin (top spectrum) with that of sample PF-8#2 phenolic cation resin (bottom spectrum).



5 0618

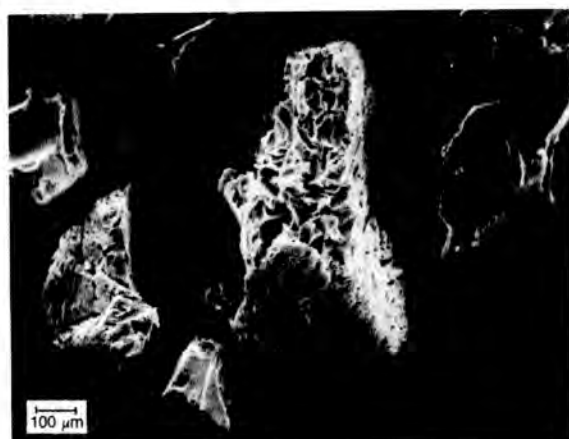
Fig. 4. SEM photomicrograph of unirradiated Epicor strong acid cation resin at 100 magnification.



PF-8#1

5 0619

Fig. 5. SEM photomicrograph of EPICOR-II strong acid cation resin sample PF-8#1 showing a closeup of one resin bead at 150 magnification.



PF-8#2

5 0616

Fig. 6. SEM photomicrograph of EPICOR-II phenolic cation resin sample PF-8#2 showing a closeup of one resin particle at 80 magnification.



5 0617

Fig. 7. SEM photomicrograph of Epicor unirradiated phenolic cation resin at 50 magnification.

Analytical Results

Table II presents the results from the various analytical tests performed on EPICOR-II strong acid cation resin samples PF-20 and PF-8#1. Also included in this table is a summary of results from the EPICOR-II phenolic cation resin sample PF-8#2. 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 resins.

CONCLUSIONS

The INEL study of degradation of EPICOR-II organic ion exchange resins correlates with findings of other researchers (Ref. 12, 13, 14, 15, 16, and 17); and degradation has been identified in the EPICOR-II resins at a lower than predicted total integrated dose (Ref. 2, 12). 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. Further coring and analysis of EPICOR resins will assist in determining the rate at which the resins are being degraded.

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. 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 capacity. PF-8#2, the phenolic cation with a similar low dose, showed no change. The resin sample PF-8#1 had reached a dose high enough to cause the exchange capacity to decrease, while the PF-20 sample reached a lower dose, where exchange capacity increased. The PF-8#2 phenolic cation resin had not reached the threshold of degradation. Those changes agree with findings of Ref. 13.

The findings of this study can be related to the commercial disposal of spent ion exchange media used in power reactors. The determination of on-set of degradation, and later, of significant loss of exchange capacity with resultant loss of radionuclides will provide a data base useful in the planning for and regulation of disposal of ion exchange resins.

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TABLE II

Summary of Results From Analysis of EPICOR-II Irradiated Resin Samples PF-20, PF-8#1, and PF-8#2^a

<u>Analytical Technique</u>	<u>PF-20 Strong Acid Cation</u>	<u>PF-8#1 Strong Acid Cation</u>	<u>PF-8#2 Phenolic Cation</u>
<u>ASTM Tests</u>			
● Water retention capacity	Increase	Increase	Increase
● Backwashed and settled density	Decrease	Decrease	Decrease
● Salt splitting capacity	Decrease	Decrease	Increase
● Total exchange capacity	Increase	Decrease	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	Soluble products observed because of contamination
BaCl ₂ precipitation for 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	No damage noted	Resin bead cracking observed	Damage observed on a few particles
Visual observations	Nothing unusual observed	Nothing unusual observed	Contamination with PF-8#1 resin observed
Physical observations	Nothing unusual observed	Lack of flow during elution observed	Nothing unusual observed
a. Changes in irradiated resins versus unirradiated Epicor resins.			