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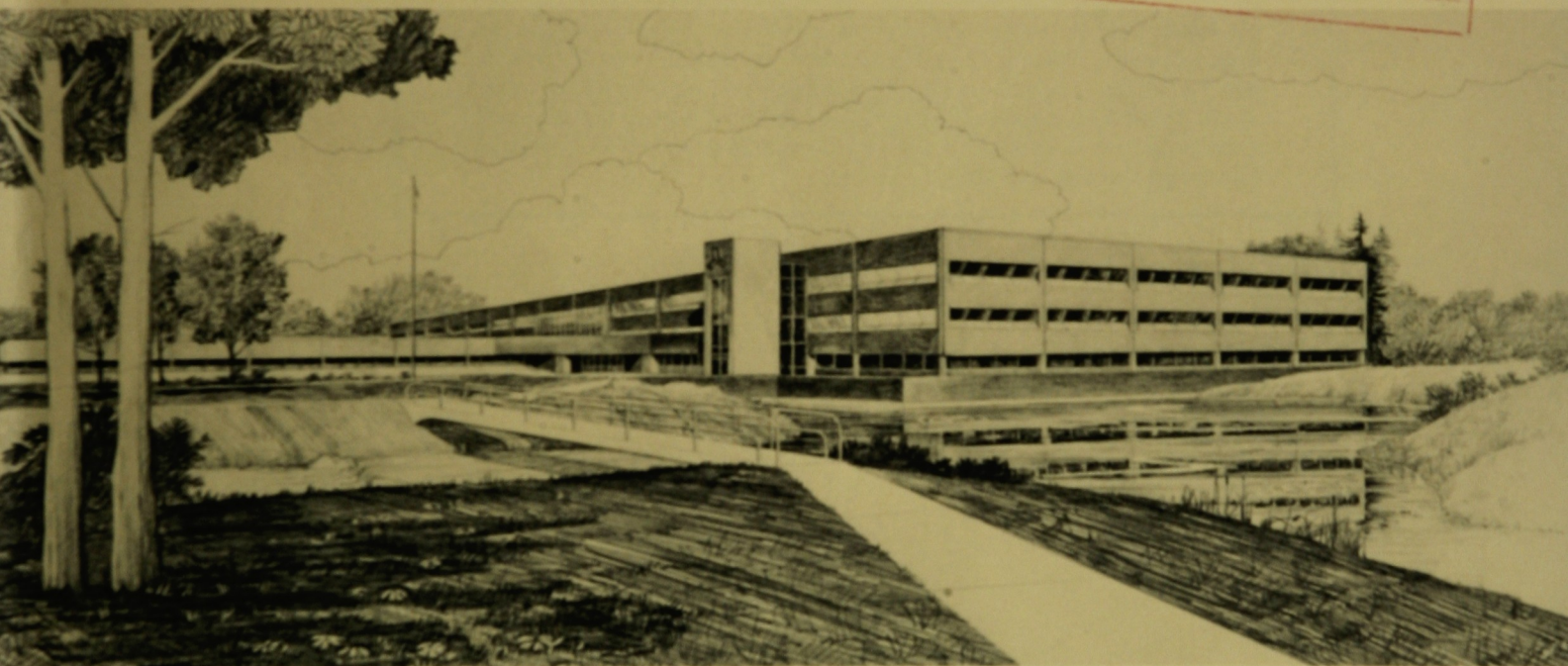
EPICOR-II RESIN CHARACTERIZATION AND PROPOSED  
METHODS FOR DEGRADATION ANALYSIS

J. D. Doyle  
J. W. McConnell, Jr.  
R. D. Sanders, Sr.

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 **EG&G** Idaho

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EG&G Idaho, Inc.  
Idaho Falls, ID 83415

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## ABSTRACT

One goal of the EPICOR-II Research and Disposition Program is the examination of the EPICOR-II organic ion-exchange resins for physical and chemical degradation. This report summarizes preliminary information necessary for the evaluation of the resins for degradation. The work was accomplished by EG&G Idaho, Inc. at the Idaho National Engineering Laboratory and was funded by the U.S. Department of Energy. The information is presented in two sections. First, a description is given of the physical and chemical characterization of unirradiated resins obtained from Epicor Inc. Second, the plan by which internally irradiated EPICOR-II resins from Three Mile Island Unit 2 will be examined for degradation is briefly described.



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EPICOR-II RESIN CHARACTERIZATION AND PROPOSED  
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INTRODUCTION

The prime objective of the EPICOR-II Resin/Liner Research is to supply useful information in the area of waste disposal on the stability of waste forms containing ion-exchange resins. Work in this area is being conducted by EG&G Idaho, Inc. at the Idaho National Engineering Laboratory under the EPICOR-II Research and Disposition Program and is sponsored by the U.S. Department of Energy. Studies of resin degradation will be conducted which will (a) determine over a 10-year period the degradation of organic ion-exchange media caused by high loadings of radionuclides and (b) determine over a 20-year period the leachability of commercial waste forms containing those highly loaded media. The main benefactors of the information will be the nuclear industry and federal and state regulatory organizations.

The accident at Three Mile Island Unit 2 resulted in the transfer of more than 1900 m<sup>3</sup> of contaminated water to the Auxiliary and Fuel Handling Buildings. The water was filtered by a three-stage ion-exchange system called EPICOR-II. The first stage consisted of a prefilter, while the second and third stages were demineralizers. During the processing of this contaminated water, the prefilters became loaded with radionuclides, mostly cesium and strontium. The ion-exchange media in the prefilters were inorganic and synthetic organic ion-exchange resins.

The majority of ion-exchange materials used in the nuclear process industry are synthetic organic resins. But one limitation of organic resins is their chemical decomposition as a consequence of their exposure to ionizing radiation. Inorganic ion-exchange materials have proven to be somewhat radiation resistant.<sup>1</sup> Therefore, the following discussion will be limited to organic resin degradation.



Most current information on the degradation of organic resins has been obtained through the analysis of resins exposed to external radiation sources. However, ion-exchange resins used in commercial nuclear applications receive an "internal" dose because the radionuclides are chemically linked to the resin matrix. The actual modes of degradation do not differ for external and internal radiation, but internal radiation has been shown to cause more extensive damage (see Reference 1). The information obtained from the degradation studies will form a bridge between external radiation test results and resin degradation produced in nuclear power plant wastes. Knowledge of resin degradation will be used to identify how long and how well ion-exchange media will retain radionuclides in a waste form. As the media retain radionuclides, dispersion of those radionuclides into the environment is limited. Thus, the media provide protection beyond that given by high-integrity containers or by solidified waste forms.

Resin degradation knowledge also will provide information on (a) leachability of radionuclides from immobilized resins, (b) an upper limit for commercial low-level waste, (c) supporting data for State Compact disposal sites, and (d) long-term behavior of those immobilized resins in several disposal environments.

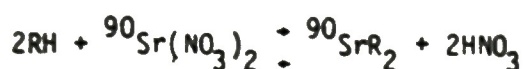
This report consists of two main parts: the results of characterization of unirradiated cation, anion, and phenolic resins procured from Epicor Inc.; and the plan for degradation analysis of expended irradiated resins removed from an EPICOR-II liner. The results should provide suitable baseline data for the degradation studies.

## BACKGROUND ON ION-EXCHANGE

### The Mechanism of Ion-Exchange

Ion-exchange is the reversible interchange of ions between a solid and liquid phase where no permanent structural change in the solid phase occurs. The following represents some typical exchange reactions:

For cation exchange



For anion exchange



where R represents the insoluble matrix of the ion-exchange solid.

Many materials found in nature possess some ion-exchange potential. Almino-silicate zeolite minerals are the most prominent of these materials and have the added, useful properties necessary to act as molecular sieves. However, the majority of ion-exchange materials available for commercial use today are synthetic organic resins because of their reasonable costs and regeneration properties.

### Applications of Ion-Exchange in the Nuclear Energy Field

Most nuclear reactors operating in the United States are light water reactors. These reactors "contaminate" large volumes of water used for cooling and moderation. Most contamination in the water is in the form of dissolved ionic materials which, if left in the water, could initiate radiolytic corrosion, increase radiation doses through activation and deposition, and reduce neutron economy through neutron capture reactions.

Ion-exchange resins remove the dissolved ionic materials through ion-exchange, thus providing a source of demineralized makeup water for the reactor.

### Properties of Synthetic Organic Ion-Exchange Resins

Synthetic organic ion-exchangers are high molecular weight polyacids or bases that are insoluble in most aqueous and nonaqueous media. In general, they are cross-linked polymer tridimensional networks to which large polar exchange groups are attached. Since the materials are not individual compounds, their composition and properties are dependent on the nature and purity of the original chemicals from which they are synthesized. Organic resins are classified according to

- o Exchangeable species (cation, anion, or multifunctional)
- o Functional group (degree of ionization)
- o Preparative process (polymerization, condensation)
- o Physical state (bead, powder)
- o Granulation (granular, membrane)
- o Rigidity of porous structures (gel, macroreticular).

Four properties of organic resins are (a) the exchange capacity, (b) degree of cross-linking, (c) moisture content, and (d) density.

### Exchange Capacity

The exchange capacity indicates the amount of ions a material is capable of exchanging. By convention, exchange capacity is measured in milliequivalents per gram of resin.<sup>2</sup>



### Degree of Cross-Linking

The amount of cross-linking is an indication of resin porosity. For synthetic polymer resins, cross-linking is defined as the percentage of divinylbenzene (DVB) that is used as the macromolecular base. The degree of cross-linking of a synthetic organic resin is inversely proportional to the exchange capacity (see Reference 2).

### Moisture Content

The moisture content of ion-exchangers is a measure of their water retention capacity. The moisture content is inversely proportional to the degree of cross-linking (see Reference 2).

### Density

The density of ion-exchangers is proportional to the amount of cross-linking. The standard units for resin density are grams per milliliter (see Reference 2).

## CHARACTERIZATION OF UNIRRADIATED RESINS

With the cooperation of Epicor Inc., unirradiated samples of organic ion-exchange resins were obtained. The resins were physically and chemically analyzed using American Society for Testing and Materials (ASTM) methods and spectrophotometric analysis.

### ASTM Tests

The ASTM standard methods consist of various chemical and physical processes performed on the resins to quantitatively analyze properties of the resins. After pretreating the resins, the following tests were conducted:

- o Total exchange capacity
- o Moisture content
- o Backwashed and settled density.

### Pretreatment

Commercial cation and anion resins usually appear in the (H<sup>+</sup>) or (OH<sup>-</sup>) forms. However, to provide a uniform basis for comparison, resin samples were converted to a known ionic form before analysis. The (Na<sup>+</sup>) form was chosen for the cation, while the (Cl<sup>-</sup>) form was chosen for the anion. Those forms were chosen since they permitted samples to be weighed and dried without concern for air contamination or decomposition.<sup>3</sup> The pretreatment process consisted of placing the resin in a standard ASTM ion-exchange column and passing the appropriate ionic solution through the resins.

### Total Exchange Capacity

Next the exchange capacities of the resins were determined. An acid-base titration was performed on the strong acid cation and phenolic cation resins to determine exchange capacities, while a Mohr, silver nitrate titration was performed on the strong base anion resin to determine exchange capacity. The results from this test are given in Table 1.

TABLE 1. RESULTS OF THE ASTM STANDARD METHODS TESTS

Resin	Exchange Capacity (meq/g)	Moisture Content (%)	Density (g/mL)
Strong acid cation	5.3	48.1	0.80
Phenolic cation	7.0	51.6	0.67
Strong base anion	3.3	44.0	0.67

### Moisture Content

The moisture content (water retention capacity) of an ion-exchange material is proportional to the pore volume. The pore volume is inversely proportional to the effective cross-linking of the material. For materials of the same functionality and polymer-type, higher values of water retention indicate lower effective cross-linking. The results of the water retention test for the three resins are located in Table 1.

### Backwashed and Settled Density

The backwashed and settled density of a hydraulically classified and settled bed was determined and correlated with the density of ion-exchange materials noted in the literature. The results from this test are given in Table 1.



## Analysis of Results

By comparing results of the ASTM tests with information available in Reference 4, a hypothesis can be formed as to the identity of the base material and active groups. The proposed structures of the resins are given in Table 2. Sulfonic acid ( $\text{SO}_3\text{H}$ ), phenolic ( $\text{ArOH}$ ), and quaternary ammonium [ $\text{N}(\text{CH}_3)_3$ ] are all typical functional groups for their respective resins. Positive identification of those functional groups was next attempted by infrared spectrophotometric analysis.

TABLE 2. PROPOSED CHEMICAL STRUCTURES OF THE RESINS

<u>Resin Type</u>	<u>Base Material</u>	<u>Active Group</u>
Strong acid cation	DVB, styrene	$\text{SO}_3\text{H}$
Phenolic cation	Phenol, formaldehyde	$\text{ArOH}$
Strong base anion	DVB, styrene	$\text{N}(\text{CH}_3)_3$

## Infrared Spectrophotometry

A Perkin-Elmer Model 1420 Infrared Spectrophotometer and Model 3600 data station were used to identify the chemical constituents of the resins. Infrared spectrophotometry involves identifying the rotational and vibrational motions of atoms in a molecule induced by infrared radiation. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum. The spectrum is uniquely characteristic of the functional groups comprising the molecule and overall configuration of the atoms.

The main objectives of this preliminary spectrophotometric analysis were to (a) identify the functional groups of the unirradiated Epicor resins to provide a baseline for analysis of irradiated EPICOR-II resins and (b) determine the accuracy of the methods to be used to analyze the irradiated EPICOR-II resins.

## Sample Preparation

All solid samples were embedded in potassium bromide pellets, and all liquid samples were deposited on sodium chloride crystals.

## Identification of Functional Groups

The identity of the functional groups sulfonic acid, phenolic, and quaternary ammonium were hypothesized from results of the ASTM tests. Another method used to determine the presence of those functional groups was a comparison of the spectrum of each type of unknown resin with that of a known resin containing the specified functional group. Each functional group has some distinguishing peaks which are easily identified, even though the functional group is locked in the resin matrix. The presence of the sulfonic acid group in the Epicor unirradiated strong acid cation was determined using the comparative method. The same procedure was performed on the Epicor strong base anion resin, and the presence of the quaternary ammonium functional group also was determined. A phenolic cation resin of known composition was unavailable, so the Epicor phenolic resin was not analyzed in this manner.

Another identifying test was performed on the strong acid cation and phenolic cation resins to determine the presence of the sulfonic acid and phenolic groups. The test was performed by assembling a composite spectrum containing various compounds suspected of being present in each resin and comparing this composite spectrum with its appropriate resin. The Epicor strong acid cation resin was assumed to consist of only three different compounds, namely styrene, DVB, and sulfonic acid. A composite "resin" spectrum was obtained by combining the spectra of styrene-sulfonic acid and DVB. The Epicor strong acid cation spectrum (Figure 1) was then compared with the composite spectrum (Figure 2). The two spectra were similar in many aspects (Figure 3), especially in the upper region of wave number.



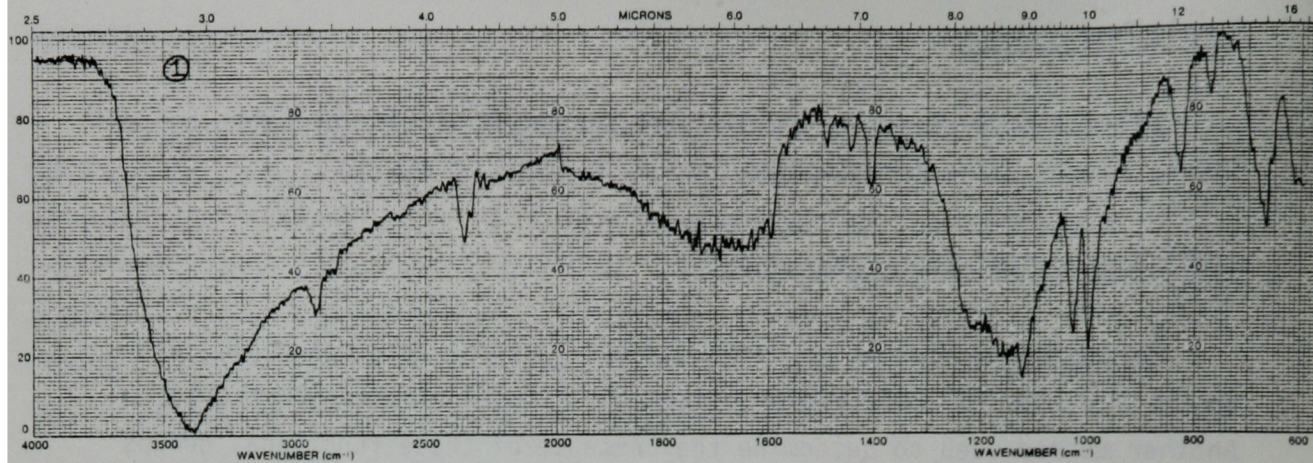


Figure 1. EPICOR strong acid cation resin (KBr pellet).

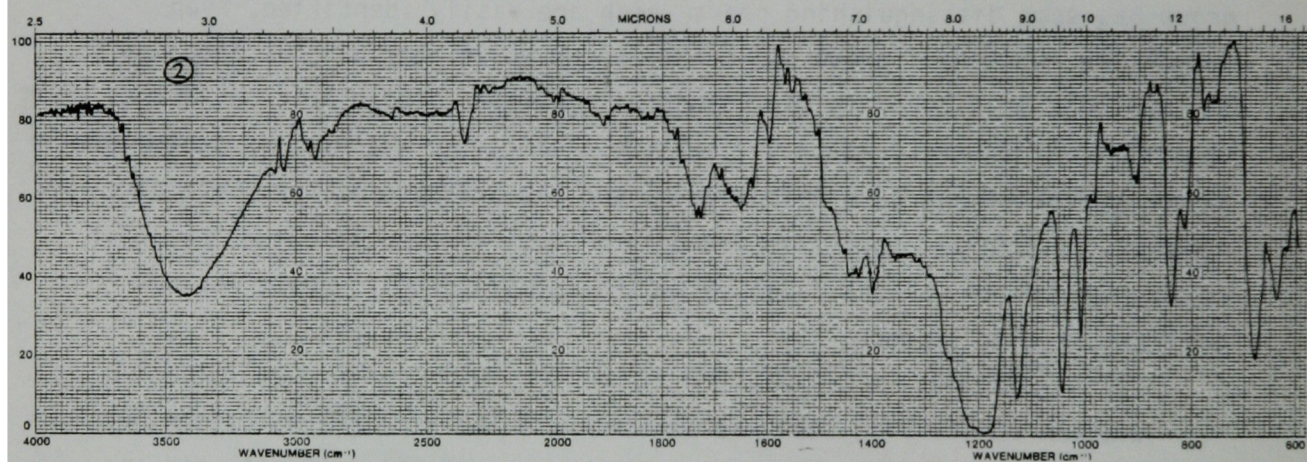


Figure 2. Composite spectrum: styrene-sulfonic acid, DVB (KBr pellet).

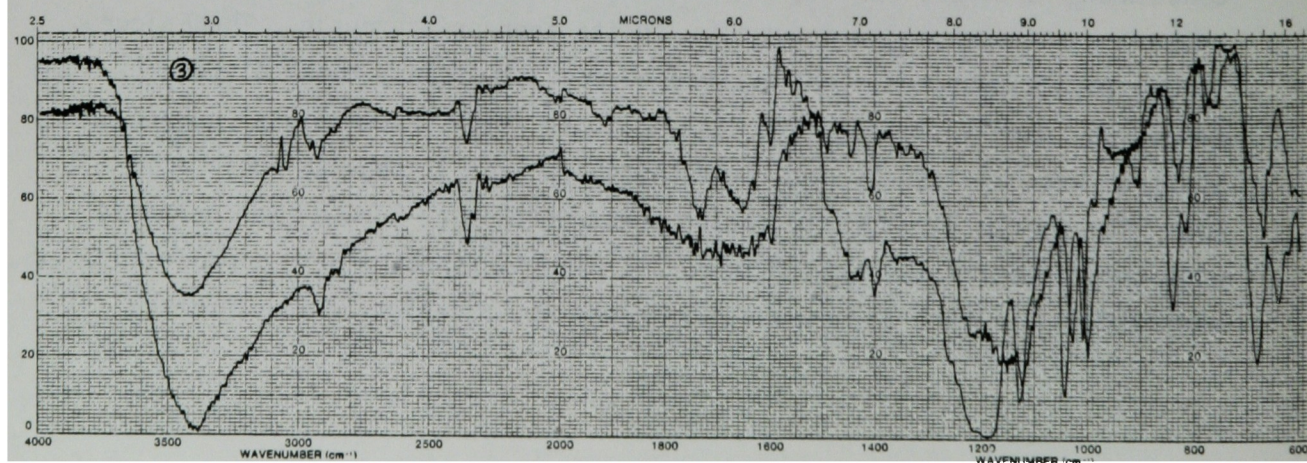


Figure 3. Comparisons of Spectra 1 and 2.



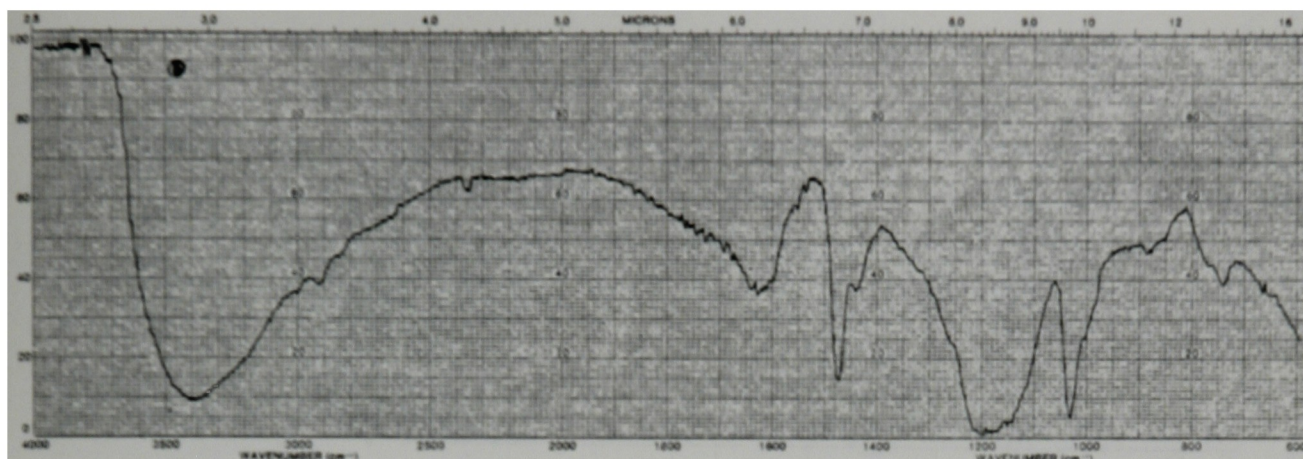


Figure 4. EPICOR phenolic cation resin (KBr pellet).

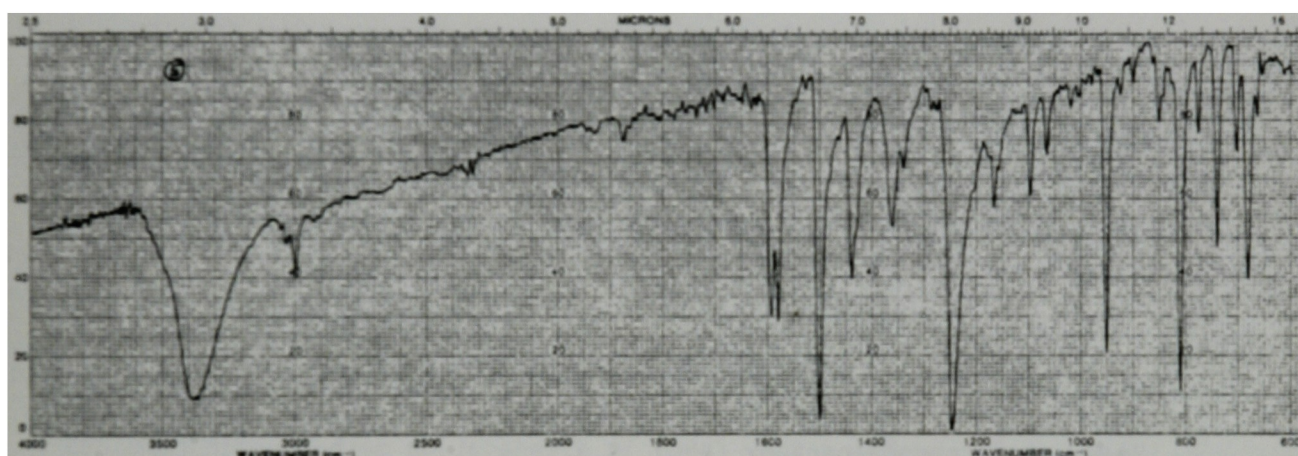


Figure 5. Composite spectrum: p-styrophenol, styrene-sulfonic acid, and DVB (KBr pellet).

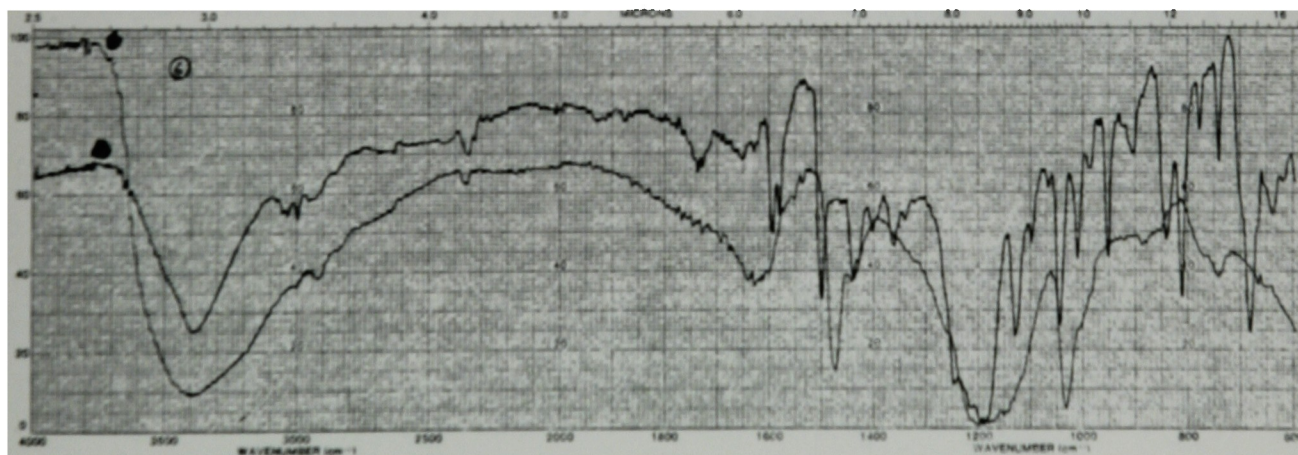


Figure 6. Comparison of Spectra 4 and 5.

The same procedure was performed on the phenolic cation resin (Figure 4). A composite spectrum consisting of (a) p-styropheno1, (b) styrene-sulfonic acid, and (c) DVB (Figure 5). The two spectra show several similarities (Figure 6). Other spectra obtained during spectrophotometric analysis were the Epicor strong base anion (Figure 7), strong base anion reference (Figure 8), and strong acid cation reference (Figure 9).

#### Analysis of the Accuracy of Spectrophotometric Methods

To determine the accuracy of the analytical methods used in the spectrophotometric analysis, a reference book of infrared spectra, "The Aldrich Library of Infrared Spectra," was used to compare known spectra with the spectra obtained.<sup>5</sup> The spectra of styrene-sulphonic acid (Figure 10), DVB (Figure 11), and styrene (Figure 12) were selected for this analysis. Upon comparison with the library spectra, it was determined that the spectra of the three compounds were accurate with respect to peak location and resolution.

#### Vapor Phase Chromatography

Vapor phase chromatography (VPC) is a separation method which combines elements of both distillation and extraction. VPC is based on the partitioning of compounds between a stationary phase (solid or liquid) and a moving phase (liquid or gas). The two types of VPC used in the analysis are Gas Chromatography and High Performance Liquid Chromatography. VPC was used to verify the presence of styrene and DVB in the resins.



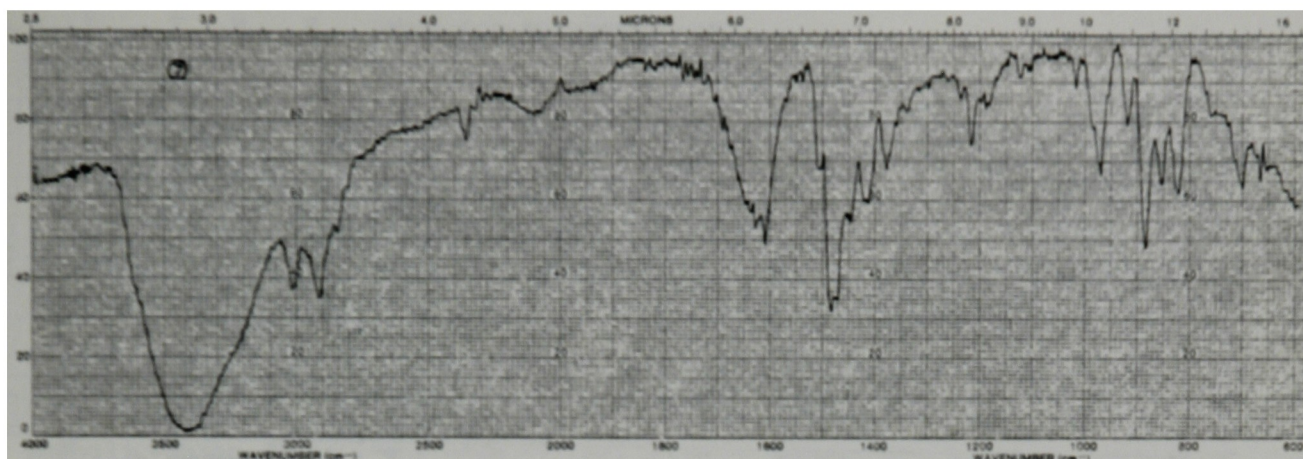


Figure 7. EPICOR strong base anion resin (KBr pellet).

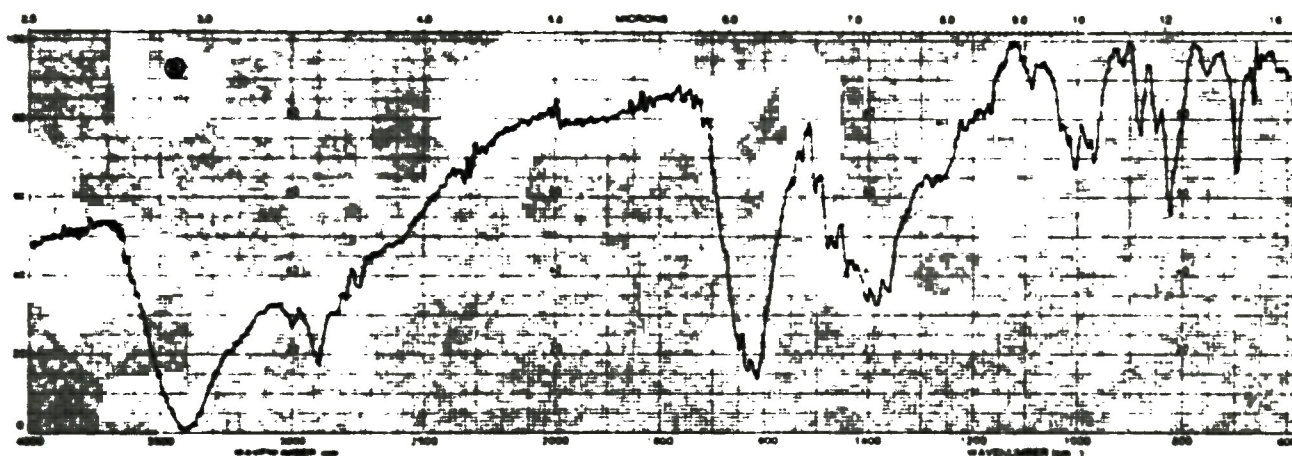


Figure 8. Strong base anion reference (KBr pellet).

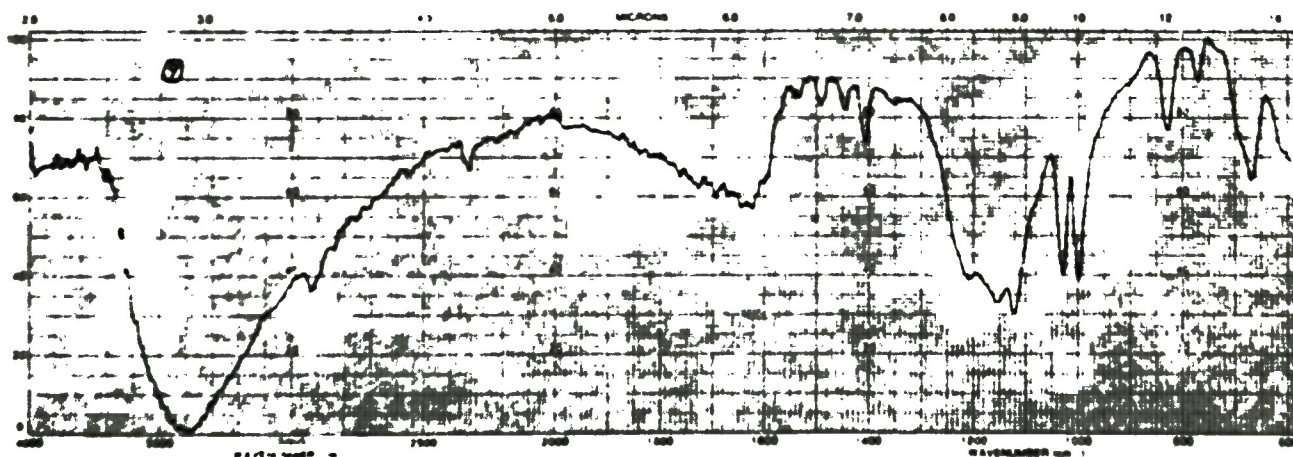


Figure 9. Strong acid cation reference (KBr pellet).



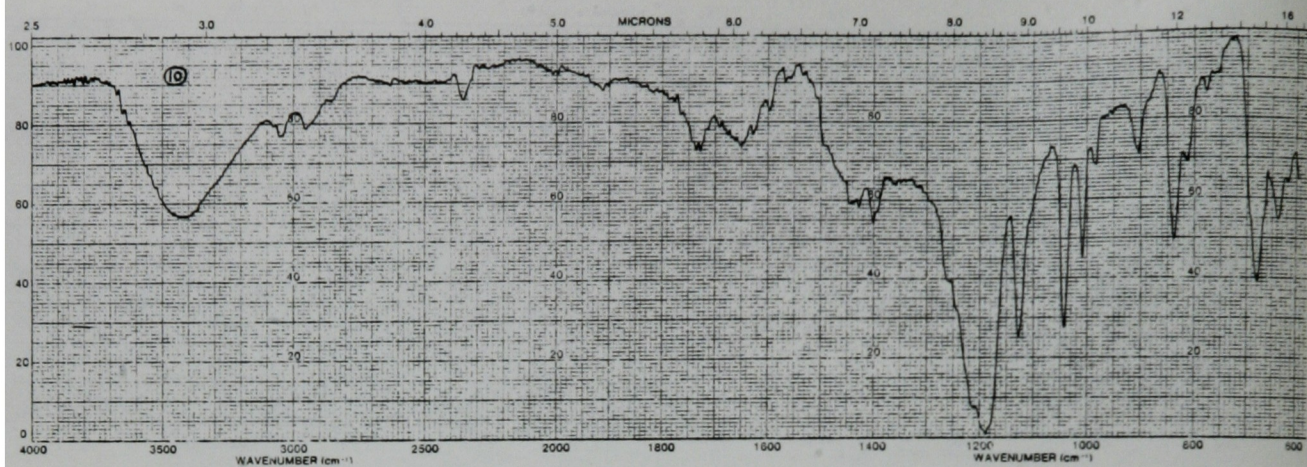


Figure 10. Styrene-sulfonic acid reference (KBr pellet).

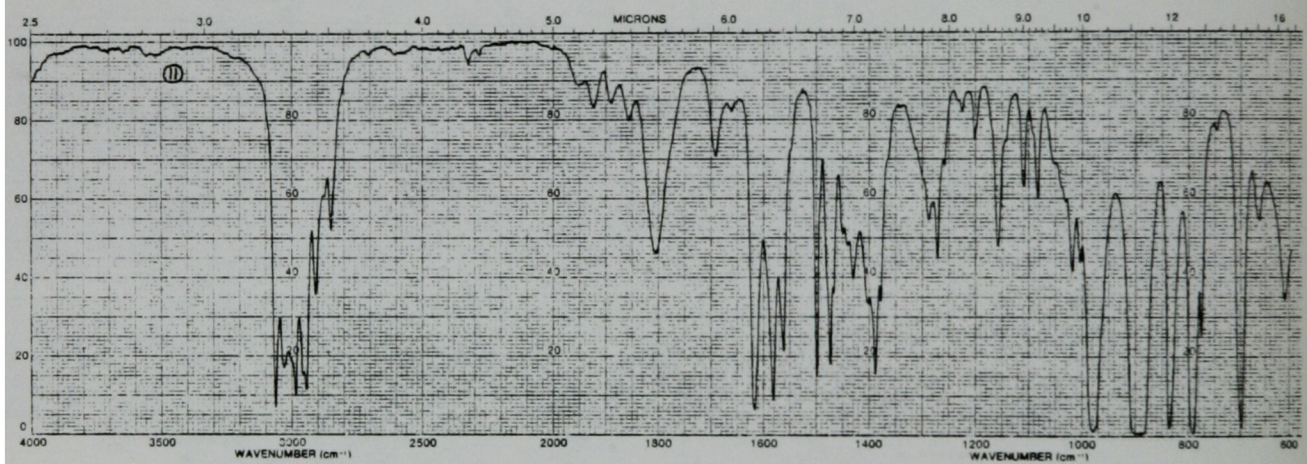


Figure 11. Divinylbenzene (DVB) reference (NEAT-Liquid).

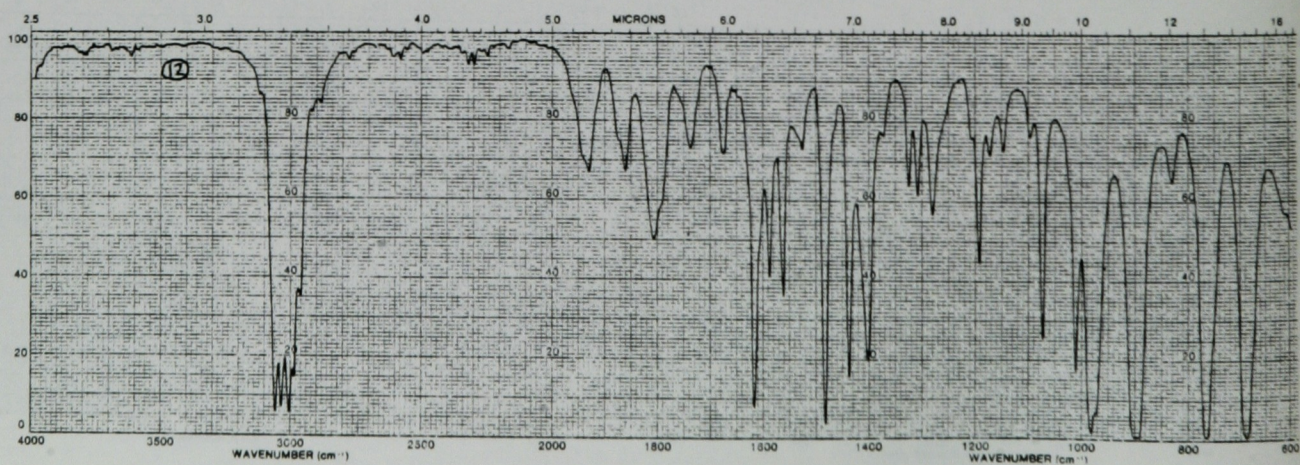


Figure 12. Styrene reference (NEAT-Liquid).



## PLAN FOR DEGRADATION ANALYSIS

The organic ion-exchange resins located inside the EPICOR-II liners received radionuclide loadings of about 2000 Ci per liner, or about  $57 \text{ Ci/ft}^3$  (Reference 6). Dose rate measurements taken inside EPICOR-II liners show that the region of highest loading is near the top of the resin bed.<sup>7,8,9</sup> Samples collected for physical and chemical degradation analyses will be taken from organic resins closest to or in the region of highest loading. If mixed beds of the cation-anion, cation-phenolic, or phenolic-anion variety are encountered, an ASTM method is available for the separation of the species before conducting the degradation studies.

The degradation plan will use the following methods:

- o American Society for Testing and Materials (ASTM) tests
- o Qualitative spectrophotometric analysis
- o Quantitative vapor phase chromatography
- o Miscellaneous chemical tests.

### Effects of Ionizing Radiation on Organic Resins

The effect of ionizing radiation on synthetic organic ion-exchange resins is the progressive conversion of the resin into a more porous material. The main mechanisms by which this conversion takes place are (a) the rupture of cross-linkage in the styrene chain, (b) the scission of functional groups, and (c) oxidation of the polymer. Three properties by which the changes induced by ionizing radiation can be measured are (a) exchange capacity, (b) moisture content, and (c) density. Radiation-induced chemical and physical changes are a direct function of the total dose, with approximately  $10^8$  rads being the degradation threshold (see Reference 4).

The following is a summary of possible degradation modes and how they will be most easily detected.<sup>10</sup>

<u>MODE 1:</u>	Rupture of cross-linkage with no oxidation.
<u>CONSEQUENCE:</u>	Increase in exchange capacity, increased porosity, no functional groups present in effluent.
<u>MODE 2:</u>	Oxidation of polymer chain.
<u>CONSEQUENCE:</u>	Increase in exchange capacity (but to a lesser degree than MODE 1), increased porosity, no functional groups in effluent.
<u>MODE 3:</u>	Scission of functional group.
<u>CONSEQUENCE:</u>	Decreased exchange capacity, decreased porosity, functional group found in effluent.
<u>MODE 4:</u>	Scission of functional group and loss of polymer segments.
<u>CONSEQUENCE:</u>	Functional group found in effluent (otherwise undetectable).
<u>MODE 5:</u>	Scission of functional group with oxidation of polymer, but no polymer loss.
<u>CONSEQUENCE:</u>	Slight increase in exchange capacity, decreased porosity, functional groups found in effluent.
<u>MODE 6:</u>	Scission of functional group accompanied by oxidative splitting of the polymer.
<u>CONSEQUENCE:</u>	Slight increase in exchange capacity, increased porosity, functional groups found in effluent.

MODE 7: Reduction of the functional group to a lower oxidation state.

CONSEQUENCE: Decreased porosity, no functional groups present in effluent.

### ASTM Tests

The ASTM methods will also be used to quantitatively analyze three properties of the irradiated EPICOR-II resins. Degradation of the resins can then be detected by comparing the values found for the irradiated resin properties to the values found for the same properties of the unirradiated resins. During the ASTM test, various fluids such as water and hydrochloric acid will be used to rinse the resin samples. The fluids, or effluents, will be examined for dissolved materials.

### Infrared Spectrophotometric Analysis

Infrared spectrophotometric analysis will be used to examine the resins and the effluents from the ASTM tests. The resin spectra will show if there is a loss of functional groups or the loss or transformation of the polymer backbone.

### Quantitative Vapor Phase Chromatography

Gas chromatography will be used to quantitatively analyze DVB and styrene content. A 0.34% Tetra-Nitro-Fluorenoeneon 80-100 Carbopack-C Column will be used. Liquid chromatography will be used to detect quaternary ammonium groups if strong base anion resins are examined. The column will contain ZORBAX-100.

### Miscellaneous Chemical Tests

A barium chloride precipitation will be performed on the strong acid cation resin to measure the sulfur content. Also, solvent extraction will be performed on all resins to be analyzed to determine their solubility.



## SUMMARY

Degradation of the synthetic organic ion-exchange resins should be efficiently and accurately measurable by using the baseline data provided by the nonirradiated resin characterization. The degradation threshold is about  $10^8$  rads, approximately the same dose rate the resins will have received by the examination date. If degradation has not occurred at the first examination point, later examinations will detect resin degradation using the same analytical methods. The results from the characterization tests will yield practical and useful data on the actual effects of radiation on commercial synthetic organic ion-exchange resins.

## REFERENCES

1. Gangwer, Goldstein, and Pillay, "Radiation Effect on Ion Exchange Materials," BNL 50781.
2. Wheaton and Seamster, "A Basic Reference on Ion Exchange," DOW Chemical Company, Reprinted from the Encyclopedia of Chemical Technology, 2nd Edition, Volume 11, 1966.
3. ASTM D2187-77, "Standard Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins," Volume 31.
4. KKS Pillay, "Radiation Effects on Ion-Exchangers Loaded with Radioactive Wastes," Department of Nuclear Engineering, the Pennsylvania State University, University Park, PA 16802, NE/RWM-80-3, October 1980.
5. Pouchert, Charles J., "The Aldrich Library of Infrared Spectra," Aldrich Chemical Company, Inc., 1981.
6. McConnell, J. W. , "EPICOR-II Resin/Liner Research Plan," EGG-TMI-198.
7. Marby, A. W., "Radiation Dose Rate Measurements Inside EPICOR-II Resin Liner PF-24-AWM-22-83," Interoffice Correspondence to J. W. McConnell, August 2, 1983.
8. Wynhoff and Pasupathi, "Characterization of EPICOR-II Prefilter Liner 3," GEND 027, April 1983.
9. Yesso, Pasupathi, and Lowry, "Characterization of EPICOR-II Prefilter Liner 16," GEND 015, August 1982.
10. Fisher, Sally A., "Effect of Gamma Radiation on Ion-Exchange Resins," Rohm and Hass Company, Philadelphia, Pennsylvania, US. AEC, Contract No. AT (49.1)-535.

