

*Effects of Ionizing Radiation
on Modern Ion Exchange Materials*

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EFFECTS OF IONIZING RADIATION ON MODERN ION EXCHANGE MATERIALS

by

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ABSTRACT

We review published studies of the effects of ionizing radiation on ion exchange materials, emphasizing those published in recent years. A brief overview is followed by a more detailed examination of recent developments. Our review includes styrene/divinylbenzene copolymers with cation-exchange or anion-exchange functional groups, polyvinylpyridine anion exchangers, chelating resins, multifunctional resins, and inorganic exchangers. In general, strong-acid cation exchange resins are more resistant to radiation than are strong-base anion exchange resins, and polyvinylpyridine resins are more resistant than polystyrene resins. Cross-linkage, salt form, moisture content, and the surrounding medium all affect the radiation stability of a specific exchanger. Inorganic exchangers usually, but not always, exhibit high radiation resistance. Liquid ion exchangers, which have been used so extensively in nuclear processing applications, also are included.

SUMMARY

We have updated earlier published reviews of the effects of ionizing radiation on ion exchangers, expanding our coverage to reflect the growing importance of inorganic exchangers, chelating resins, multifunctional resins, and liquid ion exchangers. In addition to reviewing the general effects of radiation, we have highlighted studies in which specific anion exchangers were subjected to high levels of *in situ* alpha particles. Although some investigators have tried to systematically study the effects of radiation on several new ion exchangers and confirm previous findings, appreciable gaps remain in our understanding of these radiation-damage mechanisms.

Radiation stability is a particularly important consideration when selecting materials for processing nuclear waste. We therefore cite a just-completed evaluation of 60 candidate absorbers for partitioning Hanford High-Level Tank waste. The most promising absorbers identified in that study should be evaluated for their radiation stabilities, when such information is not already available.

I. INTRODUCTION

Ion exchangers have always had a major role in pollution abatement in nature. Natural ion exchangers, such as soils, sand, clays, rocks, and decayed plant materials help protect aquifers by removing a variety of surface contaminants. The advent of synthetic ion exchangers just before the discovery of nuclear fission allowed a synergism between these two technologies that contributed to significant advances in both fields. Consequently, the nuclear industry has become a major user of ion exchange technology.

Major users of ion exchangers within the nuclear industry are the commercial nuclear power plants and the producers of fissile and fertile materials for civilian and defense applications. In particular, modern organic ion exchange resins are extensively used to purify the aqueous coolant systems of nuclear power plants. Numerous ion-exchanger systems and technologies are used worldwide to maintain the aqueous coolant systems of approximately 415 land-based nuclear power plants and an equal number of nuclear plants used for marine propulsion. The stringent requirements of reactor coolant systems make most nuclear facilities large-scale users of organic ion exchange resins. Between 10,000 and 25,000 liters of ion exchangers are used annually for coolant maintenance in a typical nuclear facility.¹ These facilities also use large quantities of organic and inorganic ion exchangers for waste management and pollution abatement.

A unique pollution abatement application of ion exchangers currently receiving much attention is in the isolation of hazardous components of high level nuclear wastes from fuel reprocessing. Decades of reprocessing irradiated fuel from production reactors at nuclear defense sites has left large quantities of highly radioactive wastes in underground storage tanks. The US Department of Energy is committed to recovering and concentrating the hazardous components from these wastes to isolate them from the biosphere. Ion exchangers that can function in an intense radiation environment are highly desirable for this application.

Ion exchangers used in the nuclear industry are subjected to ionizing radiation fields of varying intensities. Because extended exposure to ionizing radiation is known to damage ion exchangers,^{2,3} there is great interest in understanding the radiolytic damage mechanisms and in developing materials that offer greater resistance to such hostile environments. Attempts to develop a detailed understanding of the damage mechanisms have been only partially successful. Nevertheless, properties of radiation-resistant substrates have been identified and used to make improved ion exchangers for the nuclear industry. Such changes in the molecular design of organic resins have improved their radiation resistance, which in turn has resulted in superior materials for specialized applications.

During the past six decades, many hundreds of ion exchange materials have been synthesized and tested. Few, however, have achieved industrial importance. Because the nuclear industry relies heavily on synthetic organic ion exchangers, this is the type most extensively studied for radiation effects. However, improved new ion exchangers of other types are also needed for applications requiring intense radiation exposures and corrosive chemical environments. In recognition of this need, new materials are continually being examined for a variety of nuclear process environments.

Ion exchange materials used in nuclear material processing are not only subjected to ionizing radiation, they often encounter a hostile chemical environment as well. This combination of aggressive conditions can degrade many ion exchange materials. Because the behavior of ion exchangers subjected to ionizing radiation in typical processing media greatly interests chemists, it has been the subject of many published studies. Three major surveys have reviewed this literature.^{2,3,4} A concise tabulation of the key features of these studies is presented in a companion publication to one of these surveys.⁵

The objective of our review is to examine this expanding knowledge base and to highlight new developments relevant to radiation effects on ion exchangers. This report is primarily organized by generic types of ion exchangers. Because few *in situ* irradiation experiments have been published, we devote a separate section to some unique *in situ* experiments and their results.

II. SIGNIFICANT RECENT STUDIES

To locate significant new information, we examined experimental studies and literature reviews published since the last comprehensive survey,⁴ which extended through 1984. Several groups of researchers from the former Soviet Union, the Czech Republic, Egypt, and India reported the effects of radiation on ion exchange resins.⁶⁻¹³ Because these studies only confirm previous investigations, we chose not to devote space to them in this review.

Recovery operations at the Three Mile Island-II reactor, however, produced some noteworthy studies.^{14,15} Those investigations were made to determine the maximum permissible loading of the resins. The research was necessarily limited to the polymeric strong-acid cation exchange resins and the strong-base, quaternary ammonium-type anion exchange resins in use at TMI-2. The investigators measured resin-related gas generation, physical damage, increased corrosion of waste containers, and changes in resin pH and flow rate.

An extension of these TMI-2 studies by McConnel et al.¹⁶ was one of the few published *in situ* irradiation studies. The Epicor-II prefilters, which consist of a layered mixture of inorganic and organic cation exchangers, received approximately 1 MGy^a of cumulative dose from mixed fission products during nine years of TMI-2 cleanup operations. The effects of this *in situ* exposure were not significantly different from those of exposing similar resin to comparable doses of external radiation.

Other publications since 1984 established the superior radiation resistance of a new macroporous polyvinylpyridine anion exchange resin, ReillexTM IIPQ.¹⁷ The effects of *in situ* alpha particles were measured on six strong-base anion exchange resins, which included ReillexTM IIPQ.¹⁸ These studies are discussed in later sections.

A novel proposal to use well-characterized ion exchangers to measure very high dose rates, where conventional radiation dosimetry is not feasible, seems worthy of further examination.⁸ Finally, a discussion of radiation stability¹⁹ was included in a review of ion exchange technology in the nuclear fuel cycle published by the International Atomic Energy Agency.

III. GENERIC RADIATION EFFECTS

Ionizing radiation doses in the range of 10⁵ Gy significantly alter the properties of most synthetic organic ion exchangers. High absorbed doses affect exchange capacity, selectivity, and exchange kinetics. Other physical and chemical characteristics also change. In general, anion exchangers suffer more radiation damage than do cation exchangers. Radiolytic effects on ion exchangers depend on the nature of the resin itself: its chemical composition, ionic form, moisture content, swelling characteristics, and the extent of cross-linkage in the macromolecular structure. Radiolytic changes are also affected by the type of radiation and the resin environment during the irradiation.

Ionizing radiation acts on synthetic organic ion exchangers in two ways. First, direct radiolytic effects lead to the scission of functional groups, the formation of free radicals, and hydrolytic reactions of the species formed. Second, interactions occur between the ion exchanger and highly reactive radiolysis products in the surrounding medium.

Investigators have proposed mechanisms for the observed radiolytic effects on synthetic organic resins, based on knowledge of the radiolysis of synthetic polymers in water.^{2,20,23} However, our present knowledge is inadequate to evaluate the reaction-rate constants of the controlling radiolytic processes or to develop useful models for radiolysis in ion exchangers. Many radiation studies have been confirmed by investigations of similar types of resins of different origin; nevertheless, disagreements exist in several areas and some conclusions remain debatable.

Research with *in situ* radiation sources is especially desirable, but such experiments are especially challenging because all post-irradiation measurements must be done on radioactive resin. For this reason, nearly all published data are from resins exposed to external sources, such as x-ray machines, ⁶⁰Co, electron accelerators, and in a few cases research reactors. A separate section of this report discusses experiments in which modern ion exchange resins have been subjected to *in situ* alpha particles; such studies are particularly relevant because they closely simulate the actual processing environment.

^aGray is the SI unit of absorbed dose. 1 Gy = 1 J/kg = 100 rad.

Properties of ion exchange resins and irradiation effects that can be quantified for comparison purposes include (a) radiation chemical yield or G-value, (b) swelling/shrinkage of the resin matrix, (c) weight change, (d) solubility, (e) gas evolution, (f) water content and (g) formation of ionic species. These data and their original references are compiled in the two reviews cited earlier.^{2,4}

A. Polymeric Cation Exchange Resins

The commercial importance of polymeric cation exchangers, such as the styrene-divinylbenzene-sulfonic acid resins, has focused experimental studies on this type. Studies have demonstrated that the radiation chemical stability of polymeric cation exchange resins depends on the degree of cross-linkage of their macromolecular structure. (The cross-linkage of polymeric resins is defined as the percent divinylbenzene used in the resin preparation.)

Early work by Wedermeyer²⁴ and Cathers²⁵ and later contributions by Semushin²⁶ and Kiseleva²⁷ are typical of studies that demonstrate the relationship between resin cross-linkage and radiation stability. Many other investigators also have concluded that higher cross-linkage increases the radiation stability of synthetic organic ion exchange resins.²⁸⁻³⁷ However, a few exceptions to this generalization, such as those reported by Tulupov,²⁹ do exist.

A common measure of ion exchanger stability is the change in total exchange capacity as a function of radiation dose. Many commercial polymeric cation exchangers have been evaluated in this way.⁵ However, very few experimental studies of radiation-induced chemical effects yield quantitative data that can be extended to an entire class of synthetic resins.

Differing results from various experimental studies may partly reflect differences in resin constituents. Such differences can stem from common impurities in the polymerization reactants. This was demonstrated by Wiley and coworkers^{34,38,39} in their systematic comparison of the constituents of commercial divinylbenzene, and of the radiation stabilities of various resins with known constituents.

B. Polycondensation-Type Cation Exchange Resins

Cation exchange resins of the polycondensation type are more resistant to radiation damage than are polymeric resins, although their chemical, mechanical, and thermal properties are significantly worse. This generalization is confirmed by experimental studies of many organic resins.^{2,25,40-48} Changes in total exchange capacity, swelling, weight loss, gas evolution, and the appearance of new functional groups are common to both types of organic cation exchange resins; however, a comparable dose causes less change in polycondensation-type resins.

Among strong-acid type cation exchange resins containing carbon-sulfur bonds, chemically unstable phenolsulfonic acid-formaldehyde resin is more stable to ionizing radiation in many aqueous solutions than are the more chemically stable styrene-divinylbenzene-sulfonic acid resins. Studies show that weak-acid carboxylic acid resins containing carbon-carbon bonds are more resistant to radiation than are strong-acid resins containing carbon-sulfur, carbon-phosphorus, or carbon-oxygen bonds.^{42,43,45}

A polycondensation-type resin based on salicylic acid and furfural is reported to be more resistant to radiation than several condensation-type sulfonic acid derivatives.⁴² Its exchange capacity and other characteristics are unchanged after radiation doses of 2 MGy. Shigematsu and Oshio⁴³ have confirmed this generalization about the relative radiation stability of weak-acid carboxylic and phenolic-base cation exchangers.

C. Anion Exchange Resins

Polymeric resins with quaternary ammonium groups are the most important anion exchangers in the nuclear industry. These resins have been the subject of many studies during the past three decades.^{2,4,24,32,43,49-68} However, very few of these experimental studies provide useful quantitative data.

Radiation-induced chemical changes in these resins are characterized by darkening of the resin, evolution of odorous free amines, gas evolution, loss of exchange capacity, and degradation of the resin matrix. The resistance of anion exchange resins to radiation generally varies little with the basicity of the resin. Those having aromatic systems with conjugated bonds in the functional groups are more radiation resistant than other types of synthetic organic anion exchangers.

Most polymeric anion exchangers are based on styrene-divinylbenzene copolymers. Although this structure is highly resistant to radiation damage, anion exchangers that contain quaternary, tertiary, secondary, or primary amino groups do begin to show significant attrition at doses of about 0.1 MGy. By contrast, cation exchangers, based on a styrene-divinylbenzene copolymer, generally suffer little damage from a comparable dose. The attrition of anion exchangers is usually greater in the presence of water or aqueous electrolytes than in otherwise similar irradiations of dry resins.

Data for radiation effects on anion exchangers indicate that radiation-induced chemical changes in strong-base monofunctional anion exchangers follow a rather complex mechanism. There may be two types of exchange groups, which differ in their relative stability toward radiation-induced chemical changes.^{2,56,57} These groups are believed to be attached to the aromatic ring in the ortho or para positions, with the ortho groups being less stable than the para substituents.⁵⁶

Experiments suggest that quaternary-ammonium type resins decompose primarily through deamination, which breaks the carbon-nitrogen bonds that connect the trimethylamine groups to the benzyl radicals.^{53,54,57} Egarov and Novikov state in their classic work that anion exchange resins of the quaternary ammonium type lose exchange capacity primarily by decomposition of the functional groups.² These authors suggest that the decomposition depends on the nature of the functional groups and the ionic form.

Anion exchangers with quaternary ammonium base groups, when irradiated, steadily lose their strong-base exchange capacity. However, some of the strong-base groups convert to weakly basic amino groups, which temporarily increase the total exchange capacity of the resin.^{53,57} Irradiation of anion exchangers also reportedly forms oxidation-induced carboxyphenolic and hydroxy groups. As with cation exchangers, anion exchange resins with high cross-linkage experience less radiation damage.^{2,24,53}

Also, as with cation exchangers, the salt forms of anion exchangers are reported to be more radiation resistant. Although exceptions exist, the nitrate, chloride, chlorate, and sulfate forms of anion exchangers generally are more radiation resistant than the hydroxide form.^{2,32,43,53,57-59} Nitrate-form resins may be more stable than the chloride form because nitrate ions can scavenge hydrated electrons, whereas chloride radicals are strongly oxidizing.

A representative study on the loss of capacity of anion exchange resins⁴⁹ indicates that the ionic form and the environment of the resin during irradiation both influence radiation-induced chemical changes.

Several investigators characterized the radiolytic decomposition products of anion exchange resins.^{49,54,57-62} They measured yields of tertiary, secondary, and primary aliphatic amines and ammonia. Irradiation of anion exchangers having quaternary ammonium groups produces soluble amines and ammonia, with trimethylamine as the major product; however, the yields depend in a rather complex manner on the moisture content of the resin.

The radiation chemistry of polycondensation type resins has been less rigorously explored, and many features of their radiolysis remain unexplained.

IV. POLYVINYLPIRIDINE RESINS

Previous radiation stability studies^{4,22} have identified anion exchange resins with a pyridine functional group in a vinylpyridine-divinylbenzene copolymer as more resistant to radiation than polystyrene resins. Moreover, these polyvinylpyridine resins have greater resistance to attack by nitric acid, an important consideration in many nuclear industry processes.

Most conventional strong-base anion exchange resins are copolymers of styrene and divinylbenzene. Because styrene polymers can react violently with nitric acid under certain conditions, such hazardous conditions must be stringently avoided. Potential safety hazards of using ion exchange resins in nitric acid systems have been addressed by Calmon;⁶⁹ some actual failures were summarized by Miles.⁷⁰

Vinylpyridine polymers should be more resistant to nitric acid than is polystyrene. Polystyrene is susceptible to electrophilic aromatic substitution, whereas the electronegativity of nitrogen in the pyridine ring makes polyvinylpyridine highly resistant to such substitution.

More than 30 years ago PermutitTM SK, a gel-type polyvinylpyridine anion exchange resin, was reported to offer superior sorption and desorption kinetics⁷¹ and capacity⁷² for plutonium, as well as greatly increased stability against chemical attack⁷³ and radiolytic degradation.³ PermutitTM SK (no longer manufactured) is a copolymer of 2-methyl-5-vinylpyridine and divinylbenzene.

More recently, Zainutdinov et al.⁷⁴ studied the gamma-radiation resistance of anion exchange resins based on epichlorohydrin and 2-vinylpyridine or 2-methyl-5-vinylpyridine, both dry and immersed in water. Resins irradiated to 2.6 MGy were compared with their unirradiated counterparts. The capacities, wet volumes, weights, and mechanical strengths of the irradiated resins decreased by only a few percent in all cases, compared with a 30% swelling and 25% loss of strength for AN-31, an industrial anion exchange resin without pyridine functionality.

Several years ago, Reilly Industries of Indianapolis, a manufacturer of vinylpyridine polymers, began producing a macroporous polyvinylpyridine anion exchange resin. This new resin, ReillexTM HPQ, is a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene. The sorption kinetics of ReillexTM HPQ were reported to be comparable or superior to the best commercial anion exchange resin previously identified.⁷⁵ The chemical resistance of ReillexTM HPQ was evaluated by subjecting this resin to boiling nitric acid under reflux for three hours.⁷⁵ Although a small quantity of NO₂ fumes was observed, the dry weight of the resin was essentially unchanged by this severe treatment. The wet resin volume, however, increased by about 10%.

The swollen resin provided faster sorption kinetics and a capacity increase of nearly 20%, which indicated that some of the divinylbenzene cross-linking groups had cleaved.⁷⁵ Such cleavage would be expected to relax the resin structure and allow the beads to expand, in accord with the observed swelling. The more open structure of the expanded beads should make the interior anion exchange sites more accessible, which would account for the increased capacity and improved sorption kinetics.

The effects of gamma radiation on ReillexTM HPQ were compared with the effects on four conventional strong-base polystyrene resins,¹⁷ including gel-type DowexTM 1 × 4 and three macroporous resins: DowTM MSA-1, AmberliteTM IRA-900, and LewatitTM MP-500-FK. Each resin, in 7 M nitric acid, was irradiated with ⁶⁰Co to seven levels of gamma radiation ranging from 1 to 10 MGy. All irradiated resins were measured for changes in dry weight, volume in 7 M nitric acid, volume in water, strong-base and weak-base chloride exchange capacity, Pu(IV) exchange capacity, and thermal stability. Of the resins tested, ReillexTM HPQ was found to be the most stable against damage by gamma radiation, whereas LewatitTM MP-500-FK was the least stable.

The resistance of ReillexTM HPQ to *in situ* alpha particles also was compared to that of five other strong-base anion exchange resins.¹⁸ This study included the five resins used in the cited gamma-irradiation study plus one more resin, LewatitTM UMP-950, which replaced the discontinued LewatitTM MP-500-FK. Each resin was irradiated in 7 M nitric acid by sorbed ²³⁸Pu to doses of approximately 5, 8, 11, and 14 MGy. The resins were measured

for all properties cited in the preceding paragraph, except thermal stability. As in the gamma-irradiation study, Reillex™ HPQ provided the greatest stability against alpha particles, whereas Lewatit™ MP-500-FK was the least stable of the resins tested.

V. *IN SITU* ALPHA-PARTICLE IRRADIATIONS

Most investigations of the effects of radiation on ion exchange resins use an external source of gamma radiation, generally ^{60}Co . Experiments that involve *in situ* alpha-particle irradiations are relatively rare. An extensive compilation by Gangwer et al.³ lists hundreds of irradiations of ion exchange resins by a variety of external sources including gamma rays, x-rays, accelerated electrons, and spent reactor fuel. Of the cited studies, however, none involving anion exchange resin and only two involving cation exchange resin used *in situ* alpha particles. The investigators' preference for external sources is understandable. Because external sources leave no residual radioactivity in the resin, subsequent measurements of the resin can be made using benchtop procedures, rather than requiring the complication and inconvenience of glove-box operations.

Despite the added difficulty of working with *in situ* alpha particles, such studies are necessary to realistically simulate the radiation environment of ion exchangers in actinide separation processes.

Kazanjian and Horrell⁷⁶ compared the effects of gamma rays and alpha particles on Dowex™ 50W × 4 cation exchange resin. They concluded that the ion exchange sites were similarly affected, but that alpha particles caused greater damage to the polymer matrix.

Specht et al.⁷⁷ exposed Dowex™ 50W × 8 cation exchange resin to dose rates of 0.025, 0.10, 0.185 MGy per hour of *in situ* alpha particles from sorbed ^{242}Cm , and also to gamma dose rates of 0.10 and 0.185 MGy per hour from an operating nuclear reactor. The strong-acid capacity of the resin was decreased about 50% by a 20-MGy dose of either alpha particles or gamma radiation. This decrease was attributed to sulfonic acid functional groups being split off. For a given total dose of either alpha particles or gamma rays, the capacity loss was highest at the lower dose rates.

Paranonova and coworkers⁷⁸ evaluated the effects of alpha particles from sorbed plutonium on AV-23M anion exchange resin, a copolymer of 2-methyl-5-vinylpyridine cross-linked with 7% trivinylbenzene. This resin retained 91% of its initial capacity after alpha-particle exposures 2.57 MGy. Although resin weight loss was not reported, a dose of 3.42 MGy decreased the resin cross-linkage to 3.3%.

Ahrens⁷⁹ measured the effects of alpha particles on Dowex™ 1 × 4 in nitric acid, and compared his results with those of another investigator who had previously studied the effects of gamma radiation on that resin. The capacity loss caused by 1.00 MGy of alpha particles was less than half that caused by a comparable gamma dose.

The effects of alpha and gamma radiation were compared in a dissertation by Ahmed.⁸⁰ Ahmed found the capacity loss for sulfate-form anion exchange resin was 2 to 2.5 times greater from gamma radiation than from a comparable dose of alpha particles.

Marsh⁸¹ compared the effects of *in situ* alpha particles to those of external gamma radiation on five strong-base anion exchange resins: Reillex™ HPQ, a polyvinylpyridine resin, and four conventional strong-base polystyrene resins, which included gel-type Dowex™ 1 × 4 and three macroporous resins (Dow™ MSA-1, Amberlite™ IRA-900, and Lewatit™ MP-500-FK). Each resin, in 7 M nitric acid, was irradiated with ^{60}Co to seven levels of gamma radiation ranging from 1 to 10 MGy, and also to alpha doses of 5, 8, 11, and 14 MGy from sorbed ^{238}Pu . (The alpha-irradiation study¹⁸ included one additional resin, Lewatit™ UMP-950, which replaced discontinued Lewatit™ MP-500-FK.)

All irradiated resins were measured for changes in dry weight, volume in 7 M nitric acid, volume in water, strong-base and weak-base chloride exchange capacities, Pu(IV) exchange capacity, and thermal stability. Of the tested resins, Reillex™ IIPQ was the most stable to gamma radiation and alpha particles, whereas Lewatit™ MP-500-FK was the least stable.

All of these resins survived alpha particles better than gamma radiation. Weight losses were substantially higher from gamma radiation than from an equivalent exposure to alpha particles. A remarkable 97% of the initial weight of Reillex™ IIPQ resin survived even the highest alpha dose of 14.3 MGy. Plutonium(IV)-capacities of these same resins from 7 M nitric acid during a 15-minute dynamic contact confirmed that all resins were significantly less damaged by alpha particles than by a comparable dose of gamma radiation.

Resin damage from alpha particles was generally less than half that caused by an equivalent dose of gamma rays. Much of the resin damage was attributed to secondary reactions between the resin and radiolysis products of nitric acid. This is consistent with differences in experimental conditions, whereby a larger quantity of nitric acid was exposed to radiation in the gamma-irradiation study.¹⁸

VI. CHELATING RESINS

Myasoedova and Savvin⁸² presented a comprehensive review (with 247 references) of chelating sorbents and their uses in analytical chemistry. Millar et al.⁸³ reviewed approximately 50 commercial chelating resins and stated, "... only a few are in fact commercially viable, and none even approaches the original criterion (of being selective)." Sengupta and Zhu⁸⁴ have suggested applications for several chelating polymers with nitrogen donor atoms. Green and Hancock⁸⁵ studied pyridyl-imidazole and pyridyl-methyl-imidazole resins. Eccles and Greenwood⁸⁶ recently reviewed past and future applications of chelate ion exchangers. Although many chelating exchangers appear suitable for removing radionuclides from waste streams, relatively few have been studied for radiation stability.

An extensive review of the action of ionizing radiation on ion exchangers by Egorov and Novikov,² published nearly 30 years ago, devoted several pages to carboxylic cation exchangers. These authors reported that this type of exchanger is extensively damaged by doses of less than 0.1 MGy, and that most carboxylic resins cannot be used at doses above 1 MGy. They concluded (1) higher cross-linkage increases the radiation stability, (2) hydrogen-form resins irradiated dry or in water-swollen form exhibit different radiation stabilities, (3) resins irradiated in their salt forms are much more susceptible to radiation damage, and (4) phenol-formaldehyde resins, copolymers of acrylic acid, and styrene-DVB copolymers are more resistant to radiation than those based on methacrylic acid.

More recently, Murty⁸⁷ measured the effects of gamma radiation on carboxylic acid exchangers Zeocarb-226, IRC-50, and Indion-236. These resins were irradiated in the hydrogen, ammonium, and sodium forms; either air-dried, or in aqueous slurries of demineralized water or of 1:1 ethanol-water mixtures. After 1.2 MGy, at a dose rate of 30 Gy per minute, no major differences among the three resins were observed. However, the resin form and the irradiation medium both affect the loss of exchange capacity. For dry irradiations, hydrogen-form resins are generally more stable than sodium-form resins, which in turn are more stable than ammonium-form resins. In aqueous solutions, the radiation damage to hydrogen-form resin is similar to that of a dry irradiation (based on very limited data); however, the damage to sodium- and ammonium-form resins is increased. The damage to sodium- and ammonium-form resins in an ethanol-water mixture is less than that incurred in water alone.

Pfeffer et al.⁸⁸ studied the resistance of Wof MC 50 Chelon exchanger to 0.1 to 2 MGy of gamma radiation. When this resin, which has aminoacetic acid and iminodiacetic acid functional groups, was air-dried or immersed in water or 1 M nitric acid during the irradiations, the main reaction was decarboxylation, with a G-value of 13. Irradiations in nitric acid solutions of 7 M or higher concentration resulted in rapid oxidative breakdown of the functional groups, in addition to radiation-induced decarboxylation.

Egorov and Novikov² reviewed the status of phosphated cation exchangers of Soviet manufacture in the mid-1960s. Electron-beam irradiations of RF resin (with a phosphate functional group) to 28 MGy, in water and in aqueous electrolytes, caused increased swelling but little change in capacity. Irradiation of KF-1 (another phosphate cation exchanger) to 45 MGy in water, lactic acid, and acetic acid caused little change in swelling or capacity. Those reviewers concluded, from limited experimental data, that resins containing phosphate functional groups were the most radiation-resistant resins known at that time, and could be used at doses greater than 10 MGy.

Gribanova et al.⁶⁸ evaluated the radiation, chemical, and mechanical stability of porous organophosphorus exchangers irradiated by ⁶⁰Co in air, water, and 2 M nitric acid. The stability of the porous phosphonic acid exchangers was considerably higher than that of nonporous exchangers. For resins polymerized with varying ratios of iso-octane and divinylbenzene, the radiation resistance increased with the degree of cross-linkage. Resins containing at least 10% divinylbenzene and 60% iso-octane were essentially unaffected by doses to 194 MGy in any of the three irradiation media.

Tulopov et al.⁸⁹ synthesized a cation exchanger based on the bis-2,2'-chloroethyl ester of vinylphosphonic acid and divinylbenzene. The ester groups were saponified in one variation of their study to convert the arylphosphonic acid groups to alkylphosphonic acid groups. Exposures in water to doses of 1, 2, and 3 MGy, in water, resulted in capacity losses of 3.4, 4.3, and 5.7%, respectively, for the arylphosphonic acid resin; capacity losses were 8.5, 15.0, and 16.3%, respectively, for the alkylphosphonic acid resin. The chemical stabilities of these two resins in 3 M or 10 M nitric acid were comparable.

Nikolaev and coworkers⁹⁰ studied the effect of gamma radiation on a series of diallyl and triallyl esters of phosphonic acid. These esters were diallyl phosphate, triallyl phosphate, triallyl methylphosphonate, diallyl butylphosphonate, diallyl isopentylphosphonate, and diallyl allylphosphonate. Each resin, sealed in a glass tube with distilled water, was irradiated by ⁶⁰Co to a total dose of 0.9 MGy, at a dose rate of 6 Gy per second. After the irradiations, the experimenters measured changes in exchange capacity for sodium and uranyl ion, and resin swelling in water and ethanol. All resins except the diallyl phosphate gained capacity for sodium, whereas all resins lost capacity for U(VI). Resin swelling decreased in water and in ethanol. The decreased swelling and decreased capacity for the large uranyl ion were both attributed to a radiation-induced increase in cross-linkage of all resins. Moreover, these investigators proposed that the sorption mechanism was changed as a result of irradiation.

VII. MULTIFUNCTIONAL RESINS

Soviet researchers have prepared multifunctional anion exchangers from either tetraglycidyl-4,4'-thiodianiline or tetraglycidyl-4,4'-oxydianiline, combined with polyethylenepolyamine or polyethyleneimine.⁹¹ The radiation stability of these exchangers depends on the moisture content, rather than the basicity of the amine groups. Electron irradiation of tetraglycidyl-4,4'-thiodianiline:polyethylenepolyamine to 1.9 MGy caused a capacity loss of 39% when the exchanger contained 51.2% water, whereas the loss was only 19.4% when the water content was 13.3%.

Kiseleva and coworkers⁹² studied vinylpyridine-carboxylic acid ampholyte VPK, whose functional group is picolinic acid. The properties of VPK depend on the medium; in alkaline solutions it is a cation exchanger, whereas in acid solutions the protonated nitrogen behaves as an anion exchanger. In neutral and weak acid solutions the predominant intramolecular salt form exhibits a weak swelling that influences radiolysis.

The principal radiolytic degradation processes for VPK resin are decarboxylation, rupture of cross links, and oxidation of the resin.¹⁰ Sodium nitrate protects the VPK macromolecular skeleton against radiation damage, but increases the G value for decomposing the carboxylic acid from 1.2 to 2.0.

In another study, Tabakova et al.⁹³ used VPK resin loaded with Sr(II), Pr(III), or UO₂(II). The VPK was irradiated in water to doses of 2 to 10 MGy with ⁶⁰Co. No metal ions were released into solution during any of these irradiations. Metal complexes appeared to protect the carboxyl groups against decomposition, but increased the rupture of cross-links. VPK resin that was completely saturated with metal ions lost no exchange groups in the dose range of 2 to 6 MGy. Distribution coefficients for Sr(II) on irradiated VPK consistently decreased;⁹⁴ however, distribution coefficients for Pr(III) increased when VPK was irradiated in acetate buffer, but decreased when VPK was irradiated in acetate buffer that also contained sodium nitrate.

The difference in the radiolytic stability of VPK, with or without sorbed Sr(II), was explained in terms of electron density. In an ampholyte completely loaded with Sr(II), the electron density is similar to that of benzene because the complex involves not only the carboxylic acid group, but also by a slight withdrawal of electrons from the nitrogen. This shift of electron density in the ampholyte increases the reactivity of the radiolysis products with the less stable cross-links and heterocycles of the VPK, while it suppresses their reactivity with the carboxylic acid group.⁹⁵ A separate study with Ni(II) concluded that the resistance to radiation damage of VPK complexes is in the order Ni(II) > UO₂(II) > Pr(III) > Sr(II).⁹⁶

Other interesting multifunctional resins have been prepared and tested with various metal ions. Unfortunately, the radiation stabilities of these resins have not yet been evaluated. Because some of these are especially attractive candidates for radionuclide removal, however, we will discuss a few of them. We strongly encourage the developers of these sorbents or other investigators to determine their radiation stabilities.

Alexandratos and coworkers⁹⁷ synthesized and tested a series of dual-mechanism bifunctional polymers (DMBPs). These DMBPs have a hydrophilic cation-exchange ligand that provides access into the polymer network, coupled to another ligand whose reactivity determines the observed specificity. The second ligand provides a recognition mechanism based on reduction, coordination, or precipitation.

Alexandratos et al.⁹⁸ developed a bifunctional phosphinic acid resin specifically for lanthanides and actinides. More recently, Alexandratos et al. synthesized a trifunctional resin known as Diphonix, which has two phosphonic acid groups chemically bonded to a single carbon atom, and also has sulfonic acid and carboxylic acid functional groups in its styrenic-based polymer matrix. Although its radiation stability has not yet been determined, this resin has been proposed by its developers as a sorbent for actinides and other radionuclides.⁹⁹

VIII. INORGANIC ION EXCHANGERS

The term "inorganic ion exchanger" was first used by Amphlett, who published the earliest surveys of these materials.^{100,101} Vesley and Pekarek later prepared an exhaustive review of inorganic ion exchangers (with 869 references) for the period 1965-1970.^{102,103} Clearfield¹⁰⁴ and Qureshi and Varshney¹⁰⁵ also compiled extensive reviews of inorganic exchangers and their applications. Because the composition and degree of crystallinity of these materials greatly affect their sorption properties, their preparation is still being studied.¹⁰⁴

The number of natural and synthetic materials classified as inorganic ion exchangers has increased greatly during the past four decades. However, because inorganic ion exchange is accompanied by other phenomena such as molecular sieving, physical adsorption, and precipitation, the exact scope of the term "inorganic ion exchanger" is difficult to define.

For much of the past 50 years, inorganic ion exchangers have been proposed for sorbing radionuclides, based on claims of higher mechanical strength and better resistance to heat, radiation, and oxidation than organic polymers. Many of these claims should be viewed with caution, however, because they are not always supported by published studies. Another advantage claimed for inorganic exchangers is that some can be directly incorporated into the glass or ceramic materials proposed for long-term storage of radioactive waste.

Of the many publications about inorganic ion exchangers, relatively few address radiation stability.¹⁰⁴ Among those that do, many omit the irradiation medium and other important experimental conditions. Because the applications of inorganic ion exchangers in nuclear processing operations have been limited, systematic examination of the effects of radiation on these exchangers also have been few.¹⁰⁶⁻¹¹²

Hooper¹¹³ discussed the broad classes of inorganic ion exchangers: natural inorganic exchangers, synthetic zeolites, oxides and hydrous oxides, acidic salts of multivalent metals, and cyanoferrates. Hooper et al.¹¹⁴ then reviewed the published literature on inorganic exchangers in an excellent 121-page survey with 316 references. Based on this review, hydrous titanium oxide, manganese dioxide, titanium and zirconium phosphates, polyantimonic acid, and copper hexacyanoferrate were selected for experimental evaluation.

The effects of gamma radiation on these six sorbents were determined for exposures to 10 MGy.¹¹⁵ These exchangers generally showed high resistance to irradiation to this maximum dose. Manganese dioxide and copper hexacyanoferrate were unaffected by irradiation, whereas polyantimonic acid showed decreasing performance with increasing dose. The performance of zirconium phosphate, titanium phosphate, and titanium oxide decreased up to a total dose of 2.19 MGy, but then appeared to recover at higher doses. Hydrous titanium oxide was the most affected by radiation; moreover, the effects differed for the sorption of different radionuclides, suggesting that the damage mechanism involved a loss of exchange sites resulting from the loss of hydrated water.

Hydrous titanium oxide was irradiated in its hydrogen and sodium forms by Inoue and Tsuji.¹¹⁶ Because they used a low-intensity source of gamma rays, it took 1.5 years to attain the full exposure of 5.2 MGy. The capacity of the hydrogen-form exchanger decreased to about half its initial value in 1.5 years, whether it was irradiated or not, which indicates that the change was due to aging. The capacity of the sodium-form exchanger was unchanged after an identical 1.5-year irradiation.

Sodium titanate, reported to be selective for strontium, was shown to be highly resistant to gamma radiation.¹¹⁷ Essentially no change was observed in its structure or specific surface area after exposure to 10 MGy from ⁶⁰Co. However, Kenna¹⁰⁸ reported a 50% decrease in the strontium capacity of sodium titanate synthesized at Sandia National Laboratories after a gamma dose of 20 MGy.

Dosch¹⁰⁶ studied the properties of titanate, niobate, and tantalate salts. The capacity of sodium titanate powder for strontium remained unchanged to gamma doses of 0.3 MGy (from ⁶⁰Co), but decreased to 50% of its initial capacity after 20 MGy. This capacity loss was attributed to heating during the irradiation. When sodium titanate was incorporated into an organic polymer resin, however, its capacity remained unchanged to 5 MGy, but decreased to 30% of its initial capacity after 20 MGy. Anion exchange resins loaded with sodium niobate or sodium tantalate exhibited comparable sorption properties for strontium, but greater stabilities in acids. These improvements, however, were not considered sufficient to justify the higher preparation costs of the niobate and tantalate salts.

Dyer and Jamil¹¹⁸ tested six inorganic *anion* exchangers: hydrated zirconium oxide, ferric ferrocyanide, hydrated titanium oxide, hydrated aluminum oxide, lead sulfide, and mercarbide $[(CHg_3O)_n^{n+}(NO_3)_n^{n-}]$, as prepared by Weiss and Weiss.¹¹⁹ These anion exchangers were irradiated, both wet and dry, to a total dose of 1 MGy. The mercarbide and lead sulfide, when irradiated wet, showed a significant increase in capacity for perchlorate, whereas the other exchangers lost essentially all of their anion exchange capacity. Dyer et al.¹²⁰ inserted phosphorus(V) into an aluminosilicate zeolite to convert it from a cation exchanger to an anion exchanger; however, the radiation stability of this material was not tested.

Murthy et al.¹²¹ studied ammonium phosphomolybdate, polyantimonic acid, manganese dioxide, and zirconium antimonate for sorbing cesium, strontium, cerium, and sodium, respectively, in an unspecified acid from 0.2 to 10 M. Measurements before and after gamma irradiations of approximately 1 MGy showed almost no change in capacities and only slight changes in distribution coefficients.

The exchange capacity and elution behavior of zirconium arsenophosphate¹²² and antimony(V) silicate¹²³ are highly resistant to gamma doses of 1 to 3 MGy. Thorium phosphosilicate was only slightly affected by similar irradiations.¹²⁴ The exchange capacities of stannic ferrocyanide, zirconium ferrocyanide, ceric antimonate, titanium antimonate, and ceric tungstate were essentially unchanged by a gamma dose of 10 MGy, although Dowex 50W × 8 and Amberlite IR-120 lost 25% of their capacity during similar irradiations.¹²⁵

When Zr(IV), Sn(IV), and Cr(III) antimonates were exposed to 9 MGy of gamma radiation from a shut-down nuclear reactor, however, their exchange capacities decreased by 36.6%, 16.8%, and 31.2%, respectively.¹⁰⁹ In another study by different investigators,¹¹¹ zirconium phosphate, cerium phosphate, and cerium arsenate were irradiated to 10 MGy in a nuclear reactor core six days after shut-down. No change in the structure of crystalline zirconium phosphate was observed; the structure and other properties of cerium arsenate changed, and the crystal lattice of cerium phosphate was completely destroyed, causing the material to become amorphous. The difference between gamma irradiations from ⁶⁰Co and those in a shut-down reactor were attributed to the presence of neutrons in the latter case.

Although neutrons are produced by (α , n) reactions and by spontaneous fission even in a shut-down reactor, we question whether the neutron fluence explains the reported differences. Specht et al.⁷⁷ used an operating nuclear reactor as a source of high-intensity gamma radiation and concluded that the fast neutron flux, even in an operating reactor, was negligible for the two reactor positions that he used.

The high selectivity and resistance to radiolytic degradation of certain natural zeolites have made them quite useful for the separation and purification of ¹³⁷Cs and ⁹⁰Sr from the millions of gallons of highly radioactive waste stored on the Hanford reservation in Washington state.¹²⁶ The development of synthetic zeolites by the Union Carbide Corporation in 1965 and the large-scale manufacture of these materials led to the separation and purification of ¹³⁷Cs and ⁹⁰Sr at Hanford, using synthetic Zeolon-900, clinoptilolite, and Decalco. Synthetic zeolites were also used to immobilize these radionuclides during shipment from Hanford to other parts of the country.¹²⁷⁻¹²⁹

Because of inherent difficulties in studying radiation at high dose rates and very high total doses, high-dose effects are often extrapolated from lower-dose effects.¹³⁰ Zeolites, being inorganic crystalline materials, were assumed to have a high resistance to radiation until 1961, when Fullerton¹³¹ published the first study of the effects of gamma radiation on clinoptilolite. Although experimental limitations allowed only changes in the basic crystalline structure to be examined, the calcium distribution coefficient decreased by 40%, and sodium distribution also changed significantly.

Few systematic studies of the effects of radiation on zeolite were done before 1979. After the Three Mile Island-II (TMI-2) accident on March 28, 1979, numerous studies were performed using commercially available synthetic zeolites. In one such study, Wallace and Bibler¹³² measured the effects of high dose rates and high total doses on Ion SivTM IE-95, previously called Linde AW-500. They claimed that high doses of gamma radiation from ⁶⁰Co had little effect on the crystal structure of Ion SivTM IE-95 and that the distribution coefficient for cesium remained undiminished after total exposures of more than 100 MGy.¹³² This is at odds with systematic studies by Palau,¹¹² who reported decreased cesium exchange capacity of Ion SivTM IE-95 above total doses of 50 MGy.

Komareni et al.¹³³ reported that exposure of Ion SivTM IE-95 and its analogues to high doses of gamma radiation caused a slight increase in the desorption of cesium and sodium from the zeolite and a measurable increase in the leachability of the pollucite. However, a related study by Reilly, et al.,¹³⁴ of zeolites recovered from the damaged TMI-2 reactor, reported no evidence of radiation effects on the crystal structure or cesium exchange capacity, even after *in situ* exposures of 100 MGy. The obvious discrepancies among these results are attributable to the inherent difficulties of measuring dose and radiation effects at high exposures.

IX. LIQUID ION EXCHANGERS

Liquid ion exchange is a special case of solvent extraction, in which the solute is selectively transferred between two immiscible phases. Whereas solvent extraction involves the formation of a neutral species (either a chelate or an ion pair), liquid ion exchange involves only ion pairs.¹³⁵ Liquid anion exchangers are based on high-molecular-weight primary, secondary, and tertiary amines, and on quaternary ammonium salts. Liquid cation exchangers include organic compounds with sulfonic, carboxylic, phosphoric, phosphonic, or phosphorous acid groups.¹³⁶

Although the functional groups of some of these cation exchangers may also be considered as chelating agents because they coordinate directly to the metal ion, the compounds are commonly classified as liquid ion exchangers. Overlap clearly exists between the liquid ion exchangers and chelating resins. In this review, we use assignments that reflect common practice, as well as whether the exchanger is liquid or solid.

Mechanisms involving liquid ion exchangers generally resemble those of ion exchange resins. However, because liquid ion exchangers require no polymer backbone, they often permit higher concentrations of the functional group, which provide higher capacities. The liquid state of the exchanger also simplifies the design of countercurrent processes.

Moreover, the concentration of functional groups in a liquid exchanger can easily be modified by dilution, which is not feasible with a cross-linked polymer resin. Liquid exchangers also offer greater selectivity, faster exchange kinetics, and more tolerance for suspended solids, than do polymeric exchangers.¹³⁷

Liquid ion exchangers have many proven applications in inorganic analysis.¹³⁸ Because liquid ion exchangers have also been used extensively for nuclear materials processing, the radiation stabilities of many of these compounds have been investigated.

Contarini et al.¹³⁹ studied the extraction of uranium, plutonium, and fission products by Aliquat-336, after exposure to 0.24, 0.38, and 0.57 MGy of gamma radiation. Although low exposures generally decreased the extractions, higher exposures increased the extractions. Although back-extraction of fission products was relatively unaffected by gamma exposure, back-extraction of plutonium became more difficult as the dose increased. The difference between these results and those of previous studies was attributed to the fact that these researchers irradiated the Aliquat-336 in contact with nitric acid.

Triaurylamine, in contact with nitric acid solutions that contained 2 mg of Pu(IV) per ml, was irradiated with ⁶⁰Co to doses of 10 kGy and 20 kGy.¹⁴⁰ The correlation between the quantity of unextracted plutonium in the aqueous phase and the gamma dose was attributed to the formation of strong aqueous-soluble complexes of plutonium with unidentified radiolysis products.

The TRAMEX process developed at Oak Ridge National Laboratory, selectively extracts trivalent actinides from concentrated lithium chloride solution into Alamine-336 in di-isopropylbenzene.¹⁴¹ Neither the extraction and stripping of curium, nor the physical behavior of the process were impaired by a radiation dose rate of 10 W/liter and a total exposure of 100 W-hr/liter.¹⁴² The only undesirable effect, a loss of hydrochloric acid (G = 1.4), was eliminated by adding of 10 volume percent methanol, after which the solution was stable to a dose rate of 18 W/liter for 25 days.

Tachimori and coworkers studied the radiolysis products of di-(2-ethylhexyl) phosphoric acid (DEHPA) and their effects on the extraction of lanthanides¹⁴³ and americium.¹⁴⁴ In both cases, the initial increase in extraction was attributed to the formation of mono-(2-ethylhexyl)phosphoric acid (MEHPA), and the subsequent decrease to the decomposition of the DEHPA and MEHPA to phosphoric acid, which forms nonextractable complexes with these trivalent cations.

Tachimori et al.¹⁴⁵ also studied the effects of radiation on the separation of lanthanides and transplutonium elements in the TALSPEAK process. TALSPEAK preferentially extracts lanthanides into DEHPA while the trivalent actinides remain in an aqueous phase of lactic acid and diethylenetriaminepentaacetic acid (DTPA). Irradiation was found to increase the extraction but to decrease the separation factor, due to radiolytic decomposition of DTPA and formation of MEHPA. The presence of lactate, which suppressed the degradation of DTPA and DEHPA, allowed the system to operate successfully to an absorbed dose up to 200 W-hr/liter. Bond and Leuze¹⁴⁶ also observed MEHPA as a radiolysis product of DEHPA, but found that this impurity favors the aqueous phase, which provides for "self-cleaning" of MEHPA in an operating TALSPEAK process.

Tachimori and Nakamura¹⁴⁷ described general considerations and calculations involved in estimating the absorbed dose for organic extractants being considered for partitioning actinides and fission products from high-level liquid waste.

The radiolysis of DEHPA-carbon tetrachloride mixtures was studied in the presence and absence of aqueous solutions.¹⁴⁸ The decomposition of DEHPA was enhanced by the presence of carbon tetrachloride. The yield of hydrogen chloride was increased by contact with aqueous solution, and increased even more when the two phases were stirred during irradiation. Corrosion of stainless steel by the radiolytic hydrogen chloride was reported.

The effects of gamma radiation on the extraction of Am(III) by several dialkylphosphoric and monophosphoric acids were studied and compared.¹⁴⁹ Di(hexoxyethyl) phosphoric acid (DHEHPA), the strongest extractant, was the most susceptible to radiation. The radiation stability of di-(isodecyl) phosphoric acid (DIDPA), which extracts lanthanides more strongly from acid solution than does DEHPA, is nearly equal to that of DEHPA. Although DEHPA was the weakest Am(III) extractant, it was the most stable to radiation. MEHPA was highly susceptible to radiolytic degradation and was also chemically unstable. Radiolytic degradation of DIDPA, DHEHPA, and MEHPA was increased by contact with nitric acid during gamma irradiation.

X. GENERAL

Reliable partitioning agents and technologies are needed to remediate the large quantities of hazardous waste stored in underground tanks at the Hanford Reservation in Washington State. To address this need, a screening study at Los Alamos National Laboratory¹⁵⁰ measured the distribution of 14 elements on 60 different absorbers from simulant solutions that represented acid-dissolved sludge and alkaline supernate from Hanford High-Level Waste Tank 102-SY. The selected elements represented fission products (Ce, Cs, Sr, Tc, and Y); actinides (U, Pu, and Am); and matrix elements (Cr, Co, Fe, Mn, Zn, and Zr). The absorbers included cation and anion exchange resins, inorganic exchangers, composite absorbers, and a series of liquid extractants sorbed on porous beads.

Because the effect of radiation is an important factor when selecting materials to process radioactive waste solutions, the effects of radiation on the most promising absorbers identified by the Los Alamos study¹⁵⁰ should be measured, when such information is not already available.

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