LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES

3 4456 0452028 5

ORNL/TM-7782

ornl

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

A Survey: Utilization of Zeolites for the Removal of Radioactivity from Liquid Waste Streams

J. W. Roddy

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.
UCN-7969 (3 9-77)

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-7782

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

A SURVEY: UTILIZATION OF ZEOLITES FOR THE REMOVAL OF RADIOACTIVITY FROM LIQUID WASTE STREAMS

J. W. Roddy

Date Published - August 1981

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES
3 4456 0452028 5

CONTENTS

	page
ABSTRACT	1
1. INTRODUCTION	1
2. CHARACTERISTICS OF ZEOLITES	2
2.1 Crystal Structure	3
2.2 Thermal Stability	5
2.3 Ion Exchange Properties	7
3. RADIATION EFFECTS ON ZEOLITES	8
3.1 Laboratory-Scale Results	10
3.2 Plant Experience	11
3.3 Atomic Displacement by Gamma Rays	15
4. SUPPLEMENTARY INFORMATION	15
4.1 Volatility and Leachability Tests	16
4.2 Studies of Corrosive Resistance of Containment Materials	17
5. SUMMARY AND CONCLUSIONS	18
5.1 Laboratory-Scale Results	18
5.2 Plant Experience	19
5.3 Atomic Displacement	19
5.4 Volatility and Leachability Tests	19
5.5 Containment Material Tests	19
6. ACKNOWLEDGMENTS	20
7. BIBLIOGRAPHY	21

A SURVEY: UTILIZATION OF ZEOLITES FOR THE REMOVAL OF RADIOACTIVITY FROM LIQUID WASTE STREAMS

J. W. Roddy

ABSTRACT

A survey was made of the literature and of experience at selected nuclear installations to provide information on the stability of inorganic ion exchangers when used for the decontamination of both low-level and high-level radioactive liquids. Results of past campaigns at the Savannah River Plant, Oak Ridge National Laboratory, and Rockwell Hanford Operations were examined. In addition, the performance of zeolites used for controlling water quality in nuclear fuel storage basins was evaluated. The literature survey served as a guide for identifying relevant material from foreign sources and supplemented the information obtained by direct contact of domestic researchers. The study included a brief review of the physical and chemical properties of zeolites. A secondary objective of the study was to compile data on the corrosion resistance of containment materials for zeolites.

---

1. INTRODUCTION

The purification of liquids and the recovery of metals by ion exchange have been applied to industrial processes for over a century. The earliest recorded use of ion exchange was for water purification by wood ashes and bone char. In 1845, Thompson (Barrer, 1978; Breck, 1974) conducted experiments which demonstrated that certain soils, when slurried with ammonium sulfate, had the power to retain the ammonium salt while releasing calcium sulfate to the aqueous phase. Concurrently, Way (Barrer, 1978; Breck, 1974) obtained similar results with his studies of the exchange of ammonium and potassium ion for calcium and later prepared a synthetic base exchanger consisting of a sodium aluminosilicate. The reversibility of these exchanges was documented in a paper by Eichhorn in 1858 (Barrer, 1978; Breck, 1974). Chemists and engineers became interested in the years following the first industrial research efforts at Union Carbide Corporation in 1948 (Miller, 1948). Since that time, the availability of clay minerals and the synthetic silicate materials for use as sorbents, catalysts, ion exchangers, and molecular sieves has spawned a vigorous research and development program.

The advent of nuclear energy power production and weapons development has placed increased importance on the unique properties of inorganic ion exchangers.

An inevitable consequence of the production of energy by fission in nuclear reactors is the formation of a complex mixture of highly radioactive materials, including fission products, activation products, and artificial heavy isotopes. By far the largest amount of radioactivity comes from fission products which cause distinct problems during their radioactive decay. For example, in a typical mixture, the ^{90}Sr and ^{137}Cs may contribute <4% of the total activity after 100 d decay, 30% or so after 3 years, and about 98% after 30 years. During the period from 1 d to 30 years following discharge of fuel from a reactor, the total activity will have decreased by a factor of ~1000, and the activity of the strontium and cesium by a factor of ~2. Therefore, methods for the removal from liquid wastes, storage, and ultimate disposal of these isotopes have been of concern for several decades. Both natural and synthetic inorganic ion exchangers have been actively studied for this use, and a considerable body of knowledge has been acquired since the initial experiments in the 1950s.

The purpose of this study was to gather information from a comprehensive literature survey and from researchers at selected government laboratories on the use of zeolites for the adsorption of metal ions. Special emphasis was placed on the effects of ionizing radiation, processing conditions, dehydration, heating, etc., on the long-term stabilities of these exchange materials. A brief discussion of the characteristics of zeolites, including their structure and chemical properties, is presented to orient the reader to the terminology used in this report. Many monographs, reviews, summaries, and books have been written on various aspects of zeolite technology and usage, but the books by Breck (1974), Barrer (1978), and Scott (1980) have proved to be especially useful for this report and are highly recommended to the reader as excellent sources of additional information.

An attempt was made to identify all published materials on the effects of radiation on zeolites. ORNL's computerized literature facilities were used to search *Energy Research Abstracts, Nuclear Science Abstracts,* and *Chemical Abstracts* condensates (called DIALOG). To augment these techniques and to reduce the possibility of the omission of important records, a routine search was made of the various abstract publications for the past 25 years. Invaluable assistance was received from individuals at two DOE installations who supplied reports and information relating to prior experience acquired at these plants (Buckingham, 1981; Wallace, 1981). Several of the non-English articles were unavailable for translation, and the information reported here is a summary of material obtained from one of the abstract publishing services.

2. CHARACTERISTICS OF ZEOLITES

Zeolites were first recognized by Cronstedt in 1756 as a group of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths (Breck, 1974). Because the minerals exhibited intumescence when heated in a blowpipe

flame, he called them zeolites, a term which is derived from Greek words meaning "to boil" and "a stone." Natural zeolites are often found in the cavities and amygdales of basaltic and diabasic igneous rocks. In general, bulk compositions of the mineral tend to relate to the parent rock, where the aluminum-rich zeolites are associated with rocks deficient in silica and the silica-rich zeolites are associated with rocks high in silica. Massive deposits of the mineral have been formed by the action of alkaline solutions on volcanic ash deposited in lakes. Over 40 naturally occurring zeolites have been found thus far, although some are variants of similar topologies (e.g., stilbite, stellerite, and barrerite; analcime, kehoeite, viseite, and wairakite; and chabazite and herschelite).

Initial attempts to prepare synthetic zeolites met with only limited success, and the majority of this work has been discredited on the basis of improper identification. Characterization of complex compositions and structures is now possible by x-ray diffraction, which was unavailable to early investigators. A study by scientists at the Linde Division of Union Carbide Corporation was initiated in 1948 to synthesize and characterize a series of crystalline zeolites (Miller, 1964). Aqueous solutions of sodium aluminate, sodium silicate, and sodium hydroxide were used to form a highly reactive aluminosilicate gel. This gel was crystallized at temperatures ranging from ~25 to 150°C at atmospheric or autogenous pressure. The final product was a finely divided white powder consisting of very small crystals, usually only a few micrometers in size.

For nearly all industrial applications zeolites are formed into pellets having high strength and attrition resistance. In one method an inorganic binder, normally a clay, is added to the crystalline powders while they are still wet. The blended clay-zeolite mixture is extruded into cylindrical pellets or formed into beads which are subsequently calcined in order to convert the clay to an amorphorus binder of considerable mechanical strength. Kaolin-type clays are generally used as binders. The zeolites may be formed into binderless particles by hot pressing techniques. When subjected to high pressures at an elevated temperature, a mass of zeolite crystals may self-bond into a 100% zeolite pellet. This method, although widely used in the laboratory, is just beginning to see extensive industrial application. Limited success has been achieved in attempts to form single crystals in particle sizes suitable for actual use. Although single crystals up to 100 μm in size have been reported, the process has not yet attained commercial significance.

2.1 Crystal Structure

Tetrahedral SiO_4 and AlO_4 are the fundamental building units in natural zeolites (Fig. 1). Zeolites are tectosilicates; that is, they are formed by the linking together of these tetrahedra to give three-dimensional anionic networks in which each oxygen of a given tetrahedron is shared between this tetrahedron and one of four others (Fig. 2). Thus, there are no unshared oxygens in the frameworks. This means that the metal (Al + Si) to oxygen atom ratio is 1 to 2 in all tectosilicates (zeolites, feldspars, and feldspathoids). The two metals are interchangeable and not

ORNL-DWG 81-224

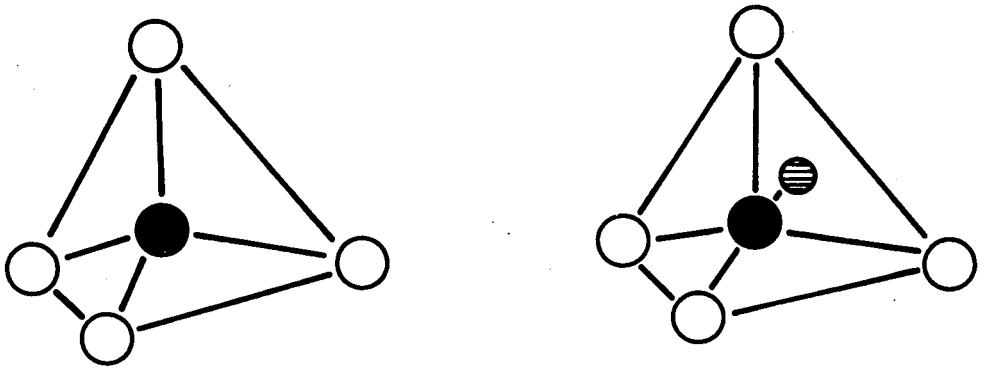


Fig. 1. Basic building blocks of zeolite crystal are tetrahedra with a silicon atom at the center and an oxygen at each of its four apexes (left). The silicon may be replaced by aluminum and an additional metal ion (right).

ORNL-DWG 81-225

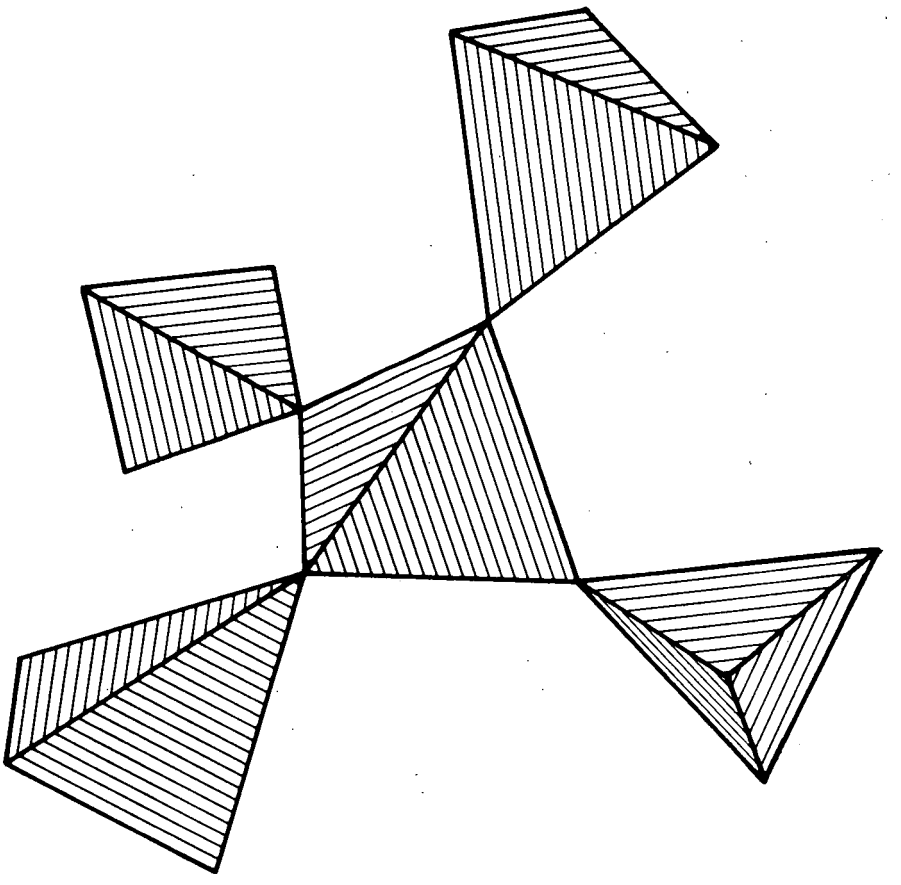


Fig. 2. The type of tetrahedral interactions characteristic of zeolites.

generally distinguishable. For every Si^{4+} ion which is replaced in the framework by an Al^{3+} ion, a negative charge is created which is neutralized by an electrochemical equivalent of cations. Additionally in zeolites, but not in feldspars or some feldspathoids, the framework (Fig. 3) is sufficiently open to accommodate water molecules as well as cations. Therefore, these ions undergo ready exchange with other cations; and the water molecules can be removed or replaced in a continuous manner, often reversibly. Sorption isotherms do not normally show steps such as are found in crystallohydrates.

The structural formula of a zeolite may be expressed for the crystallographic unit cell as:

$$M_{x/y}[(AlO_2)_x(SiO_2)_z]\cdot wH_2O,$$

where M is the cation of valence y, w is the number of water molecules, and the ratio z/x usually has values of 1 to 5 depending on the structure. The sum (x + z) is the total number of tetrahedra in the unit cell. The portion in [ ] represents the framework composition. As an example, the composition of chabazite is:

$$Ca_4[(AlO_2)_8(SiO_2)_{16}]\cdot 26H_2O.$$

The Si/Al ratio, varying between 2 and 2.6, produces an aluminosilicate framework best represented in terms of sheets or layers of linked rings of tetrahedra. The larger cavities in chabazite [Fig. 4(a)] are roughly ellipsoidal, linked by distorted eight-membered rings with dimensions of about 0.44 x 0.31 nm. Upon dehydration, the framework distorts as the calcium ions migrate from the large cavities into the hexagonal prisms. The measured void volume of approximately 50% is quite common for zeolites. Although other ions can fit the tetrahedral sites on the basis of size and charge, they are not found except in rare cases in natural zeolites.

Erionite [Fig. 4(b)] has a hexagonal structure consisting of parallel arrangements of the $(Al,Si)_6O_{12}$ rings. In order to diffuse from one cavity to another, molecules must pass through an eight-membered ring aperture into an adjacent cavity and then through another eight-ring aperture into an adjacent cavity in the original column. Continuous diffusion paths are available for molecules of appropriate size. Erionite readily adsorbs normal hydrocarbons which have a minimum diameter of 0.43 nm.

2.2 Thermal Stability

Many of the zeolites possess the ability to adsorb large quantities of water which may be removed without major alteration of their crystal structure (DeMier, 1963). Other zeolites, when completely dehydrated, undergo irreversible changes which eventually lead to structural collapse. Early dehydration studies of zeolites were based on observations of the loss in weight with increasing temperature; the results were usually expressed as a dehydration isobar.

ORNL-DWG 81-226

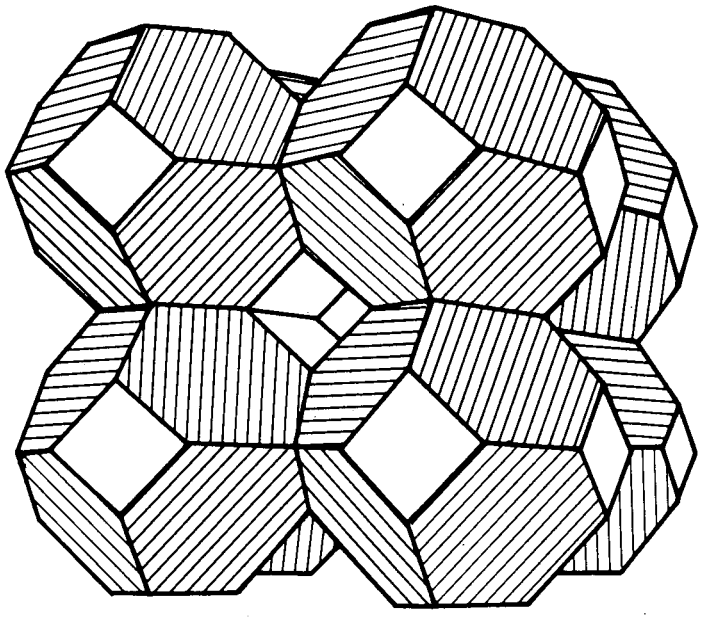
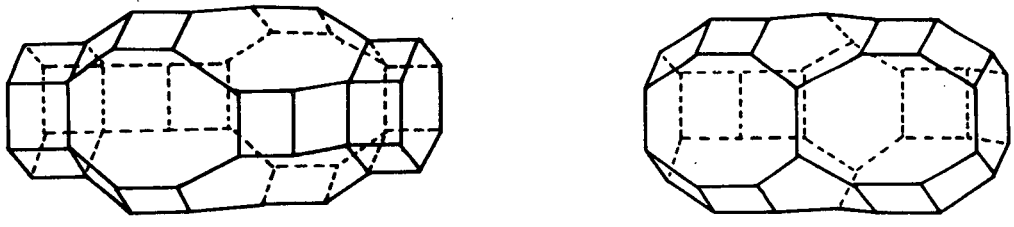


Fig. 3. The stacking of the 14–hedron structure of type I (sodalite cases) in eightfold coordination, giving the sodalite structure (Barrer, 1978).

ORNL-DWG 81-227



(a) (b)

Fig. 4. The (a) chabazite 20–hedron structure capped by hexagonal prisms, and (b) erionite 23–hedron (Barrer, 1978).

Zeolites that undergo reversible and continuous dehydration exhibit no substantial change in the topology of the framework structure. Exchangeable cations that are located in the cavities coordinated with water molecules (e.g., in chabazite, faujasite, and zeolite type X) may migrate to different sites located on the cavity walls or other positions of coordination. The effect of partial or total dehydration may be pronounced in zeolites containing several cation sites (such as type X with five sites). The water molecules are present in clusters which appear to be joined into a continuous intracrystalline hydrate because the water is present as a guest molecule in a host structure (Breck, 1974). In other zeolites such as analcime, the natrolite-type zeolites, and laminar zeolites such as stilbite, the water molecules are tightly coordinated to the exchangeable cations and the framework oxygen as well as to other water molecules. In some zeolites, complete dehydration results in irreversible changes in the framework structure in certain directions; exchangeable cations initially located in the cavities then may become trapped.

The mineral chabazite and various cation-exchanged forms have been studied extensively in terms of their dehydration behavior and ability to rehydrate. Water in these systems does not occur as a definite hydrate but is held by adsorption forces within the cavities. Dehydration is reversible after heating to a temperature of 700°C. Measurements on chabazite with a Si/Al atom ratio of 2.5 confirm that the nature of the exchanged cation exerts an important influence on the stability and dehydration behavior of the zeolite. As the size of the univalent cation increases, the temperature at which water is lost (relative ease of water loss) decreases. Zeolites containing bivalent ions retain more water than zeolites containing univalent ions of comparable radii. In several instances loss of water occurs in more than one stage. The rubidium- and cesium-exchanged forms of chabazite are stable to temperatures $>1000°C$. Recrystallization products from the different forms of chabazite vary with the cation and include four types of silica derivatives which are believed to be the "stuffed" derivatives described by Buerger (Barrer, 1978). These are eucryptite, nepheline, kaliophilite, and α-carnegeite.

2.3 Ion Exchange Properties

The cation exchange behavior of zeolites is a function of (1) the nature, size (both hydrated and anhydrous), and charge of the cation species; (2) the temperature; (3) the concentration of the cation species in solution; (4) the anion species associated with the cation in solution; (5) the solvent (most exchange has been performed in aqueous solutions, although some work has been done in organic solvents and molten salts); and (6) the structural characteristics of the particular zeolite. Cation selectivities in zeolites do not follow the typical rules that are evidenced by other inorganic and organic exchangers. Zeolite structures have unique features that lead to unusual types of cation selectivity and sieving. Because of their three-dimensional structure (Fig. 3), most zeolites and feldspathoids do not undergo appreciable dimensional change with ion exchange; however, clay minerals, which have a two-dimensional structure, may undergo swelling or shrinking.

Cation exchange in zeolites is accompanied by dramatic alteration of stability, adsorption behavior and selectivity, catalytic activity, and other important physical properties. Since many of these properties depend on controlled cation exchange with particular cation species, detailed information on the cation exchange equilibria is important. Extensive studies of the ion exchange processes in some of the more useful mineral and synthetic zeolites have been conducted (see Sect. 7). A summary of the more pertinent information available for chabazite is presented.

Exchange isotherms for all of the alkali metals and many of the alkaline earths have been measured. Of the alkali metal ions, only cesium does not displace all of the sodium ions in sodium chabazite; the extent of exchange is 84%. The positions of univalent ions in the structure of the hydrated species are unknown, but they are postulated to occupy sites in the eight-membered rings and also in the single six-membered ring or hexagonal prisms. The larger rubidium, thallium, and cesium ions would not be expected to replace any sodium ions within the hexagonal prisms. Instead, a mechanism involving migration of sodium ions into the larger cavities is likely. The cations present in these larger cavities result in less available space for water molecules with increasing cation size. A smooth decrease in the number of water molecules per unit cell with increasing cation size has been observed.

3. RADIATION EFFECTS ON ZEOLITES

Although ion exchange technology has assumed particular importance in the processing of radioactive solutions and zeolites have become the preferred exchanger for many of these applications, the number of publications found in this literature survey detailing the effects of radiation on such materials were relatively small. Many of the foreign and several of the domestic papers report the effects of exposing small samples of the adsorbent to gamma irradiation as produced by ^{60}Co. One group of researchers used a nuclear reactor as their radiative source. A few references were found which described a method for recovering fission product cesium from aged basic radioactive wastes and a means of transporting large quantities of the recovered element from one government laboratory to another for fabrication into radiation and heat sources. Several reports were found which discussed the use of zeolites for the decontamination of low-level wastewater. In 1959 three papers were published in which the authors estimated the effectiveness of gamma rays to displace lattice atoms in solids; a synopsis of their results is presented in the last section.

Several terms used in the literature are rather unique to the field of ion exchange. To prevent a misunderstanding of their meaning by the reader, the author has supplied brief definitions of several of the more important ones in the following subsections.

Adsorption - Adsorption is a process in which a substance is concentrated at the interface of a heterogeneous system. The interface is a boundary between phases of the system. Adsorption does not distinguish between mechanisms but involves the effect alone.

Adsorbent - The adsorbent is that phase upon whose surface a substance is held. This term is usually applied to solids.

Adsorbate - The adsorbate is the substance that is concentrated at the interface during the process of adsorption.

Physical adsorption - Physical adsorption is a type of reversible adsorption for which the energy is lower (<42 kJ/mol) than that required for a chemical bond.

Chemisorption - Chemisorption is a process in which the energies of bonding (>42 kJ/mol) approach those of chemical bonds and the reaction is not reversible.

Distribution coefficient - The distribution coefficient is a ratio of the concentration of a substance in the ion exchanger (meq/g) to that in the liquid phase (meq/mL). The weight of the exchanger is usually taken as the dry weight.

Exchange adsorption - Exchange adsorption is a process in which the adsorbate is exchanged for another species previously adsorbed or held by the adsorbent with similar forces. This type of adsorption usually involves ions but may also involve neutral molecules and gases.

Absorption - Absorption is usually confused with adsorption to such an extent that the term *sorption* has been coined to avoid controversies. Absorption involves the entire bulk of the solid instead of only the surface. Since ion exchange studies were originally confined to dense solids that restricted the exchange to the surface, the term *sorption* has been used to describe all exchange phenomena.

Capacity - Capacity is the most important property of an ion exchanger because it permits a quantitative determination of how many counterions can be taken up by a material. Since many different concepts and definitions for capacity have been published, care must be taken to determine which one is being considered. A few of the more common capacity modifiers and their definitions are given below.

Total - number of counterions capable of exchange.
Effective - number of counterions that can be used under given conditions.
Scientific weight - number of milliequivalents per gram of dry resin.
Technical volume - number of milliequivalents per liter of packed bed.
Breakthrough (dynamic) - point where effective capacity is reached.
Sorption - amount of solute taken up by sorption other than ion exchange per specific amount of ion exchanger.

Selectivity - Selectivity is defined as the property of certain ion exchangers to exhibit a preferential attraction for different ions. Stoichiometric and reversible ion exchange exhibits all the characteristics of an equilibrium and follows the law of mass action.

3.1 Laboratory-Scale Results

Of the well-known radioactive isotopes, ^{60}Co is by far the most widely used as a gamma-ray source in radiative chemical studies. The practical importance of this isotope has arisen partly because of the ease of its preparation and its fairly long half-life (5.3 years), and partly because the beam of gamma rays emitted [two sharp lines of equal intensity at 188 and 213 fJ (1.173 and 1.332 MeV)] is similar in penetrating power to that emitted by radium. Numerous high-activity cobalt sources [exposures $> 1 \times 10^5$ Gy/h ($> 1 \times 10^7$ rads/h)] are available, many of which have been used to study the effects of radiation on various characteristics of zeolites.

Two papers (Pionlkovskaya et al., 1965; Starodubtsev et al., 1963) from the Russian literature describe the adsorptive properties of several type A zeolites before and after exposure to gamma irradiation. Type A zeolites are aluminosilicates containing two types of polyhedra. One is a simple cubic arrangement of eight tetrahedra; the other is a truncated octahedron of 24 tetrahedra or β-cage as is found in the sodalite-type minerals (Fig. 3). The center of the unit cell is a large cavity with a free diameter of 1.14 nm. Each octahedron encloses a cavity with a free diameter of 0.66 nm. A total cumulative dose of 3×10^4 Gy (3×10^6 rads) in one study (Starodubtsev et al., 1963) and 1.53×10^5 Gy (1.53×10^7 rads) in the other (Pionlkovskaya et al., 1965) did not affect the absorptive capacity or ion exchange properties; in fact, there was a slight increase in capacity for gases at the lower exposure. A third paper from Russian researchers (Grenthe et al., 1976) reported essentially no change in sorption properties of natural calcium clinoptilolite for Ca, Ag, Tl, Hg, Sr, Ba, Pb, Cu, Co, and Zn when exposed to a cumulative dose of 1×10^7 Gy (1×10^9 rads) from a ^{60}Co source.

Lewis et al. (1966) compared the distribution coefficients of cesium on Decalso* before and after exposure to 1.5×10^4 Gy (1.5×10^6 rads) of gamma radiation and found no change in its selectivity. There was a slight darkening of the material, from white to light tan, as well as a slight increase in friability.

The flow and gas generating characteristics were determined for Ionsiv IE-95 zeolite** before and after gamma irradiation with ^{60}Co at two dose rates [0.39 and 4.5×10^4 Gy/h (0.39 and 4.5×10^6 rads/h)] (Pillay, 1980). Measured flow rates through a zeolite-packed column increased slightly (from 18 to 19 mL/min) following a dose of 2.2×10^7 Gy (2.2×10^9 rads). Analyses of the gases generated from irradiating [cumulative dose of 1.4×10^7 Gy (1.4×10^9 rads)] the sieve containing varying amounts of moisture yielded inconsistent results. The variations observed in the hydrogen/oxygen ratio data at different water concentrations were attributed to the ability of zeolites to adsorb and thereby separate a variety of gases. The effect of irradiation on exchange capacity and selectivity of the zeolite was not examined.

---

*A synthetic aluminosilicate produced by the Ionac Chemical Company; not a true zeolite.

**Formally called AW-500.

The consequences of exposing zeolites to radiation doses of ~1 x 10^8 Gy (~1 x 10^{10} rads) have been reported in two separate instances covering a time span of two decades. In 1961, Fullerton (1961) published a document summarizing his results on the post-irradiation behavior of clinoptilolite (a naturally occurring zeolite). Distribution coefficients were unchanged within experimental error for sodium, cesium, and barium after the mineral received a total gamma exposure of 9.6 x 10^7 Gy (9.6 x 10^9 rads) [absorbed dose of 8. 4 x 10^7 Gy (8.4 x 10^9 rads)], while a 40% decrease was observed for calcium. No structural changes as revealed by differential thermal and x-ray diffraction analyses were detected. Twenty years later, Wallace (1981) examined the effects of a radiation dose of 1.1 x 10^8 Gy (1.1 x 10^{10} rads) from a ^{60}Co source on Linde AW-500 zeolite. The sample was air-dried (relative humidity of 50%) overnight and then inserted into the radiation field [1.3 x 10^5 Gy/h (1.3 x 10^7 rads/h)] for 838 h. After removal, its color and distribution coefficient for cesium were unchanged, and the integrity of the pellets appeared to be unaffected. The x-ray diffraction patterns indicated a slight shift in the positions of the diffraction lines of the irradiated sample.

Nuclear reactors have been used to study the interaction of multiple types of radiation with numerous materials. One of the earliest and most comprehensive applications of their use in irradiating ion exchangers is presented in a Norwegian report (Nater, 1959). Several organic resins and one aluminosilicate exchanger, Permutit-G, were exposed to neutrons from a 450-kW research reactor. The dose rates for thermal ($E < 0.26$ eV), epithermal ($0.26 < E < 10^5$ eV), and fast ($E > 10^5$ eV) neutrons were estimated. The exchange capacity was found to be unaltered at exposures as high as 1.22 x 10^7 Gy (1.22 x 10^9 rads) (absorbed dose of 1.1 x 10^7 Gy, 1.1 x 10^9 rads).

3.2 Plant Experience

High-level liquid radioactive wastes have been generated for many years at U. S. government installations such as those at Hanford, the Savannah River Plant, and the National Reactor Testing Station. In the past two decades, zeolites have played a prominent role in the removal, storage, and transportation of certain fission products contained in these wastes. During this period, valuable knowledge was acquired on many characteristics of these ion exchangers when exposed to various levels of ionizing radiation. Summaries of plant experiences at a number of these sites are presented in the following subsections.

Zeolites have been used at the Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho, and in the General Electric Company (GE) operations near Morris, Illinois, to decontaminate low-level radioactive wastes from irradiated fuel storage basins. Both systems utilize a synthetic zeolite (Zeolon) manufactured by the Chemical Process Products Division of the Norton Company. In preliminary testing at INEL (Rhodes, 1979; Wilding and Rhodes, 1963), a 2.4-m-high by 0.9-m-diam column filled to a depth of 1.1 m with 680 L of 20- to 50-mesh size Zeolon 900 (a synthetic mordenite) absorbed approximately 75 Ci of ^{137}Cs from 2.2 x 10^7 L of water. About 3200 column volumes were discharged before 1%

breakthrough was observed. The GE process (Denio, 1977) utilizes a canister containing 2 kg of Zeolon 100 (also a synthetic mordenite). The canisters, although containing only ~28 Ci of ^{137}Cs, are changed at 3- to 4-week intervals because of problems with high-pressure drop. Both applications subject the zeolite to very low doses of radiation; however, the objective in each operation is to obtain a reasonable decontamination factor over a longer period of time.

Evaporator overheads and miscellaneous wastewaters have been treated at the Savannah River Plant near Aiken, South Carolina, with a column of AW-500* to remove ^{137}Cs (Jacobsen, 1974; Wallace, 1980). The concentration of total dissolved solids varies from 0.1 g/L in the overheads to 10 g/L in the miscellaneous wastes; the radioactivity, ^{137}Cs, approaches 0.1 mCi/L. The wastewater is pumped through a 304 stainless steel column containing 140 kg of zeolite at a flow rate of 20 to 40 L/min. When the cesium breakthrough reaches 1%, the flow is stopped and the zeolite is discharged to a storage tank. The cumulative radiation dose calculated for the top of the bed is 3.6×10^4 Gy (3.6×10^6 rads). Drastically reduced flow rates have been experienced when high pH solutions (pH = 12 to 12.5) are processed. Flushing the column with 50% NaOH is all that has been required to regenerate the zeolite. No evidence of corrosion was found when the system was disassembled for cleaning.

The waste tank farm at Hanford utilizes a cartridge containing ~0.28 m^3 of Zeolon 900 to treat the condensate produced from self-heating during the storage of processing waste solutions (Buckingham, 1981). Although the unit has treated an estimated 4×10^6 L of condensate, it has never been replaced or caused any problems. Since the cartridge is still in use, an estimate of the radiation exposure of the zeolite has not been possible. Zeolon 900 has also been used at Hanford to remove cesium and strontium from condensates generated from evaporator crystallizers. The feed to the exchanger contains traces of organic complexants which appear to attack the zeolite pellets, producing "fines." The distribution coefficient for cesium increases during this deterioration, but no breakthrough has been detected. Approximately 4 to 8×10^6 L of liquid can be treated before the Zeolon must be replaced, a condition indicated by the breakthrough of strontium but not cesium. Analysis of a sample of the discharged exchanger showed 10 μCi of ^{90}Sr and 47 μCi of ^{137}Cs per gram of zeolite. Although a cumulative dose was not calculated, it is expected to be low.

Zeolites used for the separation and purification of ^{137}Cs from processing wastes at Hanford have received considerably higher exposures (Brandt, 1970; Buckingham, 1981; Godfrey and Larkin, 1970). In the separation process, a 1.8-m-diam by 3.2-m-deep bed of 20- to 50-mesh AW-500 is contacted with the waste solution until a cesium breakthrough of 5% occurs. The feed contains large quantities of $NaNO_3$ (~5 *M*), some aluminum, and ^{137}Cs at concentrations of 1 to 4

*A synthetic chabazite manufactured by the Linde Division of Union Carbide Corporation.

Ci/L in addition to ^{106}Ru, ^{106}Rh, and ^{99}Tc. About 300 to 500 kCi of ^{137}Cs are loaded onto the bed during each cycle. The column is eluted with an ammonium hydroxide-ammonium carbonate solution, the entire cycle requiring about 4 to 5 d to complete.

After accepting ~1 x 10^7 L of supernatant waste, the column became essentially plugged and its breakthrough capacity had decreased to less than half its initial value. Aluminum in the feed was believed to have precipitated in the bed, causing the loss of capacity and plugging. Also, the retention screen at the bottom of the column had ruptured, allowing a loss of zeolite. Reloading of the column with fresh AW-500 has resulted in the processing of several million liters of waste without loss in capacity. A cumulative exposure of 5.8 x 10^6 Gy (5.8 x 10^8 rads) has been calculated for each of these two beds.

Purification of the cesium product is accomplished in much the same manner, but a 3.9-m-high by 0.3-m-diam column containing 280 L of Zeolon 900 is used (Brandt, 1970; Mercer and Ames, 1978). Nearly all of the alkali metals, as nitrates, are present in the feed (Na = 0.8 *M*, Cs = 0.1 *M*, K = Rb = 0.01 *M*). When fully loaded, the column contains about 700 to 800 kCi of activity. These columns are usually replaced after ~40 cycles because of a noticeable loss in particle integrity, resulting in a high pressure drop across the column. However, at such times the physical appearance of the zeolite appeared to be unchanged. Slightly >32 MCi of ^{137}Cs was processed with one batch of Zeolon in a 32-month period. The cumulative exposure of 2 x 10^7 Gy (2 x 10^9 rads) calculated for this column is probably conservative since additional exposure (not accounted for) has been received from a nearby tank used for the storage of purified ^{137}Cs. Over 1 MCi of radioactivity has been held in this tank for >1 week.

The transfer of radioactive materials between government sites has sometimes been required to make optimum use of existing processing facilities. Several shielded transfer tanks (STTs), previously designed for the shipment of aged fission product wastes, were modified and used to transport ^{137}Cs between Hanford and Oak Ridge (Lewis, 1966; Lewis, 1967; Lewis et al., 1965). The STTs placed in operation were of two different sizes. Six of the larger tanks, each containing 1500 L of Decalso had a designed capacity of 90 kCi of ^{137}Cs. Approximately 3.3 x 10^6 Ci of activity were transported in 27 shipments (2 to 4 tanks per shipment, for a total of 77 tanks) over a period of 68 months (Schaich, 1980). A smaller but more efficient unit, with the same nominal capacity but containing only 600 L of AW-500 zeolite, was used to transport 140 kCi of ^{137}Cs in three shipments during 1967.

In contrast to the STTs, which contained moist absorbent during shipment, a transfer system was designed at Hanford for shipment of a dry, precipitated fission product salt. The Hanford Atomic Products Operations (HAPO) system was first used to ship large quantities of ^{90}Sr as the carbonate salt, but one cask (HAPO-1C-1) was converted to a zeolite-filled cask for the transport of cesium in the early 1970s (Van Tuyl and Bray, 1961; Zahn et al., 1963). Two loadings, containing a total of 8.4 x 10^5 Ci of ^{137}Cs, was transferred on 115 L of Zeolon 900 (Schaich, 1980; Stringfield, 1971a,b). This material was dried prior to shipment by drawing a stream of dry air through the cask before it was sealed.

The exposures received by the zeolites in the three systems were calculated with the rather conservative assumption that a uniform loading of the sorbent was obtained (Campbell, 1980). In actuality, the nominal loading was to ~70% breakthrough, so that the top portion of the material received somewhat higher doses. Exposure times were estimated to be the difference between the date of shipment from Hanford and receipt at Oak Ridge, plus an additional 5 d (4 d at Hanford for leak and pressure testing, decontamination, etc., prior to shipping and 1 d at Oak Ridge for elution of the cesium product). The exposures, in grays (and rads), calculated on this basis for two of the types of adsorbent are: for Decalso, 3×10^6 (3×10^8); and for AW-500, 1.5×10^6 (1.5×10^8). The value of 7×10^7 (7×10^9) for Zeolon 900 was estimated from a Monte Carlo computer code calculation.

Apparent cesium recoveries were 89, 106, and 90% of the cesium loaded in the three systems. One of the Decalso beds was sampled after the second shipment and after the seventh shipment (Ottinger, 1963). Tests for cesium capacity gave essentially the same results in each case (10% vs 9% loss). No significant trends were indicated except for an unexpected reduction in bed volume – from 1500 L to 1000 L. A sample of the Zeolon 900 after use showed a slight color change from gray to ivory, but no deterioration of physical integrity (Oberg, 1971). The most serious problems arose when solutions containing relatively high acid concentrations were treated. Aluminum was lost from Decalso and AW-500 at pH <3 to 5, destroying their ion exchange properties and resulting in severe plugging of the columns (Kuehn, 1967). The problem was eliminated by adjusting the pH levels of all solutions to >5 with ammonium hydroxide.

Some difficulties have been experienced in the elution of ^{137}Cs from Decalso in that tailing of the last 15% of the element was observed (Lewis, 1966). Slow kinetics was suggested for this behavior, as the result of aging or the presence of a foreign ion such as iron or aluminum in the feed solution. Before the campaign, aluminum-bearing solutions originating from cladding wastes had been introduced into the normal feed solution and this aluminum-contaminated solution inadvertently contacted the Decalso bed. A solution of 0.2 *M* NaOH was effective in eluting large amounts of $Al(OH)_3$ from the column but did not prevent the tailing of cesium. The column was later replaced.

Two additional cases of plant experience at Hanford have been reported by Mercer and Schmidt (1965). Van Tuyl adsorbed 10 kCi of ^{90}Sr on a quantity of Linde type 4A zeolite, dried the material at 600°C, and sealed it in a container for ~2 years. Although a detailed physicochemical examination of the irradiated zeolite was not performed, he did find that $>80\%$ of the activity was eluted with 30 column volumes of 1 *M* HNO_3, and that the basic ion exchange properties of the zeolite were retained after being exposed to a dose of 4×10^9 Gy or 4×10^{11} rads (calculated on the assumption that all the beta energy from ^{90}Sr and its decay product, ^{90}Y, were absorbed by the zeolite). In another study attributed to DeMier, Martin, and Willingham, a zeolite containing 1% water and loaded with ^{90}Sr was sealed in a container and allowed to stand until it had received a total absorbed dose of 1×10^9 Gy (1×10^{11} rads). The maximum pressure, 280 kPa (40 psi), was

attributed to radiolysis of water and indicated that there was no cataclysmic rupture of the Si-O bonds and release of oxygen even at this high exposure level.

3.3 Atomic Displacement by Gamma Rays

Modifications of the physical properties of solids by heavy-particle bombardment have been known and reported for some time. Fewer studies (Cahn, 1959; Galavanov, 1959; Oen and Holmes, 1959) have been made on the mechanism of the action of gamma rays on materials, although they, along with other forms of radiation, have strong influence on the various physicochemical properties of substances. In contrast to the low penetrating power of electrons, gamma rays are absorbed only slightly; therefore, the effects produced by them take place almost uniformly throughout the entire thickness of the irradiated substance.

The attenuation in the intensity of gamma radiation on its passage through a substance is due principally to the production of energetic electrons. Gamma rays produce electrons energetic enough to cause displacements by three methods: (1) the photoelectric effect, (2) the Compton effect, and (3) pair production. The Compton effect, which involves the scattering of gamma rays by free electrons, is more important than the photoelectric process in producing displacements; this is especially true for elements of low atomic number. An electron-positron pair may be produced by a gamma ray having an energy of $\geqslant 1$ MeV. To conserve both energy and momentum, creation of this pair must occur in the vicinity of another particle such as a nucleus.

The fundamental structure of zeolites is composed of elements of low atomic number: oxygen with 8, aluminum with 13, and silicon with 14. The Compton effect would be expected to produce the greatest number of displacements. Oen and Holmes (1959) have calculated the atomic displacement cross sections for the production of primary displacements of lattice atoms by gamma rays through the Compton process as a function of the energy of the incident gamma rays for nine elements for atomic numbers between 4 and 92. Qualitatively, their results indicate that the gamma-ray energies, emitted by ^{137}Cs, would produce very few displaced atom-vacancy configurations. Difficulties arise in their calculations because of the lack of knowledge of the threshold energy for displacement, which must be estimated. As an example, experimentally observed damage for germanium and copper was considerably below that predicted from their calculations on the basis of a threshold at $\sim$25 eV.

4. SUPPLEMENTARY INFORMATION

The undertaking of any literature survey inevitably uncovers a wealth of information that is not directly related to the primary goals of the search but should be reported because of its usefulness. In the following sections, an attempt has been

made to describe briefly the conclusions drawn from past experience in two such areas: (1) the volatility and leachability of absorbates from zeolites, and (2) the corrosion resistance of containment materials. The references cited are considered to be representative of the data available in the literature.

4.1 Volatility and Leachability Tests

Beginning with some of the earliest research on their absorptive nature, the zeolites have been the premier choice for the long-term storage and final disposal form for many radioactive substances. Several studies have been reported on the volatility and leachability of certain fission products from these absorbents. Four reports, three from research at Hanford and one from Japan, discuss the volatility of cesium and strontium from molecular sieves.

Ames and Knoll (1962) heated columns containing several natural and synthetic zeolites loaded with one of the two elements. After 24 h at 600°C in a static system, clinoptilolite lost 0.09% of its cesium; Decalso, 0.016%; and Linde 4A, 0.01%; no losses were measured for Linde AW-500 or 13X. Knoll (1960) reported the effect of heat on the vaporization of ^{85}Sr and ^{137}Cs adsorbed on seven different exchangers. The amount of material vaporized, from 0.03 to 0.12% of that absorbed on the zeolite, was independent of temperature from 130 to 1000°C in a flowing air stream. Hilliard and Reid (1961) measured the release of radiocesium from Decalso at elevated temperature. Two samples were heated separately under isothermal conditions of 1350°C for 2 h in helium and in air. Results showed corresponding releases of 0.73 and 0.35%. In two other tests, a programmed temperature increase to a maximum of 1500°C within 2 h was employed. Releases were 0.31 and 0.25% in helium and in air, respectively.

Mimura and Kanno (1978) observed the volatilization of cesium from several zeolites at high temperature. Zeolites A, X, and Y, mordenite, and clinoptilolite were saturated with cesium and calcined for 3 h at 700 to 1200°C in an air or argon flow. The volatilization rate was fast while the zeolite structure was maintained, but slowed after structural transformation. In recalcination of calcined zeolites for 3 h at 1200°C, the mean volatilization rate was 1×10^{-5} to 1×10^{-6} mg/cm^2-min.

Numerous studies have been performed to determine the leachability of the fission products when encapsulated in highly insoluble, thermally stable aluminosilicate minerals. Strachan and Schulz (1976) found that the leach rates with water for cesium-loaded zeolites decreased from 1×10^{-4} to 3×10^{-6} g Cs/cm^2-day as firing temperatures increased from 500 to 1000°C. Barney (1975) measured leach rates after 28 d for a similar system and obtained significantly higher values, varying from 2.6×10^{-2} to 1.4×10^{-4} g/cm^2-day.

Swedish researchers (Arnek et al., 1977; Grba et al., 1975) calcined (800 to 1300°C) several zeolites containing radioactive cesium and strontium and were unable to detect the presence of any activity in their leachate after equilibration with water for 2 d. Traces of activity were found when using 0.1 *M* NaCl as the

leachate for the same time period. The lowest leach rates that were found in the survey were those reported by Kanno and Mimura (1977). Mordenite and clinoptilolite containing cesium and strontium were calcined at 800 to 1200°C for 3 h, and one sample of each was stored in water and seawater, respectively. Leach rates for cesium and strontium from zeolites calcined at 1100°C for 3 h were obtained as follows: 1×10^{-8} (H_2O) and 1×10^{-7} to 1×10^{-8} (seawater) g Cs/cm^2-day, and 1×10^{-9} to 1×10^{-10} (H_2O) and 1×10^{-8} to 1×10^{-9} (seawater) g Sr/cm^2-day.

4.2 Studies of Corrosive Resistance of Containment Materials

The necessity of separating strontium and cesium from high-level radioactive wastes with subsequent purification, conversion to an appropriate chemical form, encapsulation, and final storage of each of these elements separately in high-integrity containers has generated an abundance of knowledge in each of these areas. Difficulties associated with the containment of these substances have resulted in experimental studies to identify potential materials of construction for storage containers.

Fullam (1972) examined several containment materials for their compatibility with both radioactive and nonradioactive CsCl and SrF_2. The metals tested with CsCl were 316L stainless steel and Hastelloy C, while Haynes 25, Hastelloy C, Hastelloy X, and 316L stainless steel were evaluated for SrF_2. Capsules containing radioactive samples were tested at 400°C for periods approaching 1 year. Capsules containing nonradioactive CsCl were heated at 400 or 600°C for periods of up to 3 years; those containing nonradioactive SrF_2 were held at 400 or 800°C for periods of up to 3 years. After exposure, the capsules containing radioactivity were sectioned and examined by metallographic analysis. Interactions in the other capsules were determined by metallographic examination and by an electron microprobe scan.

The 316L stainless steel exhibited more effective corrosion resistance for CsCl. The maximum attack (as measured by the depth of surface penetration) observed after 1 year at 400°C was ~25 μm. There was little visual evidence of intergranular penetration, although some pitting and subsurface void formation were present. Haynes 25 was judged to be the preferred material for containing SrF_2. Based on the photomicrographs, exposure to radiation substantially increased interaction for all four metals; the corrosion rates were more than doubled under radioactive conditions.

Three other references discussed the results of compatibility studies of CsCl with stainless steel. To simulate the actual conditions expected for a shipment of a radioactive CsCl pellet to France, Ewing (1969) placed ~5000 Ci of ^{137}CsCl into a stainless steel capsule and heated the container so that its surface temperature was maintained at 450°C for 220 h. On completion of the test, the capsule was removed for metallographic examination. Examination of sections of the lid and weld area under 100X and 250X magnification revealed no damage or deterioration on either the capsule wall or the weld area.

In a study by Haff (1963), a 1540-Ci source of $^{137}CsCl$ contained in a stainless steel capsule was opened after 9 years of continuous use. No evidence of corrosion or deterioration of the source could be detected by metallurgical examination after receiving a cumulated dose estimated to be 1×10^9 Gy (1×10^{11} rads). A Waste Encapulation Storage Facility (WESF) capsule that contained 69 kCi of $^{137}CsCl$ and had been stored for several years was heated at 380°C for 289 d. Examination of the capsule, after being sectioned on each end and in the center, revealed pitting up to 250 μm and a general corrosion of 25 to 75 μm depth. No intergranular attack was observed. Whether this minor pitting and corrosion had occurred as a result of the elevated-temperature test or was due to normal loading and storage is not clear.

The material of construction for columns, shipping casks, and fission-product recovery systems at various government facilities is stainless steel in most cases. In the few instances when the equipment was shut down for maintenance, subsequent examination of their internal surfaces showed no evidence of corrosion (DeMier et al., 1963; Wallace, 1980).

5. SUMMARY AND CONCLUSIONS

The ion exchange nature of zeolite-type substances has been known for over two centuries, beginning with the discovery of the adsorptive properties of clays and other natural materials. The synthesis of molecular sieves in 1948 spawned an interest in their use which is as yet unabated. Zeolite ion exchangers were first considered for the decontamination of radioactive liquids in the 1950s and, since that time, have been used extensively in the nuclear processing industry.

5.1 Laboratory-Scale Results

The effects of ionizing radiation on zeolites and zeolite-like materials as determined by exposure of small samples to irradiation sources (^{60}Co gamma facilities and research reactors) have been studied for over two decades. No deleterious effects, as measured by x-ray diffraction, hydraulic behavior, differential thermal analysis, and (with one possible exception) distribution coefficient determinations, have been noted for cumulative exposures from 1×10^4 to $> 1 \times 10^8$ Gy (1×10^6 to $> 1 \times 10^{10}$ rads). The exception was a modest decrease in the rate of exchange of calcium ion (but not of sodium, cesium, and barium ions) for all samples of clinoptilolite that were irradiated, independent of radiation dose; this suggests the influence of a factor other than irradiation. Although other irradiated zeolites showed slight changes in color and were more friable after irradiation, there were no discernible differences in exchange capacity.

5.2 Plant Experience

Many government-operated nuclear facilities have routinely used zeolites for the removal, concentration, containment for shipping, storage, and purification of fission products which have been recovered from various waste streams. No serious problems have ever been detected that could be attributed directly to radiation exposure. Some difficulties were noted in the physical integrity of certain pellet formulations, but the only serious degradation of the zeolites that was observed was suspected to be caused by organic complexants present in the feed solutions and not by ionizing radiation. A few cases of decreased exchange capacity were noted when acidic solutions (pH <3 to 5) were processed. Also, the elution characteristics of Decalso used in shipping casks were slightly degraded after extended use.

5.3 Atomic Displacement

Theoretical calculations of lattice displacements in solids by gamma rays were first reported in 1959. Comparisons with experimental results indicated that the calculated values were too high. Threshold energies for displacement for most materials are unknown and must be approximated. Until more accurate methods are available for determining this information, precise calculations will be difficult. The number of atomic displacements in zeolites resulting from gamma rays produced by ^{137}Cs is expected to be small, and the displacements that do occur would probably involve return to the original sites.

5.4 Volatility and Leachability Tests

Zeolites containing cesium and strontium appear to retain these elements quite effectively upon heating. Static tests at 600°C for several natural and synthetic zeolites showed losses of less than 0.1% of the total cesium and strontium content after 24 h. Tests at higher temperatures (700 to 1200°C) in a flowing gas stream showed that the volatilization rate was fast while the zeolite structure was maintained, but slowed after structural transformation.

Although there were some discrepancies in the actual values obtained by several researchers, measured leach rates were all low for zeolites calcined at temperatures >800°C. Aqueous salt solutions produced the highest leach rates.

5.5 Containment Material Tests

Studies of the corrosive resistance of several alloys clearly demonstrate the superiority of stainless steel as a containment material for zeolites loaded with radioactivity; however, radiation does decrease their resistance (by a factor of 2 in one report). Mild steel appears to be less effective for this application.

6. ACKNOWLEDGMENTS

The author wishes to thank M. M. Beary and J. S. Buckingham of Rockwell Hanford Operations, R. M. Wallace of the Savannah River Laboratory, and especially D. O. Campbell of Oak Ridge National Laboratory for their contributions to this study.

7. BIBLIOGRAPHY

Adam, L., G. Kakasy, and I. Pallos. 1971. Removal of radioactive pollutants from water, using mineral substances of natural domestic origin. *Banyasz. Kut. Intez. Kozl.* 15(2):89.

Allen, J. 1962. Coolant cleanup in D.F.R. *Nucl. Eng.* 7:352.

Ames, L. L., Jr. 1959. *Zeolitic extraction of cesium from aqueous solutions*, HW–62607, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Ames. L. L., Jr. 1960. The cation sieve properties of clinoptilolite. *Am. Mineral.* 45:689.

Ames, L. L., Jr. 1961a. Cation sieve properties of the open zeolites chabazite, mordenite, and clinoptilolite. *Am. Mineral.* 46:1120.

Ames, L. L., Jr. 1961b. *Strontium and cesium loading characteristics of Decalso, Linde 4A, and clinoptilolite columns,* HW–70768, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Ames. L. L., Jr. 1962a. Fundamental adsorption research. In *Research and development activities, fixation of radioactive residues, quarterly progress report, January–March 1962,* HW–73412, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Ames, L. L., Jr. 1962b. Characterization of a strontium–selective zeolite. *Am. Mineral.* 47:1317.

Ames, L. L., Jr. 1962c. Effect of base cation on the cesium kinetics of clinoptilolite. *Am. Mineral.* 47:1310.

Ames, L. L., Jr. 1962d. Kinetics of cesium reactions with some inorganic cation exchange materials. *Am. Mineral.* 47:1067.

Ames, L. L., Jr. 1963. Mass action relations of some zeolites in the region of high competing cation concentrations. *Am. Mineral.* 48:868.

Ames, L. L., Jr. 1964. Some zeolite equilibriums with alkali metal cations. *Am. Mineral.* 49:127. [Also HW–SA–3031 (April 1963), Hanford Atomic Products Operation, General Electric Company, Richland, Washington]

Ames, L. L., Jr. 1965. Self–diffusion of some cations in open zeolites. *Am. Mineral.* 50:465.

Ames, L. L., Jr., and K. C. Knoll. 1962. *Loading and elution characteristics of some natural and synthetic zeolites,* HW–74609, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Ames, L. L., Jr., and B. W. Mercer. 1968. *Unidirectional cesium loading, scrubbing, and elution of AW–500 zeolite columns,* BNWL–732, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Ames, L. L., Jr., and J. L. Nelson. 1961. *^{137}Cs–loading and leaching of synthetic zeolite and clinoptilolite columns,* HW–69263, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Amphlett, C. B. 1958. Synthetic inorganic ion exchangers and their applications in atomic energy. In *Proceedings of Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva.* P/271, 28:17.

Aqudo, A. Lopez. 1975. Synthetic zeolites. I. Structure, properties, and applications. *Quim. Ind. (Madrid)* 21(3):276.

Arnek, R., A. Persson, L. Faelth, and H. Annehed. 1977. *Development of methods to extract and solidify highly radioactive waste,* STU–74–5626–a–b–c–d–e, K. Tek. Hoegsk., Stockholm.

Arnold, E. D. 1957. Personal communication.

Baetsle, L. H., and D. Huyes. 1967. Recovery of cesium–137 and strontium–90 fisson products. *Ind. Chim. Belge* 32:3.

Barney, G. S. 1975. *Immobilization of aqueous radioactive cesium wastes by conversion to aluminosilicate minerals,* ARH–SA–218, Atlantic Richfield Hanford Company, Richland, Washington.

Barrer, R. M. 1978. *Zeolites and clay minerals as sorbents and molecular sieves.* New York: Academic Press.

Barrer, R. M., J. A. Davies, and L. V. C. Rees. 1969. Comparison of the ion exchange properties of zeolites X and Y. *J. Inorg. Nucl. Chem.* 31(8):2599.

Beard, S. J., and P. W. Smith. 1965. *Status of fission product recovery at Hanford,* RL–SA–40, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Berals, L. 1963. *The sorption of strontium and cesium traces on silicate minerals and rocks,* UJV–528, The Institute of Nuclear Research, Ustav Jaderneho Vyzkumu, Rez.

Boenzi, D., and G. Lenzi. 1967. *Contribution of the study of the site of the Casaccia Nuclear Research Center,* RT/PROT–(67)7, Comitato Nazionale per l'Energia Nucleare, Rome.

Brandt, H. L. 1970. *B Plant recovery of cesium from Purex supernatant,* ARH–1639, Atlantic Richland Hanford Company, Richland, Washington.

Bray, L. L. 1967. *Recovery of cesium from Purex alkaline waste from a synthetic zeolite,* BNWL–288, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Bray, L. A., and H. T. Fullam. 1971. Recovery and purification of cesium–137 from Purex waste using synthetic zeolites. *Advan. Chem. Ser.* 101:450. [Also presented at the Second International Conference on Molecular Sieve Zeolites, Worcester, Massachusetts, Sept. 8–11, 1970]

Breck, D. W. 1974. *Zeolite molecular sieves*, New York: Wiley.

Brooksbank, R. E., and L. J. King. 1979. *Involvement of the ORNL Chemical Technology Division in contaminated air and water handling at the Three Mile Island Nuclear Power Station,* ORNL/TM–7044, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

Brooksbank, R. E., and W. J. Armento. 1980. *Post–accident cleanup of radioactivity at the Three Mile Island Nuclear Power Station,* ORNL/TM–7081, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

Buckingham, J. S. 1979. *Laboratory evaluation of an ion exchange process for removing cesium from Purex acid waste solutions,* RHO–CD–739, Rockwell Hanford Operations, Rockwell International Corporation, Richland, Washington.

Buckingham, J. S. (Rockwell Hanford Operations, Rockwell International Corporation, Richland, Washington) 1980. Letter to D. O. Campbell (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Jan. 14.

Buckingham, J. S. (Rockwell Hanford Operations, Rockwell International Corporation, Richland, Washington) 1981. Personal communication to J. W. Roddy (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), Jan. 6, 1981.

Bukata, W., and J. A. Marinsky. 1964. Ion exchange in concentrated solutions. III. Zeolite systems with salts of group I and II metals. *J. Phys. Chem.* 68(5):994.

Cahn, J. H. 1959. Irradiation damage in germanium and silicon due to electrons and gamma rays. *J. Appl. Phys.* 30(8):1310.

Campbell, D. O. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1980. Letter to R. E. Brooksbank (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Jan. 18.

Campbell, D. O. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1980. Letter to R. E. Brooksbank (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Dec. 8.

Campbell, D. O., and W. L. Pattison (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1980. Letter to R. E. Brooksbank (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Jan. 14.

Campbell, D. O., E. D. Collins, L. J. King, and J. B. Knauer. 1980. *Evaluation of the submerged demineralizer system (SDS) flowsheet for decontamination of high-activity-level water at the Three Mile Island Unit 2 Nuclear Power Station,* ORNL/TM-7448, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

Chang, Tin-Wu. 1962. The effect of irradiation on the stability of ion-exchange resins. *Hua Hsueh Tung Pao* 1962(3):26.

Collins, E. D., J. E. Bigelow, D. O. Campbell, L. J. King, and J. B. Knauer. 1980. Flowsheet development studies for the decontamination of high-activity-level water at Three Mile Island Unit 2. Presented at the 89th national meeting of the American Institute of Chemical Engineers, Portland, Oregon, Aug. 17-20.

DeMier, W. V. 1963. *Dehydration of inorganic ion exchange media,* HW-78893, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

DeMier, W. V., G. L. Richardson, A. M. Platt, and W. H. Swift. 1963. *Development of radioactive waste fractionization and packaging technology,* HW-SA-2786, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Denio, L. L., D. E. Knowlton, and E. E. Voiland. 1977. *Control of nuclear fuel storage basin water quality by use of powdered ion exchange resins and zeolites,* ASME Publ. No. 77-JPGC-NE-15, General Electric Company, Morris, Illinois.

Dlouhy, Z. 1963. *Classification of the properties of pyroclastic rocks for uptake of fission products,* UJV-951/63, Cheskoslovenska Akademie Ved. Ustav Jaderneho Vyzkumu, Rez.

Egorov, E. V., and P. D. Novikov. 1967. *Action of ionizing radiation on ion-exchange materials.* Jerusalem: S. Monson.

Ewing, S. T. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1969. Letter to R. A. Robinson (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Apr. 1.

Fedorov, V. A., A. M. Tolmachev, and G. M. Panchenkov. 1964. Exchange equilibriums of univalent ions on synthetic zeolites of the A type. *Zh. Fiz. Khim.* 38(5):1248.

Fradin, J. 1967. *Pilot waste processing plant for the recovery of cesium-137,* EUR-3625f, Commissariat a l'Energie Atomique, Saclay.

Frost, C. R. 1963. *The fixation of cesium on Australian minerals. II. Zeolite minerals,* AAEC/TM-205, Atomic Energy Commission Research Establishment, Lucas Heights, New South Wales.

Fullam, H. T. 1972. *Compatibility of cesium chloride and strontium fluoride with containment materials,* BNWL–1673, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Fullerton, R. 1961a. *The effect of gamma radiation on clinoptilolite,* HW–69256, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Fullerton, R. 1961b. *Radiation effects on some waste fixation materials – Bibliography,* HW–69257, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Gacinovic, O. M., P. D. Radovanov, and I. J. Gal. 1969. Sorption of cesium–137, strontium–90, cobalt–60, and ruthenium–106 from sodium chloride solutions on synthetic zeolite Linde 4A. *Isotopenpraxis* 5(11):420.

Galavanov, V. V. 1959. Displacement of atoms in a solid by the action of γ–rays. *Sov. Phys. Solid State* 1(1):390. [English transl. of *Fiz. Tverd. Tela* 1(3):432 (1959)]

Galli, E. 1975. The zeolites. *Rend. Soc. Ital. Mineral. Petrol.* 31(2):549.

Godfrey, W. L., and D. J. Larkin. 1970. Ion exchange tames radioactive waste solutions. *Chem. Eng. (New York)* 77(15):56.

Gorbunov, N. I., and A. V. Bobrovitskii. 1973. Distribution, genesis, structure, and properties of zeolites. *Pochvovedenie* 1973(5):93.

Gradev, G. D., M. V. Milanov, Y. D. Prodanov, and G. I. Stephanov. 1978. A study of natural calcium clinoptilolite by using radioactive indicators. *J. Radioanal. Chem.* 45:103.

Grba, V., Z. Soljic, and I. Bican. 1975. I. Synthetic zeolites and their uses as molecular sieves, ion–exchangers, and catalysts. *Nafta (Zagreb)* 26(10):520.

Grenthe, I. R., S. E. Anderson, and G. Berggren. 1976. Removal and decontamination of radioactive isotopes from aqueous solutions. Ger. Offen. 2,547,935.

Haden, W. J., Jr., and F. J. Dzierzanowski. 1965. Method for purifying radioactive waste liquid. U.S. Patent 3,196,106.

Haff, K. W. 1963. *Examination of a nine–year–old ^{137}CsCl source capsule,* ORNL–TM–584, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

Hawkins, R. H., and J. H. Horton. 1971. *Zeolite prefilter to reduce pluggage in zeolite cesium removal column,* DP–1245, Savannah River Laboratory, E. I. du Pont de Nemours & Company, Aiken, South Carolina.

Hayden, W. L., Jr., and F. J. Dzierzanowski. 1965. Method for purifying radioactive waste liquid. U.S. Patent 3,167,504.

Hilliard, R. K., and D. L. Reid. 1961. *The release of radiocesium from Decalso at elevated temperatures,* HW–69274, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Horioka, M. 1969. Separation and recovery of cesium–137 from radioactive wastes by using zeolite. *Nippon Genshiryoku Gakkaishi* 11(7):406.

Horioka, M. 1971. Experimental studies on disposal of radioactive wastes. Recovery by separation of a particular ion cesium–137 by coagulation – precipitation and ion exchange. *Gesuido Kyokai–Shi* 8(83):15.

Horioka, M. 1973. Separating and recovering cesium from fuel reprocessing waste solution. Japan Patent 73 05,438.

International Atomic Energy Agency. 1967. *Operation and control of ion–exchange processes for treatment of radioactive wastes,* Tech. Reports Series No. 78, Vienna.

Irish, E. R., ed. 1963. *Research and development activities fixation of residues quarterly progress report, January–March 1963,* HW–77299, Hanford Atomic Products Operation, General Electric Comany, Richland, Washington.

Jacobsen, W. R., W. L. Martin, D. A. Orth, and C. P. Ross. 1974. *Control and treatment of radioactive liquid waste effluents at the Savannah River Plant,* DP–1349, Savannah River Laboratory, E. I. du Pont de Nemours & Company, Incorporated, Aiken, South Carolina.

Jacobson, A. 1977. *A short review of the formation, stability, and cementing properties of natural zeolites,* KBS–TR–27, Kaernbraemslesaekerhet, Stockholm.

Jones, G. 1974. Zeolites, a brief history. *Pentacol* 12:30.

Kanno, T. 1977. Radioactive waste solution and its disposal. A trial with zeolite. *Hyomen* 15(8):459.

Kanno, T., H. Hashimoto, and T. Ohtani. 1978. Ion–exchange properties of cesium and strontium from sodium salt solutions. *Tohoku Daigaku Senko Seiren Kenyusho Iho* 34:53.

Kanno, T., and H. Mimura. 1977. Processing of radioactive waste solution with zeolites. II. Leachability of cesium and strontium from calcined natural zeolites. *Nippon Genshiryoku Gakkaishi* 19(2):113.

Kanno, T., H. Mimura, and T. Kitamura. 1976. Processing of radioactive waste solutions with zeolites. (I). Thermal transformation of sodium, cesium, and strontium type zeolites. *Nippon Genshiryoku Gakkaishi* 18(8):518.

Kato, K. 1974. Removal of cesium–137 from aqueous solutions by zeolite. *Hoken Butsuri* 9(1):11.

Katz, H, and M. Rothbart. 1968. Ion exchange process. U.S. Patent 3,380,916.

Kenna, B. T., and K. D. Murphy. 1979. Separation of ^{137}Cs from nuclear waste. *J. Inorg. Nucl. Chem.* 41(11):1535.

Knoll, K. C. 1960. *The effect of heat on the vaporization and elution of ^{85}Sr and ^{137}Cs adsorbed on zeolites,* HW–77830, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Knoll, K. C. 1964. *Removal of ^{137}Cs by ion exchange,* HW–84105, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Kuehn, P. R. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1967. Letter to R. W. Schaich (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Feb. 3.

Lambrino, Vl. 1966. Utilization of some alumino–silicates as ion exchangers for decontamination of radioactive solutions. *Rev. Chim. (Bucharest)* 17(6):371.

Lenzi, G., and A. Pozzuoli. 1969. Behavior of some natural zeolites as a function of the absorption of cesium and strontium in radioactive solutions with low activity. *Rend. Accad. Sci. Fis. Mat., Naples* 36:235.

Levi, H. W. 1967. *The behavior of crystalline silica–containing ion exchangers and their application in nuclear technology,* HMI–B–54, Hahn–Meitner–Institut fuer Kernforschung, Berlin.

Levi, H. W., W. Lutze, and E. Schiewer. 1965. Isotope exchange on mineral ion exchangers. I. Determination of exchange capacity. *Z. Anorg. Allg. Chem.* 334(5–6):250.

Lewis, R. E. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1966. Letter to T. A. Butler (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Mar. 9.

Lewis, R. E. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1967. Letter to T. A. Butler (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Feb. 13.

Lewis, R. E., T. A. Butler, and E. Lamb. 1965. *Recovery of ^{137}Cs from fission–product wastes and transport by an aluminosilicate ion exchanger,* ORNL–3765, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee. [Also *Nucl. Sci. Eng.* 24(2):118 (1966).]

Malashevich, L. N., S. A. Levina, and N. F. Ermolenlo. 1963. Regularities of the ion–exchange [process] on some synthetic zeolites. *Ionoobmen i Sorbtsiya iz Rastvorow, Akad. Nauk Belorussk. SSR., Inst. Obshch. i Noorgan Khim.* 1963:15.

Mathers, W. G., and I. C. Watson. 1962. *Waste disposal experiment using mineral exchange on clinoptilolite,* AECL–1521, Atomic Energy Canada, Limited, Chalk River.

Mercer, B. W., Jr. 1960. *The removal of cesium and strontium from condensate wastes with clinoptilolite,* HW–66276, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Mercer, B. W., Jr. 1967. *Ion exchange equilibria of trace cesium–137 and strontium–85 in multicomponent systems,* BNWL–SA–1173, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Mercer, B. W., Jr., and L. L. Ames, Jr. 1963a. *The adsorption of cesium and strontium on zeolites from multicomponent systems,* HW–SA–3199, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Mercer, B. W., Jr., and L. L. Ames, Jr. 1963b. *The adsorption of cesium, strontium, and cerium on zeolites from multi–cation systems,* HW–78461, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Mercer, B. W., Jr., and L. L. Ames, Jr. 1978. Zeolite ion exchange in radioactive and municipal wastewater treatment. In *Nat. Zeolites: Occurrence, Prop. Use, Sel. Pap. Zeolite 76, Int. Conf.* 1976:451.

Mercer, B. W., Jr., L. L. Ames, Jr., and R. G. Parkhurst. 1968. *Removal of cesium–137 from alkaline condensate wastes,* BNWL–829, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Mercer, B. W., Jr., L. L. Ames, Jr., and P. W. Smith. 1970. Cesium purification by zeolite ion exchange. *Nucl. Appl. Technol.* 8(1):62.

Mercer, B. W., Jr., and W. C. Schmidt. 1965. *Storage of long–lived fission products on aluminosilicate zeolites,* RL–SA–58, Pacific Northwest Laboratory, Battelle–Northwest, Richland, Washington.

Miller, R. 1964. Molecular sieve catalysts. *Chem. Week* 95(20):77.

Mimura, H., and T. Kanno. 1978. Processing of radioactive wastes with zeolites. IV. Volatilization of cesium from zeolites at high temperature. *Nippon Genshiryoku Gakkaishi* 20(4):282.

Minato, H. 1975. Zeolite, its natural resources and utilization. *Seramikkusu* 10(12):941.

Murat, M. 1970. Dilatometric study of the thermal evolution of natural and synthetic zeolites. *C. R. Acad. Sci. Ser. D* 270(13):1657.

Murphy, W. R. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1967. Letter to O. V. Smiset (Isochem, Incorporated, Richland, Washington), dated Jan. 20.

Nater, K. A. 1959. *Irradiation damage in ion–exchange materials,* NP–9805, Joint Establishment for Nuclear Energy Research, Kjeller, Norway.

Nater, K. A. 1962. Radiation damage of ion exchangers. *Atoomenerg. Haar Toepass.* 4(8):155.

Nelson, J. L., G. J. Alkire, and B. W. Mercer. 1962. *The recovery and purification of cesium from Purex formaldehyde–treated waste by inorganic ion exchange,* HW–74568, Hanford Atomic Products Operation, Pacific–Northwest Laboratory, Richland, Washington.

Nelson, J. L., L. L. Ames, Jr., and B. W. Mercer, Jr. 1964. *Characterization and application of zeolites for radioactive waste treatment,* HW–SA–3333, Hanford Atomic Products Operation, Pacific–Northwest Laboratory, Richland, Washington.

Nelson, J. L., and B. W. Mercer, Jr. 1963. *Ion exchange separation of cesium from alkaline waste supernatant solutions,* HW–76449, Hanford Atomic Products Operation, Pacific–Northwest Laboratory, Richland, Washington.

Nelson, J. L., B. W. Mercer, and W. A. Haney. 1960. *Solid fixation of high–level radioactive waste by sorption on clinoptilolite – scouting studies,* HW–66796, Hanford Atomic Products Operation, Pacific–Northwest Laboratory, Richland, Washington.

Ni, L. P., O. B. Khalyapina, and G. L. Perekhrest. 1966. Nature of thermal effects of some sodium hydro–aluminosilicates formed in the sodium oxide-alumina-silica-water system. *Zh. Prikl. Khim.* 39(12):2639.

Nicholls, C. M., and R. Spence. 1957. Chemical processing of nuclear fuels. *At. Nucl. Energy* 8:136.

Nikashina, V. A., G. K. Sotnikova, and E. N. Berezovskaya. 1975. Selective sorption of strontium on different types of synthetic zeolites. *Radiokhimiya* 17(3):345.

Nishimura, Y. 1973. Properties and utilization of natural zeolite. *Nendo Kagaku* 13(1):23.

Norton Chemical Company, Process Products Division, *Zeolon acid resistant molecular sieves* (Bulletin), Akron, Ohio.

Oberg, G. C. (Atlantic Richfield Hanford Company, Richland, Washington). 1970a. Letter to E. Lamb (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Oct. 12.

Oberg, G. C. (Atlantic Richfield Hanford Company, Richland, Washington). 1970b. Letter to R. W. Schaich (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Nov. 9.

Oberg, G. C. (Atlantic Richfield Hanford Company, Richland, Washington). 1971. Letter to R. W. Schaich (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Aug. 9.

Oen, O. S., and D. K. Holmes. 1959. Cross sections for atomic displacements in solids by gamma rays. *J. Appl. Phys.* 30(8):1289.

Ottinger, C. L. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1961. Letter to R. W. Schaich (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Jan. 19.

Ottinger, C. L. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1963a. Letter to R. E. McHenry (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Feb. 12.

Ottinger, C. L. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1963b. Letter to R. W. Schaich (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Dec. 18.

Pecsi–Donath, E. 1962. Investigation of the thermal decomposition of zeolites by differential thermal analysis. *Acta Geol. Acad. Sci. Hung.* 6:429.

Pillay, K. K. S. 1980. *Radiation effects on ion exchangers used in radioactive waste management,* NE/RWM–80–3, Department of Nuclear Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Pionlkovskaya, M. A., I. E. Neimark, G. S. Shameko, G. I. Denisenko, and I. N. Chervetsova. 1965. Properties of various ion–exchange forms of zeolites of type A. *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964:97.

Plodinec, M. J. 1976. *Evaluation of cesium–137 sorbents for fixation in concrete,* DP–1444, Savannah River Laboratory, E. I. du Pont de Nemours and Company Incorporated, Aiken, South Carolina.

Popovich, R. P. 1964. *Ion exchange recovery of cesium from alkaline supernatant waste – scale–up studies,* HW–83461, Hanford Atomic Products Operation, Pacific–Northwest Laboratory, Richland, Washington.

Prout, W. E., and E. R. Russell. 1964. *Removal of Cs from evaporator condensate,* DP–876, Savannah River Laboratory, E. I. du Pont de Nemours and Company Incorporated, Aiken, South Carolina.

Rees, L. V. C. 1970. Ion exchange in zeolites. *Annu. Rep. Progr. Chem. Sect. A* 67:191.

Rhodes, D. W. (Allied Chemical Corporation, Idaho Falls, Idaho). 1979. Letter to D. O. Campbell (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated May 5.

Rhodes, D. W., and M. W. Wilding. 1965. *Decontamination of radioactive effluent with clinoptilolite,* IDO–14657, Idaho Operations Office, Phillips Petroleum Company, Idaho Falls, Idaho.

Rimshaw, S. J., and E. E. Ketchen. 1969. *Compatibility data sheets for cerium–144, cesium–137, curium, and strontium–90,* ORNL–4359, Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee.

Rimshaw, S. J., and D. C. Winkley. 1960. Personal communication.

Roberts, R. C., and W. R. Herald. 1980. *Development of ultrafiltration and adsorbents: April–September 1979,* MLM–2684, Mound Laboratory, Miamisburg, Ohio.

Ruiz, J. Lopex. 1974. Molecular sieves. *Quim. Ind. (Madrid)* 20(7–8):513.

Schaffhauser, A. C. 1980. Personal communication.

Schaich, R. W. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1980. Letter to D. O. Campbell (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Dec. 3.

Schchebetkovskii, V. N. 1968. Sorption of cesium–137, strontium–90, and yttrium–91 from aqueous solutions by NaX–type synthetic zeolite. *Radiokhimiya* 10(2):151.

Schwochow, F., and L. Puppe. 1975. Zeolites, production, structure, applications. *Angew. Chem.* 87(18):659.

Scott, J. 1980. *Zeolite technology and applications, recent advances 1980.* Chem. Technol. Rev. 170. Park Ridge, New Jersey: Noyes Data Corp.

Sherry, H. S. 1966. The ion–exchange properties. I. Univalent ion exchange in synthetic faujasite. *J. Phys. Chem.* 70(4):1158.

Sherry, H. S. 1969. The ion–exchange properties of zeolites. In *Ion Exchange,* ed. by J. A. Marinsky. New York: Marcel Dekker.

Stach, H., and U. Lohse. 1975. Properties and use of natural and synthetic zeolite. *Frieberg. Forchungsh. C* C296:141.

Staff of the Oak Ridge National Laboratory and Bechtel. 1980. *A process evaluation, including laboratory tests, on the use of retired casks at TMI–2,* unpublished document.

Starodubtsev, S. V., Sh. A. Ablayev, S. E. Ermatov, and S. A. Azizov. 1963. The effect of γ–irradiation on the adsorptive properties of synthetic zeolites. *Radiats. Effeckty v. Tverd. Telakh. Akad. Nauk Uz. SSR, Inst. Yadern. Fiz.* 1963:19.

Steves, L. L., and W. V. DeMier. 1962. *Fission product and waste packaging: Effect of γ–leakage on thermal calculations,* HW–74712, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Strachan, D. M., and W. W. Schulz. 1976. *Glass and ceramic materials for the immobilization of megacurie–amounts of pure cesium–137,* ARH–SA–246, Atlantic Richfield Hanford Company, Richland, Washington.

Stringfield, H. F. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1971a. Letter to M. D. Alford (Atlantic Richfield Hanford Company, Richland, Washington), dated Jan. 21.

Stringfield, H. F. (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee). 1971b. Letter to M. D. Alford (Atlantic Richfield Hanford Company, Richland, Washington), dated Oct. 1.

Sultanov, A. S., R. I. Radyuk, D. Tashpulatov, E. D. Vdovina, and G. L. Popova. 1975. Purification of mildly active water containing long–lived isotopes using natural sorbents. *Dokl. Soobschch. – Mendeleevsk. S'ezd Okshch. Prikl. Khim. 11th* 1:240.

Sultanov, A. S., R. I. Radyuk, D. Tashpulatov, E. D. Vdovina, G. L. Popova, and E. A. Aripov. 1976. Separation of long–lived isotopes from low–activity waters by natural sorbents. *Radiokhimiya* 18(4):677.

Suzuki, N., K. Saitoh, and S. Hamada. 1978. Ion exchange properties of a synthetic mordenite on alkali and alkaline earth metal ions. *Radiochem. Radioanal. Lett.* 32(3–4):121.

Swift, W. H. 1962. *Fission product and waste packaging by inorganic zeolite absorption,* HW–73964, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Swyler, K., R. E. Barletta, and R. E. Davis. 1980. *Review of recent studies of the radiation induced behavior of ion exchange media,* BNWL–NUREG–28682, Brookhaven National Laboratory, Associated Universities, Incorporated, Upton, New York.

Takagi, S. 1975. Isolation and removal of long–lived radiocesium from the liquid waste of nuclear power stations with zeolite. *Denryoku Chuo Kenkyusho Gijutsu Dai Ichi Kenkyusho Hokoku* 1975:74064.

Takagi, S. 1975. *Preliminary research on the isolation and removal of long–lived radiocesium in the liquid waste of a nuclear power station with zeolites,* CH:74001, Central Research Institute Electric Power Industry, Tokyo.

Takagi, S. 1978. Preliminary study on use of zeolite for isolation and removal of long–lived cesium in liquid waste from nuclear power stations. *J. Nucl. Sci. Technol.* 15(3):213.

Tomlinson, R. E. 1962. The Hanford Program for Management of High–Level Waste, HW–SA–2515, Hanford Atomic Products Operation, General Electric Company, Richland, Washington. [Also Large–scale fission–product recovery. In *Proc. Intern. Conf. Peaceful Uses At. Energy, 3rd, Geneva* 10:544 (1964)]

Van Tuyl, H. H., and L. A. Bray. 1961. *Recovery of cesium from Purex tank farm supernatant solution by ferrocyanide precipitation and absorption on Decalso,* HW–70874, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

Vdovina, E. D., R. I. Radyuk, and A. S. Sultanov. 1976. Use of Uzbekistan natural zeolites for the purifcation of low–level waste waters. I. Sorption of radioactive cesium. *Radiokhimiya* 18(3):422.

Venuto, P. B., and P. S. Landis. 1968. Organic catalysis over crystalline aluminosilicates. In *Advances in catalysis and related subjects.* Vol. 18, ed. by D. D. Eley, H. Pines, and P. B. Weisz. New York: Academic Press.

Verot, J. L., and J. M. Blum. 1968. Decontamination of radioactive effluents by zeolites. *Energ. Nucl.* 10(3):210.

Verot, J. L., J. M. Blum, R. Sarfati, J. Dagnes, and Y. Cassin. 1967. *Decontamination of effluents by means of zeolites,* EUR–3452f, Etablissements Kuhlmann, Paris.

Vesely, V. 1963. *Deactivation of radioactive waste waters by countercurrent adsorption of coagulated suspensions of natural adsorbents,* UJV–973/63, Ceskoslovenska Akademie Ved. Ustav Jaderneho Vyzkumu, Rez.

Wallace, R. M. (Savannah River Laboratory, E. I. du Pont de Nemours & Company Incorporated, Aiken, South Carolina). 1980. Letter to J. W. Roddy (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Dec. 18.

Wallace, R. M. (Savannah River Laboratory, E. I. de Pont de Nemours & Company Incorporated, Aiken, South Carolina). 1981. Letter to J. W. Roddy (Oak Ridge National Laboratory, Union Carbide Corporation, Oak Ridge, Tennessee), dated Feb. 20.

Wang, Pao–Chem. 1978. Inorganic ion exchangers and the treatment of radioactive–waste water. *Hua Hsueh Tung Pao* 1978(3):159.

Wilding, M. W., and D. W. Rhodes. 1963. *Removal of radioisotopes from solutions by earth materials from eastern Idaho,* IDO–14624, Idaho Operations Office, Phillips Petroleum Company, Idaho Falls, Idaho.

Wilding, M. W., and D. W. Rhodes. 1974. *Removal of cesium and strontium from fuel storage basin water,* ICP–1048, Idaho Chemical Programs–Operations Office, Allied Chemical Corporation, Idaho Falls, Idaho.

Wilding, M. W., and D. W. Rhodes. 1976. Removal of cesium and strontium from fuel storage basin water. *Adv. Chem. Ser.* 1976:153.

Wiley, J. R. 1978. Decontamination of alkaline radioactive waste by ion exchange. *Ind. Eng. Chem. Process Des. Dev.* 17(1):67.

Wiley, J. R., and R. M. Wallace. 1975. *Removal of cesium from Savannah River Plant waste supernate,* DP–1388, Savannah River Laboratory, E. I. du Pont de Nemours & Company Incorporated, Aiken, South Carolina.

Zahn., L. L., C. W. Smith, and R. L. Junkins. 1963. Shipment of gross quantities of radiostrontium. In *Treatment and Storage of High–Level Radioactive Wastes,* Vienna:IAEA.

INTERNAL DISTRIBUTION

1. J. T. Bell
2. W. D. Bond
3. W. D. Burch
4. D. O. Campbell
5. E. D. Collins
6. A. G. Croff
7. D. J. Crouse
8. H. W. Godbee
9. W. S. Groenier
10. F. E. Harrington
11. A. D. Kelmers
12. L. J. King
13. E. H. Krieg, Jr.
14. R. E. Leuze
15. K. H. Lin
16. J. C. Mailen
17-18. A. P. Malinauskas
19. W. J. McDowell
20. J. G. Moore
21. E. Newman
22. K. J. Notz
23. W. W. Pitt
24. D. J. Pruett
25-29. J. W. Roddy
30. T. H. Row
31. A. D. Ryon
32. F. M. Scheitlin
33. S. Y. Shiao
34. R. R. Shoun
35. S. E. Shumate II
36-37. M. G. Stewart
38. O. K. Tallent
39. J. S. Watson
40. O. O. Yarbro
41. G. R. Choppin (Consultant)
42. W. H. Corcoran (Consultant)
43-44. Central Research Library
45. ORNL–Y-12 Technical Library Document Reference Section
46-47. Laboratory Records
48. Laboratory Records - ORNL R.C.
49. ORNL Patent Section

EXTERNAL DISTRIBUTION

50. Office of Assistant Manager for Energy Research and Development, DOE–ORO, P.O. Box E, Oak Ridge, TN 37830.

51. M. M. Beary, Rockwell Hanford Operations, P.O. Box 800, Richland, WA 99352.

52. W. W. Bixby, DOE/TMI Site Office, P.O. Box 88, Middletown, PA 17057.

53. R. E. Brooksbank, c/o F. Comprelli, 45/16C34, Bechtel National, Nuclear Fuel Operations, 50 Beale Street, P.O. Box 3965, San Francisco, CA 94119.

54. D. R. Buchanan, GPU Nuclear Corporation, Metropolitan Edison Company, P.O. Box 480, Middletown, PA 17057.

55. J. S. Buckingham, Rockwell Hanford Operations, P.O. Box 800, Richland, WA 99352.

56. N. N. Cole, MPR Associates, 1140 Connecticut Avenue, NW, Washington, DC 20008.

57. J. T. D'Ambrosia, Technology Division, Office of Waste Operations and Technology, Office of Nuclear Energy, U.S. Department of Energy, Washington, DC 20545.

58. H. Feinroth, U.S. Department of Energy, Washington, D.C. 20545.

59. C. Ice, 786 Boardman Road, Aiken, SC 29801.

60. D. E. Knowlton, Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

61. C. W. Kuhlman, Bechtel National, 15740 Shady Grove Road, Gaithersburg, MD 20760.

62. K. K. S. Pillay, The Pennsylvania State University, University Park, PA 16802.

63. R. B. Pope, Sandia National Laboratory, Albuquerque, NM 87185.

64. W. W. Shulz, Rockwell International, Hanford Operations, P. O. Box 800, Richland, WA 99352.

65. R. W. Wallace, E. I. du Pont de Nemours & Company, Atomic Energy Division, Savannah River Laboratory, Aiken, SC 29801.

66. A. K. Williams, Allied General Nuclear Services, P. O. Box 847, Barnwell, SC 29812.

67. H. Lowenberg, MS 396, Silver Spring, USNRC, Washington, DC 20555.

68. L. Barrett, USNRC, P.O. Box 311, Middletown, PA 17057.

69. B. Snyder, USNRC, Washington, DC 20555.

70. C. G. Hitz, General Public Utilities/TMI, P.O. Box 88, Middletown, PA 17057.

71. G. Hovey, General Public Utilities/TMI, P.O. Box 88, Middletown, PA 17057.

72. R. McGoey, General Public Utilities/TMI, P.O. Box 88, Middletown, PA 17057.

73. E. E. Anschutz, U.S. Department of Energy, Washington, DC 20545.

74. M. J. Steindler, CFN–205, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439.

75-101. Technical Information Center, Oak Ridge, TN 37830.