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Informal Report

Paul L. Piciulo



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> Brookhaven National Laboratory Upton, New York 11973 Associated Universities, Inc. for the U.S. Department of Energy

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INFORMAL REPORT

TECHNICAL CONSIDERATIONS FOR HIGH INTEGRITY CONTAINERS FOR THE DISPOSAL OF RADIOACTIVE ION EXCHANGE RESIN WASTE

DRAFT REPORT

P. L. PICIULO

DECEMBER 1981

NUCLEAR WASTE MANAGEMENT DIVISION DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY UPTON, NEW YORK 11973



Prepared for the U.S. Nuclear Regulatory Commission Office of Nuclear Materials Safety and Safeguards Contract No. DE-AC02-76CH00016

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P. L. Piciulo

Manuscript Completed: December 1981

Donald G. Schweitzer, Head Nuclear Waste Management Division Department of Nuclear Energy Brookhaven National Laboratory Associated Universities, Inc. Upton, New York 11973

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ABSTRACT

The technical rationale, for criteria which should be applied to high integrity containers for the disposal of ion exchange resin waste from the nuclear power industry, is developed in this report. A data base, on the nature of drainable liquids from ion exchange media, is compiled from information obtained from a survey of operating nuclear plants, manufacturers of organic ion exchange resins and companies which supply resin dewatering services to the nuclear industry. Factors affecting the stability of ion exchangers are reviewed, and the effects of resin decomposition products on the waste container are discussed. Methods for dewatering ion exchange resin waste are evaluated in this report.

Recommendations are given for determining the maximum limit on the amount of liquid allowed in high integrity containers used for disposal of dewatered resins. The draft copy of proposed Nuclear Regulatory Commission guidelines on high integrity container design is reviewed. For each criterion given in the guidelines, technical justification is provided, and those areas where necessary technical information is lacking are identified.

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1. INTRODUCTION

Organic ion exchange resins are widely used for water treatment in nuclear power plants. The subsequent low-level radioactive resin wastes are buried in the three commercial disposal sites currently operating, i.e., at Barnwell, South Carolina; at Beatty, Nevada; and at Hanford, Washington. Presently, the State of South Carolina(1) requires that "ion exchange resins and filter media containing isotopes with greater than five (5) year halflives having a specific activity of all these isotopes of 1 microcurie/ cubic centimeter or greater must be stabilized by solidification" and "shall have no detectable free standing (sic) liquids." The phrase "no detectable free standing (sic) liquids" is defined as "one-half percent (0.5%) by waste volume or one gallon of non-corrosive liquids per container, whichever is less." However, ion exchange resins and filter media which are dewatered and contain "liquids in excess of one-half percent (0.5%) by waste volume, but less than one percent (1%) liquid by waste volume, may be received and disposed of in approved high integrity containers." The State of Carolina has certified some high integrity containers (HIC), and dewatered ion exchange resin wastes are being buried at the Barnwell burial site in these HICs.

The U.S. Nuclear Regulatory Commission (NRC) has proposed design guidelines to be considered in the construction of a HIC, but the NRC has not yet certified such a container. The technical justification for the design guidelines and the technical rationale for determining the maximum limit on the amount of liquid allowed in high-integrity containers to be used for the disposal of dewatered ion exchange media are developed in this report.

A survey was conducted of the operating nuclear power stations to obtain information regarding their experience with organic ion exchange resins in water treatment and the subsequent disposal of these materials. Information regarding the dewatering of ion exchange resins and the characteristics of the drainable liquids was of major interest. Selected companies, which provide services to the nuclear industry, specifically related to the disposal of dewatered ion exchange media, were also contacted. In addition, the major manufacturers of organic ion exchange resins were surveyed for information about new resins and about the decomposition of resins over long periods of time. The degradation mechanisms of ion exchange resins and the corrosive behavior of the degradation products are evaluated. Conditions resulting in the release of liquids from resins are considered and suggestions are made of methods that can be used to provide information which is believed necessary to characterize the internal environment of a HIC filled with dewater ion exchange media.

The criteria or standards presented in the draft copy of proposed NRC guidelines on high integrity container design are reviewed in section 6.

Based on data compiled in the present survey and information found in the literature, the technical justification is provided for each guideline. Those areas where information was lacking are indicated and suggestions are made to alleviate those deficiencies.

2. REVIEW OF SURVEY OF NUCLEAR POWER STATIONS

2.1 Introduction

In 1973, $Lin^{(2)}$ reported an initial survey of the use of ion exchangers for water treatment in nuclear power plants. Data were compiled from sources in the nuclear industry and from manufacturers of ion exchange resins and ion exchange equipment. The decontamination of waste streams containing radionuclides in the concentration range of 10^{-7} to $1 \mu Ci/mL$ was emphasized. Decontamination factors (DFs) used by plant operators to express the performance of the ion exchange system were reported and problems associated with DF values were considered. The decontamination factor of an ion exchange system is defined as the ratio of the influent to effluent concentration of a particular isotope.

In 1978, Clark⁽³⁾ published a study which updated the Lin report on the use of ion exchange for the treatment of radioactive solutions in light water cooled reactor power plants. Data obtained in a survey of nuclear power plants (both operating and in various stages of construction), from architectengineering firms and from equipment suppliers were discussed. The methods of water treatment in nuclear power plants, using ion exchange media, were found not to have changed significantly since the report by Lin. However, resin regeneration by nuclear power stations appeared to be growing less common. Again, Clark's report emphasized the use of ion exchange in the nuclear industry, and recommendations were included for improving its efficiency.

The survey reported in the present study is not solely directed at the usage of ion exchange media for water treatment in nuclear power plants, as were the Lin and Clark reports. Rather, the characteristics and the management of the resulting radioactive waste generated by the demineralizer system were sought from the survey. The response to the questionnaires received from seven boiling water reactors (BWR) and nine pressurized water reactors (PWR) are examined, along with information obtained from discussions with radwaste personnel in a number of nuclear power plants.

The replies to the survey are reproduced in Appendix A. The responses were evaluated and an attempt was made to characterize any drainable liquids which might be present in a disposed liner of dewatered organic ion exchange media. Additionally, conditions which may result in severe changes in the waste package are identified. The information obtained from the survey was compiled and is discussed in this section.

2.2 Resins

It was found that synthetic organic ion exchange resins having a polystyrene-divinylbenzene backbone are most frequently used in the nuclear power industry. The strong acid cation exchanger with a sulfonic acid functional groups in the H⁺ form, and the strong base anion exchanger with a quaternary ammonium functional groups in the ⁻OH form are routinely used. However, other types of ion exchange media are sometimes necessary. For example, weakly basic anion exchange resins having an acrylic backbone structure

and a polyamine functionality are used to remove radioactive iodine from boric acid solutions in some PWRs. Resins are generally used as supplied by the manufacturers with no additional pretreatment by the utility. Diamond Shamrock Corporation (Duolite), Dow Chemical, USA (Dowex), Ionac Chemical Corporation, and Rohm and Hass (Amberlite) are the major manufacturers of organic ion exchange resins in the United States. The resins used for water treatment have a water content of approximately 50%, but this may vary by $\pm 20\%$. The moisture retained by ion exchangers is generally the water of hydration of the ionic functional group and counter ion. A "nuclear grade" specification is given to the resins, assuring a high percentage of exchange groups having a designated counter ion (e.g., H⁺ for cation exchangers or -0H for anion exchangers). Nuclear grade cation exchangers have a specified maximum metal ion (e.g., Fe, Cu, Na) content, and the equivalent grade anion exchangers also have a specified minimum chloride (Cl⁻) ion and carbonate (CO₃⁼) ion content.

Powdered resins (often termed "Powdex") are prepared by grinding a water slurry of bead resins. These are widely used in BWRs as thin layers (coats) on a filter septum, either alone or in conjunction with a deep bed. Powdered resins are generally mixed one part cation exchanger with one part anion exchanger. This produces a floc which provides not only ion exchange capacity but also filtration. Powdered resins are not regenerated; they are disposed of after use. A high purity organic fibrous material can be used with powdered resins. It is used as a filter coat over the powdered resin, or it is supplied pre-mixed with the powdered resin. For example, Ecodyne Graver Water Division supplies Ecocote, an organic fiberous material and Ecodex, a mixture of powdered resin and organic fibers.

2.3 Demineralizer Beds

Bead resins are generally used in a homogeneous mixed bed (one part anion exchanger to one part cation exchanger). This mixture can have a large variation and the anion beads and cation beads can be stratified in the bed. Some PWRs use anion exchange resin beds in the borate form to control the boron level in the system. Bead resin beds are often termed "deep beds", since they consist of large volumes ($20 \text{ to } 180 \text{ ft}^3$) of resin beads and provide a long contact time for the aqueous phase with the ion exchange bed. Powdered resins are always mixed, since this produces the floc which provides the filtering capacity. The layers of powdered resin are generally 0.2 inches thick; thus the contact time is shorter than in the deep bed. In some instances plants may use a powdered resin in a pre-filter system followed by a deep bed to treat the water.

Some plants use a portable demineralizing system supplied by EPICOR, Incorporated for their radwaste water treatment. An EPICOR spokesman indicated that the portable unit can have two parts connected in series -- a prefilter and a demineralizer bed.* Each component can be as large as

^{*}J. Levendusky, EPICOR, Incorporated, in a private communication with P. Piciulo, October 2, 1981.

150 ft³ (6 ft x 6 ft). The liners are supplied prefilled by EPICOR, Incorporated, and the exact contents are proprietary. However, the liners do contain organic ion exchange resins and possibly other filter media; carbon may be present to remove organic contaminants. The liners are connected to a waste water stream and after use they are dewatered and shipped for disposal. This system is similar in nature to EPICOR II used in the Three Mile Island cleanup. EPICOR reports that about eight to ten utilities use a portable demineralizer as part of their water treatment.

2.4 Operating Parameters

The operating parameters (i.e., temperature, pressure, flow rate) for the water treatment systems are consistent with those reported in the earlier reports, (2,3) and the resin manufacturers' recommendations. However, extended use of a resin bed and/or numerous regenerations of the resins can result in physical damage (e.g., bead cracking or breaking) to the resin. This may affect the ability to remove free liquid from the resin prior to disposal. Water removal will be discussed in section 4.

2.5 pH of Liquid Waste Streams

The ranges of pH for the water of the responding BWR's, and PWR's are listed in Tables 2.1 and 2.2, respectively, together with the pH ranges taken from the two earlier surveys. Lin(2) reported that the pH values in BWR plants are near neutral (pH approximately 7), while in PWR plants the pH range is from 4 to 10.5. Clark(3) indicates that in BWRs, the pH may vary from 4 to 9 and from 4 to 11 in PWRs. The present survey reveals that the overall range in the pH of water to a demineralizer is 2 to 9 for PWRs and 5 to 9 for BWRs. A pH range of 3-5 for the influent and effluent of the fuel pool demineralizer system was reported by Kewaunee Nuclear Power Plant. The Farley Nuclear Plant reported a pH range of 2-8 for the influent to the radwaste water treatment system, while the effluent is reported to have a pH of 6.

It is likely that the water remaining in a disposal liner will have a pH which is different (probably more neutral due to mixing of various streams) from the extremes listed in Tables 2.1 and 2.2, however, the large variations in pH observed are significant. Aqueous solutions having pH values less than pH = 4 are generally corrosive to carbon steel, a material commonly used in the construction of disposal liners.

Table 2.1

1.5

pH Range of Water in BWR's

Lin ^a	Clark ^b	Present Study
6.7-6.9		
6-8	5.8-8.5	5-9
	4-8	
~7		7
		70
		5.6-7.5
	Ġ.1	
7	7	7
7	7-8	
6-8	∿7	5.5-8.5
	5.2-8.7	
	4-9	7.2-7.4
	Lín ^a 6.7-6.9 6-8 ~7 7 7 6-8 	Lina Clarkb 6.7-6.9 6-8 $5.8-8.5$ $4-8\sim 7$ $$

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^aData taken from Reference 2. ^bData taken from Reference 3. ^cValue given for the liquid in the spent resin holding tank.

Table 2.2

pH Range of Water in PWR's

*

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PWR	Lin ^a	Clark ^b	Present Study
Beaver Valley Power Station		4.5-9	
Crystal River Nuclear Plant		4.8-9.0	
Donald C. Cook Nuclear Power Plant		4-8	
Fort Calhoun Station			7.83
Indian Point Station	5-10.5		
Joseph M. Farley Nuclear Plant			2-8
Kewaunee Nuclear Power Plant		5-7	5-8C
Main Yankee Atomic Power Plant		4.8-5.8	6-8
Palisades Nuclear Plant	4.5-8.0		
Point Beach Nuclear Plant	4-7.5		
San Onofre Nuclear Generating Station	4.5-10.2	4-7.5d	
Sequoyah Nuclear Plant	4.2-10.5e	4.2-10.5e	6.3-8.7
Shippingport Atomic Power Station	<7-10.3		
St. Lucie Plant		4.5-10.2	
Trojan Nuclear Plant			4-9.2
Turkey Point Plant	/	4.2-10.5	
Yankee-Rowe Nuclear Power Station	4.5-10.5	5-6	5.1-5.3
Zion Nuclear Plant	4.2-10.5	4.7-8.4	4-9

^aData taken from Reference 2. ^bData taken from Reference 3. ^cA pH range of 3-5 is given for the fuel pool water. ^dA pH = 3 is reported for the radwaste water. ^eExpected values are reported. The plant was not operating at the time of the report.

2.6 Conductivity, Total Suspended Solids, and Contaminants

A number of utilities responding have measured the conductivity and total suspended solids (TSS) in the various water streams in the plant and have given some indication of the contaminants in the waste streams. Conductance is a sensitive measure of the concentration of charged species (ions) in a solution. These ions can be radionuclides, nonradioactive corrosion products, and other ionic species which may enter a waste stream. TSS are particulates present in the various waste streams which may not be charged and are often removed by filtration. The radwaste treatment system may have a large amount of TSS and a high conductivity since this system processes aqueous waste from equipment and floor drains.

The influent conductivity is low in both PWRs and BWRs for the reactor cleanup and condensate demineralizers; usually less than 30 µmhc/cm. In PWR's borates will contribute to the conductivity. The radwaste and fuel pool demineralizer systems show much larger conductivities but have a large range from plant to plant. Kewaunee reported an influent conductivity in the radwaste system as high as 1200 µmho/cm, whereas Trojan reported a range of 1-200 µmho/cm. Only a small number of utilities indicated the conductivity of an effluent stream, it is generally lower than the conductivity of the influent.

The reported measurements of total suspended solids show a large variation from one plant to another. The radwaste and fuel pool cleanup water systems have the largest TSS values. PWR's and BWR's report TSS as high as 10⁴ ppb (parts per billion) for the radwaste system whereas condensate demineralizers and reactor cleanup demineralizers have values of <50 ppb in the influent and <1 ppb for the demineralizer effluent. This decrease is as expected because the ion exchanger (precoat or deep bed) will trap particulates.

The contaminants reported vary significantly from the different waste streams and from plant to plant. The radwaste and fuel pool cleanup show large levels of contaminants whereas the water purity is more carefully controlled in the reactor cleanup and condensate demineralizers. Chloride ion (C1-) is important to the reactor plant operation because it is a species which is corrosive to stainless steel. Thus, the presence of C1- in the drainable liquids in a disposal liner is important if stainless steel is used as a liner material. There is a large variation among plants indicating chemical contaminants and other materials, but the concentrations are usually less than 10 ppm (parts per million) and often in the ppb range. Chloride ion was reported as high as 600 ppb by one PWR. Other chemical species reported are: iron, copper, nickel, sodium, and silica. Small amounts of detergents were reported by one utility. The concentration of boron present in the fuel pool water system of PWR's varies widely, Fort Calhoun reported 2150 ppm and Yankee Rowe reported 427 ppm.

The information on effluent water quality does not describe the characteristics of water remaining in a disposal liner but it does provide some idea of the variations in the factors contributing to the drainable liquids that may be present in a liner. At many plants, the water and resins from the various water treatment systems are mixed in a spent resin holding tank (see section 2.9) or directly in a disposl liner. Large variations in conductivity, TSS, and contaminants have appeared among the different water treatment systems in a nuclear power plant. Variations also exist from plant to plant.

2.7 Radioactivity in Liquid Waste Streams

Several utilities responded to the questions on the gross α and gross β , γ activity in the demineralizer influent and effluent for various waste streams. Tables 2.3 and 2.4 summarize these values for BWR's and PWR's respectively. The gross α activity is generally very low (<1 nCi/mL) for both PWR's and BWR's. The gross β , γ activity is less than 2 μ Ci/mL for all the utilities replying and generally a few orders of magnitude lower. This is expected since the activity is being concentrated on the ion exchange media.

The levels of activity on the resin are generally much higher than that in the liquid. Activity on the resins will be discussed further in section 2.11. However, the activity in the drainable liquids in a liner will probably resemble a combination of the liquid waste streams. It is anticipated that some residual exchange capacity of the resin will be available to remove radionuclides from the water. It is concluded that:

- The activity in the free water in a disposal liner is expected to be significantly lower than the activity on the resin.
- In all probability, the activity of free water will be less than influent activity of the plant's waste streams.

The portable demineralizer discussed in section 2.3 is used at the Zion Generating Station for radwaste water cleanup. The water characteristics for the influent and effluent of this system were reported in the survey and are listed in section 2.9. (The isotopes and activities measured in the water can be found in Appendix A.) Any free water remaining after dewatering the portable demineralizer will probably have a radionuclide concentration similar to that of the system effluent.

		Inf	luent	Ef	ffluent	
BWR Sy	/stem ^a	Gross a µCi/mL	Gross β,γ μCi/mL	Gross µCi/mL	Gross B,Y µCi/mL	Radionuclides
Dresden	С	None	10-4	None	10-4	No analysis is done.
	RC	10-6	1	10-6	10-1	See Appendix A for
	RW		10-3		10-4	complete lists. Co-60, Co-58, Cs-137,
	FP		10-3		10-4	Cs-134, Mn-54. See Appendix A for complete lists.
Hatch	c	11n(b)		110		
	RC	LLD	0.1	LLD	0.001 to 0.01)	Isotones and activity
	RW			LLU	10-4 to 10-3	on resins are listed
	FP	LLD	10-3	LLD	<10-3	in Appendix A.
Peach Bottom	RC		0.05 to 0.2)	Isotopes and activity
	FP		10-4 to 10-3		}	on resins are listed in Appendix A.

Table 2.3

Gross Activities Found in BWR Waste Streams

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RW = Radwaste, FP = Fuel Pool.

^bLLD = Lowest Limit Detectable. This pertains to the sensitivity limit of the monitoring equipment. No values were specified by the utility.

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1 a	0	10	6.	-

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		Influ	uent	Effl	uent	
PWR	System ^a	Gross a µCi/mL	Gross β,Υ µCi/mL	Gross a µCi/mL	Gross β,Υ μCi/mL	Radionuclides
Farley	RW	None	5x10-4	None	5x10-6	Co-58, Co-60, Cs-137, Mn-56
Kewaunee	B RC RW FP	<lld<sup>b <lld <lld <lld< td=""><td>$\begin{array}{c} 10^{-2} \\ 10^{-1} \\ <5 \times 10^{-3} \\ <10^{-5} \text{ to } 10^{-2} \end{array}$</td><td><lld <alld <lld <lld< td=""><td>2.1x10-2 10-5 to 10-3 10-5</td><td>Na-24, F-18 Co-58, Co-60 Co-58, Co-60</td></lld<></lld </alld </lld </td></lld<></lld </lld </lld<sup>	$ \begin{array}{c} 10^{-2} \\ 10^{-1} \\ <5 \times 10^{-3} \\ <10^{-5} \text{ to } 10^{-2} \end{array} $	<lld <alld <lld <lld< td=""><td>2.1x10-2 10-5 to 10-3 10-5</td><td>Na-24, F-18 Co-58, Co-60 Co-58, Co-60</td></lld<></lld </alld </lld 	2.1x10-2 10-5 to 10-3 10-5	Na-24, F-18 Co-58, Co-60 Co-58, Co-60
Fort Calhoun	RC	<2.61x10-7	1.86			See Appendix A for
	FP		20x10-2			complete list.
Maine Yankee	RC	<1.0	1.0	<1.0	<1.0	Co-58, Mn-54, Co-60, I-13X, Rb-8X, Cs-13X
Trojan	FP	3x10-2	3x10-2			Isotopes and activity on resins are listed in Appendix A.
Yankee Rowe	FP		10 ⁻⁵ (Cs-134) 2×10 ⁻⁵ (CS-137)			See Appendix A for list of RC systems.
Zion	B RC RW FP	$ 10^{-5} \\ 10^{-5} \\ 5x10^{-5} \\ 10^{-2} to 10^{-4} $	$\begin{array}{r} 0.005 \text{ to } 0.5 \\ 0.05 \text{ to } 0.5 \\ 5 \times 10^{-5} \text{ to } 0.605 \\ 10^{-5} \end{array}$	<10-5 <10-5 <10-5	<10-5 <10-3 5x10-5_10-6	See Appendix A for complete lists.
^a Demineraliz	er System:	B = Boron Re RC = Reactor I RW = Radwaste FP = Fuel Poo	cycle Coolant,			

Gross Activities Found in PWR Waste Streams

bLLD = Lowest Limit Detectable. This pertains to the sensitivity limit of the monitoring equipment. No value was specified by the utility.

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2.8 Transport of Resins

Ion exchange resins are generally transported to and from the demineralizer tank by sluicing with a slurry pump or a hydraulic device. (3) If a resin bed is removed from service because of a large pressure drop across the bed (ΔP), it can be transported to an ultrasonic cleaner where resin fines and crud which may have clogged the bed are removed. The resin beads can be put into service in the original demineralizer tank or in another demineralizer system. This procedure is routinely used at the Dresden Nuclear Power Station.

The radionuclide loading on a spent resin bed is often larger at the top of a bed than at the bottom. When a bed is to be discarded, the resins are transported to a spent resin holding tank or directly to the disposal liner. Resins in a fluid state (i.e. during sluicing or during agitation in a spent resin holding tank) will stratify to some degree due to differences in the densities of the cation and anion resins (cation exchangers are usually more dense than anion exchangers). Resins from several beds are often stored in a single spent resin holding tank (see section 2.9). Clearly, these factors will affect the distribution of the radionuclides in the final disposal liner.

2.9 Spent Resin Holding Tank

Most nuclear power plants have one or several spent resin holding tanks which can be as large as 15,000 gallons. It is here that resins from several demineralizer beds and from various parts of the water treatment system can be mixed together. There is generally a conical bottom on the tank and a nitrogen purging system to prevent "clumping" of the resins during storage. Resins are stored here for as long as 3 to 4 years, thus allowing short-lived radionuclides to decay.

Resins being disposed of are sluiced from the spent resin holding tank to the dewatering system (a centrifuge or a disposal liner). The characteristics of the liquid remaining in a liner of dewatered ion exchange resins will be similar to characteristics of the water in the spent resin holding tank and any additional water used in the sluicing process. Most of the responding utilities did not report the water characteristics in the holding tank. The data reported are summarized in Table 2.5. The water in the spent resin holding tank is generally of neutral pH (pH = 7). The water conductivity is low although the Duane Arnold Plant reported a large range of water conductivity. The amount of TSS is variable, and there is no significant information given on the contaminants in the liquid in the spent resin holding tank. The radionuclide concentrations in the liquid are consistent with or lower than those reported for the plant's influent stream to a demineralizer. It is significant to note that all of the plants reporting indicate the presence of radionuclides with 30-year half-lifes (i.e., Cs-137, Sr-90).

To have an accurate characterization of the water remaining in a disposal liner it is necessary to analyze a portion of the water removed during the dewatering procedure. None of the plants responding nor any of the radweste personnel contacted indicated an analysis of this liquid.

Plant	pН	Conductivity µmho/cm	Gross µCi/mL	Gross µCi/mL	Radionuclides	TSS (ppb)	Contaminant
BWR							
Dresden	7	1	Unknown	Unknown	Co-60, Co-58, Cs-134, Cs-137, Mn-54	Unknown	Minimal
Edwin I. Hatch	7.3	0.1-1.0	3.0x10-10	10-3	See Table 2.8 for a list of isotopes on the resin	10-1000	Na+, SiO ₂ -
Duane Arnold	∿7	1-45,000					
PWR							
Farley	Variable	Variable	None	Very High ^a	Co-60, Co-58, Mn-56, Cs-137, H-3	Unknown	Unknown
Maine Yankee	6-8	10-50	<1.0	<10	Co-58, Mn-54, Co-60 Cs-134, Cs-137, Sr-89, Sr-90	100 ppm	<10 ppm

The Characteristics of the Water in the Spent Resin Holding Tank

Table 2.5

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aThere was no value or range specified.

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The Zion Generating Station, using the portable demineralizer from EPICOR, Incorporated for their radwaste water treatment, reported the following parameters for the influent and effluent of this water treatment system:

	Influent	Effluent
рH	4 - 8	6 - 8
conductivity (umho/cm)	10 - 200	1.0 - 10.0
gross a (µCi/mL)	5 x 10-5	<1 x_10-5
gross B, Y (µCi/mL)	$10^{-3} - 5 \times 10^{-5}$	$5 \times 10^{-5} - 10^{-6}$
TSS (ppb)	2 - 20	1 - 15
contaminants		5 ppm - SiO2

The characteristics of the effluent water of the portable demineralizer are probably a good description of any drainable liquids remaining in the liner after dewatering.

A representative of the Surry Power Station^{*} indicated that they no longer use their spent resin holding tank. The current practice involves removing a spent demineralizer from service than transferring the resins directly to a disposal liner. A number of demineralizer beds are transferred to a liner, one after another. Since more than one demineralizer bed is put in a liner, the water will be a combination of that from the various demineralizers. The characteristics of the water remaining in the liner will be dependent on the characteristics of the effluents from these systems.

2.10 Dewatering

The majority of the utilities that responded presently dewater their ion exchange resins for disposal. Table 2.6 shows that bead resins, mainly used in pressurized water reactors, are commonly dewatered in the liners. Powdered resins are mostly used in BWRs and are dewatered by centrifugation. Generally, the disposal liners capable of dewatering resins are supplied by three nuclear service companies: Chem-Nuclear Systems Incorporated, EPICOR, Incorporated, and Hittman Nuclear and Development Corporation. The liners being used for dewatered resins are constructed of carbon steel and range in size from 50 ft³ to 200 ft³. The 17H steel, 55-gallon drum is used by two utilities for the disposal of powdered resins dewatered by centrifugation. The problem of corrosion of steel by moist resins and drainable liquids is discussed in the section 3.

Two utilities reported problems with the dewatering process. Both dewater bead resins in liners equipped with underdrains. Yankee Rowe Nuclear Power Station stated that there was no visible proof of the completion of the dewatering process. A problem with shielding and the mechanical hookup was

^{*}W. Hagen, Surry Power Station, private communication to P. L. Piciulo, September 30, 1981.

stated by the Farley Nuclear Plant. In a telephone conversation with radwaste personnel at Surry Power Station, concern was expressed for these same problems. Surry aims at shipping dewatered resins with "no" free liquid, thus minimizing the possibility of more than 0.5% free liquid being found in their liners, if examined at the burial site. They also try to keep personnel exposures to a minimum by sluicing spent resins from the demineralizer tank directly to the disposal liner, thereby avoiding transferring the resins once to a spent resin holding tank and then to the disposal liner.

Table 2.6

Power Station	Dewatering Process Used	Annual Volume of Resin Disposed (ft ³)	Planning Future Use of High Integrity Containers
SWRs			
Browns Ferry	Liner with vacuum drain	30,000	Yes, when activity > 1 µCi/mL
Dresden	Solidified	540	No
Duane Arnold	Solidified	6,000	If system will accept it
E. I. Hatch	Centrifuge	15,000	Yes
Monticello	Solidified		
Peach Bottom	Centrifuge	92,700 (1980) 20,730 (1981, 6 mos)	PECO 55 gallon polyethylene drum
Vermont Yankee	Centrifuge	6,200	Yes
PWRs			
Farley	Liner with under- drain	600	Undetermined
Fort Calhoun	Liner with under- drain	100	Yes
Kewaunee	Solidified	150	Possibly
Maine Yankee	Liner with under- drain	200	Yes
Prairie Island	Liner with under- drain		Yes
Sequoyah	Liner with under- drain	1,600	Yes, if needed
Trojan	Liner with under- drain	350	No
Yankee Rowe	Liner with under- drain	80-160	Undecided
Zion	Solidified	*** ~	Being considered at corporate leve

Summary of Resin Dewatering Information

Also listed in Table 2.6 is the reported annual volume of resins for disposal. A striking feature is the difference in the amount of resin disposed of between BWRs and PWRs. Although this data base does not represent the entire industry, those utilities responding show that BWRs dispose of larger amounts of ion exchange media. This is reasonable since most of the BWRs listed use powdered ion exchange material which will be used only once (it can not be regenerated), and the service life of the precoat exchangers is short compared to deep bed demineralizers. The powdered ion exchange resin wastes will introduce more crud (particulate waste) into the final waste package because powdered resins function both as a filter and an ion exchange bed.

The survey questionnaire sought the industries' intent on using a high integrity container (HIC) for the disposal of dewatered ion exchange media. Table 2.6 gives the responses received. Most of the plants responding to this question are considering the HIC for disposal of their resin waste.

2.11 Radionuclide Loadings on Spent Resins

Several questions in the survey were aimed at finding the "normal" radionuclide loading on spent ion exchange resins. Table 2.7 lists the gross and gross β , γ activities reported for dewatered ion exchange media by the nuclear power stations. In addition, the survey requested the estimated maximum activity in a liner and the estimated maximum activity in a demineralizer bed. These data are also included in Table 2.7. Tables 2.8 through 2.11 list the radionuclides and activities measured on resin samples reported in the questionnaire received from the utilities.

Most plants did not specify any gross activity and there is no apparent trend in the gross B, y activity found on ion exchange media. However, resins from the reactor coolant cleanup demineralizers often have higher radionuclide loadings than resins from other waste streams. A liner disposed of by Maine Yankee had an estimated 125 Ci/ft³ maximum radionuclide loading. The principle radionuclides were corrosion products. A list of isotopes present in this plant's water analysis is given in Table 2.4. Assuming that the major isotope was 60Co, this loading will result in an absorbed dose of approximately 8 x 10^8 rad after 50 years. (This dose was estimated by the method described in Appendix A of Reference 4. Details of the radiation dose to ion exchange resins for loadings reported in this survey will be given in a later report. (5)) Similarly, the Hatch Nuclear Plant reported resins used in the reactor cleanup demineralizer with a maximum radionuclide loading of 41.5 Ci/ft³. As listed in Table 2.8, Cs-137 accounts for over 50% of the activity. The radiation dose from the Cs-137 having a 30-year half-life, is estimated to be greater than 3 x 10^8 rad after 10 half-lifes. Radiation doses of this magnitude could result in resin degradation and the formation of chemical species which are corrosive to container materials such carbon steel. (4,6,7,8,9) Therefore, resin degradation must be considered when estimating the environment inside a liner filled with dewatered organic ion exchange media. This topic will be discussed in section 3.

	Gross	Gross (µCi/mL)	Max. Activ. in a Liner (Ci/ft ³)	Max. Activ. in a Bed (Ci/ft ³)
BWRs	1.5.2.20			
Browns Ferry	20.20	2.47	3.73	•
Dresden	•	1.1	18	18
Duane Arnold		85	0.15	1.55
E. 1. Hatch	•	0.5 - 8ª 100 - 1000b	1.00	60
Peach Bottom		2 - 20	0.123¢	
Vermont Yankee		•	4.6-141d	-
PWRs				
Farley		1.0 - 100	3	7
Fort Calhoun	•	57.34	2.7	
Kewaunee	<10 nCi/g		-	5
Maine Yankee	<1 Ci/mL	1000-5000	125	(1500 R/hr
Prairie Island	•	Low 10-3-10-2 High 2 - 10	1	2
Sequoyah	-		.015	
Trojan	14.4 nCi/ge	<1	5.4f	5.4
Yankee Rowe		0.1 - 59	3	20
Zion			30	40

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Reported Activities on Ion Exchange Regins Disposed of by Nuclear Stations

GRange given for condensate, radwaste and fuel pool cemineralizers. BRange given for reactor coolant cleanup demineralizer. CAverage value given for 1981. dsum of values listed in Table 2.11. 4.56 uCi/g - condensate demineralizer. 140.9 uCi/g - reactor cleanup. esum of values listed in Table 2.10. fResins solidified in cement. 9Gross 8.1 of 50 uCi/cm³ reported when poor fuel was in use. *

Table 2.8

Isotope	Reactor Cleanup		Condensate Demineralize	
	Unit 1 µCi/g	Unit 2 µCi/g	Unit 1 µCi/g	Unit 2 µCi/g
Cr-51			0.832	0.7755
Mn-54		0.037	0.024	0.0100
Co-58		0.031		0.0243
Co-60	30	0.334	0.262	0.0403
Zn-65	128	1.44	0.775	0.3961
Zr-88		0.006		
Zr-95		0.048		0.0123
Nb-95		0.137	0.018	0.0191
Sb-124				0.0004
1-131			1.810	0.0033
Xe-133			0.1212	
Cs-134	547		1.06	0.0431
Cs-137	757		1.41	0.0624
La/Ba-140			0.0382	0.0046
Ba-140				0.0054

Radionuclide Loading on Powdered Resins from Edwin I. Hatch Nuclear Plant

Table 2.9

Radionclide Loading on Powdered Resins from Peach Bottom Atomic Power Station

Isotope	µCi/g
Cr-51	0.206
Mn-54	0.011
Co-58	0.105
Co-60	0.665
Zn-65	2.454
I-131	0.127
Cs-134	0.272
Cs-137	0.406
La-140	0.0238

Table 2.10

β,Y Emitting Isotope	₩Ci/g	a Emitting Isotope	µCi/g
Cr-51 Mn-54 Co-57	<0.121 2.78 0.061	Pu-239, 240 Pu-238 Am-241	1.14x10-2 2.96x10-3 5.97x10-5
Co-58 Co-60	0.532	Cm-242, 243 Cm-244	7.32x10-5 5.77x10-6
Fe-55 Fe-59	38.6 <0.059		
Ni-73 Zn-60	15.4 <0.067		
Sr-89 Sr-90	0.317		
Ru-106 Ag-110m	<0.195		
Sb-124 Sb-125	<0.0178 <0.165		
Cs-134 Cs-137	5.13 12.6		
Ce-141 Ce-144 U-235	<0.0132 0.349 <3.85x10-6		
U-238	<1.21x10-6		

Radionuclide Loading on Resin Fines from the Spent Resin Holding Tank at the Trojan Nuclear Plant

Table 2.11

Radionuclide Loading on Powdered Resins from Vermont Yankee Nuclear Power Plant

Isotope	Reactor Cleanup µCi/g	Condensate Demineralizer µCi/g
Mn-54	0.128	5.98
Co-58	0.074	5.88
Co-60	0.924	30.5
Zn-65	0.461	20.3
Zr-95		11.1
Tc-99m		0.419
I-131		0.535
Cs-134	0.702	17.8
Cs-137	2.27	48.4

As discussed earlier, the resins binding radionuclides may be more randomly distributed in a disposal liner than they are in the demineralizer bed because of numerous sluicing operations and sparging in the spent resin holding tank. However, there are two procedures being used which can result in a less homogeneous distribution of radionuclides in a disposal liner. A representative of the Surry Power Station described their practice of transferring the ion exchange media from the demineralizer tank directly to the disposal liner. Spent ion exchange beds are taken out of service and held until there are enough beds to fill a liner. They are then transferred one bed after another to the disposal liner. Since more than one demineralizer bed is put in a disposal liner, the resins from the different beds are in the liner and, hence, radionuclide loadings will be stratified.

Plants using the EPICOR portable demineralizer can dewater and ship the liner when it is removed from service. Since there is no sluicing operation of the spent resin, it is expected that the radionuclide loading in the liners is concentrated toward the top portion of the bed. The Zion Nuclear Plant uses this Epicor portable demineralizer containing a stratified mixed bed (one part anion exchanger and one part cation exchanger) of 90 ft³. Although the radionuclide loading may be low in this case, radiation damage may result from the localized accumulation of radionuclides in one region of the bed.

2.12 Storage of Resin Waste at Plants

Spent ion exchange resins are most often stored in the spent resin holding tank, as discussed in section 2.9. Generally, when a utility prepares to process its resin waste for disposal, the resins are dewatered and shipped within a couple of weeks. The utilities that solidify their resin waste were not requested to respond to the questions on this subject. The BWRs that did respond indicated that resin wastes are shipped soon after dewatering. Prior to shipment disposal containers are checked for free liquid, container integrity and the necessary dose rate measurements for transportation. Similarly, most PWR plants ship their resin waste soon after dewatering. Fort Calhoun Station indicated indoor storage (temperature 40° to 90°F) for a month, and Sequoyah Nuclear Plant stored resin waste in the transportation cask for as long as two months outdoors (60° to 90°F). The Sequoyah Plant has not been in operation long and they indicated that the only resin waste shipped has been that in the EPICOR portable demineralizers. Two utilities (Maine Yankee Atomic Company and Prairie Island Nuclear Plant) indicated indoor storage of nonsolidified resins for as long as one year (temperature <90°F). Container integrity is checked for corrosion or leakage periodically and just prior to shipment.

The Duane Arnold Energy Center stores resins indoors (70-100°F) for approximately 1 month and containers are checked for pressure changes. The following comment was made about gas buildup in their drums:

[&]quot;W. Hagen, Surry Power Station, private communication to P. L. Piciulo, September 30, 1981.

"When we were dewatering resin, we found that we would have gas built up in drums if we did not put a small amount of formaldehyde in each drum. The gas came from organic growth in the resin, the floor drains are sources of many substances, the gas was not from (radiolytic) resin breakdown."

Now all their resin waste is solidified and shipped within two or three days. This experience indicates the potential problem of gas generation from biodegradation. The need for a general practice of adding a biocide to radwaste must be evaluated. The long-term effects of the additive on the resin, the container material and the ultimate release of the biocide into the environment must be considered.

The following statements describe the utilities' practice of examining dewatered, spent ion exchange resins stored on the plant site:

- The survey responses did not indicate any quantitative utility experience of the release of liquids from dewatered ion exchange resins, nor associated changes in the liquid pH.
- No evidence of radiation damage to the resin was indicated.
- No utility checked for temperature changes in a liner of resins.
- Container integrity is generally checked to ensure no leakage.
- Gross radiation activity is checked by some of the utilities responding.

2.13 Disposal Sites

The majority of the utilities responding to the survey ship their resin waste to the Barnwell, South Carolina burial site. This is consistent with their locations in the five U.S. Nuclear Regulatory Commission regions shown in Figure 2.1. [Five in the Northeast Region (I); four in the Southeast Region (II); six in the Midwest Region (III), and two in the Western Regions (IV and V).] Several plants ship part of their radwaste to Hanford, Washington, and/or Beatty, Nevada. One plant, Trojan Nuclear Plant located in Prescott, Oregon, ships all its waste to Hanford, Washington, for shallow land burial. The cost of transportation is a major factor in the choice of disposal sites.

It is important to note that the majority of the nuclear power stations and the Barnwell burial site are located in humid regions of the United States. The precipitation at Barnwell, South Carolina is 118 cm/yr.(10) Since it is of major concern to keep water out of the trenches, it is reasonable to avoid the possible accumulation of water on a resin container before it goes into a trench. Also, to ensure drainage of precipitation, the container design should minimize the possibility of water accumulating on the surface of the disposal liner. The avoidance of water accumulation on a disposal container will help mitigate any corrosive attack.



Figure 2.1 U.S. Nuclear Regulatory Commission regions are indicated by Roman numerals and plants responding to the survey are encircled.

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2.14 Summary

Based on the information obtained in this survey and other surveys of nuclear power plants, the characteristics of any drainable liquids remaining in a liner of dewatered ion exchange resins cannot be described accurately. There are large variations in the waste streams within a plant and also from plant to plant. The variables affecting the ion exchange resin waste, generated by nuclear power plants, and the subsequent waste container, filled with dewatered resins, are iilustrated by the following points:

- Both bead and powdered ion exchange resins are being dewatered and disposed of in liners.
- The pH of the liquid in a liner can vary in the range from 2 to 11.
- There are large variations in the amount of suspended solids and contaminants reported.
- The radionuclide concentration in the free liquid in a disposal liner is expected to be lower than that on the resin.
- The activity in the free water will probably be less than the influent activity of a plant waste stream.
- Most plants combine resins from different demineralizers in a spent resin holding tank.
- Radionuclide loadings on spent resins vary among demineralizers in a plant and from plant to plant.
- Spent resins are generally contaminated with activated corrosion products but many plants indicated the presence of fission product isotopes (i.e., Cs-137).
- There is uncertainty in the spatial distribution of radioactive isotopes in a disposal liner.
- Resins are often stored for periods of one year or more in a spent resin holding tank.
- Dewatered spent resins are generally not stored very long on the plant site.
- Microorganisms, leading to gas generation due to biodegradation, can readily find their way into a liner.
- Portable demineralizers are being used and the nature of the liquid remaining in the liner after dewatering will resemble the system's final effluent.

3. ION EXCHANGE RESIN STABILITY

3.1 Introduction

The survey of operating nuclear power stations has revealed the likelihood of large variations in the chemistry of any free liquids remaining in a liner of dewatered ion exchange resins. It is also evident that the radionuclide loading on resin waste from the nuclear plants follows no predictable trend. Very high radionuclide loadings have been reported. For example:

- Maine Yankee Atomic Power Plant: 125 Ci/ft³; mainly activated corrosion products.
- Edwin I. Hatch Nuclear Plant: 41.5 Ci/ft³; over one-half of this activity is from fission product Cs-137.

As indicated in section 2.11, these loadings will produce radiation doses in excess of 10^8 rad to the resin and may result in extensive radiation damage. Thus, the possible degradation of ion exchange resin waste and the effects of the degradation products on the waste container should be considered.

This chapter will summarize the literature regarding studies of the degradation of ion exchange media. Gangwer, et al.(11) have published a review describing the radiation induced changes in the physical and the chemical properties of ion exchange materials. However, work directed toward the problems which exist in the management of nuclear waste containing ion exchange resins are of particular interest. A number of studies,(4,6,7,8,9) which are reviewed here, have emphasized the following specific areas where radiation effects might be important:

- pH changes,
- gas generation,
- resin bead agglomeration, and
- corrosion in contact with ion exchange media.

All of these can effect the stability of the ion exchange resin waste package. Additionally, preliminary results of the analysis of a disposal liner containing resin waste from the cleanup operations at Three Mile Island (TMI) are reviewed. The chemical and physical decomposition of ion exchange resins and the biodegradation of resin waste are considered. Conditions causing the release of water from ion exchange resins were discussed with manufacturers of organic ion exchange resins. The companies contacted were:

- Dow Chemical, U.S.A.
- Diamond Shamrock Corporation.
- Ionac Chemical Corporation
- · Rohm and Haas.

3.2 Chemical and Physical Stability

No direct evidence was provided by the manufacturers surveyed regarding the degradation of organic ion exchange resins over long periods of time. Degradation of ionic functional group and counterion is possible, but no physical breakdown of the resin is expected. Strong acid cation exchangers are generally more stable than strong base anion exchange resins in regard to the loss of ion exchange capacity. The quaternary ammonium group of a strong base anion exchanger will change (at ambient temperature) to a weakly basic tertiary amine exchange group with little change in total exchange capacity of the resir.(12) For example,



Strongly Basic Anion Exchanger Weakly Basic Anion Exchanger

Carbon dioxide from the air can react with the hydroxyl group of the strong base resin converting it to the carbonate form. Regeneration, which is not an option in disposal, will restore the resin to its original form.

Strong oxidizing agents such as boiling nitric acid will rapidly digest organic ion exchange reins. Oxygen or air at temperatures above 175°C (350°F) will also degrade the polymer. However, severe conditions such as these are unlikely in a liner of dewatered resins. Slower degradation with oxygen can be catalytically induced by ions of iron (Fe), manganese (Mn), and copper (Cu).(13) The demineralizers in the power plants efficiently remove the radioisotopes of iron and mangenese, present as activated corrosion products in the waste streams. The survey, reviewed in section 2, showed large variations in the contaminants present on ion exchangers and the pH of the water associated with the resins; which are factors affecting the chemical degradation of organic ion exchange resins. The stability of the C-N bond in anion resins is enhanced at low pH. In the case of cation resins, the C-S bond is less stable with respect to hydrolysis at low pH. (13) Scission of the functional groups of the resins will result in a decrease of the water retention capacity of the resins because much of the water bound to a resin is the water of hydration of the functional group and counter ion. If the functional group is released from the resin, some of the bound water will also be released, adding to the quantity of free liquid in a disposal liner and the chemical characteristics of this liquid. For example, the release of acidic species from cation exchangers will result in a decrease in the pH of the liquid. Acidic solutions

solutions are generally corrosive to carbon steel, a material often used for resin disposal liners.

Organic ion exchange resins are best stored between 32°F and 90°F. Freezing will not destroy the resins provided the material is allowed to thaw slowly. Rapid thawing can result in cracked and broken resin beads due to osmotic shock. However, it is unclear as to the effect of these phenomenon on the long-term stability of the resin waste. Powdered resins are merely ground resin beads and no distinctive differences could be found on the degradation of bead and powdered resins.

3.3 Radiolytic Effects on Ion Exchange Resins

Degradation of organic ion exchange resins used for water treatment in the nuclear power industry can be caused by radiation damage. Degradation may be either direct, resulting in decomposition of the organic material, or indirect, caused by species formed in the radiolysis of water. Strongly acidic cation exchange resins are expected to first undergo decross-linking followed by a decrease in exchange capacity. The decrease in the percent cross-linking will result in an increase in moisture retention capacity. Scission of the sulphonic acid groups causes the loss in exchange capacity and the presence of free sulfuric acid. Strongly basic anion exchange resins are generally less resistant to ionizing radiation than are the cation exchangers. The loss of exchange capacity due to scission of the functional group is prominent, resulting in free nitrogen compounds such as amines. Changes in the degree of cross-linking in anion exchangers are secondary.

3.3.1 pH Changes

Degradation products formed on the irradiation of organic ion exchange resins result in a change in the pH of an aqueous phase associated with the material. Measurements of pH reported in recent tests on ion exchangers used in the nuclear industry are listed in Table 3.1. Cation exchange resins having sulfonic acid functional groups are of major concern due to thier extensive use in the nuclear industry. These lead to large decreases in pH, producing solutions which can be highly corrosive to liner material (such as carbon steel).

Experiments reported in the literature (4,6,7,8) were done using cation exchangers or anion exchangers separately. However, when organic ion exchange resins from nuclear power plants are disposed they are generally mixed. It has been shown that resins in mixed beds can absorb degradation products. (14,15) Amine compounds released in the degradation of anion exchange resins can be absorbed by cation exchangers in the system. Likewise, anionic species released by degradation of cation exchange resins can be absorbed by remaining anion exchange resin capacity. The effect of this phenomenon on pH changes in liquid associated with dewatered ion-exchangers is unclear. One possible scenario is the neutralization of acidic and basic species released in the degradation of the mixed system. This may result in a mixture which is less corrosive to carbon steel than either of the degraded constituents. The results compiled in Table 3.1 used bead type ion exchange material. Powdered ion exchange resins are widely used in the nuclear power industry and have not been given any attention regarding their radiation induced degradation. These materials are commonly used in a mixed bed system to provide a floc like coating which will belve as a filter medium (see section 2.2). The powdered resins generally have a larger moisture retention capacity then the bead counterparts. These factors may or may not play a role in the degradation of powdered ion exchangers, nevertheless, the effects of ionizing radiation on powdered resins needs to be examined.

The cleanup operations at Three Mile Island have provided some information on pH changes in liners of ion exchange resins. Table 3.2 lists data, obtained from the dewatering tests of five EPICOR-I liners, fifteen EPICOR-II DF (second stage) liners and seven EPICOR-II DS (third stage) liners used at TMI. The data indicate that the pH of the water removed in a second dewatering was close to neutral.⁽¹⁶⁾ The pH range of the final effluent from these liners was 4.50 to 8.49. The pH of the water removed in a second dewatering performed 6 to 20 months after the liner was taken from service was 5.97 to 7.67. In all but two cases, the pH of the water from the second dewatering was closer to pH 7 than observed in the first dewatering. The gross β , γ activity ranges from <1.2 x 10⁻⁶ to 3.5 x 10⁻¹ µCi/mL which is comparable to radioactivity levels in operating plant water streams, but in this cause, the major isotope is Cs-137. Additionally, the contents of the liners which are unknown, may play a major role in the resulting pH change.

One prefilter (EPICOR II, first-stage liner) used in the water cleanup at TMI was taken to be analyzed by Battelle Columbus Laboratories. (17,18) The EPICOR-II liner, designated PF-16, contains a layer of zeolite inorganic ion exchange media, an organic cation exchange resin layer, and a layer of mixed organic anion and cation exchangers. The liner is constructed of carbon steel with an epoxy coating painted on the interior. This particular liner was selected because of the high curie loading (~ 1200 curies gross B,Y) on the resin and the low pH of the final effluent, pH=2.79. The prefilter was removed from service after processing 8,250 gallons of water in March, 1980, and examined approximately 15 months later. A gamma scan of the liner showed that the majority of the activity resulting from Cs-137 was on the upper portion of the bed. Droplets of moisture found on the manway cover had a pH measuring 2 to 3. There were 2 liters of liquid having a pH = 5.33 removed from the bottom of the liner. The pH of the condensation found in the liner is similar to that of the liquid passing through the liner during operation. However, there is clearly a change in the pH of the free water taken from the bottom of the liner.

The laboratory experiments and the analysis of PF-16 indicate that irradiation of ion exchange resins with both internal and external radiation sources results in pH changes in associated liquids. The buffering effects of mixtures of anion exchangers and cation exchangers remains unclear.
Resin	Dose (Rad)	рH	Comments	Ref.
Amberlite [R-120(H+)	0 7x107 4.4x108	3.4 1.5-1.6 3.5	a,c,f,1 a,d,1	6
Amberlite IR-120(NH4 ⁺)	0 7x10 ⁷	8.5 2.3-2.5	a,c,g,1	5
Amberlite IRA-400(C1-)	0 4.4x10 ⁸	4.6	a a,d,1	6
Dow SBR-OH (borate)	10 ⁸ 10 ⁹ 10 ⁹	8.5-9.0 8.0-8.5 7.5-8.0	b,e,m b,e,m b,e,m	7
Dow HCR-S (Na ⁺)	108 3×108 5×108 109 5×109	2.5-3.0 4.0-4.5 2.5-3.0 4.0-4.5 4.0	b,e,m b,e,m b,e,m b,e,m b,e,m	7
IRN-77 (H*)	0 107 1.25x10 ⁷ (e ⁻) 3x10 ⁷ 4.6 x10 ⁷ (e ⁻) 10 ⁸ 3x10 ⁸ 10 ⁹	3.5 2.5 2.0 2.0 1.5 1.0 0.6	a,c a,c,n a,c,o a,c,n a,c,n a,c,n a,c,n	•
IRN-77(Na*)	0 107 3x107 108 3x108 109	6.8 4.7 3.6 2.9 2.1 1.3	a,c a,c,n a,c,n a,c,n a,c,n a,c,n	4
IRN-77(H*)	0 0 3×108 3×108 3×108	2.76-3.16 3.11-3.28 3.24-3.29 1.55-1.67 1.32-1.52 1.46-1.65	a,h,n a,i,n a,k,n a,h,n a,i,n a,t,n	8
IRN-77(Na*)	0 0 3×108 3×108 3×108	3.51-3.65 3.42-3.52 3.29-3.49 2.35-2.80 2.22-2.48 2.42-2.45	a,h,n a,i,n a,k,n a,h,n a,i,n a,h,n	8

Table 3.1	_		-	
IADIA 1	T -		 -	
		-		

pH Changes on the Irradiation of Organic Ion Exchange Resins

apH measured in supernate of a mixture of 2 g of resin and 10 mL of deionized water.

bpH measured by placing samples of beads on narrow range pH paper.

CSample irradiated in Pyrex tubes, drip dry resins. dSample irradiated in aluminum tubes, drip dry resin. eSample irradiated in stainless steel tubes, drip dry resin. flrradiations were done on sample tubes containing 20 g IR-120 (H⁺ form) at the bottom and 2 g IP-120 (NH4⁺) on top; pH was taken from the bottom 2 g aliquot.

girradiations were done on sample tubes containing 20 g IR-120 (NH4⁺ form) at the bottom and 2 g IR-120 (H⁺ form) at the top; pH was taken from the bottom 2 g aloquot.

hSample in Pyrex tube, percent moisture in resins was 55.

Sample in Pyrex tube, percent mostture in resin was 27.

Sample in Pyrex tube, percent mosture in resin was 27. KSample in Pyrex tube, percent moisture in resin was 14-13. IGamma irradiation, 6000, flux 1.2 x 10⁵ R/h. ^mGamma irradiation, 6000 source, flux 5 x 10⁶ R/h. ^mGamma irradiation, 6000 source, flux not specified. 02.2 MeV electron beam, flux 5 x 10⁷ R/h.

*	1. 18		-	-	
1.2	n I	P	- X.	1	
1.04				8 fee	

		Last Eff	luent		Water Removed			
Liner Code	pH	Gross B,Y µCi/mL	Cs-137 µCi/mL	∆⊺ª	Gallons	pН	Gross βγ μCi/mL	Cs-137 µCi/mL
P-13 P-14 P-15	6.96 7.47 6.68	5.3x10-4 1.7x10-4 5.8x10-6	6.0x10-5 1.1x10-4 1.7x10-6	865	13 38 30	7.10 7.35 7.48	1.60×10-4 9.60×10-5 2.04×10-5	1.6x10-4 8.7x10-5 1.3x10-6
D-21 D-22 DF-1 DF-2	7.08 5.33 5.87	8.3x10-5 <1.2x10-6 1.1x10-1 2.5x10-1	6.0x10-3 3.9x10-7 6.8x10-4 1.3x10-3	8 5 20 19	40 20 5 5	6.98 6.93 6.4	5.75x10-3 6.43x10-6 5.02x10-3 6.29x10-4	3.0x10-3 6.9x10-6 3.2x10-3 1.8x10-4
DF - 3 DF - 4 DF - 5 DF - 6	8.10 8.49 7.11 6.37	1.6x10-2 4.5x10-2 3.5x10-1 3.8x10-2	7.4x10-2 3.8x10-2 2.3x10-1 9.5x10-4	19 19 19 18	5 3 1.5	7.67 6.49 7.54 7.66	1.29x10-2 5.98x10-5 2.46x10-1 1.14x10-2	6.5x10-5 2.0x10-1 7.1x10-3
DF-7 DF-8 DF-9 DF-10	7.56 7.66 5.56	4.9x10-3 1.2x10-2 3.4x10-2 4.5x10-4	4.2x10-4 1.9x10-3 1.3x10-5	15 15 14 14	3 7 4.25	6.80 6.41 6.26	6.89x10-4 4.22x10-4 2.76x10-4 3.86x10-4	1.2x10-4 1.3x10-4 9.6x10-5
DF-11 DF-12 DF-13 DF-14	6.93 5.24 5.53 4.50	4.8x10-3 3.9x10-2 3.8x10-2 3.4x10-3	5.1×10-3 3.7×10-3 1.5×10-3 4.0×10-6	12 12 11 11	6 6 5 4	6.21 6.52 6.40 5.97	1.06x10-4 2.4x10-3 2.55x10-4 2.57x10-5	6.2x10-5 6.2x10-4 7.8x10-5 1.8x10-5
DF-15 DS-1 DS-2 DS-3	6.17 5.68 5.18 6.21	5.8×10-3 1.6×10-4 8.8×10-2 4.8×10-3	1.7x10-4 <5.6x10-6 3.5x10-3 1.5x10-4	6 19 18 16	5 19 26 18	6.24 6.20 6.08 6.59	5.06x10-4 1.51x10-5 2.82x10-4 4.61x10-5	1.3×10-4 1.9×10-6 8.5×10-5 1.2×10-5
DS-4 DS-5 DS-6 DS-7	6.92 5.28 5.34 5.04	<1.2x10-6 6.5x10-6 1.6x10-4 9.6x10-6	<4.7x10-0 <5.2x10-6 3.6x10-6 <5.1x10-7	16 15 12 6	15 18 15 5	7.55 6.19 6.13 5.98	4.52x10-2 6.51x10-5 9.54x10-5 3.58x10-5	7.9x10-5 3.5x10-5 7.9x10-6 1.5x10-5

Epicor Liner Dewatering(12)

^aThe period of time in months between the first and second dewaterings.

3.3.2 Gas Generation

The radiolytic degradation of organic ion exchangers will result in gaseous products. (4,7,11,12) Table 3.3 summarizes the yields of gaseous products reported in the literature for the irradiation of various resins. (11) Hydrogen and carbon dioxide are the major gases produced on radiolysis. Gaseous products resulting from the irradiation of cation exchangers are: H₂, CO₂, CO, SO₂, O₂ and CH₄. The irradiation of anion exchangers produced: H₂, CO₂ CO, N₂, N₂O, and NO. The water content of the resin will effect the gaseous products. In the irradiation of dry cation ion exchange resins SO₂ will be liberated, however, sulfur dioxide gas is not produced in water swollen resins, rather acids are formed on dissolution of SO₂ in water. The yield of hydrogen is larger in wet resins then in dry. This is probably due to the radiolysis of water. (20)

Table 3.3

G-Values^a for Gaseous Product Formation During the Radiation Decomposition of Ion Exchange Resins

Resin	Ionic Form	Irradiation Condition	G(H2)	G(S02)b	G(C0 ₂)	G(CO)
Dowex 50W x4	H*,Na* and 0.1 N HC1	Air-dry	0.1 .			
Dowex 50W x 10	H*	Dry	0.026	0.087	0.035	0.009
KU-2 x S	н*	Dry	1.1		0.06	
Zeo-Karb 215	н*	Dry	0.051	0.001	0.019	
Dowex 50W x 10	н*	12-47% water	0.04 to 0.12	0.14	0.023	0.022
Dowex 50W x 10	L1*	Dry	0.001	0.26	0.007	0.002
KU-2 x 8	Na ⁺	Dry	1.0		0.03	***
Dowex 50W x 10	L1+	Swollen	0.095	0,006	0.019	0.009
KB-4P-2	н*	Swollen	1.22		0.60	0.39
Dowex 50W x 10	н+	Swollen	0.095	0.006	0.019	0.027
KB-4P-2	Na *	Swollen	3.10		0.09	
Zeo-Karb 215	H+	Swollen	0.12	0.005	0.046	0.005
Zeo-Karb 215	н*	Immersed in water	1.7	0.002	0.43	
Dowex 50W x 10	н*	Immersed in water	1.7		0.41	
Dowex 50W x 10	Li*	Immersed in water	1.3		0.41	•••
Dowex 1 x 4	NO3"	Air-dry	0.09			0.02
Dowex 11	NO3-	Air-dry	0.10		0.06	0.01
Dowex 1 x 4	NO3-	In 7N HNO3	0.02		0.6	

 $^{\rm a}{\rm G}\textsc{-value}$ is defined as number of molecules produced for 100 eV absorbed radiation. $^{\rm b}{\rm G}\textsc{-values}$ for the lowest absorbed dose.

McFarland(7) has studied gas productin on the irradiation of organic ion exchange resins used in the nuclear industry. The strong acid cation exchanger, Dow HCR-S, in the sodium form, and the strong based anion exchanger, Dow SBR-OH, in the borate form were examined under Co-60 irradiation. The pressure buildup was monitored and is apparently a linear function of the accumulated dose for both cation and anion exchangers. There appears to be an initial minimum dose which must be achieved before the linear portion of the data is reached. This threshold is not discussed in the report. The threshold for gas generation for the anjon exchanger is 4.7 x 107 rad whereas for the cation exchanger it is 8 x 107 rad. (4,7) A dose of 7.9 x 108 rad was required to reach a gas pressue of 200 psi (13.6 atm) for anion exchange resins whereas, a dose of 2.6 x 10^9 rad to the cation exchanger produced the same pressure. Activated charcoal, treated with sodium borate prior to irradiation was also examined for gas production. The results are markedly different from the resin experiments. There is rapid increase in pressure after an apparent threshold of 1.6×10^8 rad. The pressure in the vessel stops increasing at 5 psi and a dose of approximately 1×10^9 rad above which the pressure is slightly less than 5 psi. The samples were irradiated to 5 x 109 rad.

Analysis of the gaseous samples and the maximum amounts of each compound produced were normalized to one gram of resin. The results are listed in Table 3.4. The values for the hydrocarbons produced were taken from Figures 12, 13 and 14 of Reference 7. The total gas yields reported are: 12.6 cc/gm resin (7.9 x 10^8 rad) from the anion exchangers and 6.8 cc/g resin (2.5 x 10^9 rad) from the cation exchangers. It was suggested that branched chain and/or unsaturated hydrocarbons may also have been produced in the capsule containing anion exchangers and receiving the maximum dose.

The prefilter demineralizer PF-16, used in the TMI cleanup and described in Section 3.3.1, was analyzed for gas composition.(17,18) It was estimated that the liner contents received an integrated dose of 9 x 10⁷ rad in the 15 months since it was removed from service. The gas analysis of the liner on examination by Battelle Columbus Laboratories is given in Table 3.5. There is a major change in the hydrogen present and a depletion of oxygen, assuming that the gas content initially was that of air (see Table 3.6). The observed gases are consistent with the findings of other laboratory experiments.(7,9)The gas composition in PF-16 was not fully explained, but it is attributed to a combination of air, gas production via radiolysis, and gas from desorptiondissolution processes during shipment.(18)

Table 3.4

Gas	Resina	Amount of Gas cc/g of resin	Dose ^b rad
H2	Anion	6.8	7.9 x 10 ⁸
	Cation	2.8	2.5 x 10 ⁹
CO2	Anion	1.1	7.9 x 10 ⁸
	Cation	0.83	2.5 x 10 ⁹
CO	Anion	1.3	7.9 x 10 ⁸
	Cation	1.0	2.5 x 10 ⁹
0 ₂	Anion	0.56	7.9 x 10 ⁸
	Cation	0.71	2.5 x 10 ⁹
N ₂	Anion	0.68	7.9 x 10 ⁸
CH4	Anion	0.81	7.9 x 10 ⁸
	Cation	0.12	2.5 x 10 ⁹
C2H6	Anion	1.4 x 10-2	7.9 x 10 ⁸
	Cation	2.5 x 10-2	3 x 10 ⁹
C ₃ H ₈	Anion	5.5×10^{-4}	7.9 x 10 ⁸
	Cation	7.4 × 10^{-4}	3 x 10 ⁹
C4H10	Cation	7.8 x 10 ⁻⁴	3 x 10 ⁹
Sulfur gases	Cation	0.09 µg S/g	2.5×10^9

Gas Generation Experiments(7) Maximum Yields Observed

Anion exchange resin: DOW SBR-OH (Borate form). ^bDose rate: approximately 4.8 x 10⁵ rad/h.

.

Tahl	a	2	5
Iavi	e	5.	2

Components	Volume Percent			
N2 H2 C02 Ar 02 C0	$\begin{array}{r} 80.6 \\ 12.4 \\ \hline + 0.2 \\ 5.52 \\ \hline + 0.06 \\ 0.96 \\ \hline + 0.05 \\ 0.20 \\ \hline + 0.02 \\ 0.20 \\ \hline + 0.02 \end{array}$			
Hydrocarbons	<0.1			
Hydrocarbon	Parts Per Million by Volume			
Methane Ethylene & Acetylene Ethane Propylene Propane Iso-butane n-Butane Hydrogen sulfide	500. + 2.5 0.7 + 0.1 42. + 4 <0.1			
Sulfur dioxide Unknown compounds	<10 <10 <20			

PF-16 Gas Analysis(16)

T - L 7		-	~
120	0		-
1 au			0
		~ •	-

Constituent	Content (percent) by Volume	Content (ppm) by Volume
N ₂	78.084 + 0.004	
02	20.946 ± 0.002	
C02	0.033 + 0.001	
Ar	0.934 ± 0.001	
Ne		18.18 + 0.04
Не		5.24 + 0.004
Kr		1.14 + 0.01
Xe		0.087 ± 0.001
H2		0.5 -
CHA		2
N20		0.5 + 0.1

Components of Atmospheric Air(21)

3.3.3 Resin Bead Agglomeration

The observation of physical changes such as bead cracking and discoloration, and resin bead agglomeration are evidence of radiation damage to organic ion exchange resins. The major concern of radiation induced degradation of ion exchange media is the possible release of water and the release of chemical species corrosive to the disposal vessel.

Pillay(6) addressed agglomeration by measuring the flow rate of water through columns containing ion exchangers before and after gamma irradiation. Samples of Amberlite IR-120 (cation exchanger), Amberlite IRA-400 (anion exchanger) and IONSIV-IE-90 (synthetic zeolite) were assembled either individually or in layers in aluminum tubes and the flow rate of water through the bed was measured. The samples were then irradiated to a cumulative dose of 2.2 x 109 rad (dose rate: 4.5 x 106 R/hr). After irradiation the flow of water through the columns was recorded. There was no flow of water through any of the columns containing the organic ion exchange resin. Only the sample of synthetic zeolite showed no change in flow of water after irradiation. The flow was initiated in all but one of the remaining samples by submersing the columns in a tank full of water before the flow rates were measured. The collapse of gas pockets and bed channeling were suggested to explain the reestablished flow through the columns. The anion exchanger, IRA-400, was the only sample which did not allow water to pass through, after irradiation and soaking in water.

Work at Brookhaven National Laboratory⁽⁴⁾ showed no severe agglomeration on gamma irradiating Amberlite IRN-77(Na⁺), IRN-77(H⁺) and "C-66%" (a cation exchanger) to a dose of 10^8 rad. However, as the dose increased to 10^9 rad, the samples become more agglomerated. On addition of water, the agglomeration was reversed, although IRN-77 (H⁺) formed a "gel-like" solution.

The physical properties of the irradiated samples examined by McFarland(7) are summarized in Table 3.7. Anion exchangers show the release of liquids at a dose of 10^8 rad along with fracturing of the resin beads. The smell of amines is indicative of functional group degradation in anion exchange resins. No additional liquids were observed on irradiation of the cation exchangers to a dose of 5×10^9 rad. Microscopic examination of the resin beads and the sticking together of resin beads. The addition of water to the resin samples showed no significant changes in the anion resin beads. However, water added to the cation exchangers irradiated from 3×10^8 to 5×10^9 rad produced a "floculent red-brown precipitate."(7) The chemical composition of this material was not reported.

A core sample was taken from demineralizer PF-16 (described in section 3.3.1). The sample extended 16 inches into the top of the bed of exchange media. The exact makeup of the demineralizer bed is unknown although it does consist of layers of both inorganic and organic ion exchange media. The top five inch section was found to be dry and free flowing, containing irregularly shaped granular particles. The next eight-inch section consisted of regularly shaped translucent spherical particles somewhat mixed with the top layer. Near the bottom of this region opaque spherical particles were observed and there was apparent agglomeration and moisture. The final section showed agglomerates of opaque spherical particles and appeared to have a gelatinous consistency. (18)

Those sections containing spherical particles are likely to be either inorganic or organic ion exchangers or possibly a mixture of both. However, this analysis revealed agglomeration and the apparent release of liquid from ion exchange media which received radiation from an internal source (i.e. 137Cs loading) to a dose of < 10^8 rad.

Table 3.7

Physical Changes in Irradiated Resins(7)

Resin	Dose (rad)	Bead Appearance	Comments
Anion	108	Some fractured beads, shedding layers of mate- rial transparent and slightly brown.	Little liquid present, smell of amines.
	109	Fractured beads, rough scaling surfaces.	Flowing slurry of liquid and resin.
Cation	108	Beads slightly darkened.	No additional liquid, no noticeable odor.
	3 x 10 ⁸ 5 x 10 ⁸	Beads darkened but not black.	
	10 ⁹ 5 x 10 ⁹	Fractured beads, dark black, beads cling together or to surfaces.	No additional liquid found.

3.3.4 Corrosion of Steel

A number of studies (4, 6, 7, 8) have shown that the radiation induced degradation of organic ion exchange material in contact with a metal surface results in corrosion of the metal.

Pillay⁽⁶⁾ used moist forms of IONSIV-IE-95 (synethetic zeolite), Amberlite IR-120 (cation exchanger) and Amberlite IRA-400 (anion exchanger) to examine the corrosion of mild steel (ASTM-1018). Samples consisted of a single resin type or stratified combination of resins in aluminum tubes with a mild steel coupon imbedded in the ion exchange material. The samples were exposed to a $^{60}\mathrm{CO}$ gamma flux and to the fission product gamma spectrum of a research reactor in the shutdown mode. Table 3.8 summarizes the observations of this corrosion study.

The sample containers, made of AISI type 304 stainless steel, used in the McFarland(7) experiments were examined for corrosion effects one year after sample irradiation. The nominal composition of type 304 steel is: 18-20% Cr, 8-10.5% Ni, max. 0.08% C, max. 2% Mn, Max. 1% Si, Max. 0.045% P, max. 0.030% S, balance Fe. The results of these tests are complied in Table 3.9. Examination of the interior surfaces by low power microscopy and scanning electron microscopy (SEM), metallographic examination of both radial and axial sections and mechanical tensile testing to determine yield strength, ultimate-tensile strength and elongation at fracture were used to test each of the samples. Large percentages of sulfur, nickel and chromium were discovered by x-ray analysis of deposits in the pits. Since sulfates were present in the water extracts of cation exchange resin samples it is likely that the deposits contained sulfates of nickel and chromium. It is suggested that the environment contains sulfuric acid.

The conclusions drawn from the corrosion study were:(7)

- The irradiated anionic resin and its products of decomposition did not significantly attack the Type 304 stainless steel containers.
- The irradiated cationic resin and its products of decomposition caused significant localized corrosion of the Type 304 stainless steel containers. The attack was in the form of etching under surface deposits, and pitting. The pits were of different sizes, including some large and deep depressions.
- Although the corrosion attack did not cause loss of strength of the test cylinders, the localized nature of the attack might cause perforation of the walls at longer exposures.

BNL(4) has studied the corrosion effects of IRN-77 (H⁺) and IRN-77 (Na⁺) cation exchangers on mild steel and type 304 stainless steel coupons. The corrosion of mild steel was increased by irradiation. The hydrogen form of IRN-77 being more corrosive then the sodium form. No corrosion was observed for stainless steel although the contact time was only 3 days (significantly shorter than that in McFarland's(10) experiment) and the dose was 3×10^8 rad.

The effects of moisture content of organic ion exchangers on the radiation induced corrosion of mild steel (ASTM 1020) coupons were examined by BNL.(8) Table 3.10 summarizes the corrosion of mild steel measured as weight loss of the coupons. The following observations were reported:

- Without exception, corrosion of mild steel is decreased in resins of lower moisture content. At the lowest moisture content, there was no obvious evidence of coupon corrosion in either the irradiated or unirradiated specimens.
- In all cases where corrosion was observed in the irradiated resins, there was a pronounced darkening of the resin adjacent to the metal coupon at the bottom of the sample tube.

Sample No.	Ion Exchangers Used	Irradiation Facility	Weight Los % initial wt.	mg/cm ²	Qualitative Features of Corroded Metal Coupon Surfaces
7	IONSIV-IE-95	60 _{Co} a	0.9	6.4	Spotty rusted areas with zeolite beads strongly adhering.
8	IONSIV-IE-95/ Amberlite IR-120	60 _{Co} a	2.6	19	One half covered with rust only. The other half had rust and resin beads.
9	Amberlite IR-120	60 _{Co} a	3.3	24	Covered with rust throughout. One end had white spots in addition to rust.
10	Amberlite IRA-400	60 _{Co} a	1.9	13	Uniform thin layer of rust. No crust formation.
11	IONSIV-IE-95/ Amberlite IRA-400	60 _{Co} a	4.4	32	No significant crust, but significant pitting on surfaces.
12	10NSIV-IE-95/ Amberlite IR-120/ Amberlite IRA-400	60 _{Co} a	4.1	30	Covered fully with black beads and rust.
7-8	IONSIV-IE-95	none	0	0	Bright surfaces. Barely visible rust spots at the edges.
9-8	Amberlite IR-120	none	0.3	2.0	Almost all of the surface of the coupon was covered with a very thin layer of corrosion product.
10-B	Amberlite IRA-400) none	0	0	Bright surfaces like the original sample. No visible corrosion products or rust spots.
41	IONSIV-IE-95	TRIGAD	0.5	3.1	Distinct, but spotty crust formation with zeolite particles adhering to the corrosion product.
42	Amberlite IRA-120	D TRIGAD	3.5	27	Significant corrosion product build-up. Uniform throughout the surface.
43	Amberlite IRA-400	O TRIGAD	0.7	5.2	Spotty corrosion product build-up, especially around edges of the coupor.
44	IONSIV-IE-95/ Amberlite-IR-120, Amberlite-IRA-400	TRIGAD	0.8	6.2	Uniformly distributed surface layers of corrosion products.

Table 3.8 Corrosion Study Experiments(6)

aDose = 2×10^9 rad; flux = 4.4×10^6 R/hr. bDose = 4.4×10^8 rad; flux = 7.6×10^5 R/hr.

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Corrosion of Stainless Steel in Contact With Irradiated Ion Exchange Resins(7)

Codea	Container ^b	Resin	Dose (Rads)	рнс	Comments
Cq	1	Cation	2.5x10 ⁹		Crusty deposits, surface etched, pits and de- pressions.
Dq	1	Cation	2.5×10 ⁹		Deep pits, dark deposits.
W	2	Cation	5x10 ⁹	4	Heavy deposits in pits, depressions up to 200 m deep.
Ρ	2	Cation	1x10 ⁹	4.0-4.5	Deposits, pitted and etched.
U	2	Cation	5x10 ⁸	2.5-3.0	Small number of sites of attack, circular deep pits, heavy deposits.
Q	2	Cation	3x10 ⁸	4.0-4.5	Similar to P, deeper depressions.
T	2	Cation	1x10 ⁸	2.5-3.0	Clean surface, etched circular areas with pits in the center.
βd	1	Anion	7.9x10 ⁸		No evidence of corrosion for samples with anion resin.
Х	2	Anion	1×10 ⁹	8.0-8.5	
٧	2	Anion	1×10 ⁹	7.5-8.0	
S	2	Anion	1x10 ⁸	8.5-9.0	
Control	2	None	None		

^aCode refers to sample designation given in Reference 7.
^bThe container dimensions are: 1 - 1.0 in 0.D., 0.037 in wall thickness, 2 - 0.5 in 0.D., 0.034 in wall thickness.
^cpH of the environment in the containers at the end of the exposure, as measured with narrow range pH paper.
^dPressurized containers.

Moisture content is clearly an important variable affecting corrosion. The results suggest that corrosion can be greatly reduced if the resins are dried before storage. The pH measurements (see Table 3.10) indicate the radiation induced degradation of the functional groups in all cases. It was tentatively concluded that moisture is important as a transport/electrolytic medium in the corrosion process.

Corrosion was observed on PF-16, the prefilter used in the TMI cleanup.(17,18) Thus far, a visual examination was made of the exterior surfaces of the liner and of the interior of the liner above the demineralizer bed. No significant external corrosion was found, however, the internal surface of the manway cover was corroded. Areas where the epoxy coating peeled away from the interior walls, also showed signs of corrosion. Below the bed surface there was no corrosion observed in the area examined. The environment of PF-16, a liner filled with dewatered ion exchange material, is indeed corrosive to carbon steel. The epoxy coating has apparently provided some protection from corrosion, however, it is not clear why the coating peeled away from the container surface. The epoxy coating may be degraded by the chemical environment of the liner or by radiation. The behavior of this coating upon irradiation should be examined in order to access the effectiveness of the coating as a means of extending the container life.

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Effect of Moisture Content on Irradiated and Unirradiated Resins(8)

Resin Form	Percent Moisture	pH of D.I.W. Coupon Perc M'xturesa.b Weight Lo	Weight Loss	
nirradiated		9.5.6		
H+	55	2.76, 3.10, 3.07		
H+	27	3.28, 3.11		
H+	14	3.24, 3.29		
Nat	50	3.65, 3.51, 3.55 4, 4, 4		
Nat	25	3.52, 3.42 1, 1		
Na+	13	3.29, 3.49 0, 0		
- 108 rad				
H+ 100	55	top 1.67, 1.57 20, 8		
H+	27	top 1.52, 1.32 4, 7		
		bottom 1.36, 1.36		
H+	14	top 1.65, 1.50 0, 0		
Na+	50	top 2.53, 2.35 4, 5		
Na+	25	top 2.31, 2.22 2, 3		
nu .		bottom 2.48, 2.42		
Na+	13	top 2.45, 2.42 0.0		
Contract + impr	for corresion	experiments		
unirradi	ated samples:	190 h		
Irradiat	EET moisture:	78 h unirradiated + 75 h irradiate	d.	
50.	37 moisture.	75 h unirradiated + 75 h irradiate	ed.	
13	-14% moisture:	6 h unirradiated + 75 h irradiate	ed.	
		and a minimum of 2 g of resin an	đ	

10 mL of defonized water (D.I.W.). DEntries separated by commas are values of replicate specimens.

3.4 Biodegradation

The importance of biodegradation to the decomposition of organic ion exchange resins and to the stability of the internal environment of a waste package was evidenced by the survey response from the Duane Arnold Energy Center (see section 2.12). They described a pressure buildup in drums of dewatered ion exchange resins. The gas generation was attributed to organic growth in the resin waste container, citing floor drains as a source of organic matter. There is, however, little information available about the biodegradation of radioactive ion exchange resin waste.

Water samples from the influent and the effluent of a demineralizer plus resin samples from the demineralizer were obtained from the High Flux Beam Reactor at Brookhaven National Laboratory and analyzed for growth of microorganisms.* Bacteria growth was monitored by measuring CO₂ generated from the decomposition of organic carbon. The bacteria activity was greater in the influent water samples than in the effluent water samples. Measurements of CO₂ generation performed on the resins showed the largest growth of microorganisms. The radioactivity on the resins was described as low, but no values were specified.

The results of these tests indicate biodegradation of organic matter. However, there is no direct evidence distinguishing the digestion of organic contaminants in the water and trapped on the resin from the digestion of the organic backbone of the resin bead.

Information about biodegradation on organic ion exchange resins is needed in three areas. First, the types of organisms must be isolated, preferably using samples from utility reactors. Second, the stability of the organisms to radiation must be evaluated; complications can result from the formation of mutations. Third, the environment in which the organisms propagate should be understood. To predict the potential problems from biodegradation, it is necessary to determine both the rate of bacteria growth and the extent of the attack on the environment.

Bacteria growth in resin waste having high radionuclide concentrations (approximately 40 Ci/ft³ as in the EPICOR-II prefilter liners used in TMI cleanup) is expected to be completely retarded. However, it is claimed that demineralizers with lower activities (approximately a thousand times lower than the EPICOR-II prefilters) may support bacteria growth after 35 to 100 years giving CO₂ gas.⁽²²⁾

3.5 Summary

It should be apparent from this discussion that ionizing radiation at high doses is a major factor causing the degradation of ion exchange resins.

^{*}A. J. Francis, Brookhaven National Laboratory, in a private communication to P. L. Piciulo, November 16, 1981.

Thus, radiation damage must be considered when addressing the long-range stability of a waste package containing dewatered ion exchange media. The following general statements are intended to summarize the discussions on resin degradation in this chapter:

- Radiation doses on the order of 10⁸ rad result in significant chemical and physical changes in organic ion exchange resins.
- The scission of resin functional groups (e.g., sulfonic group from cation exchangers; quaternary ammonium group from anion exchangers) will release water and various chemical species.
- Marked lowering of the pH of water associated with irradiated cation exchangers has been observed.
- Some evidence shows changes in the pH of drainable liquids from ion exchange demineralizers several months after the systems were removed from service at TMI. There is a trend for the pH to approach neutral (i.e., pH = 7). However, the unknown contents of the liners, upon which this conclusion is based, limits the ability to interpret the observation.
- Gas generation is significant at doses >10⁸ rad for both cation and anion exchangers. It may be necessary to have a vent on a container to avoid the buildup of pressure and the possible failure of the container integrity.
- Hydrogen gas is liberated whereas oxygen is apparently consumed in a radiation environment.
- Anion resins are generally less stable than cation resins.
- Both cation and anion exchangers show signs of agglomeration due to radiation.
- Liquids are released from anion exchange resins after a radiation dose of 10⁸ rad.
- Amines released by anion exchange resins may buffer the acidic products released on the irradiation of cation exchangers.
- Irradiated ion exchange resin beads accelerate the corrosion of both mild steel and some stainless steel.
- As the moisture content of ion exchange resins decreases there is a decrease in the corrosive effects on mild steel.

- The analysis of the TMI first stage liner has revealed an apparent protection of the carbon steel container by an epoxy coating. (EPICOR, Incorporated claims* that the epoxy lined carbon steel liner is being considered by them as a possible high integrity container.)
- There is limited information about long-term resin decomposition due to normal aging and biodegradation.

A number of questions still remain.

- Utilities generally dispose of mixed beds of ion exchange resins.
 What are the resulting chemical and physical changes of mixed bed resins resulting from ionizing radiation?
- Powdered resins are commonly used in the nuclear industry. What, if any, are the differences in the radiation damage of mixed bed powdered resins as compared to the work reported for bead resins?
- What are the effects of radiation induced degradation of products from ion exchange media on candidate materials for future high integrity containers like epoxy and high density crosslinked polyethylene.
- What are the corrosion rates of resin degradation products on metals and on nonmetallic materials being considered for the construction of disposal containers?
- To what extent does biodegradation effect the stability of a waste package of organic ion exchange resins?

The technical basis for establishing maximum loading limits on organic ion-exchange resins is presently being evaluated at BNL.(5) The NRC has suggested, in a draft Branch Technical Position on Waste Form, that resins should not be loaded to bulk specific activities greater than 10 Ci/ft³. A loading of this concentration of 137Cs and/or 90Sr will result in an accumulated dose of approximately 10^8 rad. A radiation dose in excess of 10^8 rad may result in the degradation of organic ion exchange media. If a limit is established on the allowable radionuclide loading on ion exchange media being buried, then problems resulting from pH changes, gas generation, agglomeration, and metal corrosion may contribute less to the instability of the waste package.

*J. Levendusky, EPICOR, Incorporated, in a private communication with P. L. Piciulo, August 19, 1981

4. RESIN DEWATERING

4.1 Introduction

A survey of four manufacturers of organic ion exchange resins was conducted by telephone. The information described in this chapter is taken from the discussions with personnel at Diamond Shamrock Corporation (Duolite), Ionac Chemical Corporation, and Rohm and Haas (Amberlite). Dow Chemical, U.S.A. responded in a letter to the questions submitted. Table 4.1 summarizes their comments. In addition, three companies which supply services to the nuclear industry, Chem-Nuclear Systems, Incorporated (CNSI), EPICOR, Incorporated (EI), and Hittman Nuclear and Development Corporation (HNDC), were questioned regarding the dewatering of radioactive ion exchange resins. The information obtained in these communications is summarized in Table 4.2.

Also discussed in this chapter of the report is information found in the literature and information regarding the experience with dewatering ion exchange resins used in the cleanup at TMI.

	Dow Chemical U.S.A.a	Diamond Shamrock Corp.b.c	Ionac Chemical Co.d	Rohm and Haas ^e
Dewatering Method	continuous vacuum filter	drain and vacuum filter	screened underdrain, vacuum filter	column drain, air or inert gas passed through resin
Amount (% by volume) of free liquid in dewatered resin	0.75 typical	minimal (no value given)	~0.7	minimal (no value given)
Amount of free liquid released during storage	none if in a sealed container	moisture can evaporate if open to air	stored in air-tight drum no moisture lost	moisture can evaporate if open to air
Amount of free liquid released during transportation	none			
Environmental factors causing release of moisture	evaporation, stream of dry air, heating above 100°C	evaporation, heating will remove moisture	hot air drying	evaporation, heat will in- crease rate of moisture loss, resin heated at 110°C overnight is considered to be dry resin

Table 4.1

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Summary of Comments From Ion Exchange Resin Manufacturers

^dF. McGarvey, Ionac Chemical Company, in a private communication with P. Piciulo, July 31, 1981. ^eE. Feeney, Rohm and Haas Company, in a private communication with P. Piciulo, August 26, 1981.

	Chem-Nuclear Systems, Inc.ª	EPICOR, Incorporated ^b	Hittman Nuclear and Development Corporation ^C
Dewatering Method	Vacuum filtration conical bottom, three filter levels	Vacuum filtration "pancake" screen underdrain, dewatering cartridge	Vacuum filtration full underdrain
Dewatering time to reach 1 gallon free liquid 0.5% free liquid 1.0% free liquid	4 hrs (15 ft ³) 1-1/2 days (300 ft ³ liner)	24 hrs (150 ft ³ liner)	∿2 weeks (6'x6' liner)
Changes in volume of free liquid during storage	none	none	none
Changes in volume of free liquid during transportation	none	none (vibration test)	none (vibration test)
Comments on high integrity containers (HIC)	Presently supply a HIC made of HDXL ^d poly- ethylene. Dewatering equipment is the same as for steel liner	Three are planned: 1. steel and epoxy 2. fiberglass 3. polyethylene	Considering HDXL ^d polyethylene as the construction material.

Table 4.2

Summary of Comments From Vendors of Ion Exchange Resin Dewatering Liners

aG. Allen, Chem-Nuclear Systems, Incorporated, in a private communication with P. Piciulo, August 4, 1981.
 bJ. Levendusky, EPICOR, Incorporated, in a private communication with P. Piciulo, August 12, 1981.
 CC. Mallory, Hittman Nuclear and Development Corporation, in a private communication with P. Piciulo, August 11, 1981.
 dHDXL = High density cross-linked.

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4.2 Dewatering New Resins

Vacuum filtration is most often used by the manufacturers for dewatering organic ion exchange resins. The procedure involves sluicing the resins into a large tank equipped with an assembly of screens at the bottom and a drain. The water is allowed to gravity drain and then the resin beads are dried further by the suction of air through the resin bed. A second technique uses a continuous vacuum filter to dewater ion exchange resins. In this case, the resins are slurried onto a moving screen belt and the water and air are pulled through the screen by a vacuum. The dewatered resin is unloaded into a storage hopper.

Resins dewatered by these methods will generally contain less than 1.0% free moisture by volume. This is controlled by the amount of time the resin is in the vacuum filter. A fiber drum with a polyethylene liner (bag) is generally used to ship ion exchange resins. It is possible that a drum filled with new resin beads can have "dry" beads on the top, whereas the resins at the bottom can be a little "soupy" due to free liquid. However, the dewater-ing procedures used by the manufacturers are intended to minimize the water in a package containing resin in order to avoid the expense of shipping water.

4.3 Dewatering Spent Ion Exchange Resins

Three companies which supply services to the nuclear industry were surveyed regarding the dewatering of ion exchange resins. Each of the companies supply liners specifically designed for resin dewatering. All of the liners are equipped with underdrains. This may be a stainless steel strainer or "pancake" (EI), a conical bottom with a dewatering "spider" (CNSI), or a screened bottom and standpipe (HNDC). The water is initially gravity drained from the liner then a vacuum is applied, pulling large volumes of air through the resin thereby reducing the volume of free liquid. Usually a cycle of gravity draining followed by pumping is used. The amount of free liquid remaining in the liner is dependent on the pumping time and the physical condition of the resins.

New ion exchange resins are easier to dewater than used resin beads. Organic ion exchange beads which were in use for a long period of time and repeatedly regenerated, often have associated resin fines and broken beads. Some utilities use an ultrasonic cleaner to remove resin fines (particles smaller than 0.3 mm) and any "crud" which may be filtered by the ion exchange bed. Abrasion encountered in sluicing, and mechanical shock from the pressure drop across a resin bed, cause beads to crack and/or break. Repeated regeneration can result in a decrease in the cross-linking of the resin beads making them more sponge-like. All these factors make it more difficult to dewater spent resin beads.

The dewatering of powdered resins (e.g., Powdex, Ecodex) can be done in the liners described above or with a high speed centrifuge. To use the dewatering liners it is necessary to incorporate an underdrain which will accommodate the smaller particle size of powdered resins. The powdered resin/water slurry has been described as having a mud-like consistancy. As water is removed, air does not pass freely through, but rather a partial vacuumn results and the water is sucked from the material. The final consistency is that of dry mud.

Some power stations use a nigh speed centrifuge to dewater the powdered resins (see Section 2.10, Table 2.6). A system described by one utility spins the water/resin slurry to remove the water and an auger is used to push the dry material from the centrifuge to the disposal liner. Vermont Yankee Nuclear Power Station, Edwin I. Hatch Nuclear Plant, and Peach Bottom Atomic Power Station claim they have no problem meeting the free liquid requirements using centrifugation to dewater powdered resins.

4.4 Dewatering Tests

4.4.1 Chem-Nuclear Systems, Incorporated

Tests have been conducted by CNSI on the dewatering of liners containing both depleted and new organic ion exchange resins.* The depleted resins, which had been regenerated several times, came from a paper mill and are believed to provide for a more realistic test than dewatering new resins. Work started with the largest CNSI container, 300 ft³ (2240 gallons). In the liner there were used resins and about 400 gallons of free water. The exact measure of this water was difficult because the amount is dependent on evaporation, the void space above the resin, and temperature. The dewatering procedure required pumping water from the liner containing resin for a given time until no water could be pumped out, then allowing the liner to sit and gravity drain for a given time. This pump-drain sequence can be repeated as necessary. Measurements of the amount of water removed from the liner versus time indicated that there is initially free water, which drains quickly from the liner, followed by water absorbed on the resin beads, which is released very slowly. CNSI repeated the tests three to five times with averages and deviations determined to obtain confidence limits. It is claimed that the plotted data are best described by two regions; one for the fast drainage of water and the second is an asymptotic portion of the plot showing the slow release of water from the bed of resins. (Data of this type is discussed in section 4.4.4.) The drainage versus time curves can be used to determine the dewatering time necessary to reach a certain volume of free water remaining in the liner. It is also possible to fit the easily removed water (points at short times) to a single curve and extropolate to long time. CNSI claims that this practice does not give a true representation of the dewatering of ion exchange resins.

There is a relationship between the liner size and the time necessary to dewater to a given amount of free water. The following examples were described by CNSI:

^{*}G. Allen, Chem-Nuclear Systems, Incorporated, in a private communication with P. Piciulo, August 4, 1981.

- A 300 ft³ liner was dewatered to 1% free liquid within 1-1/2 days. This required eight hours of pumping, 16 hours of draining, and an additional four hours of pumping.
- A 15 ft³ liner was dewatered to 1/2% free water within approximately 4 hours of pumping. This test, however, was done using new resins which are generally easier to dewater.
- Activated carbon required several days to dewater. This extended time was attributed to the porosity of the material.

The bulk of the water is said to be removed from the liner within the first four hours of pumping, whereas the water on the bead surface is released slowly. CSNI contends that liners smaller than 20 ft³ can be pumped to 1 gallon free water with little difficulty. For the large liners (300 ft^3), the 1 gallon limit (0.045%) is not practical. Core samples taken from liners which were dewatered showed that the resins at the bottom of the liner are as "dry" as the resins at the top of the liner.

4.4.2 EPICOR, Incorporated

Dewatering tests were performed on 150 ft³ liners containing approximately 120 ft³ of resins; both new and depleted resins (not radioactive) have been used in these experiments.* A known amount of water is added to the liner containing the resins and then water is measured as it is removed. The procedure involves pumping the water from the liner for a set time followed by a period of time the liner is allowed to stand without pumping. This cycle is repeated until a certain amount of free water is believed to remain in the liner. (The uncertainty in the determination of the quantity of free liquid is dependent on the initial condition of the resins. It may be easier to remove all of the water added to the liner at the beginning of the test if the resins have a large amount of associated water (i.e., surface water) then if the resins were initially drier.) EPICOR, Incorporated has reached the limit of 1 gallon free water, after a 24-hour period of dewatering which included tipping the liner slightly on edge. Tipping presumably directs water toward the underdrain outlet(s). EPICOR, Incorported, believes that 0.5% free liquid is a reasonable limit, since it would allow 4 gallons of free water in the 150 ft³ liner, which can be readily achieved. The dewatering tests performed at TMI used the EPICOR liners and the results are discussed in section 4.4.5.

4.4.3 Hittman Nuclear and Development Corporation

Dewatering tests have been performed by HNDC with used resin (not radioactive) which had been previously regenerated.** A positive displacement

^{*}J. Levendusky, EPICOR, Incorporated, in a private communication with

P. Piciulo, August 12, 1981.

^{**}C. Mallory, Hittman Nuclear and Development Corporation, in a private communication with P. Piciulo, August 11, 1981.

pump is used to remove water from a liner equipped with a full underdrain. Based on measurements of water removed from a liner vs time, Hittman claims that a predictable relationship exists between dewatering time and free water remaining in the liner. (Resin dewatering is dependent on the resin condition, as well as the liner dimensions. Thus, it is not clear that a dewatering curve for a given liner will be applicable to the large variations of resin waste found in the nuclear industry.) The limit of 1 gallon free water in a 6 ft diam x 6 ft high (170 ft³) right cylindrical liner was reached after dewatering for a couple of weeks. Tipping the liner on edge was required to reduce the free liquid to this volume. HNDC maintains that 0.5% free liquid remaining in a liner of dewatered resins is a realistic limit.

4.4.4 Turkey Point Dewatering Test

A dewatering test was conducted at Turkey Point Units 3 and 4 (Florida Power and Light Company) to show that a Hittman HN-100 liner equipped with an underdrain and a bottom drain plug could be dewatered such that less than 1 gallon of water remains in the liner.⁽²³⁾ Residual water was removed from the liner containing mixed resin beads (presumably cation and anio. exchangers) by pumping from the bottom drain while the liner was tipped at 10°. With the 170 ft³ liner set in a horizontal position, 540 (540.4) gallons of demineralized water were added. About half of the water (253.5 gallons) was removed from the liner during 15 hours of gavity draining. The liner was again tipped to a 10° angle with the bottom drain at the low point and an additional 208 (208.7) gallons were removed on pumping. Dewatering by pumping was conducted at approximately 24-hour intervals until an insignificant amount of water was removed. Two-hundred milliliters (0.053 gallons) were arbitrarily defined as this endpoint. No additional dewatering was done for about a week. A final dewatering at this point would determine if a significant amount of water remained. Table 4.3 presents the test data.

The extent of the initial resin dewatering is not clear. The "dryness" of the resins at the start of the test and at the end of the test should be compared. The large difference existing between the amount of water initially added to the liner (540.4 gallons) and the total amount of water removed (472.3 gallons) presents an error of $\sim 12\%$. It was postulated that near the end of the gravity drain period the velocity of water passing through the effluent water meter was too low to be registered by the meter. An independent test of the flowmeter showed that a -20% error was possible. Also, they claimed that 540 (540.0) gallons of water were required to refill the liner. The water volumes reported imply a measuring accuracy of one part in 5000 (i.e., 0.02%), however, the errors observed are of the order of 10% to 20%. The Turkey Point workers concluded that it is possible to meet the criteria of 1 gallon free liquids with reasonable assurance when dewatering the Hittman HN-100 liners equipped with a bottom drain using the procedure described above. The conclusion is based on the observation that only 0.11 gailons of additional water was removed from the liner on day 31, 9 days after the dewatering routine was stopped. It is questionable that in this 170 ft³ (1270 gallons) liner there is only one gallon (~0.08% of the container volume) of free water remaining. The uncertainty in knowing the volume of free water remaining in a liner should be evaluated.

Table 4.3

Data Sheet(23) Liner Dewatering Test

Day	Volume of Water Removed (Gal.)	Remarks
1	253.3a	Gravity drain, 15 hr, liner flat
20	208.7	Liner tipped 10 degrees, pumped
3	2.1	Dewatered twice
3	•4	Pottom dasin
4	•0	
5	1 1	underdrain
6	1 48	Bottom drain
6	14	linderdrain
7	.14	Not dewatered
à	93	Bottom drain
8	0	Underdrain
9		Sideraram
10	.,.	Not dewatered
11	. 52	nou dend ver ed
12	.264	
13	.264	
14	.232	
15	.124	
16	.127	
17	.132	
18		Not dewatered
19	.063	
20	.074	
21		Not dewatered
22	.032	
23		
24		
25		
26	>	Not dewatered per test plan
27		
28		
29)	
30		
31	.11	End of test

aSuspected error. See text. ^bAll dewatering from day 2 on was done by pumping with the liner tipped approximately 10 degrees. Note: Container: Hittman, HN-100, with bottom drain. Media: Ion exchange resin.

The Turkey Point data were analyzed by the Hittman Nuclear and Development Corporation and they also concluded that less than 1 gallon of free water remained in the liner after the 22-day dewatering operation. The method used by HNDC was to plot gallons removed vs time (24-hour intervals) as shown in Figure 4.1 and fit the points to an unspecified power series of time. The data used is given in Table 4.4, the water removed on days 1 and 2 were omitted from all three of the numerical analyses performed:

Analysis 1 - fit Days Counting from 1 through 20; the last point was dropped.

Analysis 2 - fit all data; Days Counting 1 through 29.

Analysis 3 - fit Days Counting 4 through 29.

Table 4.4

Turkey Point - Liner Dewatering Drainage Data(23) (12/29/80)

Draining No.	Date	Days Counting	Volume-Gallons
3 and 4	11/30	1	2.5
5	12/1	2	1.3
6	12/2	3	1.1
7	12/3	4	1.88
8	12/5	6	.93
9	12/6	7	.70
10	12/8	9	.52
11	12/9	10	.264
12	12/10	11	.264
13	12/11	12	.232
14	12/12	13	.124
15	12/13	14	.127
16	12/14	15	.132
17	12/16	17	.063
18	12/17	18	.074
19	12/19	20	.032
20	12/28	29	.11
Note: Data fro	m Drainings	1 and 2 were not u	sed.

There are a number of confusing points in Table 4.4. Although the Days Counting are consistent with the days on the data sheet if the counting starts at day 3, the Draining Number is misleading. Apparently, all water removed on a single day was combined into one value. The Volume-Gallons associated with





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Days Counting number 4 in Table 4.4 is 1.88 gallons and is presumably in error. This value should be 1.62 gallons, which is the sum of the gallons removed in 2 dewaterings on day 6, listed in Table 4.3. It is not close as to the effect of this error on the analyses performed.

The integral of the power series equation fit to the 3 cases listed was evaluated to determine the time, t, necessary to reach the 1 gallon remaining limit. The observations reported for each analyses are:

- Analysis 2 t = 128 days, the correlation (not specified) of the data fit is lower than desired. The point at Days Counting = 4 was considered as affecting the correlation coefficient, but not corrected.
- Analysis 1 Dropping the last point shortened the predicted dewatering time to t = 98 days.
- Analysis 3 The total quantity of water remaining in the liner after the Days Counting = 20 was estimated at 0.71 gallons. Nine days later 0.11 gallons or 15% of this was removed.

Once again it is unclear as to what effect the error in point 4 would have in the above caluclations and the ability to predict when the 1 gallon limit is reached. The plot of the data and the results of Analysis 3 support the claim, made by Chem-Nuclear Systems, Incorporated (see section 4.4.1), that it is necessary to treat the dewatering data in two distinct regions when performing an analysis.

• In this test as in the others discussed, no determination is made of the total amount of water inside the liner. The distinction between water associated with the resins (e.g., water of hydration and surface water) and that which is free water should be understood.

Since the approximate volume of the Hittman HN-100 liner is 170 ft 3 or 1270 gallons it follows that:

- 0.5% of the volume is approximately 6.4 gallons,
- 1.0% of the volume is approximately 12.7 gallons,
- 1 gallon is approximately 0.08% of the total volume.

Assuming that less than 1 gallon of free liquid remains in the liner at the end of the 31-day dewatering test, then, from Table 4.3, the following is observed:

• The volume of water remaining in the liner after day 5 of dewatering is approximately 5.2 gallons. This volume plus the 1 gallon free liquid assumed to remain in the liner totals 6.2 gallons which are less than 0.5% of the liner volume.

• The volume of water remaining in the liner after day 2 of dewatering is approximately 11.1 gallons including the 1 gallon of free liquid assumed to remain in the liner. This volume is less than 1.0% of the container volume.

Clearly, the bulk of the water is removed from the liner in a short time as suggested by CNSI.

4.4.5 TMI-2 Resin Liner Dewatering Study

A liner dewatering study was done on the EPICOR-I and EPICOR-II Radwaste System Liners used in the water treatment at Three Mile Island.(24) It has been learned from the survey responses and a private communication with personnel at EPICOR, Incorporated, that a number of portable demineralizers are in use in nuclear power stations. Since the liners presently in use are similar to those used at TMI, the findings of the dewatering study are relevant to this report.

The testing was performed with 6 ft x 6 ft (approx. 145 ft³) liners. Five hundred eighteen gallons of water were added to the liner. This free water is defined as water existing above the resin bed and within the resin intersticial void space. Table 4.5 summarizes the volume of the container, resin and water for these tests. The liner is equipped with an arrangement of "laterals" at the bottom allowing water and not resin to pass through on pumping. The basic method used for dewatering is outlined in Table 4.6.

Several other tests were conducted and the results are summarized in Table 4.7. In the tests, the dewatering time was varied, hot air was used to help remove the water, a liner was transported 900 miles to observe the effects of road vibrations on water, and the effects of reversing the airflow were examined. This latter method of reversed airflow may have just dispersed the water to different parts of the bed. It is possible that this water will be released at a later time. The results indicate that less than 1.63 gallons of free water remained in the liner after dewatering. The transportation cest released only 2 additional quarts of water more than the static dewatering test. The use of heat and variations in pumping time had little effect on the overall dewatering of the resins.

*J. Levendusky, EPICOR, Incorporated, in a private communication with P. Piciulo, October 2, 1981.

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Water Retention in a Typical EPICOR, Inc. 6 ft x 6 ft Resin Liner(24)

and the second se		and the second se
Ι.	Total container volume	145 ft ³
11.	Volume of resin in liner accounting for compaction and liner internals	116.0 ft ³
	Volume of free water above and within resin	58.8 ft ³
IV.	Total free water	518.4 gallons
۷.	Gallons of water electrochemically bound by resin	433.8 gallons

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The Basic Test Procedure Used in the TMI Dewatering Study(24)

Basi	Method:	Dewatering Air drying	with with	Sandpiper Sandpiper	pump pump			
	Step				Date	[Jura	tion
1.	Liner fill	ed with wat	er	9	9/26/79 (1130)		-	
2.	Liner deca suction 1	ost	gpm un	til				
3.	Liner air a. Air dr b. Allowe c. Air dr d. Allowe e. Air dr	dried ried (~ 150 ed to settle ried (~ 150 ed to settle ried (~ 150	scfm) scfm) scfm)				1 1 1 1	h h h h h h
4.	Bottom dra	ain removed		9)/26/79 (1830)			
5.	Liner drat	ined		9	9/27/79 (2030)		14	h
Resu	lts: Relat Relat Water	tive humidit, tive humidity drained in	y of i y of e step	nlet air ffluent a 5	= 55 air = 56 = 1.3	gallons	5	

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	Test	Water Drained Following Dewatering Procedure	Percent (%) of Total Container Volume	Percent (%) Free Water ^a
Ι.	Dewatering with Sandpiper pump Air drying with Sandpiper pump IA. Timing and IB. Sequence was IC. Altered	1.3 gallons 1.7 gallons 1.2 gallons	0.12% 0.15% 0.11%	0.25% 0.33% 0.23%
11.	Dewatering and drying with Sandpiper pump, air drying with heated air exhauster	1.13 gallons	0.10%	0.22%
	Dewatering with Sandpiper pump air drying with air exhauster	1.13 gallons	0.10%	0.22%
IV.	Test III coupled with shipping 900 miles over the road	1.63 gallons	0.15%	0.31%
۷.	Dewatered with Sandpiper pump air drying with Sandpiper pump (Reversing airflow direction)	0.25 gallons	0.02%	0.05%

Summary of Liner Dewatering Test Results(24)

aRelative to 518.4 gallons.

An independent dewatering test included a mathematical model to evaluate the ability to predict free water removal. (24) Factors such as resin mixture, resin exhaustion, electrolytical charge, compaction and interstitial void space were considered, although no details of the model were given. The model established that 312.7 gallons of water had to be removed from a resin bed by the dewatering process. The field test run in parallel with the modeling work showed that 326.8 gallons of water were removed from the resin bed under conditions as assumed in the mathematical model. The report concludes that the close agreement (approximately 4.3%) shows both a sound understanding of water retention in a resin bed and the ability to predict water removal efficiencies. However, the 4.3% error in this test is an indication of the inability to accurately determine the volume of free water present in a liner.

4.4.6 Vermont Yankee Nuclear Power Station

Powdered ion exchange resins are extensively used in boiling water reactors (see section 2) and several of these plants dewater the resins using centrifugation. The quantity of water in the remaining in powdered resins after centrifugation was determined at the plant." The water present in a sample of Powdex resin, as supplied by their vendor, was measured by weight difference before and after drying under controlled conditions. The same test was performed on a sample of resin which was dewatered in their centrifuge. The amount of water measured in the sample dewatered in the Vermont Yankee centrifuge was smaller than that found in the fresh resin sample. Since there is no free liquid in the Powdex resin received from the supplier, it was concluded that there is no free liquid in the disposal liner prior to shipping.

4.5 Release of Liquid During Storage and Transportation

The manufacturers and vendors surveyed agree that no additional water should be released during the storage or the transportation of dewatered organic ion exchange resins. After all the free liquid is removed, some moisture will remain adsorbed on the surface of the resin bead and as water of hydration of the functional groups. This water can be released to give additional free liquid in the container. However, the release is unlikely to occur during storage (at ambient temperature) or due to mechanical shock resulting from transportation.

A number of factors can affect the removal of water retained by ion exchange resins. The water retained in an ion exchange resin is primarily that hydrating the exchange groups. The water of hydration can account for 30% to 70% of the resin volume. Heating resins in an oven at 105°C for 16 hours is a method indicated by one manufacturer to prepare "dry resin beads," considered to contain no water. Less severe conditions can remove a substantial portion of the bound water. In contact with dry air, water can be lost by evaporation and as the temperature of the air increases (and relative humidity decreases), the rate of water loss will increase. The degree of drying is dependent on the exposure time. Passing the resins through a stream of hot air can result in a decrease in moisture content from approximately 50% to approximately 10%. The resin will subsequently shrink to almost 50% of its original volume. Dry resins are a strong desicant, and when rehydrated, will expand. The pressure resulting from the expansion on contact with water can destroy the container.

4.6 Resin Drying

A method has been patented for the dehydration of spent radioactive ion exchange resins. (25) The organic resins are vacuum filtered in a chamber which can be heated to between $40^{\circ}C-150^{\circ}C$ (preferably between $70^{\circ}C-80^{\circ}C$) and evacuated to a pressure between 380-740 Torr. The second step uses superheated steam at a temperature between $93^{\circ}C-260^{\circ}C$ to fluidize the resin bed. The fluidized bed is subjected to a partial vacuum and as the resin loses moisture, heat is continuously added to the fluid bed to maintain the bed temperature in a range consistent with the thermal stability of the resin being dried. The water removed is expected to be of high purity and can be

^{*}G. D. Weyman, Vermont Yankee Nuclear Power Station, explained the procedure to P. Piciulo during a site vist, June 30, 1981.

recycled back to the water system of the nuclear plant. The dried resins can be packaged for disposal. Volume reductions of 45-50% are claimed. The thermal stability of the ion exchange resin must be considered when selecting the operating parameters in order to minimize the release of decomposition products and, possibly, radioactive species. 20

It is not known that the resin dehydration technique is being utilized in the nuclear industry at present.

EPICOR, Incorporated, is developing a dewatering cartridge that will take up any residual water when injected into a liner of dewatered resins." Although the details of the device are proprietary; it is claimed that the cartridge has been tested in demineralizers used in the TMI cleanup (presumably EPICOR-I or EPICOR-II liners).

The consideration of moisture-absorbing materials is discussed in a report on TMI liner dewatering. (24) The criteria established for the selection of the absorbing substances are:

- 1. Nonreactive to resin beads and impurities fixed on resin.
- Highly moisture absorbent.
- 3. Easily pumpable.
- 4. Able to mix within a resin bed.

Two materials chosen after laboratory testing were silicate and cellulose. It is claimed that these can be added to the liner in sufficient excess to assure no free liquid. No details of the testing were given.

4.7 Summary

It is apparent from this review that the dewatering of organic ion excharge resins is dependent on the dewatering time. New resin beads are considered easier to dewater than beads which are old and may be cracked or broken. The three vendors of dewatering services to the nuclear industry agree that it is not practicle to dewater a liner containing ion exchange media such that less than 1 gallon of free water remains in the liner. The time requied to reach this limit can range from hours for small containers to weeks for liners of 150 ft³ and larger.

Dewatering liners are generally equipped with underdrains. One company, CNSI, uses a liner with a conical bottom to direct the water to a low point. This is advantageous since liners with flat bottoms often need to be tipped on edge. Powdered resins are easily dewatered via centrifugation, assuring less than 1 gallon free liquid in the disposal container.

A method exists for dehydrating resins, and absorbent materials are being considered to help remove residual water from a liner of dewatered resins.

*J. Levendusky, EPICOR, Incorporated, in a private communication with P. Piciulo, August 12, 1981.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Characteristics of Environment Inside a High Integrity Container

The survey of nuclear power plants, reviewed in section 2, revealed extreme variations in the water chemistry within the different water treatment systems in a plant and from one plant to another. Thus, it is not possible to define the characteristics of water remaining in a HIC. However, the following points are apparent:

- The pH of the liquid can vary from 2 to 11. Solutions with pH <4 are generally corrosive to carbon steel.
- Chloride ions (Cl⁻) may be present in the drainable liquids in a disposal liner at concentrations of hundreds of parts per billion. Chloride is corrosive to stainless steel and, therfore, the effect of Cl⁻ on the container lifetime must be considered if stainless steel is used as a liner material.
- The resin waste inside a liner may come from a single demineralizer in a plant or from a spent resin holding tank where resins from several demineralizers are mixed.
- The radionuclide concentration in the free liquid remaining after dewatering will be lower than that on resins.
- The gross β, γ activity on ion exchange resins being disposed of varied from <1 to 5000 µCi/mL. This coupled with the large variations in the radioisotopes present will affect the total radiation dose to the resins during burial, thus, affecting resin degradation.
- In several cases ion exchange resins have been disposed of with large radionuclide loadings which can result in radiation doses to the resins greater than 10⁸ rad. Section 3 presented evidence of radiation induced degradation products of ion exchange resins which are corrosive to carbon steel, a liner material used at present. Thus, a HIC must not only withstand any degradation effects of free liquid in the liner, it must also maintain its integrity when in physical contact with the waste.
- Gas buildup inside a disopsal liner may result from both radiolysis and biodegradtion. The radiolysis of water or the ion exchange resins will produce primarily hydrogen gas. Biodegradation of organic carbon will yield carbon dioxide.

It is recommended that liquid removed during the dewatering of resins by the utilities, be analyzed to establish a data base on the chemistry of the water inside a liner. This is necessary to assess the corrosivity of the liquids. Additional information about the long-term chemical and physical decomposition of organic ion exchange resins is necessary to evaluate the stability of a high integrity container filled with resins throughout the hazardous liftetime of the waste.

There is little data in the literature describing biodegradation in organic ion exchange resin waste. Reseach is needed to identify the type(s) of microorganisms present in radioactive ion exchange resin waste, their rate of growth, and the extent of multiplication. In addition the effects of the degradation rate and the degradation products on the waste package should be assessed.

5.2 Maximum Limit on Free Liquid in High Integrity Containers

Of primary concern in establishing a maximum limit on the amount of free liquid remaining in a high-integrity container (HIC) filled with dewatered organic ion exchange resins, is the protection of the public health and safety. It is undesirable to have large amounts of radioactive liquids spilling from a liner of organic ion exchange resins in the event of an accident during transportation or being released into a burial trench due to container failure. The radiation exposure to the plant personnel responsible for dewatering the liner must also be considered. Since long dewatering times may increase the radiation exposure to the operator, the allowable volume of drainable liquids should be achieved in a reasonable dewatering time.

It is difficult to account for all the water in a liner filled with ion exchange resins because these resins generally contain about 50% water. For example, one manufacturer, Dow Chemical, USA, specifies a range of water retention capacity for their resins. Dowex HCR-S, a strong acid cation exchanger supplied in a nuclear grade, has a range of water retention capacity of 50-56%. Several factors will affect the water retention capacity for spent resins such as repeated regeneration, cracked beads, and radiation damage. Environmental factors like temperature and humidity can cause a change in the amount of water that is held by the resin. Consider an example where 150 ft³ (1122 gallons) of resins are dewatered in a liner to the limit of 1 gallon free liquid. Since the resin beads are spherical and packed randomly in the liner, about 35% of the 150 ft³ volume of resins is interstital void space. Thus, there are about 97.5 ft³ (729 gallons) of resin material in the liner. If the water retention capacity ranges from 50 to 56% for these resins then there are 365 to 408 gallons of water in the liner. A temperature change causing evaporation of water from within the resin bead followed by condensation outside the resin, can significantly change the volume of free water in a liner. Likewise, it is possible for the resins to take up moisture. Clearly it is difficult to account for 1 gallon of water in a liner of resins containing almost 400 gallons of water bound to the resins. It is interesting to consider that, in a large liner, for example, a 6 ft x 6 ft right cylinder with a flat bottom, 1 gallon of water equally distributed across the bottom of the container will be approximately 0.06 inches (1.45 mm) deep. One company, CNSI, has a conical bottom on the dewatering liner which will direct any free liquid to a low point to be removed. This design is

better than having a utility tip a disposal cask and liner to direct the water to a low point. A disadvantage of the conical bottom is the likelihood of collecting any corrosive liquids in a small area rather than having the solution dispersed over a larger area. It may, however, be safe to assume that a liner placed in a burial trench will not lie perfectly flat. Thus liquid in the liner will collect in the low point of the container in any event.

Liners used for the disposal of ion exchange resins vary in volume from the 55-gallon drum to the CNSI 300 ft³ (2240 gallon) liner, it may be reasonable to express the limit of free liquid as a percentage of the volume of waste in the container. Consider the disposal of 300 ft³ of dewatered resin, in a 300 ft³ (2244 gallons) liner, 1 gallon of free liquid would be allowed. Since dewatering to this limit is difficult in the large liner, disposing of the resins in six 50 ft³ (374 gallon) liners may be preferred. One gallon of free liquid is allowed in each of these six liners or 6 gallons. If 6 gallons of free liquid were allowed in the 300 ft³ liner, dewatering to this limit (approximately 0.3% of the container volume) would have been easier, and in the end less material would have been buried (assuming it requires less material to construct one 300 ft³ liner than six 50 ft³ liners).

If a HIC fails during the required containment time (say 300 years) in the burial trench, it is preferred that only a small amount of liquid is released from the container to the trench. Remember, however, that the radionuclide concentration is much smaller in the free liquid than in the ion exchange resins. Because the resins are largely water, after the liner is breached, it is possible that the water and/or radionuclides in the resins will exchange with water and/or ions in the trench soil. The equilibrium resulting in this scenario may be as important as the release of free liquids when considering the transport of radioisotopes into the environment.

Since ion exchange resins generally have a moisture content of 50% of the resin volume, the effects of this water on the waste package should be considered. Data presented in section 3 indicated that removal of water retained by the resins significantly reduces the corrosion of steel by resin degradation products. Thus, little is gained by reducing the allowable free liquids from 1% or 0.5% to 1 gallon if corrosive species can still be transported to the liner wall by water by the resins.

The vendors of services to the nuclear industry agreed that water removal is a function of dewatering time. Excessively long dewatering times may achieve the desired small amount of free water (e.g., 1 gallon), but it may also result in larger radiation exposures to a worker.

It is recommended that the amount of free liquid allowed in a high integrity container be as low as reasonably achievable. Given the findings of this study the limit should be based on the volume of waste in a liner. It is apparent that allowing only one gallon of free liquid in a liner is not practically achievable in large liners. Therefore, a limit of 0.5% free water is suggested. However, in order to establish a limit on the amount of free water to be allowed in a high integrity container, information is needed in the following areas:

- The water defined as free water remaining in a liner must be defined. The water held by the resins, water absorbed on the surface of the resins and water adsorbed on the interior surface of the liner must all be considered. These factors cause a large uncertainty in quantifying the amount of free liquid in a liner.
- The accuracy of the dewatering method to be used by a utility must be substantiated by the vendor of the dewatering equipment. The suggested procedure for dewatering resin filled liners to a certain limit of free liquid is apparently based on the interpretation of water removed vs dewatering time data.

6. TECHNICAL JUSTIFICATION FOR THE DRAFT COPY OF THE NRC HIGH INTEGRITY CONTAINER DESIGN GUIDELINES

6.1 Introduction

A major concern in the shallow land burial of radioactive waste is the stability of the burial site, which can be achieved through a stable waste package. Solidification is a common method to stabilize radioactive waste. The use of a high integrity container (HIC) for the disposal of low level radioactive waste is intended as an alternative to solidification. Design of a HIC should be based on the specific type of waste to be buried. The high integrity container design addressed in this chapter is for the disposal of dewatered ion exchange resin waste from nuclear power plants. Some of the problems of high integrity container development have been considered in a number of recent reports. (22,26,27,28)

The State of South Carolina presently allows dewatered ion exchange resin waste with specific activity greater than one microcurie per cubic centimeter to be buried in a high integrity container at the Barnwell disposal site. Design criteria for the construction of a HIC have been established by the state in a memorandum, which is reproduced in Appendix B. The South Carolina Department of Health and Environmental Control, Bureau of Radiological Health has, thus far, issued a certificate of compliance for HIC to Chem-Nuclear Systems, Incorporated and Philadelphia Electric Company.

The United States Nuclear Regulatory Commission has proposed a draft regulatory guide for high integrity container design also presented in Appendix B. The guide is applicable to a HIC containing dewatered ion exchange resins with a specific activity of 350 Ci/cm³ or less of radionuclides with half-lives greater than 5 years. This is just a guide and no HIC has yet been certified by the NRC. This section shall review each criterion and present the technical justification based on information available in the literature. Those areas where data is lacking are indicated and methods to aleviate the deficiencies are suggested.

6.2 HIC Design Guidelines

<u>Guideline A</u>. The container should maintain its physical integrity for 10 half-lives of the longest lived significant isotope. For routine resin wastes, the isotopes of primary concern are Cs-137 and Sr-90 having 30-year half-lives. Therefore, the design lifetime of a container for routine resin wastes should be a minimum of 300 years. For wastes containing isotopes having half-lives less than 30 years, containers may be designed with lifetimes less than 300 years.

To establish the minimum lifetime for a high integrity container filled with routine resin wastes from light-water reactors (LWR) the protection of humans from the radioactivity in the waste must be considered. The possible
pathways of transfer of radioactive materials from the waste form and the relation between radioactive nuclide concentration or total amounts and human exposure are important. (22,29) The Draft Environmental Impact Statement (DEIS) (29) on 10 CFR Part 61 provides the rationale for the waste categories and the allowable limits in the wastes of various nuclides.

In general, the most restrictive limit on allowable radioactivity in wastes is determined by the possibility of an intruder coming in contact with the wastes after 100 years.⁽²⁹⁾ This is the postulated period of institutional control over the waste site. The intruder can construct a building, live in this building and farm the area, or on first digging, find large quantities of foreign material (i.e., waste packages) and quickly leave to find information on the material. Table 6.1 is reproduced from 10 CFR Part 61 and present the proposed waste classification. The Class A wastes are considered innocuous and indestinguishable from natural soil after 100 years. Class B wastes require the stability of the waste form or container (HIC) to warn an intruder of possible danger, in addition to, preventing the loss of waste to the environment. Class C wastes must be stabilized and must provide protection from intruders either by the depth of burial or engineered barriers.

If the level of radioactivity of Class A waste at the end of the 100-year institutional control period is assumed safe for general access by man, then the time necessary to reach this safe level can be calculated for various nuclides with initial activities as given for Class B wastes. Table 6.2 shows the major isotopes of concern, the half life, and decay constants. The maximum concentration for Class A segregated waste as defined in 10 CFR Part 61 and the concentration after 100 years are listed in lines 3 and 4, respectively. The maximum concentration for Class B segregated waste as defined in 10 CFR Part 61 is given (line 5) and the time for this concentration to decay to the safe level (line 6) is also listed. Clearly, if the resin waste is loaded with H-3 or Sr-90 to the maximum concentration allowable for Class B waste, the necessary lifetime of the container would have to be greater than 300 years. The survey results discussed in this report have not shown any utility loading resins with radionuclides to the concentrations given in Class B for H-3, Co-60, and Sr-90, however, the Edwin I. Hatch Nuclear Plant (see Table 2.8) and the Vermont Yankee Nuclear Power Plant (see Table 2.11) have reported loadings of Cs-137 of 757 µCi/g and 48.4 µCi/g, respectively. These values are above the value suggested in 10 CFR Part 61 for Class B segregated wastes and the materials should be buried as Class C, intruder wastes. The loading of 757 uCi/g would require about 385 years to decay to the level considered safe (see line 4 of Table 6.2). An estimated upper-range maximum radionuclide concentrations for a number of waste streams in both BWR and PWR power stations is given in Table 7.4 of DEIS. (29). The values for the ion exchange resins loaded with the nuclides of interest in this discussion are listed in line 7 of Table 6.2. The time necessary to reach the level of activity considered safe is shown in line 8. Only the estimated upper range of Sr-90 expected from pressurized water reactors will not decay to the accepted safe activity level within 300 years.

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Waste	0	lass	i	fica	tions	
Table 1	F	rom	1	OCFR	Part	61

Isotope	Column	Column	Column
	11	22	33
Any with half-life less than 5 years	700	70,000	Theoretical maximum specific activit
H-3	40	10 ⁸	Theoretical maximum specific activit
C-14	0.8	0.8	0.8 ⁴
N1-59	2.2	2.2	2.2
CO-60	700	70,000	Theoretical maximum specific activit
N1-63	3.5	70	70 .
Nb-94	0.002	0.002	0.002
Sr-90	0.04	150	700
I-129 Cs-235 Cs-137	0.008 84 1.0	0.008 84 44	0.0084 84 4600
Enriched uranium Natural or depleted uranium Alpha-emitting transuranic isotopes Pu-241	0.04	0.04 0.05	0.04 0.05 10 nC1/g 350 nC1/g

 $^{1}\text{Maximum}$ concentration for Class A segregated waste. Above this, it is Class B stable waste $^{\mu\text{Ci}/\text{cm}^3}$

²Concentrations above which some wastes become Class C intruder waste uCi/cm³.

³Maximum concentration for any waste class µCi/cm³.

⁴Near-surface disposal facilities will be limited to a specific quantity for the disposal site. This quantity will be determined at the time the license is issued and will be governed largely by the characteristics of the site. Therefore, the total activity of these isotopes in each package of waste must be shown on the shipping manifest (see §20.311 of this chapter).

For isotopes contained in metals, metal alloys, or permanently fixed on the metal as contamination, the values above may be increased by a factor of ten, except natural or depleted uranium which can be the natural specific activity.

For isotopes not listed above, use the values for Sr-90 for beta emitting isotopes with little or no gamma radiation; the values for Cs-137 for beta emitting isotopes with significant gamma radiation; and the values for U-235 for alpha emitting isotopes other than radium. Wastes containing chelating agents in concentrations greater than 0.1% are not permitted except as specifically approved by the Commission.

For mixtures of the above isotopes, the sum of ratios of an isotope concentration in waste to the concentration in the above table shall not exceed one for any waste class. Concentrations may be averaged over volume of the package. For a 55-gallon drum multiply the concentration limits by 200,000 to determine allowable total activity. Until establishment and adoption of other values or criteria, the values in this table (or greater concentrations as may be appoved by the Commission in particular cases) shall be used in categorizing waste for near-surface disposal.

It is recommended that all high integrity containers have a minimum lifetime of 300 years if they contain ion exchange media with radionuclide loadings greater than those suggested for Class A waste in 10 CFR Part 61. A container designed with a shorter lifetime and allowing the release of its contents in fewer than 300 years may cause a change in the soil characteristics of the trench. This in turn can result in the premature failure of other containers which are expected to last 300 years. Line 9 of Table 6.2 presents the estimated maximum concentrations to be buried in containers with a 300year lifetime. The activities listed will decay after 300 years to the level considered safe given in line 4 of Table 6.2. Resin wastes having radionuclide loadings greater than those listed in line 9 should be disposed of in a waste form or HIC designed to maintain its integrity for more than 300 years.

Table 6.2

Comparison of Radionuclide Concentrations With Timea

	Isotope	H-3	Co-60	Sr-90	Cs-137
1)	Half-life (yrs)	12.26	5.26	28	-30
2)	Decay-const. (yr ⁻¹)	5.654x10-2	1.318x10-1	2.476x10-2	2.310x10-2
3)	Maximum concentration for Class A segregated waste ^b (µCi/cm ³)	40	700	0.04	1.0
4)	Concentration for Class A segregated waste after 100 yrs (µCi/cm ³)	0.140	1.32x10-3	3.36x10-3	9.93x10-2
5)	Maximum concentration for Class B segregated waste ^b (µCi/cm ³)	108	70,000	150	44
6)	Time for maximum concen- tration for Class B waste to reach concen- tration given in line 5 (yrs)	360	135	432	264
7)	Estimated upper-range maximum radionuclide concentration (µCi/cm ³) ^C for BWR's PWR's	227 144	73.4 25.4	2.17 71.0	53.4 112
8)	Time for values in line 8 to reach levels listed in line 5 (yrs) for BWR's PWR's	131 123	83 75	261 402	272 304
9)	Maximum radionuclide concentration to be buried in a container having a 300 year lifetime (µCi/cm ³)	3x106	Theoretical Maximum Specific Activity	5.65	102

CTaken from Table 7.4 in Reference 29.

<u>Guideline B.</u> As a minimum the following should be evaluated in assessing the integrity of the container over the design lifetime: B.1. Corrosion of the container under storage and burial conditions.

Generally, nuclear plants do not store dewatered ion exchange resins in the disposal container for long periods of time on the plant site (see section 2). Therefore, since the waste package should retain its integrity for hundreds of years, corrosion of the container under burial site conditions is of major concern. However, the container is also expected to resist corrosion during short-term storage prior to burial.

Liners presently used for the disposal of dewatered ion exchange resins are generally constructed of carbon steel. The survey of vendors of disposal liners to the nuclear industry (see section 4) revealed that one company, EPICOR, Incorporated, is considering epoxy-lined steel for a HIC. Since corrosion is a major failure mechanism for metallic containers, the corrosive effects of the burial environment must be addressed when designing a HIC.

Gause, et al.⁽²⁶⁾ made a thorough report on the corrosion of container metals in soil incorporating a number of laboratory and field studies. A number of factors affect the corrosiveness of soil such as moisture, pH, conductivity, permeability of water and air, oxygen, salts, stray electrical currents, and biological organisms. Simple relationships between these factors and the corrosiveness of soil are not always valid. Pitting is the most common form of corrosion in most soils. For a nuclear waste container, the penetration rate or pitting rate should be considered when selecting a metal as a container material.

B.2. Corrosion of the container due to the contents

Section 3 of this report reviews the degradation of organic ion exchange resins. Studies (4,6,7,8) of the radiation-included degradation of ion exchange media have shown corrosion of both mild steel and stainless steel by chemical species released from the resins. Moisture in the resin beads acts as a transport medium for corrosive species from cation exchange resins to the metal surface resulting in corrosion. (8) If metals are choosen as construction materials for a HIC it is recommend that the resistance to the corrosive action of the resins, drainable liquids and degradation products of the ion exchangers be evaluated for that material.

The use of coatings, like epoxy, used in EPICOR-II liners at TMI, may be choosen as a method of protecting the metal surface of a HIC. To provide protection against metal corrosion, the coating must be resistive to moisture, acids, alkalis, and salts (30) which may be present inside a liner. The coating material should adhere to the metal surface and remain in tact for the intended life of the container. It is also necessary that the coating be free of holidays (areas of metal not covered) which can provide a surface for corrosion to occur.

Plastics, such as high density cross-linked polyethylene, are being used as HIC materials. Work is necessary to demonstrate the corrosion resistance of HDXL polyethylene to species released on the radiation-induced degradation of organic ion exchanging resins.

B.3. Mechanical strength of the container to withstand a load placed directly on the top of the container equivalent to 35 feet of material having a density of 120 lb/ft³.

The HIC is to be used for segregated waste with radionuclide loadings greater than suggested for Class A waste in 10 CFR Part 61 ruling. This waste is disposed of in the uppermost 10 to 20 meters (33 to 66 feet) of the earth's surface. The container should have a minimum mechanical strength to support the load of 10 meters of earth overburden. The three operating burjal sites construct trenches having a depth in the range of 5 to 8 meters. (10)

Appendix C lists the soil characteristics of National Bureau of Standards test sites in the United States. (26) Column 19 gives the apparent specific gravity of the soil for 53 of the sites. The average value is 1.72 and the standard deviation of these values is 0.2. Assuming a normal distribution of apparent specific gravities, then approximately 68% of the values will differ from the mean by less than 1 standard deviation. Therefore, 84% of the values will be less than the mean plus one standard deviation or 1.92 (1.72 + 0.20). Examination of the table shows that approximatley 80% of the values do fall below the value of 1.92. A density of 1.92 g/cm³ corresponds to 120 lbs/ft³. Therefore, the values of 35 feet of overburden having a density of 120 lbs/ft³ are a conservative requirement for mechanical strength of the container.

B.4. Mechanical strength to withstand routine loads from disposal site operations, such as trench compaction operations.

The HIC should be safe during the routine handling operations at a disposal site. Once a container is placed in a trench, it should maintain its physical integrity through the entire operation of filling the trench and finishing the trench cap. Collapse or slumping of the trench cap or cover can result in water entering the trench. To minimize the settling of the earth in the trench, it is necessary to compact the dirt, hence, the waste package must be able to withstand the load resulting from this operation. This load may be larger than that of the earth overburden which must be supported for the intended life of the container.

B.5. Thermal loads from processing, storage, transportation, and burial.

Several mechanisms exist, which can result in a thermal load on a HIC filled with dewatered ion exchange resins. The use of dry hot air in the resin dewatering process was discussed in section 4. No information was given, however, on the air temperatures used or the subsequent thermal exposure to the liner. The survey reviewed in section 2 showed that

short-term storage of dewatered resins at nuclear plants can be either indoors or outdoors, and a liner can also be exposed to a large variation in temperatures during transport from the reactor station to the burial site. Table 6.3 lists temperature ranges for a few states in which some nuclear plants are located. The thermal load possible inside a liner of resin due to radioactive decay heating has been discussed(22,31) for the EPICOR-II liners used to process water from the Auxiliary Building at TMI. Based on assumptions specific to the cleanup operation, the maximum temperature difference across the ion exchange media was estimated to be 11°C to 44°C (52°F to 111°F) for a total thermal inventory of 1.0 to 4.0 watts, respectively. This evaluation may serve as an upper bound approximation for resin waste from operating nuclear plants.

Table 6.3

	Mean Minimum Temperature (°F) Range January ^a	Mean Minimum Temperature (°F) Range Julya
Illinois	14-28	84- 90
Maine	0-14	70- 84
Nevada	10-36	76-104
South Carolina	30-42	80- 92
Washington	8-36	64- 92

Temperature Variations for Several States

^aThe range given is taken from the lowest and highest isoline values from the appropriate maps in Reference 32.

The possible temperature variations discussed here indicate the necessity to address the thermal stability of a waste package when designing a high integrity container. Recommendations of test procedures are presented in a recent review of methods for testing the thermal stability of a waste form. (38)

B.6. Radiation stability of the container material and the contents to include effects produced by irradiation of the resins, including gas generation and acid formation.

It is essential that a container maintain its integrity for the hazardous life of the waste to prevent the release of radionuclides to the environment. Therefore, the stability of the waste (e.g., ion exchange resins), and the container material to radiation must be assessed in a high integrity container design.

Section 3 of this report reviews the effects of ionizing radiation on ion exchange resin media. In general, radiation doses to resins in excess of

10⁸ rad result in gas generation, and the corrosion of steel due to acidic species released from cation exchangers. The corrosive effects of resin degradation products on alternate container materials (for example high density cross-liked (HDXL) polyethylene which is being used for the dispoal of dewatered ion exchange resins at the Barnwell, SC, burial site) must be evaluated on a case-by-case basis.

The use of orgnaic materials like HDXL polyethylene and epoxy coatings on steel in high integrity containers possess a question of their radiation stability. Organic compounds yield gaseous products on irradiation. (33) Hy-drogen is the primary gas generated in the radiolysis of polyethy-lene, (33,34) and there is subsequent deterioration of the mechanical properties of the plastic. (33) A minimum accumulated radiation dose usually exists above which these changes occur. However, if a limit is established on the allowable radionuclide loading on ion exchange media being buried, (5) then failure of the waste package due to radiation damage of the contents of the container materials may be negligible. Where data is lacking on the radiation stability of candidate container materials, the information should be determined and limits established if the materials are to be used in HICs.

B.7. Biodegradability of the container and contents under storage and burial site conditions.

Microorganisms can be responsible for the degradation of natural and man-made organic materials. Thus, the possibility of biodegradation must be considered in the design of an HIC to be used for the disposal of organic ion exchange resins. The survey of the utilities revealed a potential problem of gas generation due to bacteria growth in ion exchange resin waste. There is, however, limited data on the biodegradation of organic ion exchange media, as discussed in section 3.4 of this report.

High density cross-linked polyethylene is presently in use as a construction material for HICs buried at the Barnwell, SC, disposal site. Since microorganisms are present in resin waste and also abundent in the biosphere, particularly in shallow land burial trenches, (10) the possible biodegradation of the waste package resulting in the release of radionuclides to the environment must be addressed. A recent report (35) showed that low density polyethylene was degraded slowly by microbial action. The initial rate of degradation was measured between 0.005 and 0.10% per month. High density polyethylene has been reported to have good resistance to soil microorganisms. (39)

There is need for work in the area of microbial decomposition of both waste packages and the waste itself (i.e., ion exchange resins) in order to assess the extent of the problem on nuclear waste management.

<u>Guideline</u> C. The container should be able to meet the requirements for a Type A package as defined in 49 CFR Section 173.398(b). The free drop test may be performed in accordance with 10 CFR Part 71, Appendix A. Since it is necessary to transport the high integrity container, filled with dewatered ion exchange resins, from the nuclear plant to the burial site, as a minimum, the container should meet the requirements of the Department of Transportation [i.e., 49 CFR Section 173.398(b)]. The NRC regulation defining the free drop test (i.e., 10 CFR Part 71 Appendix A) is a conservative requirement for the packaging of radioactive material. Appendix C contains the two regulations of concern. These requirements include tests in heat, cold, pressure, vibration, water spray, free drop, penetration, and compression environments, and they have contributed to the safe packaging and transport of radioactive waste at the present time. (36)

<u>Guideline D</u>. The container and the associated lifting devices should be able to withstand the forces applied during lifting operations. This includes adding a safety factor to cover "abrupt lifting." As a minimum, the container should be able to withstand a 3 g vertical load.

If a container used for the transport and disposal of dewatered spent ion exchangers is to retain its integrity for 300 years in burial, then, it should be designed to withstand the normal operations necessary to fill the package with waste, transport the package to the disposal site, and move the package to its final resting place in the burial trench. Burial site operations may include as a minimum, the use of fork lifts and cranes to lift the container from the transport vehicle to the trench. Since the public safety is of major concern when handling radioactive waste, the HIC design must address all uncertainties which may be encountered during these operations. Abrupt lifting is an example of an operation which can result in large stress on the container from the lifting device. The existing regulation for waste package standards, 10 CFR Section 71.31(c) (see Appendix C) requires that lifting devices on the waste form must be capable of supporting three times the weight of the loaded package. The weight w, of a package is simply the mass, m, of the material multiplied by the acceleration due to gravity, g.

w = mg

Since the mass of the package is constant during abrupt lifting, a minimum load of 3 g is equal to three times the weight of the package. Therefore, this vertical load is a minimum requirement which is consistent with the existing regulation.

<u>Guideline E.</u> The container should avoid the collection or retention of water on container surfaces.

The survey of operating nuclear stations, discussed in section 2 of this study indicates that the majority of the nuclear plants either operating or in various stages of construction are located in humid regions of the United States. Figure 2.1 shows the approximate location of the nuclear power reactors in the United States, which are the source of the organic ion exchange resin waste to be disposed of in a HIC by shallow land burial. The "Low Level Waste Policy Act Report," (37) also shows that the majority of low level

waste from reactors is produced in humid regions and is presently disposed of at the Barnwell, South Carolina, burial site where the precipitation is 118 cm/yr.(10) Public law 96-573(37) calls for each state to provide the availability of disposal capacity for LLW. A large portion of ion exchange resin waste is produced and buried in wet areas of the United States, hence, it is reasonable to expect the waste package design to address the problem of the collection and retention of water on the container surface. To ensure water drainage in a burial trench, the container design should minimize the possibility of water accumulation on the surface. The avoidance of water collecting in a single area on a container surface will help mitigate any corrosive attack.

<u>Guideline</u> F. The container should remain sealed for the design lifetime of the container. Special vent designs which do not cause radionuclide migration over the design lifetime of the container may be considered if needed to relieve excessive internal pressures.

The high integrity container is an alternative to solidification as a means of stabilizing ion exchange resin wastes for disposal. In both cases, it is expected that the radionculides will not be released to the environment during the hazardous lifetime of the waste. For the HIC, the construction material is the ultimate barrier to the environment for the release of radioactive contaminants to the environment. Additionally, the caps and covers used for the closure of the construction material.

Both radiation induced degradation and biodegradation of organic ion exchange resin waste can result in gaseous products. Experimental evidence for gas generation is discussed in section 3 of this report. Gases of major concern are hydrogen, H₂, produced on the radiolytic degradation of organic ion exchange media and the radiolysis of water, and carbon dioxide, CO₂, resulting from biodegradation of material inside the container. Although the radiolytic gas generation may be negligible if a limit for radionuclide loading on ion exchange media is established, (5) the potential problem of gas production from biodegradation must be assessed. Pressure buildup inside the container may result in failure of the HIC. To prevent a failure of this type, a vent for gaseous compounds may be necessary. Vent designs incorporated into high integrity containers should not allow the release of radionuclides from the waste package to the environment, thereby defeating the purpose of containment. Additionally, chemical and biological substances from the trench environment should not pass through the vent if they can cause a decrease in the stability of the resin waste package.

6.3 Conclusions

The high integrity container discussed in this study is for the disposal of dewatered ion exchange resin waste from nuclear power plants. The NRC suggests that the radioactivity in the container does not exceed 350 μ Ci/cc of

nuclides with half-lives greater than 5 years. Based on the waste classifications defined in the proposed ruling, 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste," it is recommended that the HIC have a minimum 300-year design lifetime. Maximum activities for H-3-Co-60, Sr-90, and Cs-137 to be disposed of in this HIC are estimated above which a disposal container having a longer liftime should be used.

The container should maintain its structural integrity and prevent the loss of the contents for the design lifetime. Corrosion is a major failure mechanism for metallic containers and corrosion can be caused by the internal and the external environment of the HIC. Mechanical strength and thermal stability must be considered in the design of a HIC. If a limit is established for the radionuclide loading on ion exchange resins being disposed of there may be no deleterious effects to the resins or the container material resulting from radiation.

Information on the biodegradation of the contents (i.e., ion exchange resin waste) of the HIC is sparse, thus work should be done in this area.

It may be necessary to incorporate a vent in the HIC to relieve excess gas pressure resulting from bacterial activity. It is recommended that the effects of radiation and of biodegradation on the HIC stability be evaluated on a case-by-case basis.

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APPENDIX A

COMPLETED QUESTIONNAIRES

This appendix contains the completed questionnaires received from seven boiling water reactors (BWR) and nine pressurized water reactors (PWR). Included is any additional information supplied by the utilities.

A.1 Boiling Water Reactors

Responses were received from:

Bronws Ferry Nuclear Power Station Dresden Nuclear Power Station Duane Arnold Energy Center Edwin I. Hatch Nuclear Plant Monticello Nuclear Generating Plant Peach Bottom Atomic Power Station Vermont Yankee Nuclear Power Station

A.2 Pressurized Water Reactors

Responses were received from:

Fort Calhoun Station Joseph M. Farley Nuclear Plant Kewaunee Nuclear Power Plant Maine Yankee Atomic Power Plant Prairie Island Nuclear Generating Plant Sequoyah Nuclear Plant Trojan Nuclear Plant Yankee-Rowe Nuclear Power Station Zion Nuclear Plant

The contents of this appendix are given in the attached microfiche.

APPENDIX B

- 1. HIGH INTEGRITY CONTAINER DESIGN GUIDELINES
- 2. SOUTH CAROLINA DEPARTMENT OF HEALTH AND ENVIRONMENTAL CONTROL, "STAFF POSITION ON GENERAL CRITERIA FOR HIGH INTEGRITY CONTAINERS"

HIGH INTEGRITY CONTAINER DESIGN GUIDELINES

Scope:

This guide is applicable to a high integrity container to be used for the disposal of nuclear power plant dewatered resins containing up to $350 \,\mu$ Ci/cc of nuclides with half-lives greater than 5 years. The resins are assumed to be dewatered to the extent that the remaining drainable liquid upon receipt at the disposal site would not exceed 0.5% of container volume or 1 gallon, whichever is less, and has a pH within the range of 4 to 11.

Guidelines:

- A. The container should maintain its physical integrity for 10 half-lives of the longest lived significant isotope. For routine resin wastes the isotopes of primary concern are Cs-137 and Sr-90 having 30-year halflives. Therefore, the design lifetime of a container for routine resin wastes should be a minimum of 300 years. For wastes containing isotopoes having half-lives less than 30 years, containers may be designed with lifetimes less than 300 years.
- B. As a minimum the following should be evaluated in assessing the integrity of the container over the design lifetime:
 - 1. corrosion of the container under storage and burial site conditions;
 - 2. corrosion of the container due to the contents;
 - mechanical strength of the container to withstand a load placed directly on the top surface of the container equivalent to 35 feet of material having a density of 120 lb/cf;
 - mechanical strength to withstand routine loads from disposal site opertions, such as trench compaction operations;
 - 5. thermal loads from processing, storage, transportation, and burial;
 - radiation stability of the container material and the contents to include effects produced by irradiation of the resins, including gas generation and acid formation.
 - biodegradability of the container and contents under storage and burial site conditons.
- C. The container should be able to meet the requirements for a Type A package as defined in 49 CFR Part 173.398(b). The free drop test may be performed in accordance with 10 CFR Part 71 Appendix A.
- D. The container and the associated lifting devices should be able to withstand the forces applied during lifting operations. This includes adding a safety factor to cover "abrupt lifting." As a minimum, the container should be able to withstand a 3g vertical load.

- E. The container design should avoid the collection or retention of water on container surfaces.
- F. The container should remain sealed for the design lifetime of the container. Special vent designs which do not cause radionuclide migration over the design lifetime of the container may be considered if needed to relieve excessive internal pressures.

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RETYPED FOR LEGIBILITY

October 22, 1980

MEMORANDUM

TO: Heyward G. Shealy, Chief Bureau of Radiological Health

FROM: Division of Rad. Material Licensing & Compliance Bureau of Radiological Health

SUBJECT: Staff Position on General Criteria for High Integrity Containers

In October 1979, the low-level waste facility license was, again, amended in its entirety. This revision to the burial license specifically defined our requirements for free standing liquids and set goals for their implementation. Also discussed were the Department's goals to enhance the stability of the high concentration waste forms buried at the South Carolina site. One method to increase stability and containment of these waste forms is to require complete solidification. Another option is to improve the integrity of the burial containers.

High integrity containers could be a viable option to increase stability and long term containment of high concentration waste forms. High concentration waste forms are defined as ion exchange resins, filter media and other media used to concentrate and remove activation and corrosion products from plant process systems having specific activity of one (1) microcurie/cubic centimeter or greater of all radionuclides with greater than five (5) year half-lives. The high integrity containers for these waste forms should be designed and constructed to minimize any impact on the industry but also to meet the criteria established below. These containers should be designed to be used in conjunction with existing Type A and Type B specification shipping containers to meet the U. S. Department of Transportation requirements.

The general criteria for high integrity containers to be used for high concentration waste forms is as follows:

- The container must be capable of maintaining its contents until the radionuclides have decayed, approximately 300 years since two of the major isotopes of concern in this respect are Strontium 90 and Cesium 137 with half-lives of 28 and 30 years, respectively.
- (2) The structural characteristics of the container with its contents must be adequate to withstand all the pressure and stresses it will encounter during all handling, lifting, loading, offloading, backfilling, and burial.
- (3) The container must not be susceptible to chémical, galvanic or other reactions from its contents or from the burial environment.
- (4) The container must not deteriorate when subjected to the elevated temperatures of the waste streams themselves, from processing materials inside the container, or during storage, transportation and burial.

Memorandum Page two October 22, 1980

- (5) The container must not be degraded or its characteristics deminished by radiation emitted from its contents, the burial trench or the sun during storage.
- (6) All lids, caps, fittings and closures must be of equivalent materials and construction Commet all of the above requirements and must be completely sealed to prevent any loss of the container contents.

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APPENDIX C

49 CFR Section 173.398 SPECIAL TESTS

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10 CFR Part 71 - APPENDIX A - NORMAL CONDITIONS OF TRANSPORTATION

10 CFR Section 71.31 - GENERAL STANDARDS FOR ALL PACKAGING

Table C.1 - CHEMICAL AND PHYSICAL PROPERTIES OF THE SOILS AT THE NBS TEST SITES

§ 173.398

defined in paragraph (a) of this section.

[Amdt. 173-90, 39 FR 45243, Dec. 31, 1974]

§ 173.398 Special tests.

(a) Special form material: To qualify as special form material, the radioactive material must either be in massive solid form or encapsulated. Each item in massive solid form or each capsule must either have no overall dimension less than 0.5 millimeters, or must have at least one dimension greater than 5 millimeters. Each item, or the capsule material, must not dissolve or convert into dispersible form to the extent of more than 0.005 percent, by weight, by immersion for 1 week in water at pH 6-8 and 68' F., and a maximum conductivity of 10 micromhos/centimeter. and by immersion in air at 86° F. If in massive solid form, the radioactive material must not break, crumble, or shatter if subjected to the percussion test prescribed in this section, and must not melt, sublime, or ignite at temperatures below 1,000° F. If encapsulated, the capsule must retain its contents when subjected to all of the performance tests prescribed in this section, and must not melt, sublime, or ignite at temperatures below 1,475° F.

(1) Free drop. A free drop through a distance of 30 feet on to a flat essentially unyielding horizontal surface, striking the surface in such a position as to suffer maximum damage.

(2) Percussion. Impact of the flat circular end of a one inch diameter steel rod weighing three pounds, dropped through a distance of 40 inches. The capsule or material shall be placed on a sheet of lead, of hardness number 3.5 to 4.5 on the Vickers scale, and not more than one inch thick, supported by a smooth, essentially unyielding surface.

(3) *Heating*. Heating in air to a temperature of 1,475° F. and remaining at that temperature for a period of 10 minutes.

(4) Immersion. Immersion for 24 hours in water at room temperature. The water shall be at pH6-pH8, with a maximum conductivity of 10 micromhos/cm.

Note 1: Each shipper of special form radioactive material shall maintain on file for

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at least one year after the last shipment, and be prepared to provide the Department, a complete certification and supporting safety analysis (see Note 2) demonstrating that the special form material meets the requirements of paragraph (a) of this section. This requirement is effective December 31, 1974.

Note 2: Prior to the first shipment of a special form radioactive material outside of the United States, each shipper shall obtain a Certificate of Competent Authority for the specific material. Each petition sust be submitted in accordance with § 173.303b (b) and (c), and must additionally include the following information:

A detailed description of the material, or if a capsule, the contents. Particular reference must be made to both physical and chemical states;

b. A detailed statement of the design of any capsule to be used, including complete engineering drawings and schedules of material, and methods of construction;

c. A statement of the tests which have been done and their results, or evidence based on calculative methods to show that the material L capable of meeting the tests, or other evidence that the special form radioactive material meets the requirements of paragraphs (aX1) thru (4) of this section.

(b) Standards for Type A packaging:

(1) Type A packaging must be so designed and constructed that, if it were subject to the environmental and test conditions prescribed in this paragraph:

(i) There would be no release of radioactive material from the package:

(ii) The effectiveness of the packaging would not be substantially reduced; and

(iii) There would be no mixture of gases or vapors in the package which could, through any credible increase of pressure or an explosion, significantly reduce the effectiveness of the package.

(2) Environmental conditions:

(i) Heat. Direct sunlight at an ambient temperature of 130° F. in still air.

(ii) Cold. An ambient temperature of -40° F. in still air and shade.

(iii) Reducid pressure. Ambient atmospheric pressure of 0.5 atmosphere (absolute) (7.3 p.s.i.a.).

(iv) Vibration. Vibration normally incident to transportation.

(3) Test conditions: The packaging shall be subject to all of the following tests unless specifically exempted therefrom, and also to the consecutive

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application of at least two of the following tests from which it is not specifically exempted:

(i) Water spray. A water spray heavy enough to keep the entire exposed surface of the package except the bottom continuously wet during a period of 30 minutes. Packages for which the outer layer consists entirely of metal, wood, ceramic, or plastic, or combinations thereof, are exempt from the water spray test.

(ii) Free drop. Between 1% to 2% hours after the conclusion of the water spray test, a free drop through a distance of 4 feet onto a flat essentially unyielding horizontal surface, striking the surface in a position for which maximum damage is expected.

(iii) Corner drop. A free drop onto each corner of the package in succession, or in the case of a cylindrical package onto each quarter of each rim, from a height of 1 foot onto a flat essentially unyielding horizontal surface. This test applies only to packages which are constructed primarily of wood or fiberboard, and do not exceed 110 pounds gross weight, and to all Fissile Class II packagings.

(iv) Penetration. Impact of the hemispherical end of a vertical steel cylinder 1% inches in diameter and weighing 13 pounds, dropped from a height of 40 inches onto the exposed surface of the package which is expected to be most vulnerable to puncture. The long axis of the cylinder shall be perpendicular to the package surface.

(v) Compression. For packages not more than 10,000 pounds in weight, a compressive load equal to either five times the weight of the package or 2 pounds per square inch multiplied by the maximum horizontal cross section of the package, whichever is greater. The load shall be applied during a period of 24 hours, uniformly against the top and bottom of the package in the position in which the package would normally be transported.

(c) Standards for hypothetical accident conditions of transportation for Type B packagings:

1) Type B packaging must meet the applicable Type A packaging standards and must be designed and constructed and its contents so limited that, if subjected to the hypothetical

accident conditions prescribed in this paragraph, it will meet the following conditions:

(i) The reduction of shielding would not be enough to increase the radiation dose rate at three feet from the external surface of the package to more than 1,000 millirem per hour.

(ii) No radioactive material would be released from packages containing Type B quantities of radioactive material. The allowable release of radioactivity from packages containing large quantities of radioactive material is limited to gases and contaminated coolant containing total radioactivity exceeding neither 0.1 percent of the total radioactivity of the package contents nor 0.01 curie of Group I radionuuclides, and 10 curies of Groups III and IV radionuclides, except that for inert gases the limit is 1,000 curies.

(2) Test conditions: The conditions which the package must be capable of withstanding must be applied sequentially, to determine their cumulative effect on a package, in the following order:

(1) Free drop. A free drop through a distance of 30 feet onto a flat essentially unyielding horizontal target surface, striking the surface in a position for which maximum damage is expected.

(ii) Puncture. A free drop through a distance of 40 inches striking, in a position for which maximum damage is expected, the top end of a vertical cylindrical mild steel bar mounted on an essentially unyielding horizontal surface, the bar shall be 6 inches in diameter, with the top horizontal and its edge rounded to a radius of not more than one-fourth inch, and of such a length as to cause maximum damage to the package, but not less than 8 inches long. The long axis of the bar shall be perpendicular to the unyielding horizontal surface.

(iii) Thermal. Exposure to a thermal test in which the heat input to the package is no less than that whicn would result from exposure of the whole package to a radiation environment of 1,475° F. for 30 minutes with an emissivity coefficient of 0.9, assuming the surfaces of the package have an absorption coefficient of 0.8. The

§ 173.426

package shall not be cooled artificially until 3 hours after the test period unless it can be shown that the temperature on the inside of the package has begun to fall in less than 3 hours.

(1v) Water immersion (fissile radioactive materials packages only). Immersion in water to the extent that all portions of the package to be tested are under at least 3 feet of water for a period of not less than 8 hours.

(d) It is not necessary to actually conduct the tests prescribed in this section if it can be clearly shown, through engineering evaluations or comparative data, that the material or item would be capable of performing satisfactorily under the prescribed test conditions.

(Amdt. 173-3, 33 FR 14929, Oct. 4, 1968; 33 FR 19823, Dec. 27, 1968, as amended by Amdt. 173-90, 39 FR 45244, Dec. 31, 1974; 40 FR 2435, Jan. 13, 1975]

Subpart I—Special Requirements for Certain Rail Shipments or Movements

\$ 173.426 Cars, truck bodies or trailers containing lading which has been fumigated or treated with flammable liquids, flammable gases, poisonous liquids or solids, or poisonous gases.

(a) Delivery of rail cars, freight container, or trailers containing lading, fumigated or treated with flammable liquid or flammable gas for transportation by rail carrier is prohibited until 48 hours have elapsed after such fumigation or treatment, or until cars, truck bodies or trailers have been ventilated so as to remove danger of fire or explosion due to the presence of flammable vapors.

(b) Rail cars, truck bodies or trailers containing lading which has been formigated or treated with poisonous liquid, solid, or gas, such as carboliacid, liquid or solid, chlorpicrin, hydrocyanic acid, methyl bromide, etc., must be placarded on each door or near thereto with placard as described below (for cleaning cars see § 174.615 of this subchapter):

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(Reduced size)

(Red lettering on white cardboard)



[29 FR 18773, Dec. 29, 1964. Redesignated at
 32 FR 5606. Apr. 5, 1967; Amdt. 173-94. 41
 FR 16087. Apr. 15, 1976. and amended by
 Amdt. 173-94A, 41 FR 40684, Sept. 20, 19761

\$\$ 173.127-173.131 [Reserved]

173.132 Tank car shipments.

(a) Tank cars containing any flama mable gas or flammable liquid, except liquid road asphalt or tar, must not be offered for shipment unless originally consigned or subsequently reconsigned to parties having private-siding (see Note 1 of this section) or to parties using railroad siding facilities which have been equipped for piping the liquid from tank cars to permanent storage tanks of sufficient capacity to receive contents of car.

(b) A tank car containing any compressed gas must not be offered for transpertation unless the car is consigned for delivery (see paragraph (c) of this section) and unloading on a private track (see Note 1 of this section) except that where no private track is available, delivery and unloading on carrier tracks is permitted provided the following conditions are complied with:

(1) Any tank car of DOT-106A or 110A type (see §§ 179.300 and 179.301 of this subchapter) may be offered for transportation and the loaded unit tanks may be removed from car frame on carrier tracks, provided the shipper has obtained from the delivering carri-

APPENDICES

APPENDIX A-NORMAL CONDITIONS OF

Each of the following normal conditions of . transport is to be applied separately to determine its effect on a package.

1. Heat-Direct sunlight at an ambient temperature of 130° F. in still air.

2. Cold-An ambient temperature of -40°F. in still air and shade.

3. Pressure - Atmospheric pressure of 0.5 times standard atmospheric pressure.

 Vibration - Vibration normally incident to transport.

5. Water Spray-A water spray sufficiently heavy to keep the entire exposed surface of the package except the bottom continously wet during a period of 30 minutes.

6. Free Drop-Between 1-1/2 and 2-1/2 hours after the conclusion of the water spray test, a free drop through the distance specified below onto a flat essentially unyielding horizontal surface, striking the surface in a position for which maximum damage is expected.

FREE FALL DISTANCE

Pac	(pound	weight ds)	Distance (feet)
ess than 10	.000		4
0.000 to 20	000.0		3
0,000 to 30	000,0		2
fore than 30	0.000		1

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7. Corner Drop-A free drop onto each corner of the package in succession, or in the case of a cylindrical package onto each quarter of each rim, from a height of 1 foot onto a flat essentially unyielding horizontal surface. This test applies only to packages which are constructed primarily of wood or fiberboard, and do not exceed 110 pounds gross weight, and to all Fissile Class II packagings.

8. Penetration-Impact of the hemispherical end of a vertical steel cylinder 1-1/4 inches in diameter and weighing 13 pounds, dropped from a height of 40 inches onto the exposed surface of the package which is expected to be most vulnerable to puncture. The long axis of the cylinder shall be perpendicular to the package surface.

9. Compression-For packages not exceeding 10,000 pounds in weight, a compressive load equal to either 5 times the weight of the package or 2 pounds per square inch multiplied by the maximum horizontal cross section of the package, whichever is greater. The load shall be applied during a period of 24 hours, uniformly against the top and bottom of the package in the position in which the package would normally be transported.

10 CFR Section 71.31 - GENERAL STANDARDS FOR ALL PACKAGING

Subpart C-Package Standards

§71.31 General standards for all packsging.

(a) Packaging shall be of such materials and construction that there will be no significant chemical, galvanic, or other reaction among the packaging components, or between the packaging components and the package contents.

(b) Packaging shall be equipped with a positive closure which will prevent inadvertent opening.

(c) Lifting devices:

(1) If there is a system of lifting devices which is a structural part of the package, the system shall be capable of supporting three times the weight of the loaded package without generating stress in any material of the packaging in excess of its yield strength.

(2) If there is a system of lifting devices which is a structural part only of the lid, the system shall be capable of supporting three times the weight of the lid and any attachments without generating stress in any material of the lid in excess of its yield strength.

(3) If there is a structural part of the package which could be employed to lift the package and which does not comply with subparagraph (1) of this paragraph. the part shall be securely covered or locked during transport in such a manner as to prevent its use for that purpose.

(4) Each lifting device which is a structural part of the package shall be so designed that failure of the device under excessive load would not impair the containment or shielding properities of the package.

(d) Tie-down devices:

(1) If there is a system of tie-down devices which is a structural part of the package, the system shall be capable of withstanding, without generating stress in any material of the package in excess of its yield strength, a static force applied to the center of gravity of the package having a vertical component of two times the weight of the package with its contents, a horizontal component along the direction in which the vehicle travels of 10 times the weight of the package with its contents, and a horizontal component in the transverse direction of 5 times the weight of the package with its contents.

(2) If there is a structural part of the package which could be employed to tie the package down and which does not comply with subparagraph (1) of this paragraph, the part shall be securely covered or locked during transport in such a manner as to prevent its use for that purpose.

(3) Each tie-down device which is a structural part of the package shall be so designed that failure of the device under excessive load would not impair the ability of the package to meet other requirements of this subpart.

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Table C.1

Chemical and Physical Properties of the Soils at the NBS Test Sites^a, (26)

		•	Inter-		-	S	mposition	a of water	extract	hə-Bui '	per 100	g of soil		Ican	An- M	-tio	Ap	Untr- V	-lo
No. *	Type	Location	drain- sge of test	Result- ivity ut ut	II	Total acid-	Na + K	3	314	co,	liC0,	5	80,	-una -una	ion -	ent - p		Nity -	1 5
	Attis sitt tosts.	Jeveland, Ohio. Jallan, Ter. Ulanta, Ga.		Ohm-cm 1, 215 681 681 6 670	0.12	1.5	0.72	0 32	0.13	88	88	0.0	0.83	2.001	13.8% 13.2% 1.2% 1.2% 1.2% 1.2% 1.2% 1.2% 1.2% 1	100-08	0000	2928	22.000
	Chester foam. Dublin clay adole. Everett gravelty aandy loam. Pargo clay loam.	cattationer, Calif. Dakland, Calif. Stattle, Wash. Sincinnati, Ohio	a craa	1,315	0.1	20.8	. 93	4 1 72	3.55	8 8		10	1	0.12 2.02 2.02 2.02	338.6	12.22	00000	500 000 000 000 000 000 000 000 000 000	21.0
og 192	Generee sitt loam Gloucester sandy loam Il accretoran loam Il andord fine sandy loam	Middleboro, Mass. Loch Raven, Md. Loch Raven, Md. Pattersheld, Calif.		7,460	0 0100	3.6 2.5 5.4	0.30	0.50	0.16	88 8	97 1 99	00 13	3.76	522 C C C C C C C C C C C C C C C C C C	15.2 27.2 27.2	12110	00041	6 28 08	8 6 0 1 39 8
11 11	llempataad ait loam llouaton black clay . Kalmia fino anady loam Keyport loam Kor ait loam	Baa Antonio, Ter. Mobile, Ala Alcandria, Ve. Omaha, Nebr	a 2200	480 5,080 1,410 1,410		8.101	0.27	83 93 93	878	888	10.0	838	25 15	55. 3 50.6 10.5 10.5	61.6 27.8 33.0	128.855	07938	32828	3.8
222 22	Lundey ait loam. Makhoning ait loam. Meanphia ait loam. Meanphia ait loam.	Cleverand, Ohio Kansas City, Mo Memphas, Tean. Buttonwillow, Calif	4 2020	2,870 5,150 5,150 11,400	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	S 88 8	9 88 94	8	8	1.87	1 12	5.57	51.4 61.6 65 50 46.1	37.1 47.7 6.1 30.1	238.4 238.4 23.74 23.0 23.0 23.0	80.08	1.66 1.67 1.60	8.8 0.2 0.2
55.65	Micrimae gravely sandy toom- Mismi clay foam. Mismi att toam. Minite clay.	Milwaukoe, Wia. Springfield, Ohio Bunkle, La. San Diego, Calif.	A CLAN	2, 986 576 1, 270	N N N N N	28 A 4	2.15		31 33	88888	0.70 0.12 0.12 0.12	23.00	1.51 0.80 0.24	50.19 50.19 50.19	37 56 57.4 32.1	16.4 21.6 21.6 29.4	20.0	2.01	32.5
88 2823	Nuce ait loam. Nucetue ait loam. Nucetuk foe and Ontario loam. Peat	Davenport, Iowa Jacksonville, Fla Rochester, N. Y. Miliwaukee, Wis. Norristown, Pa.	* 005+0	20,50 5,700 4,900 2,000		30.05	1 53	7.30	1.06	88 8	57. 1.10	2.27 0.06	2.13	69.3 17.6 16.1 51 62.4	47.4 32.8 30.1 40.1	172.8 23.4 18.0	111.0	1.85	1.00
35 33	R-mona joan. Ruaton aandy loam. St. John'a fino aand Sasaafraa aitt loam. Sasaafraa aitt loam.	Meridian, Miss Ackaouville, Fla Camdea, N. Bel Wilmagton, Del New Orleana, La	OLGRA	38,500	00000 989900	48-80	8	58		8 8	0.03	10	28	61.0 54 54 54 54 54.4	1.12 1.12 1.12	7.0 33.0 33.1	32.1	1 73	2000 27 28 28 29 29
20021	Summit ailt loam Susquehenna clay Tidal marsh. Wabash ailt Joam	Kausaa City, Mo Meridian, Miss Elizabeth, N. J Ounaha, Nebr.	77720 77720	13.70	0000 C	308	45.10 8 15.00 8 15.00	. 08 1.08 3.70	0.06	888	0 24	43 30 0.82 18	37 00 0 41 11 98	61.0 52.6 47.2	51.0 27.8 15.3	31 8 55.4 14.8 14.8	18.7	1 22	0 0
52 51 52 52 52 52 52 52 52 52 52 52 52 52 52	Unidentified andy loam. Unidentified all loam. Acadia clay Lake Charles clay loam. Ceel clay loam.	Denver Colo. Salt Lake City, Utah. Spindletop, Tex. League City, Tex.	04440	1,72	1000	5 B.S.	10.07	0.33	50 SE	883	88 50 1 30	5 15 1 33	0 48 1.26 1.26	50.00 61.0	18	25.7 21.8 33.78	2.6	1.672	33.6

See footnotes at end of table.

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Table C.1, Continued

Chemical and Physical Properties of the Soils at the NBS Test Sites^a, ⁽²⁶⁾

Type Lease Addite Data Data <thdata< th=""> Data Data <</thdata<>		Boil		Inter-	Resist-		Co	mposition	a of water	extract	ba-But .	per 100	g of soi		Mean	An.	fois-	AL AL		-tot
		Type	Location	drain- age f toot	wity #1	H	Total acid-	Na + K	3	MG	00°	1001	5	80.	pera- turo .	preci-	ture optiv-	All'	fic the	rink-
	1 -	Chimmen all lane	Cincinnati, Ohio	-	880	7.0		0.56	10.10		8	0.70	0.08	9.05		Inches 38.6	Per-	Per-	89	Per-
$ \begin{array}{c} \label{constraint} \math {\bf k} \ma$:2353	Is accedition from the first second s	Lach Raven, Md. El Viata, Tex. Tranquility, Calif. New Orleana, La.	97-7	5, 210 406 128 712	8-1-8	10.0	23.40	13.50	1.20	888	818	1.15	37.50		82.4	28.1 40.9 57.8	32.0	285	1.0.0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3953	Cartiala muck Ridt part Sharkey clay Suargechana clay	Kalamaroo Mich. Plymouth, Ohio. New Orleana, La. Meridian, Miaa.	3442S	1,660 218 013 6,920	0084	12.0 12.0	2.91	3.08	2.80	888 8	887 8	0.000	1.01	1000 1000 1000 1000	31 37 53.6 53.0	43.4	233.2	1288	1.01
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	5 33853	Talat marah Docaa clay China witi bam Mulave fac graveliy bam Guiders	Chairteaton, S. C. Cholame, Calif Wilhuington, Calif Phoenix, Arri. Milwaukee, Wia.	e and	62 118 1332 455	4000	****	28.10	12.20 0.51 3.03	0.76	8888	0.73	28 80 6 05 0 08	0.26 16.90 22.80 22.80	60.7 60.7 60.7	16.2 15.2 30.1 7.8	41.1 26.4 116.5	20.1	8=2	545
33 Unitatified aft learn Murvanity M_{12} <td>22222</td> <td>Micreel ait ham. Matomar ait ham. Pa, waating aity clay ham. Oteo clay ham.</td> <td>Buttonwillow, Calif West Austintown, Ohio Deerheld, Ohio East St. Louis, III. Rocky Ford, Colo.</td> <td>22472</td> <td>2,582 2,582 521 436</td> <td></td> <td>A 11 0 0</td> <td>8.38 0.22 0.11</td> <td>0.38</td> <td>18883</td> <td>.02</td> <td>1.87 0.33 1.75 0.77</td> <td>0.03</td> <td>6.67 0.27 11.58 1.00 20.22</td> <td>65</td> <td></td> <td></td> <td>-</td> <td>8</td> <td>;</td>	22222	Micreel ait ham. Matomar ait ham. Pa, waating aity clay ham. Oteo clay ham.	Buttonwillow, Calif West Austintown, Ohio Deerheld, Ohio East St. Louis, III. Rocky Ford, Colo.	22472	2,582 2,582 521 436		A 11 0 0	8.38 0.22 0.11	0.38	18883	.02	1.87 0.33 1.75 0.77	0.03	6.67 0.27 11.58 1.00 20.22	65			-	8	;
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	718	Unidentified ailt loam Chino ait loam Suanuchanna clay Caddo Ane santy Joam	Alluquerque, N. Mes. Los Angeles, Calif Louaville, Miss. Louaville, Miss. Lates, Tes.	20222	2,650 9,390 9,390 821 201	*****	21 × ×	5.21 5.21 5.21	0.87 005 114 19.24	0.16	.16	1.23	1.56	0.15 0.15 05 71 22.48	62.0	80	30.0			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	28133	Hilings aitt loam (mod. alkali) Bulings aitt loam (high alkali) Ceell chy Ceell chy	Grand Junction, Colo. Charlotte, N. C. Salabury, N. C.	**000	103 8,500 28,000 25,000	****	A A 1122.00 A A	22 63	16.56	38	88	18	11.00	36.82	80.23 80.23	88.88 40.14 40.14	20.4 30.6 31.1 38.8			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	101100	Cecil fire andy loam Cecil gravely loam Cecil gravely loam Freuo fine andy loam (low alkah) Fremo fine andy loam (tick alkah).	Raleigh, N. C. Atlanta, Ga. Frenco, Calif. Kernell, Calif.	00111	54, 400 44, 400 531 531	****	11 17 17 18	3 53	0.07	0.10	18 - 0 18 - 0	1.07 0.58	0.79	0.48	82232	6.89 6.89 6.99 6.99 8.99 8.99 8.99 8.99	29.0 31.3 18.6 18.4 22.1			
Nitzud Gravely ann adole Tranquility, Calif. P 100 8.3 A 30.19 11.60 6.31 6.31 6.3 6.31 6.3 <th6.3< th=""> 6.3 <th6.3< th=""></th6.3<></th6.3<>	20112	Imperial clay (mod. alkali) Imperial clay (jugh alkali) Lake Charles clay Membra alt loam Mereed clay	Niland, Calif. do El Vista, Tex Vickaburg, Miss. Los Banos, Calif.	++20×	3,450 320 320 3,450	PP-20	**	22 18 26 50 50 50 50 50 50 50 50 50 50 50 50 50	0.81 0.81 0.8	201	888 9	36 63 77 77	10.01	23.98 4.00 0.93 1.57	71 221	\$1.0 \$1.0 \$1.0	31.6			
Parache day houn Mendofa, Calif. F 6.832 7.4 A 2.32 0.03 70 0.07 1.40 63.3 81.4 31.6 1.40 63.4 31.6 1.40 63.4 31.6 1.41 23.1 1.40 63.8 1.41 23.1 2.32 0.05 70 0.07 1.40 63.4 31.6 1.41 32.4 31.6 1.41 31.6 1.41 23.4 1.4 23.4 31.6 1.41 31.6 1.41 23.4 1.4 23.4 31.6 1.41 31.6 1.41 23.4 1.4 23.4 31.2 31.6 1.41 31.4 31.2 31.6 1.41 31.4 31.2 31.6 1.41 31.4 31.2 31.6 1.41 31.4 31.2 31.6 1.41 31.4 31.2 31.6 1.41 31.2 1.41 31.2 31.4 31.2 31.2 1.41 31.2 1.41 31.2 31.4 31.2 31.2	118	Merced chy loam adobe Nihaud gravely and (low alkali) Nurfolk and Norfolk and	Tranquility, Calif. Niland, Calif. Macon, Ga Penacola, Fla. Taupa, Fla.	12000	100 34,400 16,400	80000	3	36.19	38	8	88 88	0.20	5.01	6.53	35.35	8 41.8 57.95	31.0 31.0 31.0			
	3853	Panochu clay Ioam Buequeianna clay do Buequelanna fine saudy ham	Mendofa, Calif. Blueveport, La. Troup, Tex. Blueveport, La.	****	6.81 1.100 5,770	N++1	21 9 28 1 28 1	2.32	0.03	16,	8	.70	0.01	01 1	1233		2010			

drainage; C, good; F, fair; P, pour; VP, vury poor. dA, alkaline reaction. Obata for mean temperature and annual pr United States Weather Bureau. Values with no figures to the right of the decimal point are for some nearby city.

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