Adsorption and Desorption Behavior of Selected 10 CFR Part 61 Radionuclides From Ion Exchange Resin by Waters of Different Chemical Composition

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U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001

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Abstract

Two sets of laboratory experiments were conducted to determine the sorption and desorption behavior of a selected group of long-lived radionuclides on nuclear grade ion exchange resin in contact with several types of groundwater. The first experiment used a slightly modified version of ASTM Method D 4319-83, "Distribution Ratios by the Short-Term Batch Method" to determine Kd values for 13 radionuclides (^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, and isotopes of Th, U, Np, Pu, and Am) on EPICORE AC-32 mixed-bed ion exchange resin in contact with three different water types; 1) Chalk River groundwater (pH 6.6), 2) Hanford groundwater (pH 7.9), and 3) Soap Lake water (pH 10.1). These measurements gave high Kd values (10^4 to 10^5) for the Hanford and Chalk River groundwaters, and much lower Kd values for the Soap Lake water. The relatively high dissolved salt content and high alkalinity of the Soap Lake water either saturated the resin or provided high concentrations of competing ions for the adsorption sites on the resin. The second experiment involved determining the leaching rate and magnitude for nine radionuclides (^{14}C, ^{36}Cl, ^{63}Ni, ^{99}Tc, ^{129}I, and isotopes of U, Np, Pu, and Am) previously sorbed onto the same type of EPICORE AC-32 ion exchange resin. A slightly modified version of the INEEL leaching method described in NUREG/CR-5224 was used to determine equilibrium desorption coefficients (1/Kd) of radionuclides leached from the resin by two different water types; 1) Hanford groundwater (pH 7.9), and 2) a "cement water" (pH 12.1) prepared by equilibrating Hanford groundwater with Portland cement. The desorption coefficients were very small (mainly in the range of 10^{-5} to 10^{-7}), indicating that the radionuclides were very tightly sorbed to the resin and not easily leached during contact with the test groundwater samples. The measurements from these two experiments have provided LLW site performance assessment modelers with empirical data to more effectively estimate the retention fraction, or conversely, the release fraction of radionuclides on ion exchange resin during contact with infiltrating groundwater types.

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Executive Summary

A major concern associated with the disposal of low-level radioactive waste (LLW) is the eventual infiltration of water into the waste trenches, followed by leaching of the waste forms and subsequent transport of radionuclides away from the disposal site via groundwater. The requirements of 10CFR Part 61 (Licensing Requirements for Land Disposal of Radioactive Waste), subpart D, section 61.50(a)(2) state that any proposed LLW disposal site must be capable of being characterized, modeled, analyzed, and monitored. In order to model the performance of an existing or potential LLW disposal site, it is necessary to have empirical data that provides a measure of the sorption and desorption properties of radionuclides associated with the various waste forms. Spent ion exchange resins constitute a major waste form for a large inventory of radionuclides at LLW waste disposal facilities. A knowledge of the retention behavior of radionuclides on these resins is critical to accurately estimating the release of radionuclides from the resins and their subsequent transport in site and offsite groundwater.

An extensive literature review indicated a scarcity of useable data on the sorption/desorption behavior of radionuclides on ion exchange resin in contact with solution phases that were typical of representative natural water or groundwater types. Because of this lack of information, a study was initiated that developed empirical measurements of the adsorption and deposition behavior of radionuclides on nuclear grade, mixed-bed ion exchange resin in contact with various groundwater types.

This study was initiated to provide modelers with empirical measurements of laboratory-derived distribution coefficients (Kd's) and desorption coefficients (1/Kd) of selected long-lived radionuclides for the type of ion exchange resin typically used at commercial nuclear power stations for cleanup of primary coolant and liquid radwaste.

Two sets of experiments were performed. The first set of experiments was designed to determine the binding strengths of 13 selected radionuclides (^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, and isotopes of Th, U, Np, Pu, and Am) on nuclear grade ion exchange resin that was in contact with groundwater. The resin sample was EPICORE AC-32 mixed-bed bead resin. Three groundwater types were used: 1) Hanford groundwater, 2) Chalk River groundwater, and 3) Soap Lake water (a high dissolved salt, high alkalinity water). A slightly modified version of ASTM Method D 4319-83, "Distribution Ratios by the Short-Term Batch Method" (ASTM, 1990) was used for the Kd measurements. Batch contact times of 30 minutes and 7 days were used. The radionuclide Kd's were very large (10^4 to 10^5) in Hanford and Chalk River groundwater when a long contact time (7 days) was used, while a short contact time (30 minutes) gave Kd's 100 to 1000 times lower. This suggests that a rather slow exchange rate between ions in solution and on the resin occurred. Soap Lake water, with its higher dissolved salt and alkalinity content gave much lower Kd's that varied by only a factor of 2-3 between the 7-day contact time and the 30-minute contact time. This observation strongly indicated that the resin had become saturated by the high dissolved salt content of the Soap Lake water, which resulted in a competing ion effect that produced the relatively smaller Kd's.

The second set of experiments involved the determination of leaching rates of nine selected radionuclides from EPICORE AC-32 mixed-bed resin by two different water types. A series of leaching experiments

were conducted to simulate the desorption of radionuclides from spent ion exchange resins by waters expected to be infiltrating into buried low-level radioactive waste. The leaching characteristics and "desorption coefficients" (defined as 1/Kd) were determined for nine long-lived 10CFR Part 61 radionuclides, including ^{14}C, ^{36}Cl, ^{63}Ni, ^{99}Tc, ^{129}I, and isotopes of U, Np, Pu, and Am which had been loaded onto mixed-bed ion exchange resin. The desorption coefficient may also be viewed as the leach fraction of the radionuclides entering into solution from the resin. Two types of water samples, a Hanford Groundwater (pH 8.0) and a cement-equilibrated groundwater (pH 11.3) were used for the resin leaching studies. The cement water was chosen to simulate groundwater which had percolated through concrete, a condition that might exist at an engineered barrier LLW disposal facility that had been infiltrated with water. The desorption coefficients determined in this experiment reflected the desorption of radionuclides from the resin by the water. The pH, chemical species, chemical concentrations, ionic strength of solution and complexing anions varied widely in the two waters used to measure the desorption coefficients. The desorption coefficients were small (mainly in the range of 10^{-5} to 10^{-7}) for both water types and appeared to achieve equilibrium values within a few days for most radionuclides. Initial measurements for all radionuclides indicated a small (0.00034% to 0.14%) but

very rapid desorption of the tracers from the resin during the first day of contact with the water. After the first day of contact, the fraction of the radionuclides in solution either increased slightly over the next 100 days, or actually decreased in concentration, indicating re-adsorption onto resin, or to a smaller degree, onto the container surfaces for some of the radionuclides. To further define the initial (day-1 to day-11) desorption behavior, the first few days of the experiment were repeated using the same resin samples used in the 100-day test, but with new water replacing the old water. Data from this repeat experiment showed a significant decrease in the day-1 release of radioactivity from the resin into the water, compared with the first experimental results, giving lower desorption coefficient values. This was probably due to the longer equilibration time of the tracers on the resins for the repeat test.

These empirical measurements of the adsorption and desorption behavior of a number of long-lived radionuclides on ion exchange resin in contact with various groundwater types have provided performance assessment modelers with data to more accurately estimate the retention, or conversely, the leaching of radionuclides from the resin waste forms by groundwater. These assessments will, in turn, provide more accurate radiation dose estimates to individuals living near commercial LLW disposal facilities.

Acknowledgments

1 Introduction

The technical requirements for land disposal of low-level radioactive waste (LLW), as published in 10 CFR Part 61, require that the disposal be performed in a manner such that radiation exposures to humans, as specified in 61.41, are not exceeded. The behavior of the disposed waste under ambient environmental conditions and upon contact with water therefore becomes a very important factor in minimizing radionuclide releases from disposal facilities.

Ion exchange resins used for the removal of radionuclides from various reactor coolant systems and liquid waste streams within commercial nuclear power stations are disposed in LLW disposal sites and represent a significant fraction of the radionuclide inventory of a disposal facility. The adsorption properties of the resin for the various radionuclides, together with the leachability or desorption of the radionuclides from the waste ion exchange resin by infiltrating water contacting the waste is of great interest and importance. This is because the radionuclide adsorption and desorption behavior of the resin will, in large measure, determine the environmental fate and transport of radionuclides residing in LLW disposal facilities which become infiltrated with water. Therefore, in order to conduct meaningful performance assessment modeling of a disposal site, it is necessary to have empirical data that describes the binding strengths and desorption properties of the radionuclides on the resin waste forms.

The adsorption or desorption of any radionuclide from an ion exchange resin in an aqueous media can be measured by comparing the radionuclide concentration per unit volume of liquid to the radionuclide concentration per unit weight of the resin. The equilibrium adsorption ratio is traditionally referred to as the distribution coefficient (Kd), and is unique to individual elements. The

desorption of radionuclides from the resin can be operationally expressed as the inverse Kd (1/Kd), and may be viewed as a leach fraction. Several factors can affect the adsorption or desorption of a particular element and, therefore, it's leachability by waters coming in contact with the resins.

The present study consisted of three tasks: 1) a literature review of radionuclide distribution coefficients determined for ion exchange resin in contact with near-neutral pH solutions, 2) the laboratory determination of equilibrium distribution coefficients (Kd) for a group of thirteen radionuclides by nuclear grade mixed-bed ion exchange resin, and 3) the laboratory determination of desorption coefficients (1/Kd) for a group of nine radionuclides on the same type of ion exchange resin.

In the first task, an extensive literature review was conducted to access distribution coefficients for the 10CFR Part 61 radionuclides for ion exchange resin in contact with neutral or near-neutral pH water. This review is presented in Appendix A of this report. This review revealed very few such studies had been conducted, and that most of the Kd experiments used distilled water adjusted to natural pH values. The vast majority of previous studies examined the adsorption of radionuclides onto ion exchange resin from acid solutions of various strengths, and were not applicable to environmental pH levels of natural groundwater or surface water.

In the second task of this present study, distribution coefficients (Kd's) were determined for thirteen 10CFR Part 61 radionuclides using three goundwaters of differing pH and chemical composition. The study employed the experimental methods in ASTM D 4319-83, "Distribution Ratios By Short Term Batch Methods" to determine the distribution coefficients (Kd) for the 10CFR Part 61 radionuclides using groundwater as the

solution phase and EPICORE AC-32 mixed bed anion-cation bead resin as the solid phase. The radionuclides were initially dissolved in the aqueous phase, which was then contacted with the solid resin phase. The Kd's reflected the adsorption of the radionuclides from the water onto the resin. Two contact times (30 minutes and 7 days) were used to measure the kinetics of the processes by which the radionuclides were being adsorbed on the resin. At the conclusion of this study it was felt that to more closely reflect the actual adsorption/desorption mechanisms, a study should be undertaken that would determine "desorption" distribution coefficients for radionuclides already loaded onto ion exchange resins brought in contact with groundwater and also with groundwater that had previously been equilibrated with cement. This latter water (hereafter referred to as cement water) simulated the water composition that would result from infiltrating water percolating through concrete cap and wall barriers at an engineered LLW disposal facility.

The third task in this study measured the desorption coefficients (1/Kd) as a function of time from EPICORE AC-32 resin for nine 10CFR Part 61 radionuclides, including ^{14}C, ^{36}Cl, ^{63}Ni, ^{99}Tc, ^{129}I, and isotopes of U, Np, Pu, and Am. Hanford ground water and Hanford groundwater previously equilibrated with Portland cement constituted the aqueous phases. An adaptation of the leaching procedure reported in NUREG/CR-5224, EGG-2549, "The Leachability of Decontamination Ion-Exchange Resins Solidified in Cement at Operating Nuclear Power Plants", was used for this task. The procedure was modified for the laboratory determination of desorption coefficients for given geochemical conditions. In the specific NUREG procedure, the volume of leachate used was based on the surface area of the solid as shown in the following equation:

$$\frac{V_L(cm^3)}{S_a(cm^2)} = 10 \pm 0.2$$

Where: V_L = volume of the leachate solution (cm³)
S_a = the surface area of the solid substrate (cm²)

In our modified study, which used ion exchange resin as the solid phase, the ratio of the volume of leachate in mL to solid substrate was based on the weight in grams of resin and not the surface areas, as is shown by the following equation:

$$\frac{V_L(cm^3)}{S_G(g)} = 10 \pm 0.2$$

Where: V_L = volume of the leachate solution (cm³)
S_G = the weight of resin (g)

The desorption coefficient, 1/Kd, was calculated as the ratio of the activity on the water multiplied by the grams of resin to the activity in the resin multiplied by the volume of water in mL. The desorption coefficient was used to assess the degree to which each radionuclide would be removed from the resin if infiltrating water were to contact the resin. The desorption measurements could also be used to assess the rate at which radionuclides would be removed from an ion exchange resin by water. The desorption coefficients usually apply to ionic species only and are measured under conditions where the species of interest are present solely as dissolved ions. The pH values at which these tests were run were not conducive to the formation of soluble species for some of the radionuclides, particularly if the solubility product of the tracers was exceeded. Consequently, some of the resin loading of the radionuclides may represent physical adsorption of insoluble tracer species onto the resin, rather than true ion exchange adsorption.

2 Background Information

The long-term stability of nuclear waste forms being disposed in LLW burial facilities is of concern from an environmental and radiological standpoint. Many leaching studies of both low- and high-level radioactive materials have been conducted over the past several decades with nuclear waste form materials such as spent ion exchange resins solidified in cement and bitumin, solidified sludges and liquid radwastes, neutron activated metals, spent nuclear fuel, high-level waste solidified in glass and ceramic materials, and other high- and low-level waste materials. A variety of leaching techniques have been utilized, ranging from static batch contact experiments to dynamic flowing systems.

Numerous studies of the distribution coefficients of radionuclides on ion exchange resins from acid solutions of various strengths have been conducted, and summaries of this information have been published (Dean 1995). However, a detailed literature review (see Appendix A of this report) has indicated that very few studies of the adsorption and desorption of radionuclides on unsolidified ion exchange resin of the types used at commercial nuclear power stations have been conducted using natural water types as the solution phase. This information is important because untreated (except for dewatering) spent ion exchange resin LLW from commercial nuclear power stations represents a major source term for radionuclide inventories at commercial LLW disposal facilities.

Ion exchange resins have very high affinities for many radionuclides and would be expected to retain most of the radionuclides if water infiltrated the waste trenches and began leaching the LLW materials. Therefore, when conducting performance assessment modeling of the release of radionuclides to the environs from a LLW facility, it would be reasonable to give credit to the binding capacity of the radionuclides by the resins which would hold the radionuclides on the resin until the resins themselves degraded.

Ion exchange resins made by copolymerizing polystyrene with divinylbenzene are very stable polymers in the environment and may hold their chemical and physical integrity for many years.

Cation exchange resins are most commonly produced by the sulfonation of styrene-divinylbenzene polymer beads. Cation exchange resin converted to the Na form retain cations from solution by a reaction such as:

$$(RSO_3)Na + M^+ \rightarrow (RSO_3)M + Na^+$$

where: RSO_3 represents a styrene-divinylbenzene polymer with an attached sulfonic group and M represents a monovalent metal cation.

Anion exchange resins usually incorporate a quaternary ammonium functional group on the polymer. Anion exchange resin in the hydroxide form retains anions from solution by a reaction such as:

$$(RNR'_3)OH + A^- \rightarrow (RNR'_3)A + OH^-$$

where: (RNR'_3) represents a polymer with an attached quaternary ammonium functional group, and A^- represents a monovalent anion species.

Nuclear grade ion exchange resins used at nuclear power stations for demineralization of the primary coolant and liquid radwastes are usually mixtures of cation and anion resin and are referred to as mixed-bed ion exchange resin. Most of the long-lived radionuclides specified in 10CFR Part 61 have relatively high distribution coefficients on mixed-bed resin from dilute acid solutions (Dean 1995), but little information has been available that describes distribution coefficients on resin from natural waters.

The soluble species of the various long-lived radionuclides of environmental concern have different bonding strengths to the resins. All ion exchange resins have preferences for the particular type of ions they will hold if given a

choice. This preference is defined as the selectivity of the resin. The resin phase shows these preferences with regard to bonding strengths:

1. The ion of higher charge.
2. The ion with the smaller solvated radius.
3. The ion that has the greater polarizability.

Thus, in solutions containing complex mixtures of radionuclides, the various ions will compete for the functional group sites on the resin. This competition is dependent on a number of variables, including the type of functional groups on the resin, the valence and nature of the exchanging ions, the total ionic strength of the solution, the pH and redox conditions of the solution, the relative concentrations of the different solutes, and the presence of complexing ions and dissolved organic constituents.

Two series expressing qualitatively the decreasing selectivity of strong-acid cation exchange resin for the long-lived radionuclides of concern and other common cations are:

$TRU(III)>Th(IV)>U(VI)>Ba^{++}>Pb^{++}>Sr^{++}>Ca^{++}>Ni^{++}>Cd^{++}>Cu^{++}>Co^{++}>Zn^{++}>Mg^{++}>Ag^{+}>Cs^{+}>Rb^{+}>K^{+}>NH_4^{+}>Na^{+}>H^{+}>Li^{+}$

Similarly, for strong-base anion exchange resin, the following selectivity series exists:

$Tc(VII)>CNS^{-}>I^{-}>NO_3^{-}>Br^{-}>CN^{-}>HSO_4^{-}=HSO_3^{-}>NO_2^{-}>Cl^{-}>HCO_3^{-}>OH^{-}>F^{-}$

Thus, mixed-bed ion exchange resins will have strong bonds between the functional groups and the soluble species having the higher selectivities. This high specificity will result in most of the long-lived radionuclides of interest in LLW disposal being strongly retained on the resin during contact with groundwater.

This present study was conducted to determine the distribution coefficients for these radionuclides on mixed-bed ion exchange resin of the type used at nuclear power stations from natural water types. Following the adsorption study, the degree of retention of the radionuclides was determined by leaching radionuclide-tagged resin with the natural waters or cement-equilibrated groundwater. This work has developed the needed information to more accurately model the release of radionuclides from LLW disposal facilities as a function of time.

3. Experimental

3.1 Distribution Coefficients (Kd) for Selected 10 CFR Part 61 Radionuclides Between Ion Exchange Resin and Three Different Water Types

This section of the report describes the experimental methods used for conducting the distribution coefficient (Kd) determinations of selected 10CFR Part 61 radionuclides (^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, and isotopes of Th, U, Np, Pu, and Am) on EPICORE AC-32 mixed-bed ion exchange resin and Portland cement from three different water types. The Kd measurements were determined for two different contact times, 1) a 30-minute contact time to determine the rapid ion exchange uptake by the resin, and 2) a 7-day contact time to determine the equilibrium adsorption of radionuclides onto the resin by ion exchange, adsorption, precipitation, and other mechanisms. For the Portland cement, only a 30-minute contact time was used, and equilibrium adsorption conditions were most likely not achieved. Therefore, the Kd measurements for the Portland cement should be viewed as minimum values.

3.1.1 Physical and Chemical Characteristics of EPICORE AC-32 Ion Exchange Resin

The resin used in this study was EPICORE AC-32, a bead type mixed-bed (cation + anion) resin, made by EPICORE, INC. This resin is used at many nuclear power stations to remove radionuclides from primary coolant and various liquid radwaste systems. The characteristics of the resin are shown in Table 3.1. The resin is a chemically equivalent mixture of strong-base gel anion resin, Type I, in the hydroxide form, and strong-acid gel cation resin, (sulfonic acid type) in the hydrogen form. The total capacity of one mL of resin (assuming a 1:1 mixture of anion and cation types) is 1.53 meq/mL, while the effective capacity will be somewhat less. The bead size distribution of the resin was as follows:

< 2% of the beads were > 1 mm diameter; 96% of the beads ranged from 0.4 mm to 1.0 mm diameter; <3% of the beads ranged from 0.32 mm to 0.4 mm diameter; while < 0.5% of the beads were < 0.32 mm diameter. Impurities in the cation resin of Na^+, Al^{+++}, Fe^{++}, and Cu^{++} were listed as < 50 ppm, while Pb^{++} was listed as < 10 ppm. Impurities in the anion resin were listed as Cl^- (1%), CO^{-3} (5%), and SO_4^{-2} (0.5%).

3.1.2 Groundwater Characteristics

The groundwater used for this study was selected to give a pH range from slightly acid to quite basic. The groundwater characteristics are shown in Table 3.2. Freeze and Cherry (1979) have shown that the difference in pH of groundwater is mainly due to the carbonate equilibrium that exists between CO_3^{-2}, HCO_3^-, and H_2CO_3. This correlation between pH and the concentration of the various carbonate species can result in variations in groundwater pH's ranging from 4 to 12. The groundwater from Hanford, Washington, had a pH of 7.9 and contained 1.67 mg of cations and 5.10 mg of anions as dissolved salts per 30 mL, which represented 0.055 meq and 0.0846 meq, respectively. The ratio of HCO_3 to CO_3^{-2} was 27.6. Groundwater from Chalk River, Ontario, Canada, had a pH of 6.6 and contained 4.76 mg of cations and 9.13 mg of anions as dissolved salts per 30 mL, which represented 0.161 meq and 0.179 meq, respectively. The ratio of HCO_3^- to CO_3^{-2} was 872. The surface water from Soap Lake, Washington had a pH of 10.1 and contained 199 mg of cations and 333 mg of anions per 30 mL which represented 8.36 meq and 5.63 meq, respectively. The ratio of HCO_3^- to CO_3^{-2} in Soap Lake water was 1.24. The Soap Lake water was selected as a simulant for groundwater which had infiltrated through a concrete barrier and which contained high concentrations of salts typical of those leached from concrete.

Table 3.1 Ion Exchange Resin Specifications

Identification .... EPICORE AC-32 Bead Resin

Description .... Chemically equivalent mixture of
strong-base gel, Type 1, anion
resin in the hydroxide form
with strong-acid gel sulfonic
acid cation resin in the
hydrogen form.

Total Cation Capacity, meq/mL 1.90

% H^+ . ... >99

Total Anion Capacity, meq/mL 1.15

% OH^- . ... > 95

% Cl^- . ... < I

% CO_3^{-2} / SO_4^{-2} .... < 5 / <0.5

Screen size .... % retained

+ 16 .... < 2

-16 to + 40 96

+ 50 .... < 3

- 50 .... < .5

Table 3.2 Groundwater Geochemical Data

Constituent	Hanford Groundwater		Chalk River		Soap Lake	
			30 mL groundwater			
	mg	meq	mg	meq	mg	meq
Ca^{+2}	0.765	0.019	1.85	0.045	0.063	0.002
Mg^{+2}	0.390	0.016	1.05	0.045	0.036	0.002
Na^+	0.369	0.016	1.38	0.058	183	0.94
K^+	0.144	0.004	0.483	0.013	16.3	0.42
	-----	-----	------	-----	-----	-----
Total Cations	1.67	0.055	4.76	0.161	199.0	8.36
Cl^-	0.744	0.021	3.85	0.107	58.8	1.68
HCO_3^-	1.66	0.027	3.14	0.049	99.5	1.63
NO_3^-	1.293	0.021	0.040	0.001	0.072	0.001
SO_4^{-2}	1.338	0.014	2.09	0.022	94.5	0.98
CO_3^{-2}	0.060	0.001	0.0036	<0.0001	79.9	1.33
F^-	0.012	0.0006	0.001	$<6x10^{-6}$	0.216	0.011
	-----	------	------	-------	-------	-----
Total Anions	5.10	0.0846	9.12	0.179	333.0	5.63
pH	7.9		6.6		10.1	

3.1.3 Description of the Method for Kd Determinations

The study used the ASTM Method D 4319-83 "Distribution Ratios By The Short-Term Batch Method" (ASTM, 1990) to determine the Kd's for the 1OCFR Part 61 radionuclides using groundwater as the fluid and ENCORE AC-32 mixed-bed of anion-cation bead resin as the solid substrate. Two contact time periods were used to help in understanding the kinetics and the chemical processes by which the radionuclides were being adsorbed from the solution onto the ion exchange resin. A short period of 30 minutes was used to estimate what fraction of the Kd might be attributed to rapid ion exchange kinetics. Dorfner (1979) has shown that in a batch system, using high cross-linked resin, such as the resin used in this study, 80% of the capacity of the resin will be attained during the first minute of contact. In addition to the 30-minute contact period, a much longer contact period of 7 days was used to study the equilibrium Kd which would include partitioning factors due to ion exchange, adsorption, co-precipitation, and filtration.

The method consisted of first measuring the pH of the groundwater to be used, then taking a 30 mL aliquot, adding a radionuclide tracer of interest, measuring the pH, readjusting the pH if necessary using either dilute NaOH or HCl, filtering the aliquot, and then adding the filtered aliquot to a mixing chamber containing one gram of mixed anion-cation resin and contacting for the specified time.

The distribution coefficient was determined by:

$$Kd = \frac{(resin\ activity)(mL\ water)}{(water\ activity)(grams\ resin)}$$

Where: resin activity = d/m of 1 gram resin

water activity = d/m 30 mL water

3.2 Desorption of Selected 10 CFR Part 61 Radionuclides from EPICORE AC-32 Ion Exchange Resin by Two Water Types

This section of the report describes the experimental methods used for conducting the radionuclide desorption studies from the EPICORE AC-32 ion exchange resin. These measurements provided the data from which the desorption coefficients (1/Kd) were determined as described in section 4.2 of this report.

3.2.1 EPICORE AC-32 Ion Exchange Characteristics

The EPICORE AC-32 ion exchange resin is the very same type used for performing the Kd determinations and the resin characteristics were described previously in section 3.1.1 of this report.

3.2.2 Test Water Characteristics

The two waters used for this study were a filtered (0.2μ) Hanford groundwater (HW) and a Hanford groundwater that had been equilibrated with Portland cement and then filtered (0.2μ) and is hereafter referred to as cement water (CW). The chemical composition of these two water types is given in Table 3.3. The cement water was chosen since spent resin LLW will be disposed in future engineered-barrier facilities having concrete walls and caps. Infiltrating water will eventually percolate through this concrete barrier and would have a chemical composition similar to that of the cement water used in these experiments (i.e., high pH and dissolved salts).

The cement water was prepared by adding several hundred grams of Portland cement to several liters of Hanford groundwater and gently mixing the suspension for several days until chemical equilibrium conditions were

approached. The suspension was then allowed to settle and the supernate water decanted off and filtered through a 0.2μ membrane filter to remove any remaining particulates.

The cement water composition was much different from the Hanford groundwater as shown in Table 3.3. The cement water became quite basic (pH = 12.1) due to hydroxyl ions formed by reactions of the cement with the water. Also, the cement water contained much higher concentrations of Ca^{++}, K^+, and Na^+ which would compete for exchange sites on the cation resin, and SO_4^{-2} and OH^- which would compete for exchange sites on the anion resin. The expectation would be for the cement water to be a much more aggressive leachant of resin-bound radionuclides compared to the Hanford groundwater. However, this was generally not borne out by the experimental results described in Section 4 of this report.

Since 2.5 mL of mixed-bed resin was used for each contact test, the data from Table 3.1 indicates that the total cation exchange capacity for the test aliquots and anion exchange capacity would be 2.4 meq and 1.4 meq, respectively, assuming equal fractions of each resin type. From the water analysis data in Table 3.3, the 25 mL of cement water used in each contact test contained 0.31 meq of total cations and 0.13 meq of total anions. The anion balance was obviously low and was probably due to uncertainties in measuring the pH of the highly basic cement water, where small errors in the pH measurement would result in large differences in hydroxyl ion concentrations. The true anion meq should be close to the cation meq value of 0.31 meq. In any case, it was obvious that the exchange capacity of the mixed- bed resin was not exceeded by either the cations or anions present in the 25 mL of cement water used in each test. The Hanford groundwater contained much lower total ion concentrations than the cement water and would therefore have an even smaller effect on resin saturation.

Table 3.3 Hanford Groundwater and Cement Water Geochemical Data

Constituent	Hanford Water		Cement Water	
	25 mL water			
Cations	mg	meq	mg	meq
Ca $^{+2}$	0.638	0.032	3.78	0.189
Ba $^{+2}$	-	-	0.0033	4.7E-5
Mg $^{+2}$	0.325	0.027	<0.0009	<0.0001
K$^+$	0.120	0.0031	2.50	0.0641
Na$^+$	0.308	0.013	0.665	0.0288
Sr $^{+2}$	-	-	0.026	0.0006
total cations	1.390	0.075	6.94	0.31
Anions				
F$^-$	0.010	0.0005	0.0125	0.0007
Cl$^-$	0.620	0.018	0.45	0.0127
NO$_3^-$	1.078	0.018	0.28	0.0044
PO$_4$ $^{-3}$	-	-	<0.013	<0.00003
SO$_4$ $^{-2}$	1.115	0.023	3.90	0.081
CO$_3^{-2}$	0.050	0.0017	-	-
HCO$_3^-$	1.380	0.023	-	-
OH$^-$	-	-	5.5	0.31
total anions	4.253	0.083	9.33	0.41
pH	7.9		12.1	

3.2.3 Radionuclide Measurement Methods

The radionuclide tracers used in this sorption/desorption study were measured by liquid scintillation counting using a Quantulus Liquid Scintillation Analyzer. One mL of tracer solution was mixed with 15 mL of Ultima Gold Scintillation cocktail and counted from 10 to 100 minutes, depending upon the activity of the tracer.

3.2.4 Description of the Desorption Coefficient Method

This task employed a modified version of the methods described in NUREG/CR-5224 to determine the desorption coefficients for nine of the 10 CFR Part 61 radionuclides (^{14}C, ^{36}Cl, ^{63}Ni, ^{99}Tc, ^{129}I, and isotopes of U, Np, Pu, and Am) using Hanford groundwater (HW) and Hanford groundwater previously equilibrated with cement (CW) as the aqueous phase and EPICORE AC-32 mixed-bed anion-cation bead resin as the solid phase. In these experiments ^{125}I was used as an analog tracer for ^{129}I because of easier availability and better counting features. Known amounts of each radioisotope were loaded onto two, 2.5 gram aliquots of resin in 50-mL conical plastic centrifuge tubes and allowed to contact for several hours. The resin was then washed with distilled water until the amount of activity in the wash became minimal. The loading efficiency of the radionuclides onto the resin was greater than 99.9% except for plutonium where the loading efficiency was 96.3%. Twenty-five mL of HW was added to one set of nine radionuclide-tagged resins and 25 mL of CW was added to the other set.

The 18 samples were placed on a tilt-board mixer and allowed to gently mix continuously. After one day, 1 mL of water was removed from each sample and counted and 1 mL of new water was added and the mixing continued. This sampling procedure was repeated after 5 days, 11 days, 40 days, 70 days, and 100 days. After observing significant amounts of activity on day-1, as compared to the other days, it was decided to empty the water after day-100, transfer the resin to new tubes, acid wash the old tubes and count the wash to determine wall adsorption losses. Then 25 mL of new water was added to each new tube and the contact procedure was repeated for an additional 1, 5, and 11 successive days. These sampling days were called day-101, day-105, and day-111.

The desorption coefficients were determined using the following formula:

$$Desorption\ Coefficient = \frac{1}{Kd}$$

$$\frac{1}{Kd} = \frac{(water\ activity)(grams\ resin)}{(resin\ activity)(mL\ water)}$$

Where: resin activity = d/m of 2.5 grams resin
water activity = d/m in 25 mL water

4 Results and Discussion

4.1 Distribution Coefficients (Kd) for Selected 10 CFR Part 61 Radionuclides Between EPICORE AC-32 Ion Exchange Resin and Three Different Water Types

The results of the Kd determinations are shown in Tables 4.1 and 4.2. The Kd's from the 7-day contact time using Hanford and Chalk River groundwaters were consistently in the 10^5 range for all radionuclides except ^{14}C and ^{137}Cs. These very high Kd's indicated that the radionuclides would be highly retained on the ion exchange resins if the resins ever came in contact with Hanford or Chalk River type groundwater infiltrating a LLW site. The 30-minute contact time of resin and groundwater from Hanford and Chalk River gave Kd values in the 10^3 range, and apparently reflect non-equilibrium conditions. The Kd values for the 7-day contact times, as compared to the Kd values for the 30-minute contact times, showed an increase of two to three orders of magnitude.

The rate of exchange of ions in the ion exchange process is extremely fast with high cross-linkage ion exchange resins, reaching 80% of capacity in less than one minute according to Dorfner (1977). Thus, comparing the Kd values for the two contact time periods would strongly suggest that other slower sorption processes were also involved during the 7-day contact experiment, including adsorption, co-precipitation, and/or filtration. These slower processes were apparently governed by weakly charged or neutral groups of atoms or colloids where both the movement of the large particles in the solution and the removal onto the resin beads was quite slow.

Soap Lake water was unique compared to either Hanford or Chalk River groundwater in that the dissolved salt concentration was very high and the pH was unusually high at 10.1. Soap Lake water was the only test solution where the salt concentration in the aliquot used for the Kd measurement exceeded the capacity of both the anion and cation resins by

nearly an order of magnitude. Consequently, the Kd's for the Soap Lake water were much lower than those for the Hanford and Chalk River groundwater because of the competing ion effect from the high concentrations of the major dissolved anions and cations in the Soap Lake water. The ratio of Kd's obtained for the 7-day to 30-minute contact times using Soap Lake groundwater showed an average increase in the ratio for all radionuclides of only about 2.5, as compared to Hanford or Chalk River groundwater where most ratio values increased by 10- to 1000-fold, with the exception of ^{14}C, ^{36}Cl, and ^{137}Cs. The latter three radionuclides only increased by a factor of 4 to 5 over the extended contact time period for the Hanford and Chalk River groundwater. Apparently, the competing ion effects override the kinetic considerations to a large degree.

It is interesting to note that the ^{99}Tc Kd's for Soap Lake water were much higher than any other radionuclides for both the short and long contact time, indicating that the high dissolved salt concentration did not have the same effect on ^{99}Tc as it did for the other radionuclides. The selectivity of the resin for ^{99}Tc was obviously much greater than that of the competing ions.

The radionuclides of nickel and cobalt behaved quite similarly in Hanford and Chalk River groundwater, but in Soap Lake water the Kd for ^{60}Co was much higher than that for ^{63}Ni. The data also suggested that the competing ion effect was smaller for cobalt compared to nickel in Soap Lake water. Strontium appeared to have relatively fast exchange kinetics as demonstrated by the relatively high Kd's in the 30-minute contact.

The actinide radionuclides (thorium, uranium, plutonium, and americium) showed relatively low Kd's for the 30-minute exposure, but very high Kd's for the 7-day exposure in the Hanford and Chalk River waters, suggesting either rather slow exchange kinetics or additional sorption mechanisms. In Soap Lake water, the Kd's for ^{232}U, and to some extent ^{241}Pu, were relatively high during the

short contact period, and possibly showed the effect of carbonate complexing of these two radionuclides. During the 7-day contact time, the Kd's of these actinide isotopes were very large for Hanford and Chalk River water, indicating the effects of other sorption processes besides ion exchange. In the 7-day exposure using Soap Lake water, uranium showed a relatively small Kd, again indicating the possible effect of carbonate complexing. The curium tracer showed very erratic behavior in both the long and short-period exposures. Chemically, curium should behave similar to americium. Both elements form tri-valent ions in solutions, both resist oxidation/reduction, both have very insoluble hydrous oxides, and both are complexed by the same ligands. In view of their chemical similarities, their much different Kd values are somewhat of a puzzle.

Since these data strongly indicate that other processes besides ion exchange are occurring in the removal of radionuclides from groundwater onto ion exchange resin, it was decided to measure the radionuclide desorption kinetics from ion exchange resin by leaching tracer-loaded resins with the various types of groundwater, as described in section 4.2 of this report.

4.2 Desorption Behavior of Selected 10 CFR Part 61 Radionuclides from EPICORE AC-32 Ion Exchange Resin by Two Water Types

The desorption curves for seven of the nine radionuclides which had been loaded onto the ion exchange resins and contacted with the two water types are shown in Figures 4.1 to 4.7. Curves for ^{99}Tc and ^{36}Cl were not included because very little of these two tracers desorbed from the resin into the aqueous phases during the course of the testing. The tabulated experimental data for all nine radionuclides are given in Table 4.3.

As described in section 3.2.4, the loss of tracers from solution due to adsorption onto the walls of the centrifuge tubes was

evaluated after day-100. These data are given in Table 4.4, and show that wall losses ranged from less than 1% of the total desorbed activity for ^{129}I to 99% for ^{99}Tc. These wall losses are further discussed in Section 4.3.

The most striking feature of these data was the very rapid (within one day) initial desorption of a very small fraction of the tracers from the resins. Table 4.5 shows the percentage of the radio-tracers desorbed from the resins after one day of contact with the test waters, which ranged from a low of 0.00034% for ^{99}Tc to a high of 0.14% for ^{129}I. This rapid initial desorption was followed by either very minimal additional releases of the tracers from the resin over the next 100 days of contact, or by actual re-absorption of the tracers onto the resins during this time period. Only ^{241}Pu showed a continual gradual desorption from the resins.

The behavior of each tracer is discussed in the following section. Figures 4.1 to 4.7 show the change in radio-tracer concentrations in solution after introduction of the tagged resin to the water samples. The concentrations are reported in units of disintegrations per minute (dpm) per 25 mL of solution. Depending on the radiosotope and the water type, the concentrations of the radionuclides in solution either increased or decreased from the initial desorption value.

4.2.1 Carbon-14

Figure 4.1 shows the desorption behavior of ^{14}C for the resin/water phases. After the first day of contact, approximately 0.07-0.08% of the ^{14}C tracer was desorbed from the resins by both water types (see Table 4.6). The resin in the Hanford groundwater continued to release small quantities of ^{14}C until about day-40, when an equilibrium desorption condition prevailed. At equilibrium, 0.14% of the resin-sorbed ^{14}C was desorbed if both the activity in the solution and that adsorbed to the walls of the centrifuge tubes were considered. For the cement water, about 22% of the ^{14}C initially in solution gradually re-adsorbed to the resin by day-70. No significant wall losses of ^{14}C from the cement water occurred.

Table 4.1 Measured Distribution Coefficients (mL/g) on EPICORE AC-32 Mixed-Bed Resin Using Groundwater from Hanford, Chalk River, and Soap Lake– 30 Min. Contact

| Radionuclide | Groundwater Types | | |
	Hanford pH 7.9	Chalk River pH 6.6	Soap Lake pH10.1
	...............Distribution Coefficient ± % error..................		
^{14}C	3519 ± 28	2590 ± 12	8.3 ± 8
^{36}Cl	37,890 ± 8	44,720 ± 4	14.0 ± 5
^{60}Co	1822 ± 13	2000 ± 6	616 ± 8
^{63}Ni	2906 ± 5	2332 ± 24	14.1 ± 11
^{90}Sr	3450 ± 41	6909 ± 5	108 ± 4
^{99}Tc	3049 ± 7	4949 ± 10	3013 ± 5
^{137}Cs	4695 ± 9	6145 ± 5	13.8 ± 5
^{230}Th	27 ± 9	69.1 ± 7	68.3 ± 11
^{232}U	168 ± 13	401 ± 20	550 ± 5
^{241}Pu	110 ± 7	374 ± 13	105 ± 8
^{241}Am	138 ± 13	69.4 ± 10	16.9 ± 30
^{244}Cm	809 ± 22	385 ± 11	99.2 ± 5

(1) Used ASTM D 4319-83 Procedure, 30 MINUTE EXPOSURE

Error bar is at one sigma

Table 4.2 Measured Distribution Coefficients (mL/g) on EPICORE AC-32 Mixed Bed Resin Using Groundwater from Hanford, Chalk River, and Soap Lake–7 Day Contact

<u>Groundwater Types</u>

Radionuclide	Hanford pH 7.9	Chalk River pH 6.6	Soap Lake pH 10.0
	.............Distribution Coefficient ± % uncertainty (1σ)...............		
^{14}C	10,300 ± 8	9,800 ± 5	14.7 ± 10
^{36}Cl	116,200 ± 5	166,100 ± 13	17.6 ± 5
^{60}Co	242,900 ± 20	176,800 ± 21	494 ± 10
^{63}Ni	192,000 ± 5	179,000 ± 12	48.9 ± 24
^{90}Sr	94,130 ± 19	117,600 ± 18	2170 ± 10
^{99}Tc	708,100 ± 6	332,300 ± 17	9000 ± 8
^{129}I	197,400 ± 11	148,200 ± 12	550 ± 9
^{137}Cs	18,840 ± 15	41,500 ± 14	31.9 ± 9
^{230}Th	102,000 ± 12	167,400 ± 5	365 ± 7
^{232}U	489,300 ± 5	704,500 ± 8	1173 ± 6
^{241}Pu	213,000 ± 15	136,000 ± 13	343 ± 12
^{241}Am	560,000 ± 8	517,000 ± 5	45.4 ± 12
^{241}Cm	328,100 ± 18	2266 ± 22	175 ± 14

(1) Used ASTM D 4319-83 procedure, 7-DAY exposure

Table 4.3 Tracer Activity Desorbed from Resin into 25 mL Water as a Function of Time

-- dpm/25 mL --

Isotope	dpm on Resin	Water* Type	Day 1	Day 5	Day 11	Day 40	Day 70	Day 100
^{14}C	9.21E6	HW	6625±271	7331±283	7716±290	8490±303	8325±301	8467±302
		CW	7150±280	6823±274	6650±271	7066±279	5595±251	5965±258
^{36}Cl	~2.35E7	HW	673±120	<88	<89	<90	228±98	<89
		CW	141±93	178±95	113±91	<86	<88	<88
^{63}Ni	2.52E7	HW	1407±171	361±119	418±122	368±119	525±128	188±102
		CW	3961±257	1364±169	2359±207	1470±173	138±104	95±95
^{99}Tc	2.61E7	HW	<91	<89	103±94	<89	<88	<87
		CW	139±96	108±94	<93	180±98	<94	<89
^{129}I	4.44E7	HW	62602±886	64295W±898	57680±851	66925±1217	63825±1420	17800±477
		CW	18421±470	20243±509	17899±479	24180±742	20395±823	5635±277
^{232}U	8.64E6	HW	3036±525	224±72	536±190	<107	<102	496±159
		CW	1573±538	148±44	425±75	275±67	210±58	723±160
^{241}Pu	9.45E6	HW	777±175	2111±249	2514±262	6640±400	10646±498	7791±428
		CW	1411±211	2029±245	2657±268	2281±251	2259±252	1846±228
^{241}Am	1.15E7	HW	3986±198	6089±245	8075±281	7498±271	2190±148	2206±180
		CW	248±56	372±66	173±49	61±36	<32	<26
^{237}Np	1.12E7	HW	4368±207	1835±135	1261±113	645+86	345±62	263±60
		CW	1078±105	990±101	1086±105	553±77	433±67	371±68

HW = Hanford groundwater
CW = Hanford groundwater previously equilibrated with cement

Table 4.4 Fraction of Resin-Desorbed Activity Attached to Plastic Container Walls

Isotope	dpm on Resin	Water* Type	Activity on Wall (dpm)	Total Resin-Desorbed Activity,** (dpm)	% Desorbed Activity on Wall @ Day 100
^{14}C	9.21E6	HW	3314±37	13321±304	24.9
		CW	87±7	7383±258	1.2
^{36}Cl	2.35E7	HW	10±4	123±89	8.2
		CW	16±4	94±88	72.5
^{63}Ni	2.52E7	HW	822±22	1133±104	72.5
		CW	1086±25	1553±108	69.9
^{99}Tc	2.61E7	HW	6909±37	6980±95	99.0
		CW	24121±98	24225±132	99.6
^{129}I	4.44E7	HW	27±5	30440±477	<1.0
		CW	35±5	9716±277	<1.0
^{232}U	8.64E6	HW	160±94	820±185	19.5
		CW	33±105	861±191	3.8
^{241}Pu	9.45E6	HW	16285±120	24984±445	65.2
		CW	334±18	2605±229	12.8
^{241}Am	1.15E7	HW	731±17	4051±181	18.0
		CW	30±4	86±26	34.8
^{237}Np	1.12E7	HW	36±4	637±60	5.7
		CW	31±3	568±68	5.5

HW = Hanford groundwater
CW = Hanford groundwater previously equilibrated with cement

**Activity on wall plus activity in solution corrected for the one mL removal during each time period.

Table 4.5 Percentage of Radio-tracers Desorbed from the Resins After One Day and 100 Days of Contact with the Test Water

Isotope	Water Type	Total dpm on Resin	% of Tracer in Solution @ Day I	% of Tracer in Solution @ Day 100
^{14}C	HW	9.21E6	0.072	0.092
	CW		0.078	0.065
^{36}Cl	HW	2.35E7	0.0029	<0.00038
	CW		0.00060	<0.00037
^{63}Ni	HW	2.52E7	0.0056	0.00075
	CW		0.016	0.00038
^{99}Tc	HW	2.61E7	0.00034	<0.00033
	CW		0.00053	<0.00034
^{129}I	HW	4.44E7	0.14	0.040
	CW		0.041	0.013
^{232}U	HW	8.64E6	0.035	0.0057
	CW		0.018	0.0084
^{241}Pu	HW	9.45E6	0.0082	0.082
	CW		0.015	<0.019
^{241}Am	HW	1.15E7	0.035	0.019
	CW		0.0022	0.00023
^{237}Np	HW	1.12E7	0.039	0.0023
	CW		0.0096	0.0033

HW = Hanford groundwater
CW = Hanford groundwater previously equilibrated with cement

Figure 4.1 C-14 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time
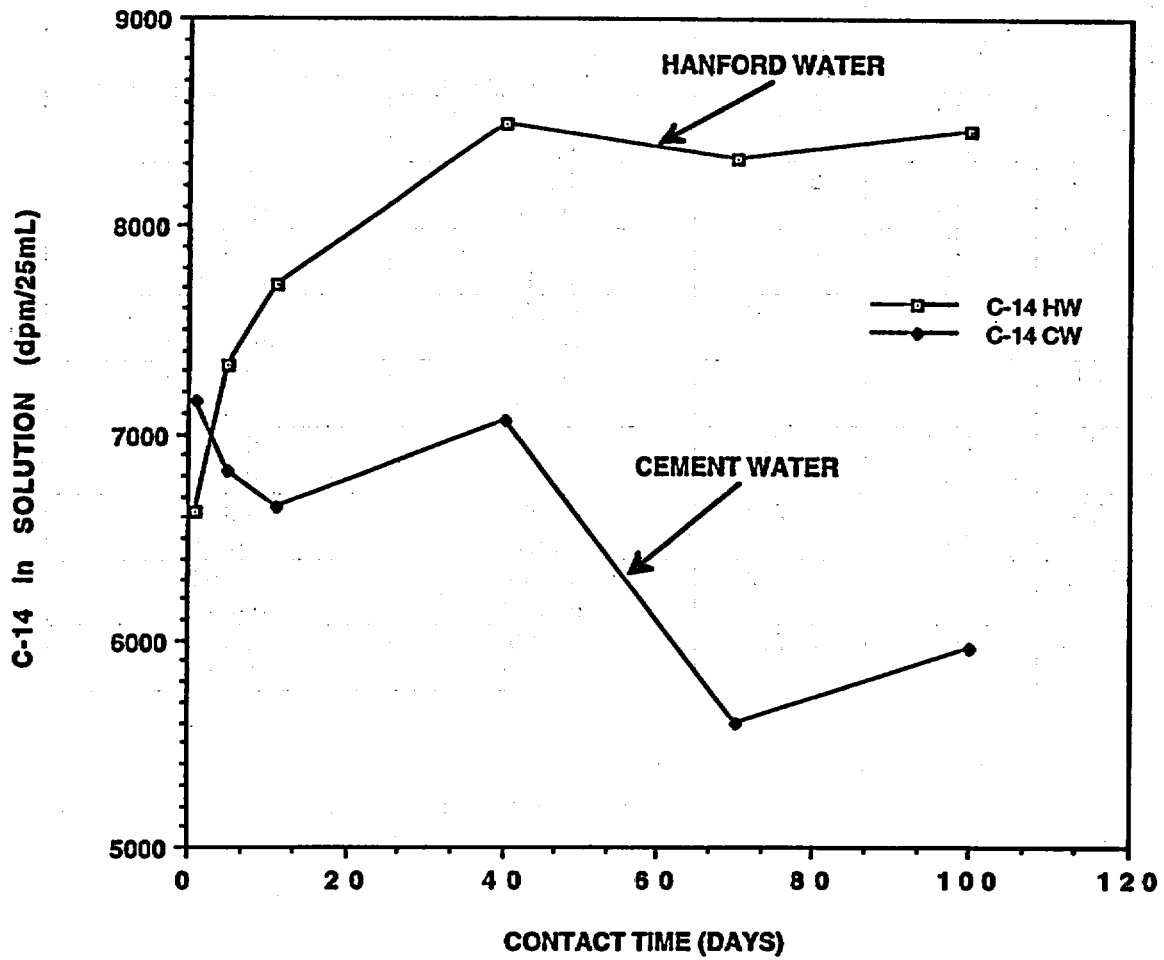
4.2.2 Nickel-63

Figure 4.2 shows the desorption behavior for ^{63}Ni. After day-1 the Hanford groundwater and the cement water desorbed 0.0056% and 0.016%, respectively, of the total ^{63}Ni initially sorbed on the resins (see Table 4.6). During the next 100 days, the ^{63}Ni in solution decreased by over a factor of 10 in both water types. Table 4.4 shows that most (70-73%) of the desorbed ^{63}Ni attached to the walls of the centrifuge tubes during the contact period. The ^{63}Ni appears to be firmly bound to the resin and does not significantly desorb during the 100 days of contact.

4.2.3 Iodine-129

For these experiments ^{125}I was used as an analog tracer for ^{129}I, and its desorption behavior is shown in Figure 4.3. After day-1 the Hanford groundwater and cement water desorbed 0.14% and 0.041%, respectively of the total ^{125}I initially sorbed to the resin (see Table 4.5). Between day-1 and day-70, the fraction of ^{125}I in the solution phases remained nearly constant, but between 70 to 100 days a significant re-adsorption onto the resin occurred. The wall losses for ^{125}I were insignificant.

4.2.4 Uranium-232

The desorption behavior of ^{232}U is show in Figure 4.4. After day-1, the Hanford groundwater and the cement water desorbed 0.035% and 0.018%, respectively, of the ^{232}U initially adsorbed to the resins (see Table 3.3). After day-1, a 10-fold re-adsorption of the ^{232}U onto the resin occurred and the fraction in the solution phase remained relatively constant throughout the remainder of the test. The ^{232}U appeared to be strongly bound to the resin and did not leach from the resin after the initial equilibrium conditions were established. The desorption behaviors for the cement water and the Hanford groundwater were quite similar.

4.2.5 Neptunium-237

The desorption behavior of ^{237}Np is shown in Figure 4.5 and is very similar to that observed for uranium. The initial (1-day) desorption of ^{237}Np from the resins was followed by a very systematic 10-fold re-absorption onto the resin as evidenced by the decrease in ^{237}Np in the solution phase. Very little ^{237}Np adsorbed onto the container walls.

4.2.6 Plutonium-241

Figure 4.6 shows the desorption curves for ^{241}Pu. After an initial desorption of 0.0082% and 0.015% of the ^{241}Pu from the resins by the Hanford groundwater and the cement water, respectively, (see Table 3.3) the Hanford groundwater continued to leach ^{241}Pu from the resin for up to about 70 days until an equilibrium condition was reached. About 65% of the ^{241}Pu which was desorbed from the resin by the Hanford groundwater attached to the walls of the container. In the cement water, ^{241}Pu leached from the resin by the cement water adsorbed onto the walls of the container.

4.2.7 Americium-241

The initial (1-day) desorption behavior of ^{241}Am, shown in Figure 4.7, indicated that 0.035% and 0.0022% of the ^{241}Am was leached from the resin by the Hanford groundwater and the cement water, respectively (see Table 3.3). The Hanford groundwater continued to gradually leach ^{241}Am from the resin over the next 10 days, but then began to re-adsorb to the resin between 40 to 70 days. After 70 days an equilibrium desorption condition was established. The cement water showed a gradual 10-fold re-adsorption of the ^{241}Am to the resin between days 5 and 100, with very little ^{241}Am remaining in solution after day-100.

Figure 4.2 Ni-63 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time

Figure 4.3 I-125 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time

Figure 4.4 U-232 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time

Figure 4.5 Np-237 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time

Figure 4.6 Pu-241 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time

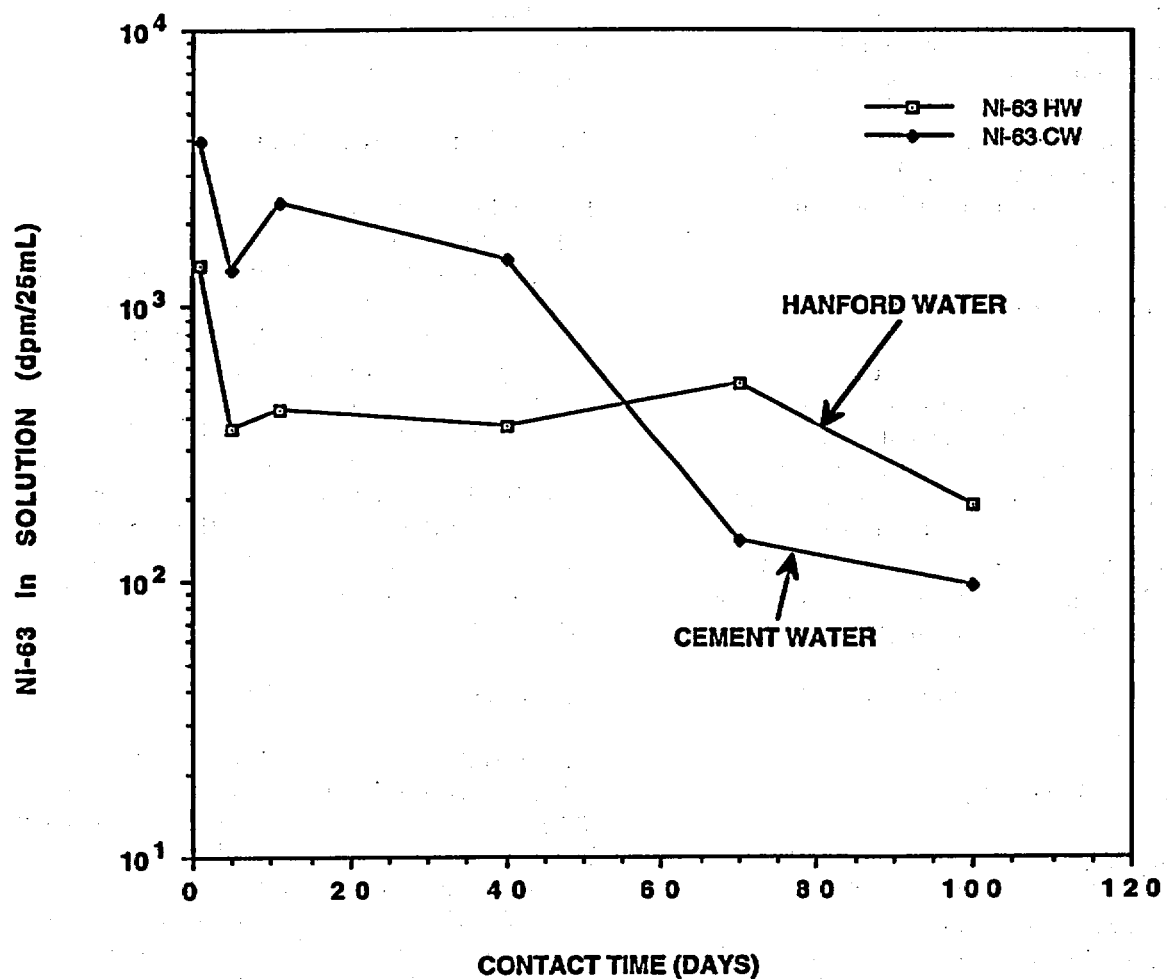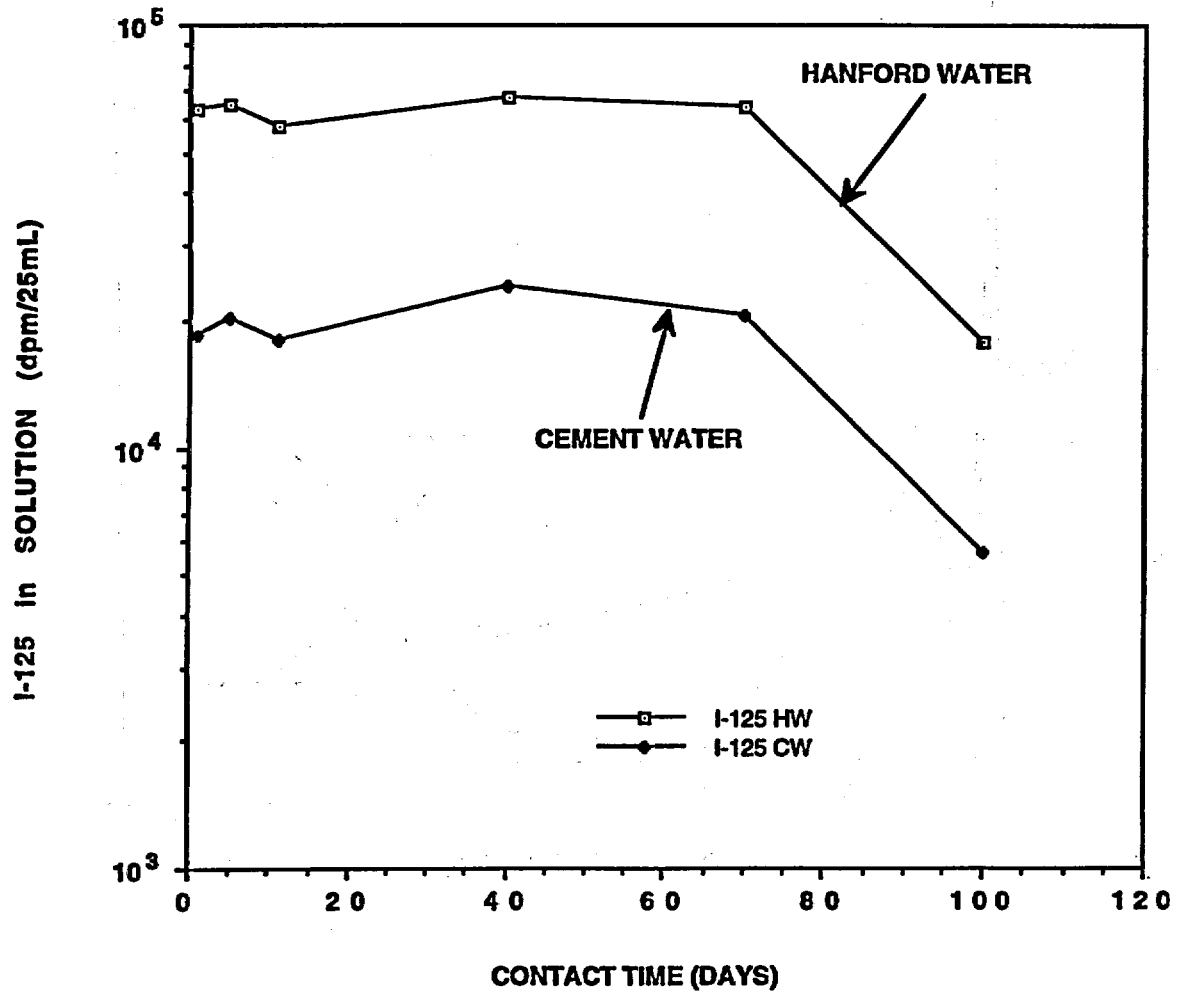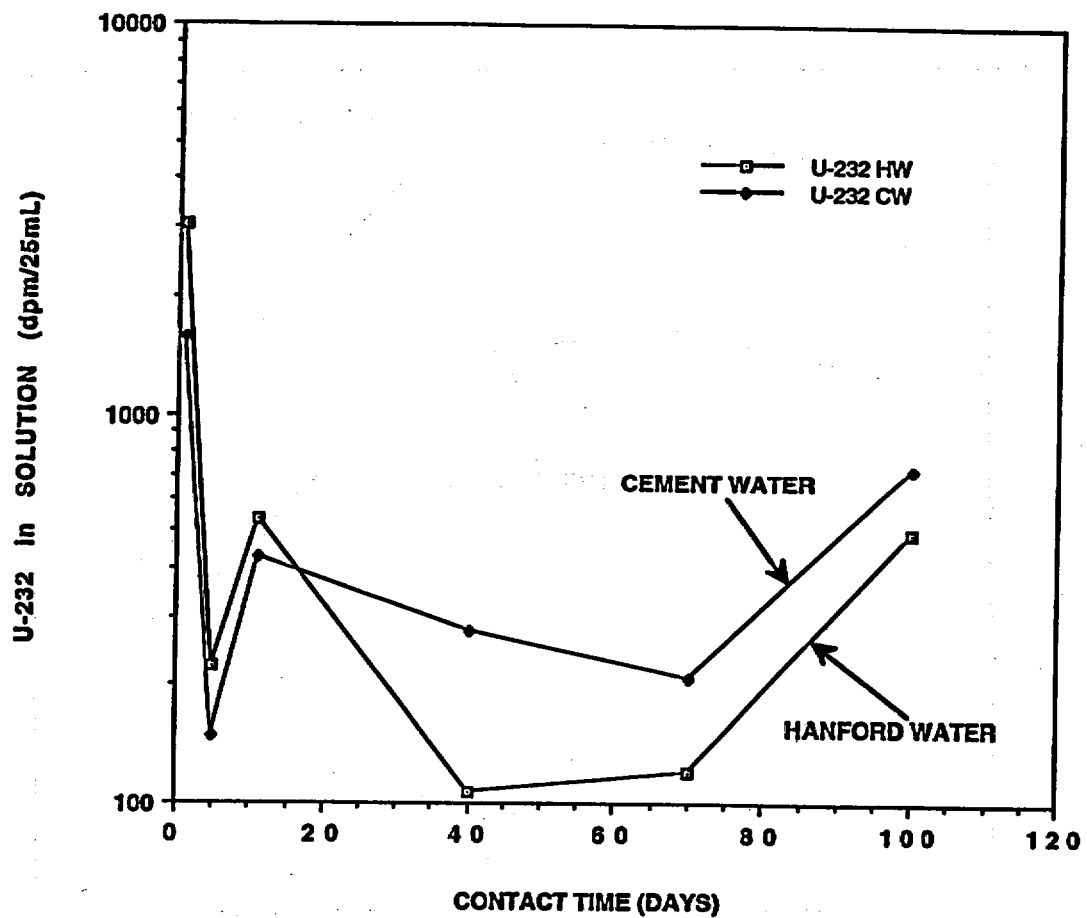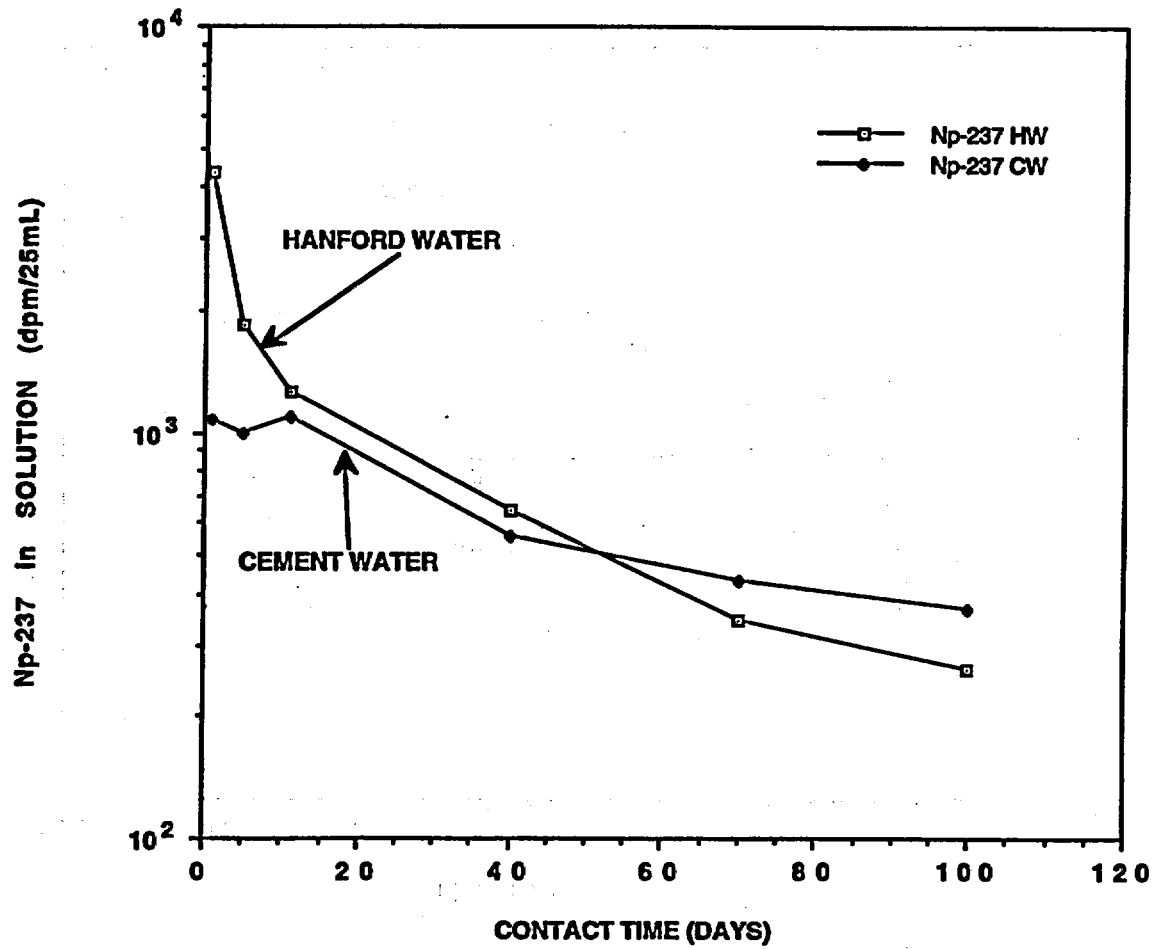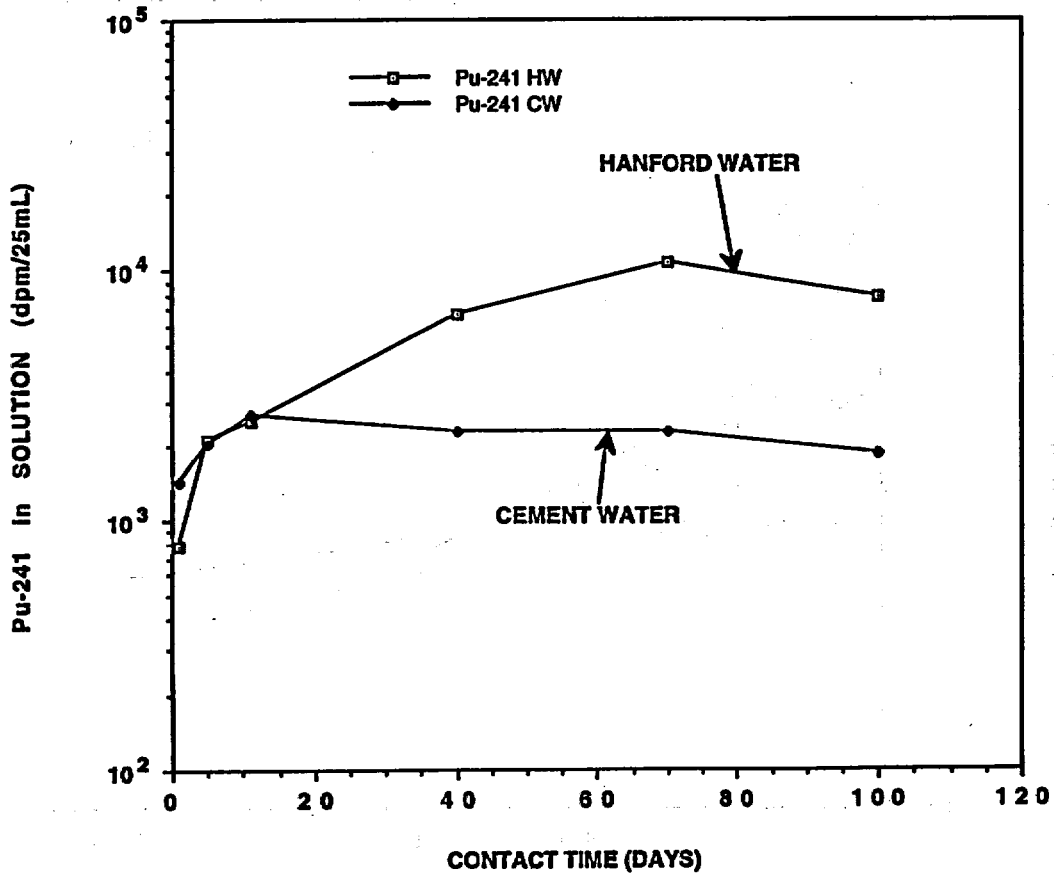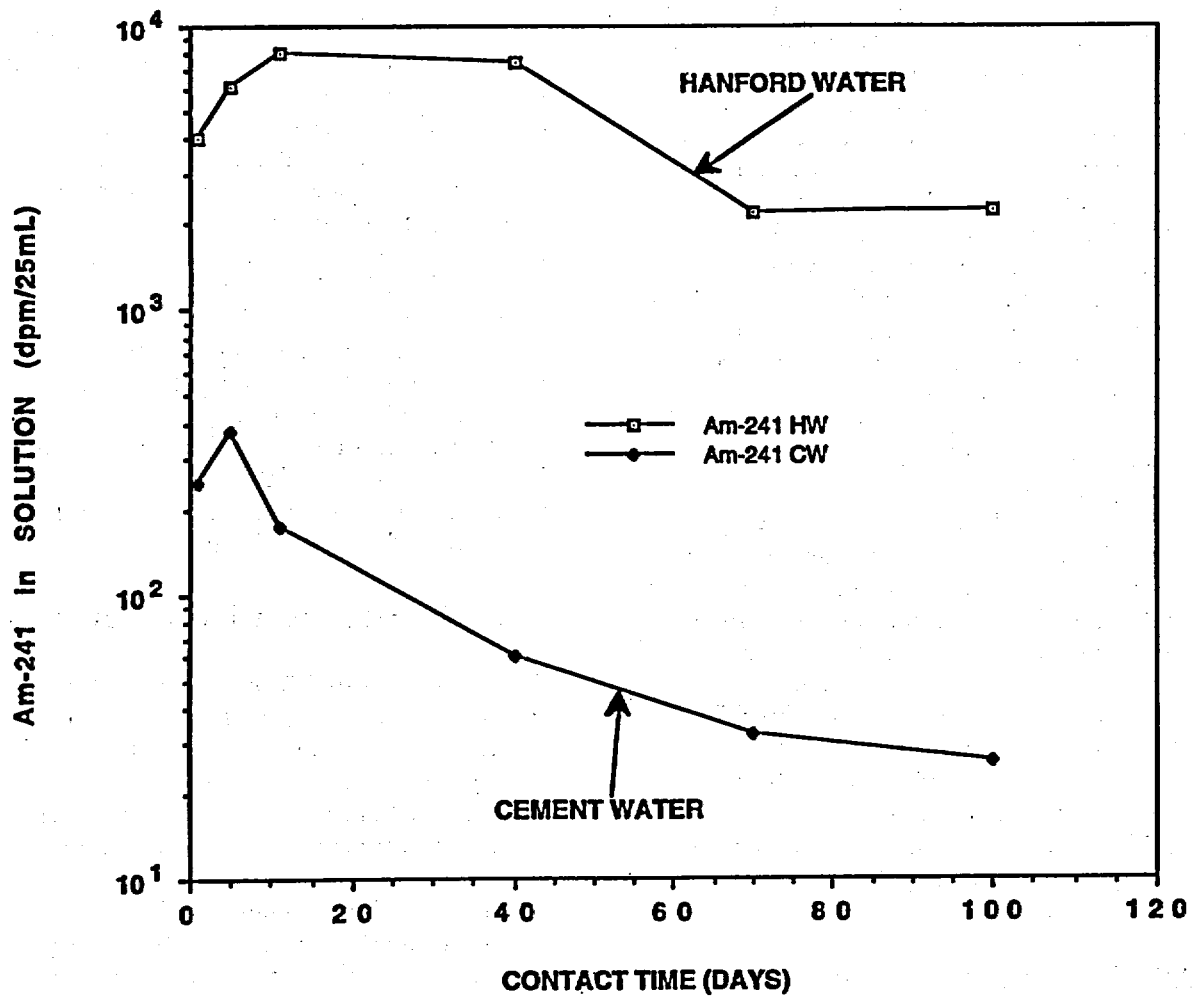**Figure 4.7 Am-241 Concentrations in Solutions in Contact with EPICORE AC-32 Mixed-Bed Ion Exchange Resin as a Function of Time**

4.2.8 Chlorine-36 and Technetium-99

The desorption behaviors of ^{36}Cl and ^{99}Tc were not graphed because these two radionuclides were so tightly bound to the resins that insignificant fractions of the resin-sorbed tracers were ever leached from the resins by the two water types (see Tables 4.1 and 4.2). Thus, it can be expected that these radionuclides will not be significantly released from spent ion exchange resins by infiltrating groundwaters at LLW disposal facilities. This observation was not unexpected for ^{99}Tc because of its very high affinity for anion exchange resin. However, the tenacious behavior of the ^{36}Cl on the resin was surprising because chloride normally has a relatively low selectivity for anion resin and can be exchanged by other anions having higher selectivities. This sorption behavior was especially surprising when compared with the behavior of the ^{125}I. Iodine has a much greater selectivity on anion exchange resin compared to chloride, but 50 times more ^{125}I than ^{36}Cl was desorbed from the EPICORE AC-32 resin by the waters. Perhaps if a dynamic contact experiment was conducted where a fresh supply of ions were continually available to the resins, the desorption of ^{36}Cl due to replacement by higher selectivity anions would be observable.

4.2.9 Summary of Desorption Behaviors

As stated earlier, only ^{241}Pu in both water types, and ^{14}C and ^{241}Am in Hanford groundwater showed a gradual, continuing desorption from the resins into the water phases up to about 10 to 70 days of contact time. All other radionuclides showed gradual re-sorption onto the resins as the experiment continued to a contact time of 100 days. Thus, it appears that most of the desorption that will occur will happen very rapidly (within 1 day) and that much of the desorbed radionuclides will actually re-sorb to the resin, perhaps by physical adsorption of hydrolyzed chemical species, rather than by true ion exchange. In any case, the tenacious binding capacity of the mixed-bed ion exchange resins for the radionuclides studied here will help

insure that these radionuclides will not be readily released to infiltrating groundwaters during breaching of an LLW disposal facility.

As long as the ion exchange resins are not chemically or physically degraded by ionizing radiation or environmental parameters, this effective fixation of sorbed radionuclides by the resins should continue indefinitely. In conducting site performance assessment modeling of new and existing LLW disposal facilities, some credit for retention of radionuclides by the spent ion exchange resins should be considered. The data from these desorption experiments suggest that small percentages of the various radionuclides (0.0003 to 0.1%) may be rapidly released to infiltrating groundwaters, but that continued, long-term leaching of the spent resin waste would not release significant additional quantities of sorbed radionuclides.

4.3 Desorption Coefficients

The data generated from the desorption measurements shown in Table 4.1 and Figures 4.1 - 4.7 can be converted into desorption coefficients, 1/Kd, as described in Section 3.2.4 of this report. These desorption coefficient values are given in Table 4.6.

The most striking conclusion obtained from the data was the small desorption coefficients measured over the entire time period for both Hanford groundwater and cement water, as shown in Table 4.6. The desorption coefficient values ranged from 3.2E-4 for ^{129}I to 2.1E-7 for ^{99}Tc, and their change as a function of contact time showed the same trends as discussed in Section 4.2. The results of this study compliment very well the results of the 1995 study, which also showed very small desorption coefficient values for this resin type. The rate of exchange of ions in the ion exchange process is extremely fast with high cross-linkage ion exchange resins such as that used in this study, reaching 80% of capacity in less than one minute, according to Dorfner[6]. Therefore, comparing the 1996 desorption coefficient values for the two waters on day-1 to the other time periods would strongly suggest that the small amount of activity which left the resin did so with a very rapid

exchange rate between solution and resin and would be typical of ion exchange kinetics. After this small amount of rapid exchange which took place during day-1, very little of the activity left the resin during the ensuing contact times, as discussed in Section 4.2. Consequently the desorption coefficients remained quite low throughout the study. Iodine-129 was the most noticeable exception, in that its desorption coefficient from day-1 and throughout the study ranged from 3.2E-4 to 1.3E-4 for the Hanford groundwater. This would indicate that an appreciable amount of ^{129}I activity moved rapidly from the resin into the water during day-1. Since both Hanford groundwater and the cement water contained only small amounts of dissolved salts, the relatively high desorption coefficient values could not be attributed to competition from high concentrations of ions as was the case in the 1995 study where high desorption coefficients occurred when the dissolved salt concentration in the aliquot of test water exceeded the capacity of both the anion and cation resin by nearly an order of magnitude.

It is interesting to note that a common characteristic between the cement water and the Soap Lake water used in the 1995 study was the high pH values of 11.1 and 10.1, respectively. Comparing the data from these two water samples, which gave relatively high desorption coefficients for Soap Lake water and relatively low desorption coefficients for cement water would indicate the controlling factor in the desorption coefficient was not the pH of the groundwater, but rather the competing salt concentration of the solution.

It was apparent that some of the activity of day-1 which desorped from the resin and went into solution either re-attached to the resin or deposited on the wall of the container (see Table 4.3). To ascertain if a lack of equilibrium between resin and solution phases caused the initial small, but rapid, desorption of radionuclides from the resin, a follow-on experiment was conducted using the same tagged resin specimens from the 100-day contact experiment. A repeat of days 1, 5, and 11, designated as day 101, 105, and 111 was performed after the sampling of day 100. The resin specimens were transferred to new

container tubes, rinsed, and fresh Hanford groundwater and cement water was added to the respective resins and the contact test resumed. The old container tubes were acid-rinsed several times and the combined rinses were counted to measure any activity that had been adsorbed onto the container walls.

The desorption behavior for the repeat leaching test is shown in Table 4.7. These data were subsequently re-calculated into desorption coefficients as described earlier, and these values are given in Table 4.8. The results of the repeat test were similar to those from the initial experiment and showed that a small fraction of the resin-sorbed radionuclides was rapidly desorbed by the Hanford groundwater and cement water during the first day of the repeat test (referred to as day 101). In all cases, except for ^{241}Pu in the Hanford groundwater, the rapid day-1 desorption of radionuclides from the resin was less in the repeat test compared to the initial experiment. Therefore, the resulting desorption coefficients from the repeat test were significantly lower (except for ^{241}Pu in Hanford groundwater) than those observed in the initial experiment. The desorption coefficients from the repeat test, where equilibrium conditions between the resin and water phases were probably better established, are considered the most representative of in situ conditions at an LLW disposal site which has been infiltrated by water.

The container wall acid rinse data, shown in Table 4.4, indicate that appreciable amounts of radionuclides deposited on the walls, namely, ^{14}C from the Hanford groundwater, ^{63}Ni from both water types, ^{99}Tc from both water types, and ^{241}Pu from Hanford groundwater. Although it is not known at what time during the course of the experiment these radionuclides attached to the walls of the containers, the amount on the walls can be compared to the amount in the water at day-100 when the two phases were separated. Tables 4.3 and 4.4 show the activity in the water at each sampling time. If the wall activity is compared to the sum of the wall activity plus the activity in the water for day-100, as shown in Table 4.4, this will give

Table 4.6 Measured Desorption Coefficients (g/mL) for EPICORE AC-32 Mixed Bed Resin Contacted With Hanford
Groundwater and Cement Water as the Aqueous Phases

Isotope	dpm on Resin	Water Type*	Day 1	Day 5	Day 11	Day 40	Day 70	Day 100
14C	9.21E6	HW	7.19E-5	7.94E-5	8.40E-5	9.17E-5	9.01E-5	9.17E-5
		CW	7.75E-5	7.41E-5	7.19E-5	7.69E-5	6.06E-5	6.49E-5
36Cl	2.35E7	HW	2.87E-6	2.40E-7	3.10E-7	3.60E-7	9.70E-7	2.90E-7
		CW	6.00E-7	7.60E-7	3.60E-7	2.90E-7	2.50E-7	2.40E-7
63Ni	2.52E7	HW	5.59E-6	1.43E-6	1.67E-6	1.46E-6	2.08E-6	7.50E-7
		CW	1.57E-5	5.41E-6	9.35E-6	5.85E-6	5.50E-7	3.80E-7
99Tc	2.61E7	HW	2.10E-7	2.40E-7	3.90E-7	2.20E-7	2.80E-7	2.10E-7
		CW	5.20E-7	4.00E-7	3.00E-7	6.80E-7	2.10E-7	3.00E-7
129I	4.44E7	HW	1.61E-4	1.72E-4	1.65E-4	2.72E-4	3.22E-4	1.27E-4
		CW	4.65E-5	5.44E-5	5.16E-5	9.80E-5	1.03E-4	4.02E-5
232U	8.64E6	HW	3.52E-5	2.59E-6	6.21E-6	1.72E-6	1.71E-6	5.75E-6
		CW	1.82E-5	1.72E-6	4.93E-6	3.18E-6	2.43E-6	8.33E-6
241Pu	9.45E6	HW	8.20E-6	2.23E-5	2.66E-5	7.04E-5	1.13E-4	8.26E-5
		CW	1.49E-5	2.15E-5	2.81E-5	2.42E-5	2.39E-5	1.95E-5
241Am	1.15E7	HW	3.46E-5	5.29E-5	6.99E-5	6.49E-5	1.90E-5	1.91E-5
		CW	2.15E-6	3.23E-6	1.50E-6	5.30E-7	2.40E-7	1.80E-7
237Np	1.12E7	HW	3.89E-5	1.64E-5	1.12E-5	5.81E-6	3.08E-6	2.34E-6
		CW	9.62E-6	8.85E-6	9.71E-6	4.93E-6	3.77E-6	3.31E-6

* HW = Hanford groundwater
CW = Hanford groundwater previously equilibrated with cement

$$\text{Desorption Coefficient} = 1/Kd = \frac{\text{(activity in water) (2.5 grams resin)}}{\text{(activity on resin) (25 mL water)}}$$

Table 4.7 Repeat Test of Desorption Behavior of Radionuclides Between Resin and Water Phases Activity in 25 mL of Water vs. Time

| Isotope | Total dpm on Resin | Water Type | ---- dpm in 25 mL of water vs time---- | | |
			Day 101	Day 105	Day 111
^{14}C	9.21E6	HW	2030±162	2149±165	2938±188
		CW	1597±76	2453±172	2659±181
^{36}Cl	2.35E7	HW	435±109	415±105	558±116
		CW	292±101	339±101	
^{63}Ni	2.52E7	HW	148±91	215±97	717±132
		CW	91±44	238±99	430±253
^{99}Tc	2.61E7	HW	<89	95±95	115±92
		CW	96±90	102±87	130±93
^{129}I	4.44E7	HW	2589±195	3219±213	3400±219
		CW	1122±140	1274±145	1413±153
^{232}U	8.64E6	HW	1386±193	<145	<203
		CW	673±111	<148	<141
^{241}Pu	9.45E6	HW	5607±364	3457±293	1823±227
		CW	361±132	344±132	161±39
^{241}Am	1.15E7	HW	787±94	336±64	445±71
		CW	<31	48±36	<26
^{237}Np	1.12E7	HW	739±91	397±71	359±62
		CW	1071±107	742±91	498±73

HW = Hanford groundwater
CW = Hanford groundwater previously equilibrated with cement

Table 4.8 Repeat Test for Measured Desorption Coefficients (g/mL) for EPICORE-AC-32 Mixed-Bed Resin Using Hanford Groundwater and Cement Water

Isotope	Total dpm on Resin	Water Type*	------------Desorption Coefficient---------------		
			Day 101	Day 105	Day 111
^{14}C	9.21E6	HW	2.20E-5	2.33E-5	3.19E-5
		CW	1.73E-5	2.66E-5	2.89E-5
^{36}Cl	2.35E7	HW	1.85E-6	1.77E-6	2.38E-6
		CW	1.24E-6	1.43E-6	2.18E-6
^{63}Ni	2.52E7	HW	5.90E-7	8.50E-7	2.84E-6
		CW	3.60E-7	9.40E-7	1.17E-6
^{99}Tc	2.61E7	HW	2.60E-7	3.60E-7	4.30E-7
		CW	3.60E-7	3.80E-7	4.90E-7
^{129}I	4.44E7	HW	1.85E-5	2.30E-5	3.06E-5
		CW	8.00E-6	9.09E-6	1.27E-5
^{232}U	8.64E6	HW	1.61E-5	1.71E-6	1.72E-6
		CW	7.81E-6	1.71E-6	1.70E-6
^{241}Pu	9.45E6	HW	5.92E-5	3.66E-5	1.93E-5
		CW	3.80E-7	3.64E-6	1.70E-6
^{241}Am	1.15E7	HW	6.85E-6	2.92E-6	3.86E-6
		CW	2.70E-7	4.20E-7	1.80E-7
^{237}Np	1.12E7	HW	6.58E-6	3.53E-6	3.19E-6
		CW	9.52E-6	6.62E-6	4.44E-6

$$\text{Desorption Coefficient} = 1/K_d = \frac{(\text{activity in water}) (2.5 \text{ grams resin})}{(\text{activity on resin}) (25 \text{ mL water})}$$

* HW = Hanford groundwater
  CW = Hanford groundwater preciously equilibrated with cement

the fraction of the total desorbed activity remaining on the container wall. This comparison shows that the ^{63}Ni wall activity for the Hanford groundwater and the cement water was 81% and 92%, respectively, while ^{99}Tc wall activity for both types was >99% for each. The ^{241}Pu wall activity for Hanford groundwater was 68%. These data would indicate that a large fraction of the ^{63}Ni and ^{99}Tc which was desorbed from the resin by both water types and a significant amount of ^{241}Pu in Hanford groundwater eventually became attached to the container walls. Also, the data from Table 4.4 showed that only a small fraction of the ^{241}Pu from cement water, and ^{14}C, ^{36}Cl, ^{129}I, ^{232}U, ^{241}Am, and ^{237}Np from both water types was deposited on the container walls. These data would also indicate that an appreciable amount of the activity which left the resin at day-1 re-absorbed onto the resin by day-100 for the radionuclides ^{36}Cl, ^{63}Ni, ^{129}I, ^{232}U, ^{242}Am, and ^{237}Np for both water types.

It was decided to compare desorption coefficient values calculated using different data sets and select what appeared to be the most representative value. Table 4.9 shows the desorption coefficients obtained by four different methods of calculation.

Method 1 simply used the day-100 water activity for the aqueous phase and neglected the fraction of the tracers that had desorbed from the resins and became attached to the container wall surfaces. Thus, it is a true measure of what actually remained in solution after 100 days of contact time between resin and water. This method provides the recommended desorption coefficient values to be used by performance assessment modelers, since it provides a true measure of the actual leach fraction remaining in solution for migration from the waste trenches via groundwater transport.

Method 2 used for the aqueous phase of the activity in the water at day-100, plus the wall activity. This method assumed that the activity leaving the resin was a

sum of the activities in the day-100 water (corrected for the 1 mL removed at each sampling time period prior to day-100), plus the activity that was on the container tube surface.

Method 3 assumed that the wall activity was deposited uniformly throughout the study. Thus, the wall activity was equally added to the water from each sampling time period and the average of the re-adjusted water activity was then used for the calculations.

Method 4 assumed that the start of the study (sample days 1, 5, 11) should be similar to days 101, 105, and 111 if the resin had been sufficiently equilibrated with the water phases. The sum of the wall activity and the average activity in the water for these three sampling time periods was used for the calculations.

Although the desorption coefficients measured during the initial test sampling periods were probably relatively high, the values obtained during days 105 and 111 were compared to the desorption coefficient values obtained in 1995 for day 7, where in both instances Hanford groundwater was used. These data are presented in Table 4.10. These data are in reasonable agreement with the possible exception of ^{129}I, where the 1996 data indicates a significantly higher desorption coefficient value. The lower values suggest that there may be more than one oxidation state for iodine in the 1996 tests.

At day-11, day-70, and day-111, the pH of the solutions were taken to determine if significant pH changes of the solutions occurred during the sampling time periods, a condition which was indicated during the 1995 study. These results indicated that both the Hanford groundwater and cement water under-went a significant pH change. The data show that both water types ended up at essentially the same pH values for each specific radionuclide test. The waters containing the anionic radionuclide species, plus Ni and Np, had pH values

ranging from 5 to 6 for all time periods, while the water containing cationic species of the actinide radionuclides U, Pu, and Am had equilibrated to pH values of 2.5 to 3.5.

Table 4.9 Average Desorption Coefficient (g/mL) Values Based on Four Different Calculation Methods

Isotope	Water Type	Method 1*(A)	Method 2**	Method 3***	Method 4****
^{14}C	HW	9.17E-5	1.17E-4	7.25E-5	6.62E-5
	CW	6.49E-5	6.45E-5	5.75E-5	3.41E-5
^{36}Cl	HW	2.90E-7	4.20E-7	6.80E-7	1.81E-6
	CW	2.40E-7	3.20E-7	2.90E-7	1.45E-6
^{63}Ni	HW	7.50E-7	3.62E-6	2.12E-6	4.20E-6
	CW	3.80E-7	4.98E-6	5.24E-6	5.45E-6
^{99}Tc	HW	2.10E-7	2.16E-5	3.26E-6	2.17E-5
	CW	3.00E-7	7.46E-5	1.10E-4	7.52E-5
^{129}I	HW	1.27E-4	5.53E-5	1.01E-4	3.01E-5
	CW	4.03E-5	1.74E-5	3.24E-5	1.14E-5
^{232}U	HW	5.75E-6	7.63E-6	7.35E-6	8.47E-6
	CW	8.33E-6	8.06E-6	4.72E-6	4.57E-6
^{241}Pu	HW	8.26E-5	2.13E-4	6.33E-5	1.81E-4
	CW	1.95E-5	2.22E-5	1.82E-5	9.62E-6
^{241}Am	HW	1.19E-5	2.84E-5	3.58E-5	1.72E-5
	CW	1.80E-7	6.10E-7	1.08E-6	7.00E-7
^{237}Np	HW	2.34E-6	4.59E-6	1.05E-5	6.62E-6
	CW	3.31E-6	4.08E-6	5.43E-6	7.04E-6

1*   Calculated using Day-100 water activity as reported in Table 3.4. These values do not take into account the activity attached to the container walls.

2**   Calculated using Day-100 water activity plus wall activity corrected for 1 mL removal for each period.

3*** Calculated by assuming wall activity was deposited equally throughout the time period. Therefore, equal aliquots were added to the solution activities and the average solution activity was used.

4**** Calculated similar to #1 except the average days of 101, 105, and 111 were used in place of day-100.

(A)   Recommended method for calculating most reasonable desorption coefficient values.

Desorption Coefficient = 1/Kd = $\frac{\text{(activity in water) (2.5 grams resin)}}{\text{(activity on resin) (25 mL water)}}$

Table 4.10 Comparison Between 1995 and 1996 Desorption Coefficient (g/mL) Studies Using Hanford Groundwater

| | | ----------------------------Desorption Coefficient----------------------------- | |
| | 1995 Study* | 1996 Study** | |
Isotope	Day 7	Day 105	Day 111
^{14}C	9.71E-5	8.00E-5	8.40E-5
^{36}Cl	8.62E-6	2.40E-7	3.20E-7
^{63}Ni	5.21E-6	1.43E-6	1.66E-6
^{99}Tc	1.41E-6	2.40E-7	3.90E-7
^{129}I	5.08E-6	1.72E-4	1.66E-4
^{232}U	2.04E-6	2.59E-6	6.21E-6
^{241}Pu	4.69E-6	2.23E-5	2.66E-5
^{241}Am	1.79E-6	5.29E-5	6.99E-5

*   Desorption coefficient values determined by adding clean EPICORE-AC-32 resin to spiked, equilibrated Hanford groundwater.

**   Desorption coefficient values determined by leaching radionuclide-loaded EIPCORE-AC-32 resin with clean Hanford groundwater.

$$\text{Desorption Coefficient} = 1/Kd = \frac{(\text{activity in water}) (2.5 \text{ grams resin})}{(\text{activity on resin}) (25 \text{ mL water})}$$

5 Summary, Conclusions, and Regulatory Implications

The sorption and desorption behavior of long-lived 10CFR Part 61 radionuclides on EPICORE AC-32 mixed-bed ion exchange resin from natural water solutions has been determined in laboratory tests. These measurements have provided estimates of the retention of these radionuclides on the type of resin used at nuclear power stations for demineralization of primary coolant and liquid radwastes. This information is important to performance assessment modelers for predicting the leaching of radionuclides from low-level radioactive waste (LLW) materials disposed at shallow-land burial facilities which may become infiltrated with water. Using these data, credit for retention of the radionuclides on the ion exchange resin (a major LLW radionuclide source term) can be taken into account, thereby giving more reasonable estimates of the offsite transport of radionuclides by groundwater.

The short-term batch Kd determinations indicated that most of the radionuclides had a very high affinity for the mixed-bed ion exchange resin from the water solutions. These results indicate that radionuclides are tightly held by the functional groups on the resin, and may have very long environmental half-lives attached to the resin LLW materials, even when leached with groundwater.

The results of these short-term batch desorption tests indicated that a very small fraction of the resin-sorbed radionuclides would rapidly (within one day) desorb from the resin. Thereafter, either very little leaching of the radionuclides from the resin occurred, or the initially desorbed radionuclides actually re-absorbed to the resin. It was shown that the exchange capacity of the resin samples used in the tests was not exceeded by the amounts of dissolved salts in the test waters used in these batch contact experiments. Therefore, the competing ion effect (i.e. dissolved ionic species in the water samples replacing resin-sorbed radionuclides) would have been minimized.

From these two experiments, it is clear that some credit for the retention of radionuclides by the ion exchange resin disposed of in LLW facilities, even when leached by groundwater, should be taken into account by performance assessment modelers. It appears that a very small fraction (10^{-5} to 10^{-7}) of most radionuclides attached to the resin would be leached by infiltrating groundwater, even over long time periods. These release fractions could be used to estimate the fractional release of radionuclides from LLW ion exchange materials into contacting water. Thus, the radiation dose to offsite individuals could be much lower compared to predictions based on the conservative approach which assumes that all of the radionuclides in the LLW material would be quickly leached from the waste materials by infiltrating groundwater.

Several factors still could complicate this assumption. First, the chemical composition of the filtrating groundwater could be substantially modified by other materials leached from the wide variety of LLW waste forms present in the disposal trenches. It is well-known that actual LLW trench leachates have relatively high concentrations of dissolved salts, metals, and organic materials (Dayal, Pietrzak, and Clinton 1986; Kirby 1982; Kirby et al. 1991). In addition, trench leachates are usually quite anoxic. These chemical and redox conditions could affect the degree of retention of radionuclides by ion exchange resin LLW being leached by such trench leachates. Second, bacterial action on the organic polymers and functional groups that comprise ion exchange resin may shorten the environmental half-life of the ion exchange resin LLW. Although these polymers are relatively stable organic materials, their biological stability over long time periods is not known.

Several follow-on experiments could be conducted that would give further confidence in the retention capacity of ion exchange resin to hold radionuclides over long time periods while being leached by infiltrating groundwater. It would be very desirable to repeat the resin leaching tests using a dynamic, flow-through contact system where the test waters were continually being renewed. The continuous supply of fresh test waters would provide a more realistic simulation of the in situ leaching of spent ion exchange resin by infiltrating waters at a breached LLW disposal facility. In this way, the effects of resin exchange capacity and saturation could be better evaluated,

as well as the lowered pH values observed for the batch contact tests for U, Pu and Am. It would also be desirable to use test waters that more closely resembled the composition of LLW trench leachate waters which have relatively elevated concentrations of both organic and inorganic constituents, as well as reducing conditions. Simulated waste trench waters kept at reducing conditions could be prepared for use in future experiments. The aim of this additional research would be to more precisely mimic the real-world leaching environment that disposed ion exchange resin wastes would be exposed to in breached LLW facilities.

6 References

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Appendix A

Literature Review of Adsorption and Desorption of Radionuclides from Ion Exchange Resins by Near-Neutral pH Solutions

1.0 Introduction

The requirements for disposal of radioactive waste in a low-level waste (LLW) repository, as specified in 10CFR Part 61, indicate that radionuclides contained in the waste must not breach the disposal site boundaries in quantities greater than allowed. Ion exchange resins used for the removal of radionuclides from the primary coolant system of commercial nuclear power plants and other liquid waste streams are collectively one type of waste sent to LLW disposal facilities. Spent ion exchange resins are dewatered and packaged in high integrity containers for burial at the disposal facilities. However, these containers will eventually degrade and come in contact with infiltrating water. The mobility of the various radionuclides in groundwater will depend on how tightly the radionuclides are bound on the ion exchange resins. This literature study was undertaken to evaluate the binding strength of the radionuclides present on waste ion exchange resins in contact with near-neutral pH (5-8) solutions which might simulate contact with groundwater.

The distribution coefficients (Kd's) of resins for various radionuclides indicate the binding strength or selectivity of the resins for those radionuclides. Distribution coefficients are a ratio of the quantity of a radionuclide (or ion) per unit weight of exchanger (resin) compared to the quantity of a radionuclide or ion per unit volume of the liquid in an equilibrium situation, and Kd's are usually expressed in units of mL/g. These ratios are influenced significantly by the chemistry and pH of the liquid phase involved. Present methods of calculating

radionuclide releases from ion exchange resins involve a simple rinse model using distilled water. The chemistry and pH of distilled water differs significantly from that of ground water and therefore the Kd's determined for radionuclides on ion exchange resins in distilled water are not completely representative of what would occur in a LLW facility infiltrated with ground water.

2.0 Literature Survey

An extensive survey of the literature was undertaken to find information on distribution coefficients for resins in contact with aqueous solutions which simulated the groundwater pH range of 5-8. A literature search vendor service available at the Hanford Technical Library, Dialog Information Service, Inc. (Dialog), was employed in this survey. Dialog database included National Technical Information Services (NTIS); Nuclear Science Abstracts; Compendex Plus Energy Science and Technology (formerly DOE); Nuclear Science Abstract, Analytical Abstracts, and Chemical Abstract Search. This literature review is not presented as being totally complete or exhaustive. In addition, personal contacts were made with numerous individual researchers, laboratories, and resin suppliers to assist in obtaining pertinent information.

The literature review did not identify a single study that used actual or simulated groundwater to determine Kd's or to elute radionuclides from waste resins. All of the available data showed the removal of radionuclides from resins by water (usually distilled water) adjusted to pH's near those of ground water. From these

data, Kd's were given or estimated by the authors of this paper. The problem encountered with this approach is that each study involved a unique waste stream with different chemical additives characteristic of the individual operation. None of the studies employed an eluant that approximated the chemistry of groundwater. Many of the chemicals involved were strong complexing agents capable of removing radionuclides from the resin by complexation. In some instances, the chemical additives were oxidizing or reducing agents that can remove radionuclides from the resin by their oxidizing or reducing potential. There were numerous studies determining the leachability of ion-exchange resins solidified in cement or cement and fly ash. The majority of these studies used distilled water as the leaching solution.

The following compilation from several studies presents the Kd's determined for pH 5, 6, 7, and 8. Not all studies cover the entire pH range of interest. One study (Campbell, Lee and Dillow, 1990) did measure Kd's for ^{90}Sr and ^{137}Cs for the pH range of 11 to 13.

2.1 Amberlite IRN-77 and Powdex PCH Resins

The distribution coefficients for ^{137}Cs and ^{90}Sr at neutral pH were calculated from data found in NUREG-CR-0619 (Columbo 1979). This study measured the release rates for ^{137}Cs and ^{90}Sr from Amberlite IRN-77 (Rohm and Haas Co.,) and Powdex PCH (Ecodyne Corp.) cation exchange resins using a modified IAEA leaching test in distilled water. Amberlite IRN-77 is a strongly acidic polystyrene based nuclear-grade, cation-exchange resin with sulfonic acid groups. It has an exchange capacity of 4.7 meq/g (dry), a maximum moisture content, as received, of 55% and an effective bead size of 0.45 to 0.60 mm. Powdex PCH is a strongly acidic sulfonated styrene-divinylbenzene copolymer and, as a powdered resin, has a much higher specific area. This resin has a particle size of 100-400 mesh (0.15 to 0.37 mm) with the majority falling within the 200-400 mesh size. The exchange capacity of this resin is approximately 4.6 meq/g with an average moisture content, as received, of 50%. Table 1 shows the Kd's calculated from these data.

Table A1. Calculated Distribution Coefficients (mL/g) for ^{85}Sr and ^{137}Cs on Amberlite IRN-77 (Bead) and Powdex PCH (powdered) Cation Exchange Resin

Isotope	Resin Type	pH5	pH6	pH7	pH8
^{137}Cs	bead	-	-	329	-
	powdered	-	-	10890	-
^{85}Sr	bead	-	-	7900	-
	powdered	-	-	94340	-

2.2 BioRad AGMP-50 Resin

Distribution coefficients for 14 elements were estimated by Horwitz (Horwitz et al. 1993a, b) using BioRad AGMP-50 cation resin at pH's of 5, 6, 7, and 8. BioRad AGMP-50 is a sulphonic acid cation resin

with an exchange capacity of 4.6 meq/g and mesh size of 100-200. In this study, the resins were converted to the calcium form using 2M Ca(NO$_3$)$_2$. The Kd's were determined using, as the aqueous solution, a 0.1 M ammonium acetate buffer whose pH had been adjusted to 5, 6, 7, or 8 by

the addition of acetic acid or ammonia. By buffering the solution with ammonium acetate and adjusting the pH with acetic acid or ammonia, considerable amounts of acetate and ammonium ions were introduced into the system. The ammonium ion would produce co-ordinate complexes of Co, Ni, Ag, and Cu. All of these complexes, if ionized, would be cationic complexes of 0, +1, +2, and +3 depending on the influence of the acetate ion in the chelate. As a result, the Kd's can be a measure of a species quite different than expected. Table 2 lists the Kd's derived from this study. Where possible, the elements are listed as isotopes of the elements that are included in the 10 CFR Part 61 compilation.

Table A2. Measured Distribution Coefficients (mL/g) For a Number of Isotopes on AGMP-50 Cation Exchange Resin

Isotope/Element	pH5	pH6	pH7	pH8
^{108}Ag	3000	4000	4000	1500
^{59}Ni	50	40	75	130
^{63}Ni	50	40	75	130
^{60}Co	40	35	85	190
^{109}Cd	60	55	125	250
^{113m}Cd	60	55	125	250
^{121}Sn	800	2500	2000	4500
^{126}Sn	800	2500	2000	4500
U^{+6}	175	300	95	20
Cr^{+3}	100	200	1000	1200
Cu^{+2}	10	15	49	180
Al^{+3}	85	300	95	20
Hg^{+2}	4000	2500	2000	4500
Pb^{+2}	100	90	180	300
Mn^{+2}	1200	70	100	125
Zn^{+2}	60	55	150	400
Sb^{+3}	70	150	200	400

2.3 Diphonix Resin

The study by Horwitz (Horwitz et al. 1993a, b) compared BioRad AGMP-50 resin to a new resin, Diphonix, which is a styrene-divinylbenzene sulfonated ion exchange resin containing chemically-bonded gem-diphosphonic acid groups. Although this resin is a recently developed experimental resin and has not been used in large quantities at nuclear power stations, the distribution coefficients are shown for comparison purposes since the effects from the acetate and ammonium ions will be similar. Table 3 lists the Kd's for Diphonix resin. It is obvious that the Diphonix chelating resin has much higher Kd values compared to the AGMP-50 cation exchange resin under the conditions of these tests.

Table A3. Measured Distribution Coefficients (mL/g) For a Number of Isotopes on Diphonix Chelating Ion Exchange Resin

Isotope/Element	pH5	pH6	pH7	pH8
^{108}Ag	2000	1900	400	300
^{59}Ni	300	2000	6000	9500
^{63}Ni	300	2000	600	9500
^{60}Co	500	5000	17000	21000
^{109}Cd	1500	11000	35000	10000
^{113m}Cd	1500	11000	35000	10000
^{121}Sn	2000	2000	3000	15000
^{126}Sn	2000	2000	3000	15000
U^{+6}	15000	18000	10000	9000
Cr^{+3}	50000	20000	7000	6000
Cu^{+2}	1000	1000	1000	1000
Al^{+3}	300	300	300	400
Hg^{+2}	4000	4300	5000	4000
Pb^{+2}	10000	9000	50000	30000
Mn^{+3}	4000	20000	50000	50000
Zn^{+2}	15000	>100000	100000	100000
Sb^{+3}	300	80	200	300

2.4 Other Studies

Plutonium removal from the low-level waste water effluent of the Plutonium Finishing Plant at the Hanford Site was tested using several commercially available ion exchange resins (Barney et al. 1989). Batch distribution coefficients for plutonium were measured for each resin at the pH's of interest (5-9). The activity of plutonium was too low to be measured conveniently. A ^{238}Pu spike solution was added to the waste water as a tracer for plutonium. The ^{238}Pu spike solution was chemically adjusted to assure that all the plutonium was in the (IV) oxidation state before adding it to the waste water. The spiked waste waters were treated with dilute NaOH or HNO_3 to achieve the desired pH's. The resulting solutions were filtered through 0.45 mm millipore filters to remove any plutonium-containing solids. Table 4 lists the distribution coefficients measured using 4 different resins.

Table A4. Measured Distribution Coefficients (mL/g) For Pu (IV) on Four Different Ion Exchange Resins

	pH5	pH6	pH7	pH8
Duolite GT73 (cation)	2500	1500	900	500
AMB IRC718 (cation)	-	140	180	190
Dow 21K (anion)	0.3	0.9	10	500
Dow M41 (anion)	0.2	0.4	1	500

In a study reported in MLM 2684 (Roberts, et al. 1980) distribution coefficients were measured for ^{60}Co and ^{137}Cs using actual and simulated Mound Facility waste streams at neutral pH. The purpose of the study was to compare several organic and natural resins for the removal of radionuclides from waste streams. Since none of the resin columns used were allowed to run until breakthrough occurred, this data could only be used in approximating Kd's. The waste streams were spiked with ^{60}Co or ^{137}Cs and then adjusted to the desired pH. The waste influent to the column was filtered through a 10 ÿm filter, sampled and then passed through the appropriate column. It was found that a considerable amount of the ^{60}Co and ^{137}Cs remained on the filter, and as a result, the Kd's are representative of both the filtration and ionic removal by the resin in the column. Tables 5 and 6 list the distribution coefficients estimated from this data.

Table A5. Measured Distribution Coefficients (mL/g) For ^{137}Cs on Several Types of Ion Exchange Resin[a]

Resin	pH5	pH6	pH7	pH8
AG50W-x8 (cation)	>2560	-	-	>8230
HCR-W (cation)	-	-	-	-
MSC-1 (cation)	>3330	-	-	>9320
XN-1010 (cation)	>1400	-	-	>4470
IR-200 (cation)	>1230	-	-	>3660
XE-243 (anion)	>1	-	-	>2

(a) These Kd values do not represent equilibrium conditions.

Table A6. Measured Distribution Coefficients (mL/g) For ^{60}Co and Several Types of Ion Exchange Resins[a]

Resin	pH5	pH6	pH7	pH8
AG50W-x8 (cation)	>23500	.	.	4380
HCR-W (cation)	>12540	.	.	>4600
MSC-1 (cation)	>9820	.	.	>5470
XN-1010 (cation)	>10500	.	.	>3610
IR-200 (cation)	>5770	.	.	>3960
XE-243 (anion)	>6	.	.	>1

(a) These Kd values do not represent equilibrium conditions.

In a study done at Idaho National Engineering Laboratory, six small-scale specimens of cement-solidified ion-exchange resin wastes were leach-tested in deionized water at 23ÿC using the American National Standards Institute/American Nuclear Society (ANSI/ANS) Standard procedures. This study was representative of many studies done using cement solidified spent ion-exchange resins from the decontamination of primary coolant systems. Release rates, effective diffusivities and leachability indexes of radionuclides, chelating agents and metals were determined using ANS-16.1 diffusion release models. Releases of radionuclides from waste forms that degraded during leaching were similar to releases from waste forms that maintained their integrity during leaching. Table 6 indicates the cumulative fraction releases on the various waste forms tested.

Table A7. Cumulative Fraction Release Fractions of Several Isotopes From Cement-Solidified Ion Exchange Resins Used for Decontamination of Reactor Primary Coolant Systems

Waste-Form ID	^{55}Fe(a)	^{60}Co	^{63}Ni(a)	^{90}Sr(a)
AP/Citrox				
mixed-bed	1.3×10^{-2}	1.7×10^{-2}	1.5×10^{-4}	2.3×10^{-2}
cation	6.4×10^{-2}	1.7×10^{-3}	1.2×10^{-3}	9.9×10^{-1}
Can-Decon # 1	1.2×10^{-4}	1.5×10^{-3}	9.6×10^{-3}	3.8×10^{-1}
Can-Decon # 2	----b	1.3×10^{-3}	----b	$<8.8 \times 10^{-2}$
Dow NS-1	2.2×10^{-5}	6.3×10^{-2}	9.4×10^{-1}	2.4×10^{-1}
LOMI	2.7×10^{-4}	1.3×10^{-3}	5.7×10^{-4}	2.3×10^{-1}

Table 7 (Continued)

	^{137}Cs	^{241}Pu(a)
AP/Citrox		
mixed-bed	9.9×10^{-1}	$<3.4 \times 10^{-3}$
cation	6.8×10^{-1}	$<2.2 \times 10^{-2}$
Can-Decon # 1	9.8×10^{-1}	2.4×10^{-4}
Can-Decon # 2	3.6×10^{-1}	$<2.4 \times 10^{-2}$
Dow NS-1	$<8.6 \times 10^{-3}$	$<2.0 \times 10^{-3}$
LOMI	$1.0 \times 10^{+0}$	$<2.8 \times 10^{-3}$

(a) Not all leachates were analyzed for this radionuclide or metal.

(b) Concentration of radionuclide or metal in ion-exchange resin waste was not determined.

3.0 Conclusions

As a result of the literature survey, it became apparent that no studies have been undertaken to produce the desired information, i.e., there are no data on 10CFR61 radionuclide Kd's measured for ion exchange resins in contact with real or simulated groundwaters. The information available represents only simulations and approximations none of which gives a truly accurate measurement of Kd values for radionuclides attached to ion exchange resins in contact with groundwaters. Since the chemistry of groundwater is very complex and not easily reproduced in a laboratory, it would seem appropriate that a study be done using actual groundwater and fresh resins or spent ion exchange resins from the primary coolant system of a nuclear power plant. By using samples of actual groundwater taken from around a LLW disposal site and using them in leach tests of representative

resins, the desired data could be generated.

Equilibrium batch Kd measurements should be made with tracers of 10CFR61 radionuclides using the types of ion exchange resins used at nuclear power stations and using several groundwater types covering normal pH ranges (5-8). Since new LLW disposal facilities will be lined with concrete, infiltrating water will have to pass through the concrete. This will probably raise the pH of this water to 10-11. Thus, Kd measurements should also be made using high pH water altered by contact with cement.

An alternative experimental approach would be to obtain actual spent ion exchange resins from several nuclear power stations and conduct leaching studies with the groundwater types listed above. This approach would be more costly because the non-gamma-emitting 10CFR61 radionuclides would have to be radiochemically separated and measured, but this method would more closely resemble the actual environmental leaching conditions at a LLW disposal site.

4.0 Appendix A References

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2. TITLE AND SUBTITLE

Adsorption and Desorption Behavior of Selected 10 CFR Part 61 Radionuclides From Ion Exchange Resin by Waters of Different Chemical Composition

3. DATE REPORT PUBLISHED

MONTH	YEAR
July	2000

4. FIN OR GRANT NUMBER
L1808

5. AUTHOR(S)

D.E. Robertson, S.L. Pratt, C.W. Thomas

6. TYPE OF REPORT

Technical

7. PERIOD COVERED *(Inclusive Dates)*

8. PERFORMING ORGANIZATION - NAME AND ADDRESS *(If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)*

Pacific Northwest National Laboratory
Richland, WA 99352

9. SPONSORING ORGANIZATION - NAME AND ADDRESS *(If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)*

Division of Risk Analysis and Applications
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

10. SUPPLEMENTARY NOTES

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11. ABSTRACT *(200 words or less)*

Two sets of laboratory experiments were conducted to determine the adsorption and desorption behavior of a selected group of long-lived radionuclides on nuclear grade ion exchange resin in contact with several types of groundwater. In the first experiment, distribution coefficients (Kd) were determined for 13 radionuclides (^{14}C, ^{36}Cl, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs, Th, U, Np, Pu, and Am) on EPICORE AC-32 mixed-bed ion exchange resin in contact with three different water types. These measurements gave high Kd values (10^4 to 10^5) for the radionuclides. The second experiment involved determining the leaching rate and magnitude for nine radionuclides (^{14}C, ^{36}Cl, ^{63}Ni, ^{99}Tc, ^{129}I, U, Np, Pu, and Am) previously sorbed onto the same type of EPICORE AC-32 ion exchange resin. Equilibrium desorption coefficients (1/Kd) were determined for the radionuclides leached from the resin by two different water types. The desorption coefficients were very small (mainly in the range of 10^{-5} to 10^{-7}), indicating that the radionuclides were very tightly bound to the resin and not easily leached during contact with the test groundwater samples. These measurements have provided LLW site performance assessment modelers with empirical data to more effectively estimate the retention fraction, or conversely, the release fraction of radionuclides on ion exchange resin during contact with infiltrating groundwater.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

Ion exchange resin
radionuclide adsorption and desorption
low-level radioactive waste
distribution coefficients

13. AVAILABILITY STATEMENT

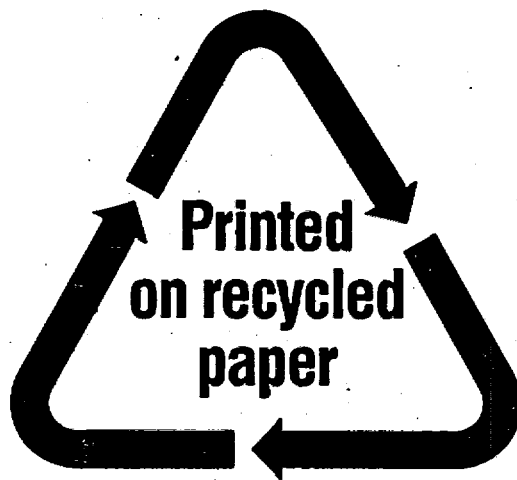unlimited

14. SECURITY CLASSIFICATION

(This Page)

unclassified

(This Report)

unclassified

15. NUMBER OF PAGES

16. PRICE

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

1975 **25** 2000
years