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Distribution Coefficients (Kd Values) for Waste Resins Generated from the K & L Disassembly Basin Facilities

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1.0 Executive Summary

Cation (CG-8) and anion resins (SBG-1) are used at the K & L Disassembly Basin Facilities to maintain the chemical quality of basin waters used to store spent fuel. The spent resins generated from the facilities contain a number of radionuclides, including ^{14}C, ^{129}I, and ^{99}Tc. The objective of this study was to measure the radionuclide distribution coefficients, or K_d values, of the spent resin that would provide information for evaluating their suitability for disposal at the E-Area Low-Level Waste Disposal. Sorption tests were conducted by mixing spent resins in the proportion that they are disposed, 42:58 cation:anion, and leaching them with either an acid-rain leachate (to simulate trench disposal) or a cement leachate (to simulate vault disposal). The resulting K_d values (mL/g) were:

	Acid-Rain Leachate	Cement Leachate
^{14}C	240	140
^{99}Tc	>680	>810

^{129}I K_d values could not be calculated because leachate and resin ^{129}I concentrations were below detection limits. A provisional ^{129}I K_d value was estimated based in part on previously measured ^{129}I concentrations in spent resin;

^{129}I K_d was >3700 mL/g for both acid rain and cement leachate.

These measured and estimated K_d values were appreciably greater than the default conservative values of 2 mL/g for ^{14}C, 0.6 mL/g for ^{129}I, and 0.36 mL/g for ^{99}Tc used in the most recent performance assessment calculations. These larger K_d values indicate that the

tendency of the radionuclides to leach into the underlying groundwater is less than the default values would predict.

2.0 Introduction

Resins are used at the K & L Disassembly Basin Facilities to maintain low dissolved salt and radionuclide concentrations in the basin waters used to store spent fuel. The spent resins from the facilities contain a number of radionuclides. Among the disposal options being considered for the spent resin is burial in the E-Area Low Level Waste Disposal Facilities. Prior to burial, it is necessary to know not only the inventory of radioactive and non-radioactive contaminants, but also the tendency of the contaminants to leach from the resins. This tendency of the contaminants to leach can be quantified by the distribution coefficient, or the K_d value. The K_d value is defined as:

$$K_d = \frac{C_s}{C_{aq}} \quad (1)$$

where C_s is the concentration of the radionuclide in the solid phase, and C_{aq} is the concentration in the aqueous phase.

Based on previous performance assessment calculations at the E-Area Low-Level Waste Disposal Area (McDowell-Boyer et al. 2000), the radionuclides that pose the greatest human health risk resulting from subsurface disposal are expected to be ^{14}C, ^{129}I, and ^{99}Tc. Previous measurements of desorption K_d values of SRS waste have been recently measured for ^{129}I (Kaplan et al. 1999, Kaplan and Serkiz 2000, Kaplan and Iversen 2001).

2.1 Objectives

The objective of this study was to measure ^{14}C, ^{129}I, and ^{99}Tc K_d values of spent resin generated from the K & L Disassembly Basin Facilities.

2.2 Scope

The scope of the work was to conduct K_d measurements of resins combined in the ratio that they are disposed, 42:58 cation:anion. Because it was not known how these spent resins would be buried, it was necessary to measure the K_d values in such a manner as to simulate both trench and vault disposal. This was accomplished by using an acid-rain simulant (a standard U.S. Environmental Protection Agency protocol) and a cement leachate simulant (both described in more detail in Section 3.0).

3.0 Materials and Methods

K_d values for ^{14}C, ^{129}I, and ^{99}Tc were measured using standard methods (ASTM 1984). A detailed description of the materials and methods used in this experiment are presented in Appendix A. The spent resin used in this experiment was provided by the Analytical

Development Services group within the Savannah River Technology Center. They, in turn, received the resin samples from the Waste Characterization and Certification Group of the Nuclear Material Management Division. The spent resin samples were identified as:

- CG8 cation resin, LIMS 150512 (Job #00446)
- CG8 cation resin, LIMS 150469 (Job #00444)
- SBG1 anion resin, LIMS 150473 (Job #00445)
- SBG1 anion resin, LIMS 150515 (Job # 00447)

Two leaching solutions were used in this study: an acid-rain simulant and a cement-leachate simulant. The acid-rain simulant was prepared by adding drops of a 60/40 wt-% mixture of sulfuric acid/nitric acid to deionized water until a pH of 3.0 was achieved (approximately 120 drops/50-L) (EPA Method 1320, EPA 1986). The cement leachate simulant was based on the chemical composition data of an actual cement leachate reported by Serne et al. (1987). The recipe for a 50-L (pH 12.3) solution included: 13.70-g $CaCO_3$, 10.55-g $CaOH_2$, 69.30-g KOH, and 173.57-g NaOH. Following a 2-hr mixing period, the leaching solution was filtered to remove any precipitated or undissolved materials.

Two K_d tests were conducted, one with the acid-rain simulant and the second for the cement leachate simulant. About 11.5 g of cation resin, 15.9 g of anion resin, and 475-mL of simulant were combined for each test. The suspensions were allowed to equilibrate for 7-days, during which time the sample bottles were gently mixed once per day for 30-sec. Following the 7-day equilibration period, leaching solutions were filtered (0.45-μ m) and the filtrates and the resins were submitted to the Analytical Development Services Group for ^{14}C, ^{129}I, and ^{99}Tc analyses. K_d values were calculated using Equation 1 and are reported on a dry weight basis.

3.1 Sample Analysis and Quality Assurance

Digestion of the solids and analysis of the digested solids and leachate solutions were conducted by the Analytical Development Section of the Savannah River Technology Center using the standard methods and quality control/quality assurance program described on their web site (http://shrine.srs.gov/html/srtc/ads/index.html). The resins were digested by the sodium peroxide fusion method. ^{129}I concentrations were determined by the LOAX HPGe gamma spectroscopy and neutron activation analysis (NAA). ^{99}Tc and ^{14}C were determined by standard liquid scintillation techniques. Standard QA practices described in the WSRC QA Manual 1Q were followed throughout this study.

4.0 Results

The results from the desorption batch K_d tests are presented in Table 1 and the raw data and calculations used to generate these values are presented in Appendix B.

Table 1. Kd Values of Mixed Resins Denerated from the K & L Disassembly Basin Facilities

	Acid-Rain Leachate	Cement Leachate

^{14}C	240	140
^{99}Tc	>680	>810

^{129}I K_d values could not be calculated from the data because both leachate and resin ^{129}I concentrations were below detection limits. The below detection limit concentration of the resin was unexpected because previous analytical results indicated ^{129}I concentrations in the resins were about 1 pCi/g, albeit a very low concentration (Personal communication with Betsy Westover, Waste Characterization and Certification Group of the Nuclear Material Management Division; Appendix C). To provide some guidance, a K_d value was estimated by assuming that the resin ^{129}I concentration (i.e., the denominator in Equation 1) equaled a previous detectable concentration (Appendix C) and that the aqueous concentration was, as measured, less than the detection limit. This yielded:

$$K_d = \frac{C_s}{C_{aq}} = \frac{(f_{cation} \times C_{cation}) + (f_{anion} \times C_{anion})}{C_{aq}} = \frac{(0.42*7.43e-7\mu Ci/g) + (0.58*3.56e-5\mu Ci/g)}{< 5.57e-9\mu Ci/mL} = >3763\,mL/g \quad (2)$$

where *f* is the volumetric fraction of resin in the mixture, and the other symbols are as defined for Equation 1. By way of comparison, ^{129}I-K_d values for the cation resin, CG-8, generated from the F-Area and H-Area Water Treatment Units range from 3 to >2150 mL/g (Kaplan and Serkiz, 2000). This wide range of values was attributed to varying methods of measuring the ^{129}I K_d (column and batch) and to widely varying concentration of ^{129}I in the spent resin. The presence of the anion resin, SBG-1, in this study would invariably increase the ^{129}I K_d value above that of the cation resin.

5.0 References

ASTM. 1984. Standard Test Method for Distribution Ratios by the Short-Term Batch Method D 4319-83. Annual Book of ASTM Standards, Vol 04.08.

EPA (U.S. Environmental Protection Agency). 1986. Multiple Extraction Procedure, Method 1320. In: Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846. Office of Solid Waste, Washington, DC.

Kaplan, D. I., and G. Iversen. 2001. Free-moisture Content and ^{129}I-Kd Values of Filtercake Material Generated from the F-Area Ground Water Treatment Unit. WSRC-TR-2001-00253, Rev. 0. Westinghouse Savannah River Company, Aiken, SC.

Kaplan, D. I., and S. M. Serkiz. 2000. Iodine-129 Desorption from Resin, Activated Carbon, and Filtercake Waste Generated from the F- and H-Area Water Treatment Units. WSRC-TR-2000-00308, Rev. 0, Westinghouse Savannah River Company, Aiken, SC 29808.

Kaplan, D. I., S. M. Serkiz, and N. C. Bell. 1999. I-129 Desorption from SRS Water Treatment Media from the Effluent Treatment Facility and the F-Area Groundwater Treatment Facility. WSRC-TR-99-00270. Westinghouse Savannah River Company, Aiken, SC.

McDowell-Boyer, L., A. D. Yu, J. R. Cook, D. C. Kocher, E. L. Wilhite, H. Homes-Burns, K. E. Young. 2000. Radiological Performance Assessment for the E-Area Low-Level Waste Facility. WSRC-RP-94-218, Rev. 1. Westinghouse Savannah River Company, Aiken, SC.

Serne, R. J., L. J. Criscenti, and D. M. Strachan. 1987. Comparison of Geochemical Code Predictions and Laboratory Test Results for Uranium Leaching/adsorption from Cement. Pacific Northwest National Laboratories, Richland, Washington.

Appendix A. One-Time Instructions for Measuring Desorption Kd Values from Spent SBG1 & CG8 Resin

One-Time Instructions for Measuring Desorption Kd Values from Spent SBG1 & CG8 Resin

Objective: Measure the I-129 desorption K_d in cement leachate and acid-rain leachates of a 42:58 vol-% of SBG1:CG8 resin mixture.

Materials:

1. CG8 cation resin, LIMS 150512 (Job #00446)
2. CG8 cation resin, LIMS 150469 (Job #00444)
3. SBG1 anion resin, LIMS 150473 (Job #00445)
4. SBG1 anion resin, LIMS 150515 (Job # 00447)
5. 475-mL Cement-Leachate Simulant
6. 475-mL Acid-Rain Simulant
7. 2 500-mL Nalgene bottles

Methods:

1. Add 475-mL Cement Leachate Simulant to a 500-mL Nalgene bottle labeled "42:58 CBG1:CG8 Cement Leachate." Add 475-mL Acid-Rain Simulant to a 500-mL Nalgene bottle labeled "42:58 CBG1:CG8 Acid-Rain Simulant."
2. Combine LIMS 150512 and LIMS 150469 into one container labeled "cation resin." Combine LIMS 150473 and LIMS 150515 into a second container labeled "anion resin." Mix contents well.
3. Weigh 21-g of the cation resin and 29-g of the anion resin into each of the leaching solutions in the 500-mL Nalgene bottles, such that both 500-ml bottles receives a total of 50-g (21g + 29g) of resin.(The proportion of cation to anion resin is based on an email from Joanna Cason (3/12/02, 16:15; "Cason samples 01564/01575"). In the email she writes: "A typical HIC contains 50 ft3 cation resin and 70 ft3 anion resin. This ends up being 42 vol% cation resin and 58 vol% anion resin. If you assume a specific gravity of 1.1 and a limiting amount of resin available from ADS of 20g, then the amounts of resin from these four samples needed to run your experiment are 20 g from Job #00445, 20 g from Job #00447 (these are both anion resins) and 14.5 g from Job #00446 and 14.5 g from Job #00444 (these are both cation resins). This should provide enough sample to run your experiment at the ratios expected in our HICs.")
4. Shake rigorously for 15 seconds twice a day, first thing in the morning and last thing before leaving at the end of the day.
5. After 7 days, separate solids and liquids through settling and filtration.
6. Send liquid and solids to ADS for C-14, I-129 and Tc-99 analyses, attention Dave Diprete.

7. Do duplicate dry weight determinations of the resins in the "anion resin" and "cation resin" composite samples created in Step #2. Use between 1 and 2 g of moist sample and dry at room temperature.

Appendix B. Raw Data and Distribution Coefficient Calculations

Dry Weight Determinations of the Rad SBG1 and the CG8 Spent Resins										
	Conducted by Cathy Coffey			5/28/02						
	QA'ed by Dan Kaplan			5/28/02						
	Lab notebook/page			WSRC-NB-2000-00045/page 54						
Sample ID	Empty pan + closed container	Wet sample + pan + closed container	Net weight of wet sample	Dry sample + pan + closed container	Sample dry wt.	Moisture in sample	% Moisture content	% Solids	% Moisture average	% Moisture Std. Dev.
	(g)	(g)	(g)	(g)	(g)	(g)	(%)	(%)	(%)	(%)
Cation-1	108.409	109.603	1.194	109.298	0.889	0.305	25.5	74.5	25.4	0.2
Cation-2	108.409	109.561	1.152	109.270	0.861	0.291	25.3	74.7		
Anion-1	108.407	110.102	1.695	109.147	0.740	0.955	56.3	43.7	57.1	1.0
Anion-2	108.410	110.053	1.643	109.103	0.693	0.950	57.8	42.2		

Carbon-14, Tc-99 and I-129 Kd Values								
File (spent fuel C14 Tc99 I129 Kd.xls)			QA�ed: Dan Kaplan					
I-129, Tc-99, and C-14 Analytical Results								
	Sample	ADS LIMS #	Units		Tc-99	C-14	I-129	
	Acid Liquid	300180006	dpm/mL	<	2.00E-01	3.64	BDL	
	Cement Liquid	300180013	dpm/mL	<	2.66E-01	15.5	BDL	
	Acid solid	300180014	dpm/g		1.36E+02	882	BDL	
	Cement Solid	300180015	dpm/g		2.16E+02	2170	BDL	

Calculating Tc-99 and C-14 Kd Values of 42:58 Mixed Resins								
					Tc-99	C-14	I-129	
					Kd (mL/g)	Kd (mL/g)	Kd (mL/g)	
			Acid	>	680	242	3763	
			Cement	>	812	140	3763	
Estimating Kd for I-129								
	I-129 Solid's concentration Data from Betsy Westover (email)							
	Problem: The solids and the liquids had no detectable I-129 in them.							
	Approach: Use the I-129 concentrations from previous solids analyses and the avg detection limit for aqueous concentrations.							
	Anion: LIMS # 300166481, Job #01412:				3.56E-05	µ Ci/g		
	Cation: LIMS # 300150469, Job # 00444:				7.43E-07	µ Ci/g		
	Below detection limit values(pCi/L):							
	9.12							
	3.94							
	3.58							
	1.96							
	3.51							
	9.09							
	6.95							
	5.40							
	5.99							

	6.14							
	5.57	=average						
	Kd of 42:58 cation:anion mixture:			>	3763.027	mL/g		
	Kd of cation resin:			>	1.33E+02	mL/g		
	Kd of anion resin:			>	6.39E+03	mL/g		

Appendix C. E-mail Describing 129-I Concentrations Previously Measured in Spent Resins

Betsy Westover 07/22/02 10:03 AM	To:Daniel Kaplan/WSRC/Srs@Srs cc: Subject:SFS Cation and Anion Max I-129 Values for Solids

Hey Dan-

To date, the following are the 2 highest I-129 values (real hits, not DLs) for our cation and anion spent resins from the DBU process. Let me know if you need anything else.

Anion LIMS# 3-166481 Job #01412 3.56E-05 µ Ci/g

Cation LIMS# 3-150469 Job #00444 7.43E-07 µ Ci/g

Thanks

Betsy