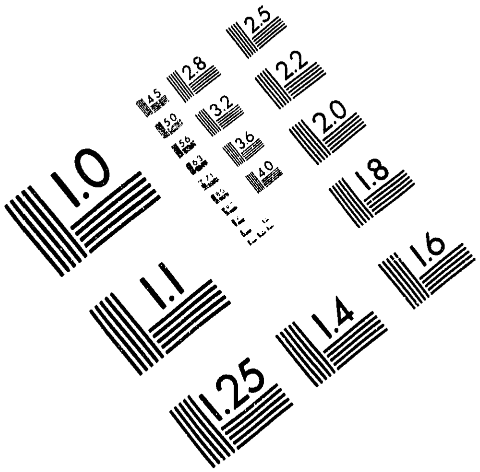

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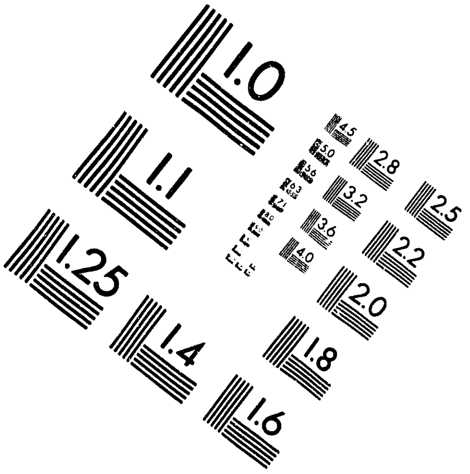

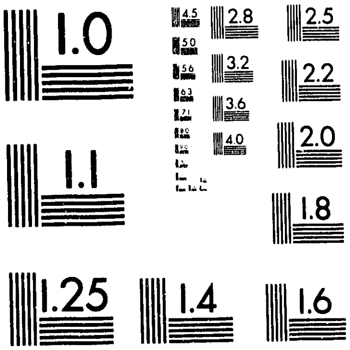

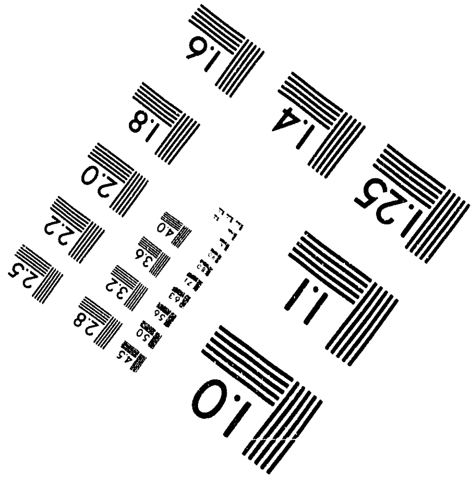

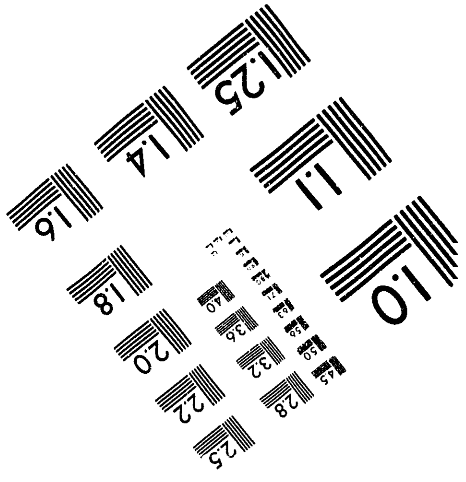

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DEVELOPMENT AND TESTING OF ION EXCHANGERS FOR TREATMENT OF LIQUID WASTES AT OAK RIDGE NATIONAL LABORATORY

J. L. Collins
D. J. Davidson
C. W. Chase
B. Z. Egan

Chemical Technology Division

D. D. Ensor
R. M. Bright
D. C. Glasgow

Tennessee Technological University

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ABSTRACT

Research and production activities involving radionuclides at Oak Ridge National Laboratory generate several low-level liquid waste and processing streams. Efforts are being made to develop methods of treatment of these streams to remove radionuclides using ion exchangers. This report addresses three areas of waste treatment: (1) treatment of newly generated low-level liquid waste and Melton Valley Storage Tank (MVST) supernate using inorganic ion exchangers; (2) treatment of processing streams at the Radiochemical Engineering Development Center (REDC); and (3) removal of radionuclides from organic solutions. Distribution of various radionuclides between simulated waste solutions and several sorbents was determined in batch tests.

Inorganic ion exchangers were prepared in the form of microspheres by an internal gelation process. Microspheres of hydrous titania, hydrous zirconia, hydrous titania containing embedded sodium cobalt hexacyanoferrate, and the corresponding phosphate forms of these materials were prepared. The composite microspheres can be effectively used in the pH range 1 to 10. Basic waste solutions with pHs in the 7 to 10 range could be treated with these microspheres to remove cesium. The phosphate forms of the microspheres can be used to remove cesium from more acidic waste streams.

Several zeolites (PDZ-140, PDZ-300, IE-96, CBV-10A) and inorganic ion exchangers (hydrous titania, hydrous zirconia, polyantimonic acid, sodium cobalt hexacyanoferrate) were tested for the removal of cesium and strontium from the acidic simulated Cleanex raffinate generated at REDC. Sodium cobalt hexacyanoferrate removed >99% of the cesium; strontium removal by different polyantimonic acid samples ranged from 24 to 96%.

A resorcinol-based ion-exchange resin developed at the Savannah River Plant and three types of sodium titanate were tested for removal of cesium and strontium from the REDC caustic dissolver solution. The resin removed 42% of the cesium. Two of the sodium titanate materials removed >99% of the strontium.

Hydrous titania, hydrous zirconia, and their corresponding phosphates were tested for the removal of Eu^{3+} from various solutions of di-2-ethylhexyl phosphoric acid (HDEHP) in toluene or dodecane. After pretreatment with HCl, zirconium phosphate and titanium phosphate removed 79 to 98% of the europium from 0.5 to 1.0 $\underline{M}$ HDEHP solutions.

DEVELOPMENT AND TESTING OF ION EXCHANGERS FOR TREATMENT OF LIQUID WASTES AT OAK RIDGE NATIONAL LABORATORY

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1. TREATMENT OF NEWLY GENERATED LOW-LEVEL LIQUID WASTE USING INORGANIC ION EXCHANGERS

1.1 INTRODUCTION

Research and production activities with radionuclides over the past five decades at Oak Ridge National Laboratory (ORNL) have generated a large volume of low-level liquid waste (LLLW). During this time, the LLLW has been treated, and the resulting salty concentrates have been stored in underground storage tanks known as the Melton Valley Storage Tanks (MVSTs). Currently, as a result of limited storage space in these tanks, efforts are being made to develop more efficient management, treatment, and disposal alternatives. The ultimate goal is a maximal waste minimization effort that will treat as many facility liquid waste streams as possible with minimal solid waste generation. Consequently, the quantities of radionuclides that will be directed toward the storage tanks will be considerably less. New LLLW treatment facilities are in the process of being designed that will be capable of treating both the salty LLLW concentrate stored in the MVSTs and LLLW generated by future research activities at ORNL. An estimated composition of LLLW used in the design of a new treatment facility has tentatively been determined and is referred to as "newly generated LLLW" or NGLLLW.[1]

One method of treating LLLW streams is the use of inorganic ion exchangers. Many inorganic ion exchangers with excellent adsorption properties are commercially available only as fine powders or granular materials that tend to degrade to fine powders when used. Consequently, these materials do not work well in columns or in continuous process applications. For example, certain transition-metal hexacyanoferrate(II) compounds are recognized for their ability to selectively remove cesium from aqueous streams, but most are available only as powders. At the La Hauge Reprocessing Plant in Cherbourg, France, the French are currently using cyanoferrates for removing cesium from various liquid waste streams. Sodium/nickel hexacyanoferrate powders are used in a large batch processing method to remove the cesium.[2]

To make hexacyanoferrates more usable in treating NGLLLW, an effort was initiated to determine the optimum formulations and process conditions for embedding $Na_2[CoFe(CN)_6]$ (abbreviated NaCoCF) powder in hydrous titanium oxide (HTiO) microspheres. These composite microspheres could be useful for treating solutions having a high salt content and high pH for removing the $^{134\text{-}137}Cs$. However, pH adjustment would be required before supernates in the storage tanks at ORNL Melton Valley and Westinghouse Hanford could be treated. In addition, these materials may be useful as a waste minimization step in treating process waste streams, such as the Cleanex raffinate stream, at the Radiochemical Engineering Development Center (REDC).

1.2 EQUIPMENT AND METHODOLOGY USED TO PRODUCE COMPOSITE MICROSPHERES BY THE INTERNAL GELATION PROCESS

A flowsheet for preparing composite HTiO microspheres by the internal gelation process is shown in Fig. 1.1. The extensive chemistry of this process will not be described in this report. However, a thorough discussion of the chemistry of the internal gelation process can be found in a previous paper.[3] The NaCoCF powder used in this experimental work was prepared by T. A. Dillow of ORNL using the preparation method of Prout.[4] The NaCoCF slurries were prepared by slowly mixing equal molar solutions of cobalt nitrate $[Co(NO_3)_2]$ and sodium hexacyanoferrate $[Na_4Fe(CN)_6]$. As in the powder preparation, the $Na_4Fe(CN)_6$ was slowly added (~1 drop/s) to the $Co(NO_3)_2$ with continuous stirring at ambient temperature. The slurries were stirred an additional 10 to 15 min in an ice bath before they were added to the chilled broth. Adding the hexamethylenetetramine (HMTA) to the $TiCl_4$ prior to adding the NaCoCF minimizes the NaCoCF adsorption of Ti ions. The titanium ions are strongly complexed with urea at ice-bath temperatures.

Much of the laboratory equipment used to produce inorganic ion exchangers as microspheres in this work is similar to the equipment described in reports by Spence[5] and Haas.[6,7] One key difference is in the design of the broth pot. A Thomas Magne-Matic Stirrer was employed to keep the fine crystalline particles of sodium cobalt hexacyanoferrate (NaCoCF) homogeneously suspended in broth formulations used to make hydrous metal oxide beads. The broth pot is made of glass with a cooling jacket. Air pressure is gently

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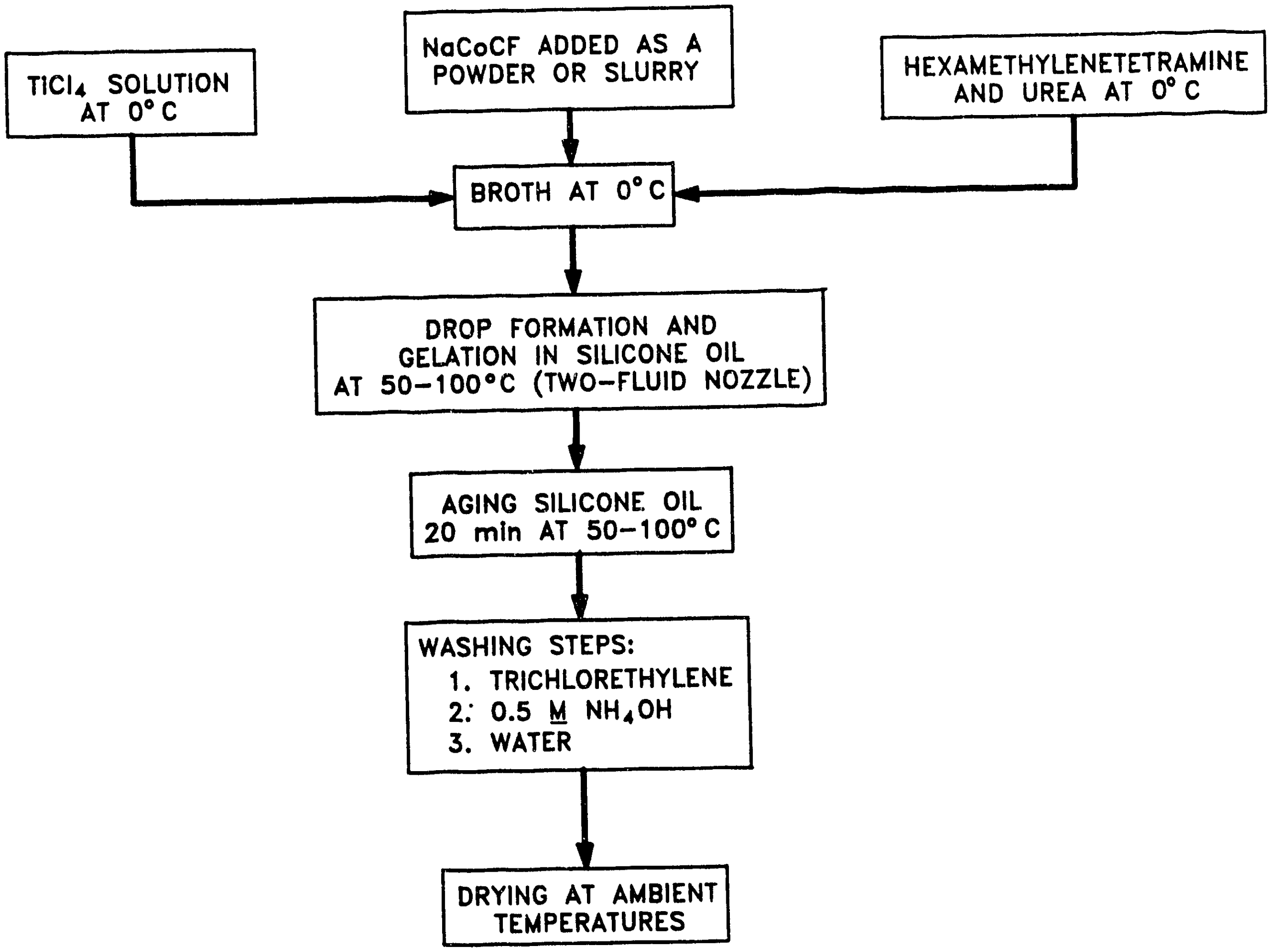

Fig. 1.1. Flowsheet for preparing composite HTiO microspheres by the internal gelation process.

applied to force the broth mixture out through a glass tube at the bottom edge of the pot into a Tygon tube which is attached to a flat-tipped 18-, 19-, or 20-gauge needle. The needle is perpendicularly inserted through a vertically positioned section of Tygon tubing through which hot silicone oil flows into the forming column. The tip of the needle is positioned at or near the center of the tube for the best control of the drop formation. A laminar-flow, orthogonal, two-fluid nozzle concept is used to control the size of the microspheres. By adjusting the flow of the silicone oil and the air pressure on the broth pot, microspheres of the desired size can be reasonably regulated. Within a few seconds after contacting the hot silicone oil in the forming column, the droplets of aqueous broth begin to gel and entrap the suspended inorganic ion exchanger particles in the gel matrix. By a siphoning effect, the gelling microspheres are slowly transported through a long section of Tygon tubing. The residence time in the tube allows the microspheres to harden before being collected in a stainless steel, wire-screen basket which is positioned above the hot silicone oil reservoir. Once the basket is filled with microspheres, it is immersed in the hot silicone oil reservoir to allow the microspheres to age for about 15 to 20 min. This is a crystal growth step. Afterward, the basket is removed from the oil and positioned over the reservoir for ~10 min to allow the oil to drain from the microspheres. To remove the residual silicone oil and the unneeded reactants and reaction products (HMTA, urea, and ammonium chloride), the microspheres are given several consecutive washes with trichloroethylene and then with 0.5 M NH_4OH. In practice, the NH_4OH washing steps are repeated until a constant conductivity is reached in the wash solution; this normally requires 3 to 5 washes. The NH_4OH wash steps also ensure that the microspheres are completely precipitated. Once this process is completed, the microspheres are washed consecutively in deionized water until a constant pH is reached in the wash solution. At this point, most of the residual NH_4OH has been removed.

In the final step, the composite microspheres are dried in large glass or stainless steel pans at ambient temperature for several days before storage or use. The microspheres can be dried in an oven at temperatures up to 75°C. However, care must be taken not to remove too much of the water of hydration; the adsorption capacity could be lessened.

For use to treat acidic streams, the hydrous titanium oxide phase of the composite microspheres is converted to titanium monohydrogen phosphate (TiHP). TiHP is insoluble in acid solutions and also adsorbs cesium from acid streams. To accomplish the conversion, the composite microspheres were given specially developed, pressurized treatments with phosphoric acid, then washed in deionized water, and air dried at ambient temperatures.

1.3 METHODOLOGY OF BATCH SORPTION TESTS

1.3.1 Simulated NGLLLW and MVST Test Solutions

Simulated MVST supernate and NGLLLW solutions were prepared by recipes provided by W. D. Arnold of ORNL'S Chemistry Division. The development of the simulated NGLLLW is thoroughly discussed in a recent report by W. D. Arnold et al.[1] and will not be discussed in this report.

Stock solutions of simulated MVST supernate and NGLLLW were prepared, and samples also were obtained from W. D. Arnold for comparison. The supernate simulant contained 0.14 $\underline{M}$ Na_2CO_3, 0.1 $\underline{M}$ NaCl, 3.9 $\underline{M}$ $NaNO_3$, 0.001 $\underline{M}$ $Zn(NO_3)_2$, 0.2 $\underline{M}$ KNO_3, 0.24 $\underline{M}$ NaOH, 0.005 $\underline{M}$ $Al(NO_3)_3$, and 0.0001 $\underline{M}$ $CaCO_3$. The pH of this solution was adjusted from 13 to 11 by the addition of HNO_3.

The composition of the simulated NGLLLW was 0.335 $\underline{M}$ NaOH, 0.061 $\underline{M}$ $NaNO_3$, 0.012 $\underline{M}$ $NaAlO_2$, 0.587 $\underline{M}$ Na_2CO_3, and 0.034 $\underline{M}$ NaCl. The pH of this solution was adjusted to a pH of 8 with HCl solution and was subsequently filtered to remove the precipitated hydrous aluminum oxide.

1.3.2 Procedure for Batch Tests

Triplicate samples of ion exchanger, as either microspheres or powders, were weighed and placed in 15-mL graduated polypropylene centrifuge tubes. The samples were then preequilibrated over a 2-d period by washing and mixing them several times with simulated NGLLLW which contained no Cs, Rb, or Sr. Ten milliliters of the NGLLLW solution containing 1.16 μg Cs/mL were added to each of the samples. The cesium was nonradioactive ^{133}Cs, which was added as $CsNO_3$ that was traced with radioactive ^{137}Cs. The samples, in sets of three, were then placed on a "Rota-Torque" rotating mixer at a rotational speed and tilt angle that provided good, gentle mixing for time periods of 3, 24, or 336 h. After mixing, the liquid was removed from the ion exchanger and centrifuged for 30 min at ~2600 rpm. (The microspheres were visually inspected for evidence of microsphere degradation or loss of NaCoCF from the microspheres.) Samples (0.5 mL) of the clarified solutions were transferred by pipet to counting vials and counted using an LKB Wallac 1282 Compugamma Universal Gamma Counter. Solutions mixed with powder or granular ion exchangers normally had to be centrifuged twice and sometimes filtered.

1.3.3 Calculations

Results of batch tests are reported in this paper as percentage removal (%R), distribution ratio (D_t), decontamination factor (DF), and posttest solution concentration (PSC). These values are calculated in the following manner:

$\%R = 100[(C_o - C_t)/C_o]$,
$D_t = [(C_o - C_t)/C_t][V/m]$ (units are mL/g),
$DF = C_o/C_t$,
PSC = posttest solution concentration of contaminant ion in ppm (μg/mL) or ppb (ng/mL).

The pretest and posttest count rates of contaminant ions (^{137}Cs, ^{90}Sr) are represented by C_o and C_t, respectively. A count rate of a specific contaminant ion is converted to a mass quantity by dividing the count rate by the predetermined effective specific activity (counts/mass of contaminant ions). The D_t is an expression of the ratio of the mass of the ions of a contaminant sorbed on a gram of ion exchanger to the mass of that ion remaining in an mL of the test solution after a specified mixing time.

Tables 1.1 and 1.2 are hypothetical results given to show the significance of the solution characterization expressions used in this report. These two sets of hypothetical results show that similar %R, DF, and PSC values can be obtained with considerably different D_t values. For liquid waste treatment, care must be taken to select or develop ion exchangers that are effective at high solution/exchanger ratios. The volume of contaminated solid waste is thereby minimized.

1.4. PREPARATION AND DEVELOPMENT OF COMPOSITE MICROSPHERES

1.4.1 Basic Criteria for Composite Microsphere Development

The development of composite HTiO microspheres required that certain criteria be met to maximize the cesium adsorption efficiency of NaCoCF powder homogeneously embedded in microspheres. First, an internal gelation formulation had to be determined which would yield microspheres that were structurally strong with adequate interconnecting porosity to allow cesium diffusion into the matrix. Second, the optimum weight percentage of NaCoCF that could be embedded for maximum cesium adsorption had to be determined. There was concern that large amounts of NaCoCF might plug the openings and pore channels and restrict cesium diffusion into the matrix. Batch tests were conducted using samples of composite microspheres to get necessary cesium adsorption data to serve as a guide for process development. Simulated solutions of NGLLLW and MVST supernate (Sect.1.3.1) containing ^{133}Cs traced with ^{137}Cs were employed.

Table 1.1. Hypothetical comparison example illustrating the relationships between the solution characterization expressions[a]

	Time (h)				
Parameter[b]	0	2	4	6	8
R,%	0	50	90	99	99.9
DF	1	2	10	100	1000
PSC, μg/mL	1000	500	100	10	1
D_t	0	10	90	990	9990

[a] These results are assumed for a 10-mL test solution sample containing 1000 ppm cesium mixed with 1.0 g of exchanger for predetermined periods of time.

[b] R = removal, DF = decontamination factor, PSC = posttest solution concentration, and D_t = distribution ratio.

Table 1.2. Hypothetical comparison similar to the one in Table 1.1 except the solution is mixed with less exchanger[a]

	Time (h)				
Parameter[b]	0	2	4	6	8
R, %	0	50	90	99	99.9
DF	1	2	10	100	1000
PSC, μg/mL	1000	500	100	10	1
D_t	0	1000	9000	99000	999000

[a] 0.01 g.

[b] R = removal, DF = decontamination factor, PSC = posttest solution concentration, and D_t = distribution ratio.

1.4.2 HTiO Internal Gelation Formulation for Making Composite Microspheres

Several potential HTiO formulation recipes were chosen from the optimum process parameters window for making HTiO by the internal gelation process. This window was previously developed by the Chemical Development Section of the Chemical Technology Division. The second formulation that was tried proved successful in providing structurally strong microspheres with embedded NaCoCF. Embedded microspheres prepared with the first formulation tended to degrade when tested. The stability of the microspheres was determined by shaking a small volume of microspheres in a nontraced, simulated supernate waste or NGLLLW for a number of days and looking for evidence of microsphere degradation.

1.4.3 Composite Microspheres Prepared from NaCoCF Powder

1.4.3.1 Optimum Weight Percent of NaCoCF

To determine the optimum amount of NaCoCF needed in HTiO microspheres to remove cesium from NGLLLW, samples of gel-derived HTiO microspheres embedded with various amounts of NaCoCF powder were first prepared by mixing the powder directly in the broth. Samples of microspheres containing 6.6, 9.3, 15.9, and 32.1 wt % of NaCoCF were batch tested. The average diameter of composite microspheres prepared and used in this series of experiments was 1.0 ± 0.2 μm. Each sample contained 0.050 g of NaCoCF; the mass of hydrous titanium oxide varied, depending on the weight percent of NaCoCF present. As an example, at the low end (6.6 wt % NaCoCF), the total mass of beads used was 0.763 g; at the high end (32.1 wt % NaCoCF), only 0.156 g of beads was used.

The results of these tests are summarized in Tables 1.3 and 1.4. These data show that the microspheres with 9.3 wt % NaCoCF removed the largest fraction of Cs: 98.7% in 3 h and 99.7% in 24 h. However, a fraction of the cesium was adsorbed by the HTiO. Similar batch tests using HTiO microspheres (no embedded NaCoCF) were conducted to determine the cesium adsorption affinity. These data are also summarized in Table 1.3. The masses of HTiO tested were equal to the masses of HTiO used in the 6.6% and 32.1% NaCoCF tests. For a 3-h test period, 0.1061 and 0.7140 g of HTiO removed 7.5 and 32.6% of the cesium, respectively. The cesium removed in 24 h was only slightly higher, 12.3% and 38.9%. If cesium adsorption by HTiO is assumed to be linear as a function of mass, then it is estimated

Table 1.3. Cesium sorption as a function of embedded NaCoCF

			Cesium removed (%)					
NaCoCF in HTiO (wt %)	Mass HTiO used (g)	Mass NaCoCF used (g)	HTiO + NaCoCF (3 h)	HTiO only (3 h)	Est. NaCoCF only (3 h)	HTiO + NaCoCF (24 h)	HTiO only (24 h)	Est. NaCoCF only (24 h)
6.6	0.714	0.05	97.4	32.6	64.8	99.3	38.9	60.4
9.3	0.489	0.05	98.7	23.3[a]	75.4	99.7	29.0	70.7
15.9	0.264	0.05	97.4	14.0[a]	83.4	99.6	19.2	80.4
32.1	0.106	0.05	93.0	7.5	85.5	99.5	12.3	87.2

[a] Calculated values.

that for the masses of HTiO (0.489 and 0.264 g) used in the 9.3% and 15.9% NaCoCF sorption tests, about 23.3% and 14.0% of the cesium would be removed in 3 h, and 29.0% and 19.2% of the cesium would be removed in 24 h, respectively. The calculated percentages of cesium removed by NaCoCF are also given. When the adsorption of cesium by HTiO is taken into account, the HTiO microspheres containing 15.9% NaCoCF were more effective. The percentages of cesium removed were slightly less, but the mass of HTiO used in the 9.3% case was a factor of 1.86 more. Table 1.4 shows that the D_t values obtained for the 9.3% and 15.9% NaCoCF microspheres in 3 h were similar, 1374 and 1191 mL/g (NaCoCF), respectively. Consequently, microspheres embedded with about 15% NaCoCF were chosen for further preparation and sorption studies.

1.4.3.2 Preparation and Batch Testing of 1.13-mm-Diameter Composite Microspheres Containing NaCoCF Added as a Powder

At this point in the composite microsphere development, a second batch (23 g dry weight) of HTiO containing 14.5% NaCoCF was prepared for testing. This weight percent of NaCoCF should represent near optimum embedment for cesium adsorption. The average diameter of these microspheres was ~1.13 mm with a "slow pour" density of 0.956 g/mL. ("Slow pour" density is determined by slowly pouring a known mass of microspheres into a graduated cylinder and measuring the volume.) The microspheres were larger than sought but were structurally strong. Batch contact studies were conducted using these microspheres to measure cesium sorption from simulated NGLLLW for contact times of 3, 24, and 336 h.

Table 1.4. Effect of weight percent of NaCoCF in microspheres on D_t

		D_t for cesium	
NaCoCF (wt %)	Contact time (h)	Microspheres (mL/g)	NaCoCF only (mL/g)
6.6	3	508	7760
	24	2000	30400
9.3	3	1370	1480
	24	5980	64400
15.9	3	1190	7470
	24	7310	45900
32.1	3	847	2640
	24	11900	36900

Triplicate samples of six different amounts of the microspheres were tested as described in Sect. 1.3. The average weights of the samples for each set and the corresponding amount of NaCoCF powder present (shown in parenthesis) were 0.0206 (0.003) g; 0.0343 (0.005) g; 0.1028 (0.015) g; 0.1718 (0.025) g; 0.2405 (0.035) g; and 0.3441 (0.050) g. The ratio of solution to NaCoCF ranged from 3338:1 to 200:1(300 to 5000 ppm NaCoCF added to the NGLLLW). Inspection of the solutions and microspheres after the mixing periods revealed no apparent degradation of the microspheres. The average percent cesium removal (%R), distribution ratio (D_t), decontamination factor (DF), and posttest cesium concentration for the above samples for the three mixing periods are shown in Tables 1.5 to 1.8. The range of percent cesium removal was 48.7 to 97.4% after 3 h, 69.8 to 99.1% after 24 h, and 98.9 to 99.7% after 336 h. The D_t ranged from 2.6×10^3 mL/g (3 h, 5 mg NaCoCF) to 3.5×10^5 mL/g (336 h, 5 mg NaCoCF). The largest DF obtained (Table 1.7) was 357. Table 1.8 shows that the lowest concentration of Cs remaining in NGLLLW after 336 h mixing was 3.3 ppb. An increase in the weight percent of NaCoCF had little effect on lowering the concentration of Cs much below 3.6 ppb. The adsorption data in Tables 1.5 and 1.6 indicate that cesium sorption was diffusion limited. The microspheres were much too large to quickly take advantage of the embedded NaCoCF in the HTiO matrix. For practical column use, the rate of sorption had to be improved.

Table 1.5. Comparison of the percentage of cesium removed from simulated NGLLLW test solutions by HTiO microspheres containing embedded NaCoCF

NaCoCF* (mg)	Cesium removal (%)		
	3 h	24 h	336 h
3	48.7	69.8	98.9
5	56.8	83.2	99.4
15	87.9	96.7	99.7
25	94.0	98.5	99.7
35	95.8	99.0	99.7
50	97.4	99.1	99.7

*Composite microspheres with an average diameter of 1.13 mm homogeneously embedded with dry NaCoCF powder.

Table 1.6. Comparison of distribution ratios obtained for removing cesium from NGLLLW with HTiO microspheres containing embedded NaCoCF

NaCoCF* (mg)	Distribution ratio (D_t)		
	3 h	24 h	336 h
3	3.2×10^3	7.9×10^3	3.1×10^5
5	2.6×10^3	1.0×10^4	3.48×10^5
15	4.9×10^3	2.0×10^4	2.11×10^5
25	6.2×10^3	2.7×10^4	1.34×10^5
35	6.5×10^3	2.8×10^4	1.01×10^5
50	7.4×10^3	2.3×10^4	7.23×10^4

*Composite microspheres with average diameter of 1.13 mm homogeneously embedded with dry NaCoCF powder.

Table 1.7. Comparison of decontamination factors obtained for removing cesium from NGLLLW by HTiO microspheres containing embedded NaCoCF

NaCoCF[a] (mg)	Decontamination factor (C_0/C_t)		
	3 h	24 h	336 h
3	2.0	3.3	91
5	2.3	6.0	172
15	8.9	30	323
25	17	68	333
35	24	97	345
50	38	116	357

[a] Composite microspheres with average diameter of 1.13 mm homogeneously embedded with dry NaCoCF powder.

Table 1.8. Comparison of posttest cesium concentration of NGLLLW solutions that were mixed with HTiO microspheres containing embedded NaCoCF

NaCoCF[a] (mg)	Posttest cesium concentration (ppb)[b]		
	3 h	24 h	336 h
3	596	350	13
5	501	195	6.7
15	140	39	3.6
25	70	17	3.5
35	49	12	3.4
50	31	10	3.3

[a] Composite microspheres with average diameter of 1.13 mm homogeneously embedded with dry NaCoCF powder.

[b] The initial cesium concentration of the solutions was 1160 ppb.

An effort was then initiated to modify the microspheres to improve the rate of cesium removal. To do so, it was decided that smaller microspheres had to be prepared with the NaCoCF added to the HTiO broth as a slurry rather than dry powder. (The slurry idea was suggested by D. O. Campbell and T. A. Dillow.) The particle size of the NaCoCF in a slurry is much smaller and provides more adsorption surface area per unit mass.

1.4.4 Composite Microspheres Prepared from NaCoCF Slurry

1.4.4.1 Preparation and Batch Testing of 0.75-mm-Diameter Composite Microspheres Containing NaCoCF Added as a Slurry

Composite microspheres were successfully prepared with NaCoCF added to the broth pot as a slurry. The average diameter of these microspheres was 0.75 mm, compared with 1.13 mm for the ones made with dry NaCoCF powder. The slurry was prepared as described in Sect. 1.2. Broths prepared with the NaCoCF slurries were much easier to control. There was little or no settling of the fine NaCoCF particles in the tube from the broth pot to the forming needle or plugging of the forming needle which occassionally occurred when dry NaCoCF powder was used. The chemical compositions of both broths were identical except for the sodium nitrate produced in the NaCoCF slurry preparation.

To determine if the rate of cesium sorption from NGLLLW solution was improved, batch contact experiments were conducted as before, and the results were compared with those results obtained using the microspheres prepared from dry NaCoCF powder. Triplicate sets of different amounts of microspheres containing 3, 5, 15, or 25 mg of NaCoCF were tested for 3, 24, and 336 h. Again, in each case, the microspheres were contacted with 10 mL of synthetic NGLLLW (pH 8) which contained 1.16 ppm cesium, traced with ^{137}Cs. These results are shown in Tables 1.9 to 1.12 as "B" values. The "A" values are the ones obtained for the larger microspheres (~1.13 mm) prepared from NaCoCF dry powder; the "C" values are described in Sect. 1.4.4.2. As expected, these results showed that the smaller microspheres made with the NaCoCF slurry removed cesium more rapidly. For example, in 24 h the microspheres containing 3 mg of NaCoCF prepared from a slurry removed approximately the same amount of cesium (98.1%) as did the microspheres containing 25 mg of NaCoCF made from dry powder (98.5%). The percentages of cesium removal for the 5-mg samples after 3 h and for the 3-mg samples after 24 h were notable; improvements by factors of 1.41 and 1.43 were obtained using the smaller microspheres prepared from the slurry. Table 1.10 shows that the D_t value (7.3×10^3 mL/g of NaCoCF) obtained for the 5-mg (slurry) sample was the same as the value obtained for the 50-mg (powder) sample in the 3-h tests. Distribution ratios were much better in the 24- and 336-h tests. In the 24-h test comparison for the 3-mg samples, the D_t for the slurry-prepared sample was 19 times larger than the powder-prepared sample. The DF for the 15-mg "B" sample tested for 24 h was 306. A value of 337 was obtained for the 3-mg "B" sample after mixing 336 h. Table 1.12 shows that the posttest concentration of cesium remaining in the NGLLLW after 24 h for the 15 mg "B" sample was only 3.8 ppb.

1.4.4.2 Preparation and Batch Testing of 0.45-mm-Diameter Composite Microspheres Containing NaCoCF Added as a Slurry

An additional attempt to improve the rate of cesium adsorption from NGLLLW solution was made by making the HTiO microspheres even smaller with an average diameter of 0.45 mm. As before, these microspheres also were made from a NaCoCF slurry. The formulation was adjusted so that the final weight percentage of NaCoCF in the dried microspheres was ~17%. While microspheres smaller than 0.45 mm could be prepared, the smaller sizes would be less desirable for column separations because liquid flow through the column would be hampered by higher pressure drop. On the other hand, microspheres in the range of 0.25 mm could be employed in cases where slower flow velocities would be acceptable. Slower velocities would increase the residence time and help compensate for the slower kinetics of the composite microspheres.

Several batch contact tests were conducted to determine the effectiveness of these microspheres in removing cesium from the synthetic NGLLLW. As in the previous batch-contact tests, triplicate sets of microsphere samples were tested for specified periods of time. In each case, the microspheres were shaken with 10 mL of synthetic NGLLLW (pH 8) that contained 1.16 ppm cesium traced with ^{137}Cs. The comparative results are provided in Tables 1.9 to 1.12 as the "C" values.

Although only a few batch tests were conducted, these results clearly revealed that the 0.45-mm microspheres were even more effective at removing the cesium. In the 3-h tests with the 15 mg of NaCoCF samples, 99.3% of the cesium was removed, compared with 87.5% removal for the "A" microspheres containing 15 mg of NaCoCF. In all direct comparisons, the smallest microspheres, prepared by adding the NaCoCF as a slurry, removed the most cesium.

Table 1.9. Comparison of the percentage of cesium removed from simulated NGLLLW test solutions by different batches of HTiO microspheres containing embedded NaCoCF

	Percentage cesium removal							
NaCoCF	3 h			24 h			336 h	
(mg)	A[a]	B[b]	C[c]	A	B	C	A	B
3	48.7			69.8	98.1	99.5	98.9	99.7
5	56.8	81.0		83.2		99.6	99.4	
15	87.9		99.3	96.7	99.7		99.7	
25	94.0	98.7		98.5			99.7	
35	95.8			99.0			99.7	
50	97.4			99.1			99.7	

[a] A = microspheres with average diameter of 1.13 mm prepared from NaCoCF dry powder.

[b] B = microspheres with average diameter of 0.75 mm prepared from NaCoCF slurry.

[c] C = microspheres with average diameter of 0.45 mm prepared from NaCoCF slurry.

Table 1.10. Comparison of distribution coefficients obtained for removing cesium from NGLLLW with different batches of HTiO microspheres containing embedded NaCoCF

	Distribution ratio (D_t)							
NaCoCF	3 h			24 h			336 h	
(mg)	A[a]	B[b]	C[c]	A	B	C	A	B
3	3.2×10^3			7.9×10^3	1.5×10^5	5.1×10^5	3.1×10^5	9.9×10^5
5	2.6×10^3	7.3×10^3		1.0×10^4		4.1×10^5	3.5×10^5	
15	4.9×10^3		1.4×10^4	2.0×10^4	1.7×10^5		2.1×10^5	
25	6.2×10^3	2.6×10^4		2.7×10^4			1.3×10^5	
35	6.5×10^3			2.8×10^4			1.0×10^5	
50	7.4×10^3			2.3×10^4			7.2×10^4	

[a] A = microspheres with average diameter of 1.13 mm prepared from NaCoCF dry powder.

[b] B = microspheres with average diameter of 0.75 mm prepared from NaCoCF slurry.

[c] C = microspheres with average diameter of 0.45 mm prepared from NaCoCF slurry.

Table 1.11. Comparison of decontamination factors obtained for removing cesium from NGLLLW by different batches of microspheres containing embedded NaCoCF

NaCoCF	Decontamination factor (C_0/C_t)							
	3 h			24 h			336 h	
(mg)	A[a]	B[b]	C[c]	A	B	C	A	B
3	2.0			3.3	54	183	91	337
5	2.3	5.3		6.0		225	172	
15	8.9		146	30	306		323	
25	17	76		68			333	
35	24			97			345	
50	38			116			357	

[a] A = microspheres with average diameter of 1.13 mm prepared from NaCoCF dry powder.

[b] B = microspheres with average diameter of 0.75 mm prepared from NaCoCF slurry.

[c] C = microspheres with average diameter of 0.45 mm prepared from NaCoCF slurry.

Table 1.12. Comparison of posttest cesium concentrations of NGLLLW solutions that were mixed with different batches of microspheres containing embedded NaCoCF

NaCoCF	Posttest cesium concentration (ppb)[a]							
	3 h			24 h			336 h	
(mg)	A[b]	B[c]	C[d]	A	B	C	A	B
3	596			350	22	6.3	13	3.3
5	501	221		195		4.7	6.7	
15	140		7.9	39	3.8		3.6	
25	70	15		17			3.5	
35	49			12			3.4	
50	31			10			3.3	

[a] The initial cesium concentration of the solutions was 1160 ppb.

[b] A = microspheres with average diameter of 1.13 mm prepared from NaCoCF dry powder.

[c] B = microspheres with average diameter of 0.75 mm prepared from NaCoCF slurry.

[d] C = microspheres with average diameter of 0.45 mm prepared from NaCoCF slurry.

Table 1.10 shows that the distribution ratios for the "C" microspheres containing 15 mg of NaCoCF were 1.41×10^4 mL/(g of NaCoCF) for the 3-h test. For the microspheres containing 3 and 5 mg of NaCoCF in the 24-h tests, the D_t values were 5.1×10^5 and 4.1×10^5 mL/(g of NaCoCF), respectively.

For the three sets of batch tests conducted using the 0.45-mm microspheres, the DF values (Table 1.11) were very good, ranging from 146 to 245. The largest concentration of cesium left in solution was only 7.9 ppb in the 3-h test using the microspheres containing 15 mg of NaCoCF. The improvements made by the development process steps for the "A", "B", and "C" composite microspheres are seen in Tables 1.9 to 1.12 for the microspheres containing 3 mg of NaCoCF that were contacted with the simulated NGLLLW for 24 h. The improvements were percentage cesium removed — from 69.8 to 98.1 to 99.5%; D_t values — from 7.9×10^3 to 1.52×10^5 to 5.10×10^5 mL/(g of NaCoCF); DF values — from 3.3 to 54 to 183; and posttest concentrations of cesium left in solution — from 350 to 22 to 6.3 ppb. The lowest cesium concentration in NGLLLW solutions after treatment with microspheres made by any of the preparation methods for any of the time periods was 3.3 ppb. After 3 h, the concentration of cesium in 10 mL of the NGLLLW decreased from 1160 to 7.9 ppb when mixed with "C" microspheres that contained 15 mg NaCoCF. It took 336 h for an identical amount of the larger microspheres "A" to decrease the cesium concentration to 3.6 ppb.

The best decontamination factor obtained in these batch test characterization studies was 357, as seen in Table 1.11. The best distribution ratio, 9.9×10^5 mL/(g of NaCoCF), was obtained for the "B" sample containing 3 mg of NaCoCF that was tested for 336 h. No "C" samples were tested for the 336-h period. For the "B" samples that were tested for 24 h, the average mass of the microspheres used was 0.0210 g, which contained 0.0036 g NaCoCF. From Table 1.3, it can be estimated that ~92% of the cesium was adsorbed by the NaCoCF and the remainder by the hydrous titanium oxide. For 1 g of these microspheres, 0.549 mg of Cs was adsorbed; of this, about 0.506 mg was adsorbed by the NaCoCF. The ratio of NGLLLW solution tested to mass of microspheres was 476:1. If related to NaCoCF only, the ratio would be 2778:1. Under these test conditions, 1 g of embedded NaCoCF in 5.83 g of microspheres would adsorb 2.95 mg Cs. The actual capacity for Cs has not been determined yet.

Several runs were conducted to build up an inventory of embedded microspheres for future testing. About 80 g of HTiO microspheres were prepared with NaCoCF added to the broth as a slurry. The average diameter of the microspheres was 0.5 mm.

1.4.4.3 Preparation and Batch Testing of 0.5-mm-Diameter Composite Microspheres Containing KCoCF Added as a Slurry

About 26 g of hydrous titanium oxide (HTiO) microspheres were prepared in which $K_2CoFe(CN)_6$ (KCoCF) slurry was added to the broth. The formulation was such that the weight percentage of KCoCF in the dried microspheres was about 21%. The average diameter of these microspheres was 0.5 mm.

Batch tests were conducted to compare the effectiveness of the HTiO/NaCoCF and HTiO/KCoCF microspheres in removing cesium from simulated MSVT supernate. Triplicate tests were conducted for 3- and 24-h contact periods using 10 mL of supernate that was adjusted to a pH of 10 and filtered. The average sample mass of the HTiO/NaCoCF microspheres was 0.0295 g containing 0.005 g of embedded NaCoCF, and the average sample mass of the HTiO/KCoCF microspheres was 0.0208 g containing 0.0044 g of embedded KCoCF. The percentages of cesium removed were very similar: 57.1% (NaCoCF) and 56.8% (KCoCF) in 3 h, and 95.4% and 93.8% in 24 h, respectively. The distribution ratios for the 24-h tests were 4.1×10^4 mL/(g of NaCoCF) and 3.5×10^4 mL/(g of KCoCF).

1.4.5 Conversion of HTiO Composite Microspheres to the Phosphate Form

Composite microspheres also were prepared to treat acidic waste streams. Since hydrous titanium oxide begins to dissolve in solutions with pHs <1, a batch of the 0.45-mm HTiO microspheres containing the NaCoCF was converted to the phosphate form to stabilize them for use in batch-test studies using acidic solutions.

Batch contact tests were conducted using a portion of the converted phosphate microspheres to remove cesium from simulated NGLLLW. Triplicate sets of 3- and 5-mg NaCoCF samples (phosphate form) removed an average of 99.7% Cs in 24 h. Table 1.13 shows that similar amounts of Cs were removed (99.5 and 99.6%) by the HTiO form. This slight difference may be the result of titanium monohydrogen phosphate (TiHP) sorbing Cs slightly better than hydrous titanium oxide under the same conditions. However, most of the cesium was likely sorbed by the embedded NaCoCF particles.

1.5 DISCUSSION

Optimum formulations and process conditions for making composite HTiO microspheres embedded with $Na_2[CoFe(CN)_6]$ or $K_2[CoFe(CN)_6]$ have been determined. The composite microspheres can be effectively used in the pH range 1 to 10. HTiO is soluble below pH 1, and the embedded cyanoferrate particles decompose at pHs above 13. Basic waste solutions with pHs in the 7 to 10 range, such as NGLLLW or MVST supernate solutions, could be treated with these microspheres to remove cesium. The phosphate forms of these composite microspheres were developed to treat waste streams that are more acidic ($\leq$ pH of 1), such as the highly radioactive acidic (~4 M HNO_3) liquid waste generated in the Fission Product Release Program in Building 4501, and the Cleanex raffinate at REDC. Hydrous titanium oxide in the composite microspheres is converted to acid insoluble TiHP by treating the microspheres with phosphoric acid. TiHP is also a good inorganic ion exchanger for removing cesium and can assist the cyanoferrate exchanger in removing the cesium in the pH range of 1 to 7, if the salt concentration of the solution is not too high, $\leq$1 M.[8-10] Furthermore, TiHP is a good ion exchanger for removing polyvalent ions,[8-12] such as Am^{3+}, Cm^{3+}, UO_2^{2+}, and Pu^{4+}.

The methodology employed to embed the cyanoferrates in HTiO microspheres also could be used to prepare microspheres embedded with other excellent ion exchangers, such as ammonium molybdophosphate (AMP), polyantimonic acid (PAA), and sodium titanate (NaT), which are commercially available only as fine powders. (NaT is also available in pellet form.) AMP and PAA are known to be very effective at removing Cs and Sr from acid waste streams.[13-16] NaT, as formulated by Sandia Laboratories,[17-19] works well at removing Sr from solutions with high salt content and high pH. PAA is more effective than TiHP at removing polyvalent cations under very acidic conditions. In addition to HTiO, other hydrous metal oxides of Zr, Hf, Ce, Fe, and Al or their phosphates could be used to prepare composite microspheres. In this work, only batch contact studies were conducted to determine the best process parameters for making the composite microspheres.

Loading capacity and column tests are needed to better define the use of these materials. However, the batch tests do indicate that microspheres could be very useful in waste minimization efforts and could have an impact on limiting the quantities of radionuclides reaching the proposed liquid waste treatment facilities.

Table 1.13. Comparison data for the composite HTiO and TiHP microspheres embedded with 17% NaCoCF

NaCoCF (mg)	Cs removed (%)				D_t (mL/g)				DF (C_o/C_t)				Cs left in solution (ppb)			
	(3 h)		(24 h)		(3 h)		(24 h)		(3 h)		(24 h)		(3 h)		(24 h)	
	A[a]	B[b]	A	B	A	B	A	B	A	B	A	B	A	B	A	B
3			99.5	99.7			5.1×10^5	8.5×10^5			183	294			6.3	3.9
5			99.6	99.7			4.1×10^5	5.8×10^5			341	245			4.7	3.4
15	99.3	99.7			8.3×10^4	1.2×10^5			146	218			7.9	5.3		

[a] A = HTiO embedded with NaCoCF (17 wt %); diameter of microspheres was 0.42 to 0.50 mm.

[b] B = Titanium monohydrogen phosphate embedded with NaCoCF (17 wt %); diameter of microspheres was 0.42 to 0.50 mm.

The improved flow dynamics offered by the composite microspheres allow for several methods of liquid waste treatment that are not practical with powders. Large gravity-flow ion-exchange columns can be used to treat liquid waste. However, if the loading kinetics of the composite microspheres proved to be too slow for normal column use, solutions could be repeatedly passed through a column bed in a cyclic fashion to remove undesired cations.

Another approach is currently being used to treat radioactive liquid waste solutions in hot cell "D" of Building 4501. TiHP, ZrHP, and/or HTiO microspheres, which are housed in a closed stainless steel mesh basket, are placed into a stainless steel tank where contaminated solutions are added for treatment. Good contact mixing is provided by bubbling air through the solution. Once the ion-exchange capacity of the microspheres is reached (determined by gamma counting of treated solutions), plans are to dry the microspheres at 300°C for several hours to remove any free water and to collapse the structure of the microspheres. The tank, which is designed for easy removal from the hot cell, will be sealed and sent to the burial ground and placed in retrievable storage. Entrapment of the radionuclides in the water-insoluble matrix of the microspheres should lessen the possibility of the radionuclides being leached into the environment if the stainless steel tank were to fail.

2. TREATMENT OF REDC WASTE STREAMS

2.1 INTRODUCTION

Waste streams produced during operations at the Radiochemical Engineering Development Center (REDC) are being included in treatment processes with other waste streams contained at the Oak Ridge National Laboratory (ORNL). The combined waste streams are designated as the NGLLLW, and processes for treatment are being developed by the Liquid and Gaseous Treatment Technology Group (LGTTG). However, if the waste streams from REDC can be treated at the point of generation, instead of being diluted with other waste streams, then the treatment of NGLLLW would become less costly and complex. Treatment at the source could considerably reduce the amount of low-level process wastewater to be treated at ORNL.

Two of the process streams at REDC, the Cleanex raffinate and the caustic dissolver waste streams, were chosen for treatment investigation. The Cleanex raffinate stream is highly acidic but contains relatively low concentrations of salt. The caustic dissolver stream is a highly alkaline, very salty stream. Radionuclides of Cs, Sr, and Ru are the primary contributors to the radioactivity of the liquid wastes. Because of limited space in the hot cells at REDC, special attention has to be given to the methods of treatment of these waste streams. It is also important that any proposed method lend itself to ease of operation and manpower time and that little new waste be generated. If feasible, the use of ion-exchange materials in the treatment methodology should offer the best solutions for removing Cs and Sr from these streams.

Zeolites and synthetic inorganic ion exchangers with good potential for removing Cs and Sr were chosen for screening tests. Zeolites are distinguished by molecular structure as well as chemical composition, especially the aluminum content,[20] and are named according to these characteristics. Certain zeolites are better suited for cesium and strontium removal, depending on their structure. The zeolites selected included PDZ-140, Ionsiv IE-96, PDZ-300, and CBV-10A. Previous work by Robinson and Begovich[21] using PDZ-140, Ionsiv IE-96, and PDZ-300 demonstrated the effectiveness of these zeolites for cesium and strontium separation in dilute waste solutions. In solutions having a total hardness of 150 ppm as $CaCO_3$ and consisting of 50 ppm Ca, 12 ppm Mg, and 30 ppm Na, the cesium distribution coefficients were >8,000 for PDZ-140, >15,000 for Ionsiv IE-95 (the H^+ form of Ionsiv IE-96), and 23,000 mL/g for PDZ-300. Tests were also conducted using a synthetic mordenite in a similar solution, and the resulting cesium distribution coefficient[21] was >14,000 mL/g. The strontium distributions were not as high; however, PDZ-300 showed the most promise for strontium separation.

Tests conducted by Ullrich et al.[22] using spherical zirconium monohydrogen phosphate (ZrHP) in solutions containing 10^{-3} $\underline{M}$ of cesium and strontium resulted in distribution ratios of 620 and 1112 mL/g, respectively, at pH 2. As reported by Beaver et al.,[23] TiHP removed 94% of the cesium present in a 1 $\underline{M}$ nitric acid solution and 98% at pH 2. Campbell et al.[24] tested the KCoCF and found that after a contact time of 1 h, the cesium distribution ratios were 5.6×10^5 and 3.3×10^6 mL/g at pH 1.0 and 2.3, respectively. Studies by Maeck et al.[25] showed that ZrHP had a cesium distribution ratio of ~100 mL/g at pH 1, but at pH 2 the value was ~1000 mL/g. Therefore, these materials were examined further for separating cesium and strontium from the REDC Cleanex raffinate waste stream.

Due to the chemical nature of the REDC caustic dissolver stream, the materials selected for this stream had to demonstrate stability under the high salt and alkaline conditions of the stream. The literature reports two materials that exhibit the characteristics that are essential for this stream — a resorcinol-based exchanger developed at Savannah River Plant, Savannah River Resin (SSR), and sodium titanate, NaT. Tests by Campbell et al.[24] using SRR and NaT in a caustic aluminate solution showed a cesium distribution ratio of 10^4 mL/g using the SRR and a strontium distribution ratio of 10^5 mL/g using NaT.

The results discussed above provided an indication of several potential ion-exchange and sorbent materials for separating cesium and strontium from these waste streams. Metal ferrocyanides, zeolites, and inorganic ion exchangers were selected for testing to determine the treatability of acidic Cleanex raffinate. For caustic dissolver solutions, SRR and NaT were selected for testing for removing cesium and strontium.

2.2 CLEANEX RAFFINATE

Initial batch studies were conducted to evaluate the capabilities of five inorganic ion exchangers for removing cesium and strontium from the Cleanex raffinate solution produced at REDC. Two inorganic ion exchangers prepared as microspheres, TiHP and ZrHP, and three zeolites, PDZ-140 (a natural Na^+ clinoptilolite), PDZ-300 (a natural chabazite), and Ionsiv IE-96 (a synthetic chabazite), were tested.

The compositions of the Cleanex raffinate solution and the simulant used for the tests are shown in Table 2.1. The concentrations of Cs, Sr, and Rb in the simulant were based on a previous Cleanex raffinate analysis and were somewhat higher than in the present Cleanex raffinate solution. Tracer amounts of ^{137}Cs and ^{85}Sr were added for analytical purposes.

The sorbents were first equilibrated with a simulant solution that excluded Rb, Cs, and Sr. Then, 10 mL of the Cleanex raffinate simulant containing the tracers was added to 50-mg samples of sorbent. Contact times on the Rota-Torque mixer were 4 and 17 h. The results of these tests are summarized in Table 2.2. In some cases, the values are reported as minimum or maximum values because of difficulty in accurately counting very low tracer levels.

Results revealed that these exchanger materials are only moderately effective for removal of cesium and strontium from the Cleanex raffinate solution. Consequently, several additional sorbent materials were chosen and tested under identical conditions. These materials included NaCoCF, PAAs, and molecular sieve CBV-10A. The NaCoCF and PAAs were tested in powder form. The results from these tests are summarized in Table 2.3.

Table 2.1. Composition of Cleanex raffinate solution

Constituent	Cleanex raffinate composition*	Simulant composition*
HCl	0.03	0.0299
NaCl	0.10	0.101
LiCl	0.04	0.04
Cs	62	124 + ^{137}Cs tracer
Sr	91	185 + ^{85}Sr tracer
Rb	4.9	14.5
Pd	1080	
Ru	720	
Al	570	
Ba	470	
Ni	280	
Cd	130	
Cu	28	
Cr	28	

*Expressed as M̲ for HCl, NaCl, and LiCl; all other data reported in parts per million (ppm).

The CBV-10 removed ~77% of the cesium and ~9% of the strontium. The NaCoCF removed >99% of the cesium and <1% of the strontium. The cesium loading equates to ~24 mg Cs/g NaCoCF. In a separate test, 15-mg samples of NaCoCF powder were shaken for 0.5 h with 10-mL samples of simulated Cleanex raffinate. In this test, 87% of the cesium was removed, giving a resulting loading value of 83 mg Cs/g NaCoCF. On a large scale, this means that if 1 kg of NaCoCF powder were mixed with 667 L of simulated Cleanex raffinate for 0.5 h, ~83 g of the cesium could be adsorbed. This corresponds to ~3600 Ci of activity if one-half of the cesium were ^{137}Cs.

Three different forms of PPA were tested. None of these removed more than 6% of the cesium; strontium removal ranged from 24 to 96%. The results for the most promising sorbents are compared and illustrated in Figs. 2.1 to 2.4.

Ammonium molybdophosphate (AMP) has been identified from the literature as another potential sorbent for removing cesium from acidic solutions. The applicability of AMP to the Cleanex raffinate needs to be evaluated. Incorporation of AMP into microspheres would be the next step to make the material more useful for column applications. Because PPA showed some promise for strontium removal, it would be of interest to prepare microspheres containing this material.

Table 2.2. Comparison of sorbents for removing cesium and strontium from Cleanex raffinate solution

Parameter	Sorbent				
	PDZ-140	PDZ-300	IE-96	TiHP	ZrHP
Cesium distribution, mL/g in 4 h	396 ± 4	120 ± 10	39.8 ± 0.8	126 ± 3	135 ± 5
Cesium distribution, mL/g in 17 h	570 ± 20	150 ± 10	33 ± 2	258 ± 2	146 ± 5
Cesium removed, % in 4 h	66.3 ± 0.2	37 ± 3	16.5 ± 0.3	38.6 ± 0.4	40.1 ± 0.9
Cesium removed, % in 17 h	74.2 ± 0.6	44 ± 2	14.1 ± 0.6	56.7 ± 0.9	42.3 ± 0.6
Strontium distribution, mL/g in 4 h	36 ± 4	<15	4.6 ± 0.4	<6	4.8 ± 0.6
Strontium distribution, mL/g in 17 h	37 ± 3	<17	<6	<13	<5
Strontium removed, % in 4 h	15 ± 1	<7	2.2 ± 0.2	<3	2.3 ± 0.3
Strontium removed, % in 17 h	16 ± 1	<8	<3	<6	<3

Table 2.3. Additional sorbents tested for cesium and strontium removal from Cleanex raffinate solution.

Parameter	Sorbent				
	CBV-10A	PAM[a]	PAHT[a]	PAS[a]	NaCoCF[b]
Cesium distribution, mL/g in 4 h	650 ± 30	<13	<1	6.1 ± 0.4	44000 ± 2000
Cesium distribution, mL/g in 17 h	680 ± 10	4.3 ± 0.5	<1	7.4 ± 0.8	49000 ± 4000
Cesium removed, % in 4 h	76.4 ± 0.9	<6	<1	2.9 ± 0.2	>99
Cesium removed, % in 17 h	76.9 ± 0.3	2.1 ± 0.2	<1	3.6 ± 0.5	>99
Strontium distribution, mL/g in 4 h	19 ± 2	590 ± 60	64 ± 1	510 ± 60	<2
Strontium distribution, mL/g in 17 h	19.7 ± 0.9	5800 ± 500	98 ± 3	4700 ± 700	<2
Strontium removed, % in 4 h	8.7 ± 0.9	74 ± 2	24.0 ± 0.2	71 ± 3	<1
Strontium removed, % in 17 h	8.8 ± 0.3	96.6 ± 0.3	33 ± 1	95.8 ± 0.7	<1

[a] PAM, PAHT, and PAS designate three different forms of polyantimonic acid.
[b] NaCoCF designates the sodium cobalt hexacyanoferrate.

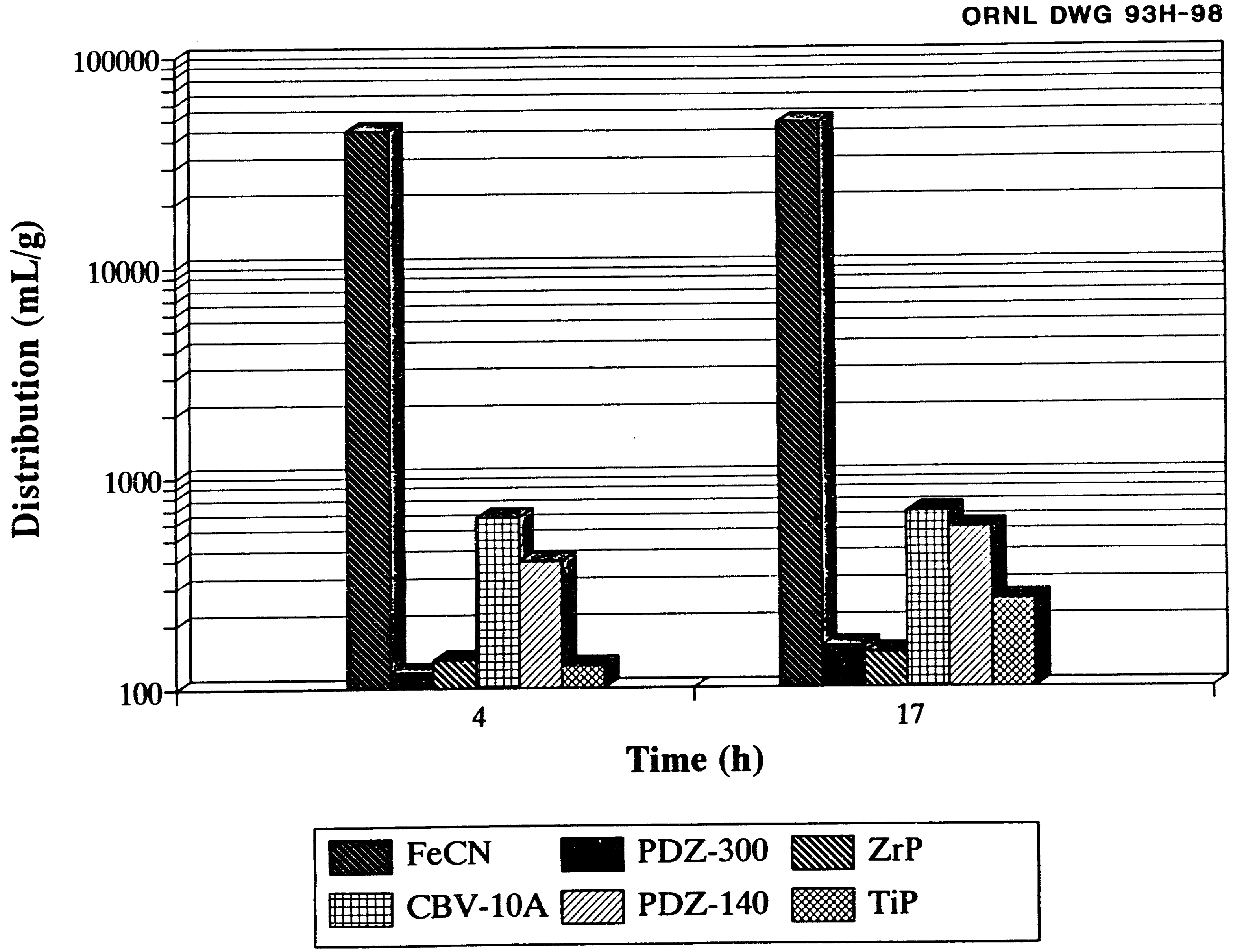

Fig. 2.1. Cesium distribution between various sorbents and Cleanex raffinate simulant.

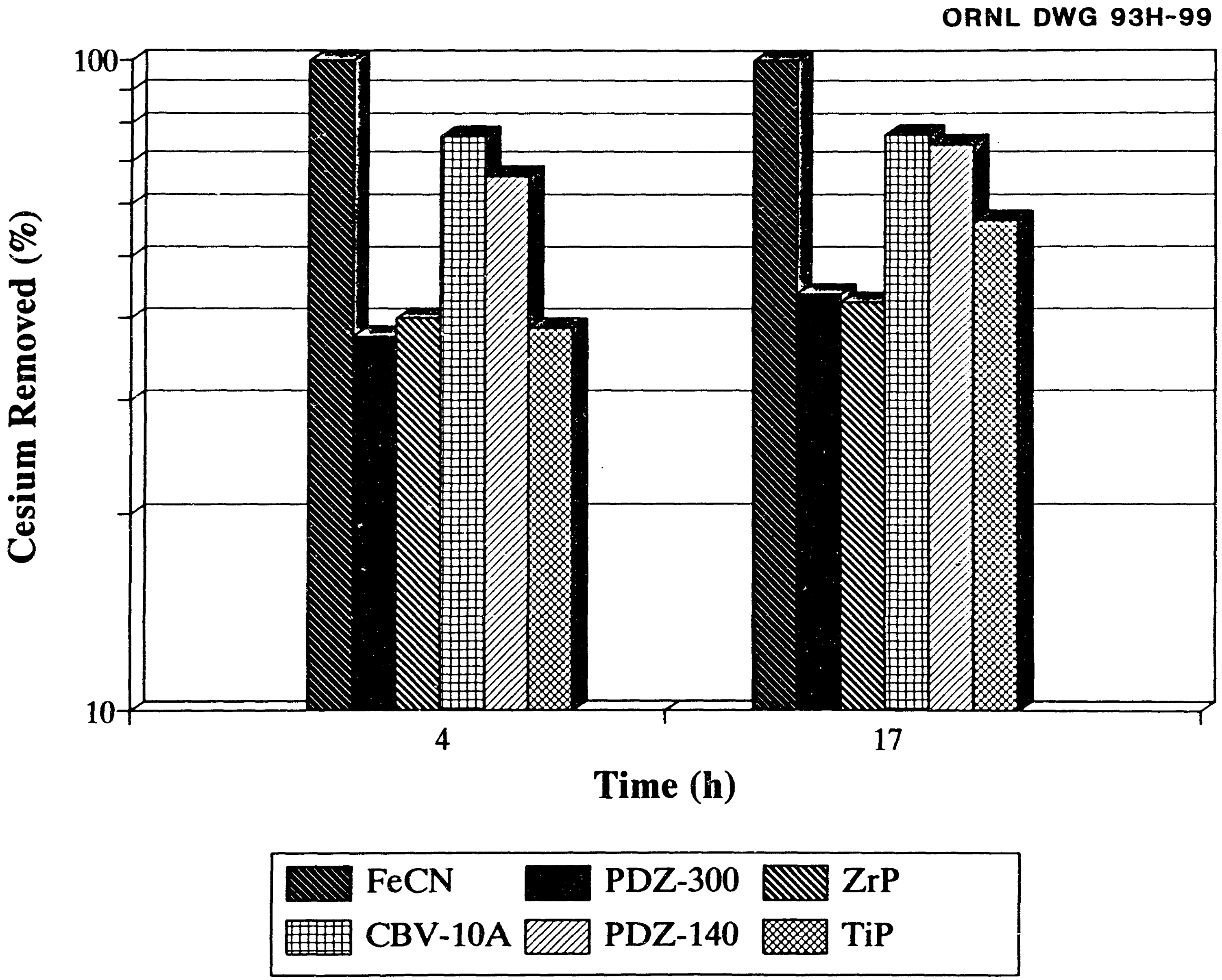

Fig. 2.2. Percent cesium removal by various sorbents from Cleanex raffinate simulant.

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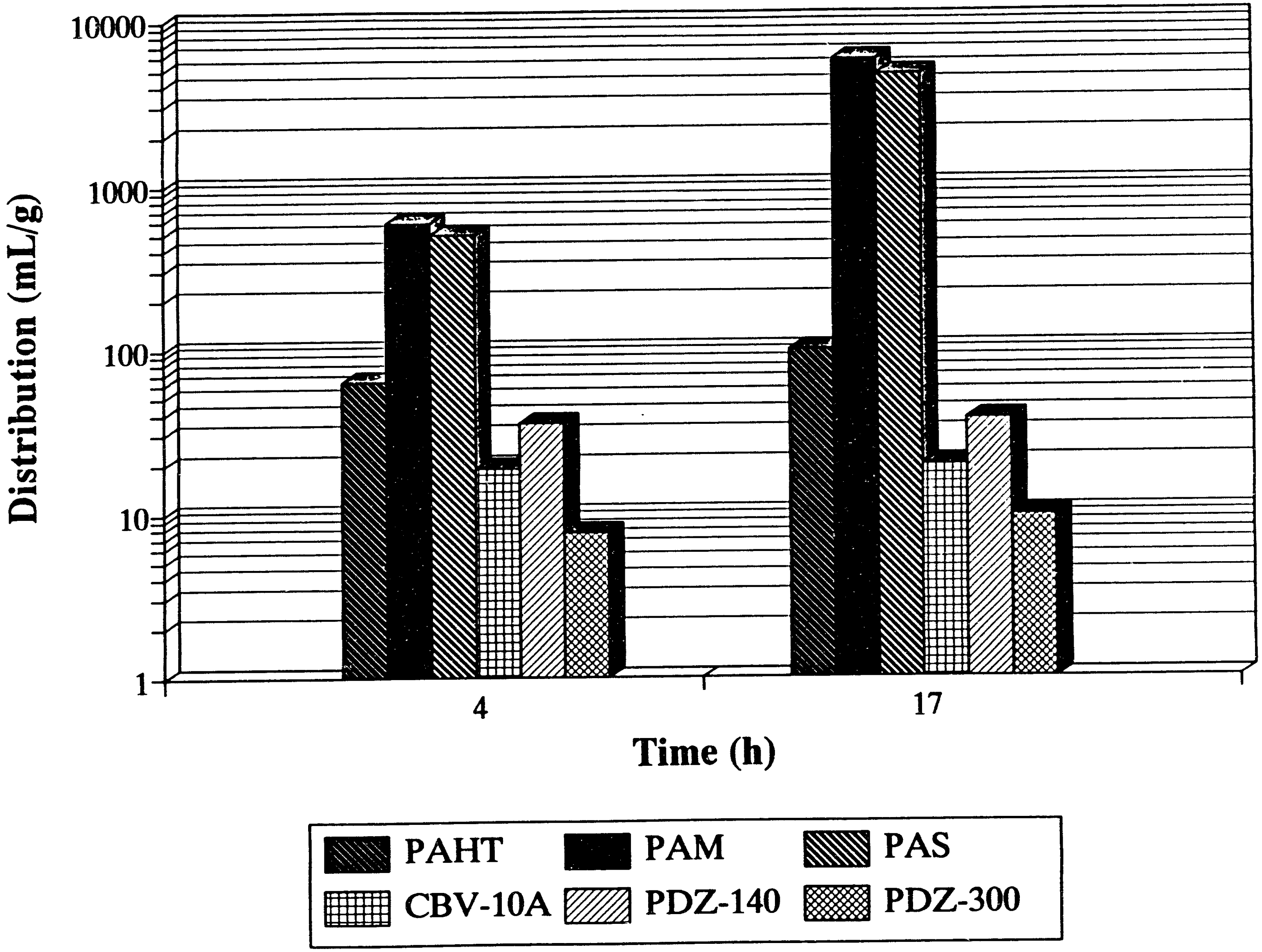

Fig. 2.3. Strontium distribution between various sorbents from Cleanex raffinate simulant.

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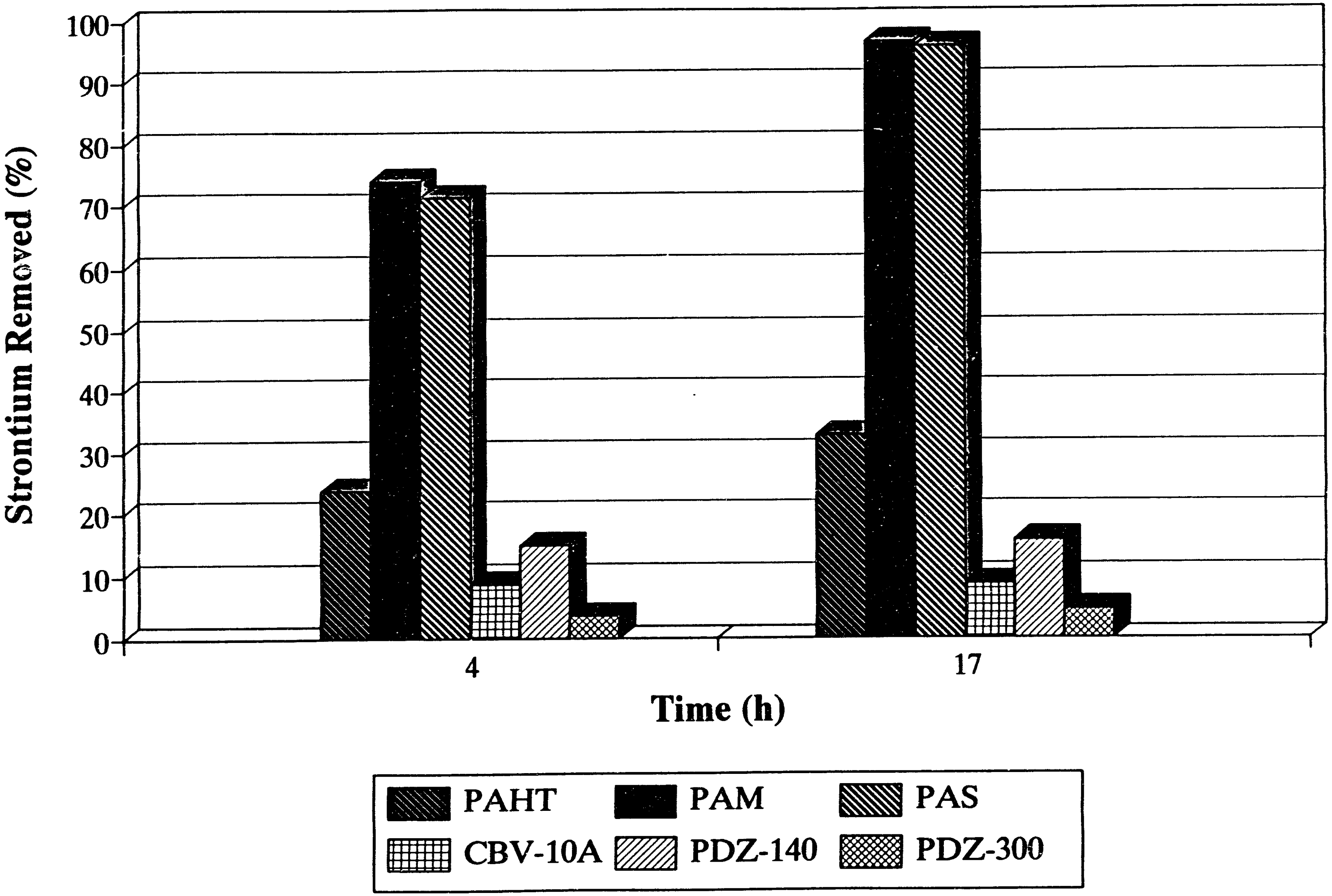

Fig. 2.4. Percent strontium removal by various sorbents from Cleanex raffinate solution.

2.3 CAUSTIC DISSOLVER SOLUTION

A solution simulating the caustic dissolver solution generated at REDC was obtained from W. D. Bond of the Chemical Technology Division (ORNL). The composition of this simulant solution is shown in Table 2.4. Tracer amounts of ^{137}Cs and ^{85}Sr were added for analytical purposes.

Table 2.4. Composition of caustic dissolver solution

Constituent	Dissolver solution composition	Simulant composition
$NaAlO_2$	0.7 - 1.0 M	1.14 M
NaOH	0.5 - 1.0 M	1.98 M
$NaNO_3$	1.0 - 1.5 M	0.85 M
$NaNO_2$		0.13 M
Cs	202 ppm	298 ppm + ^{137}Cs tracer
Sr	3.7 ppm	8.5 ppm + ^{85}Sr tracer
Rb	16 ppm	
Ba	19 ppm	

Four sorbent materials were selected for initial testing to measure their ability to remove cesium and strontium from the simulated caustic dissolver solution. The sorbent materials tested were SRR and three different forms of NaT. The three NaT sorbents were from Cerac, Inc.; R. Dosch; and Tam Ceramics, Inc.; and were used as received.

The SRR was pretreated according to the method used by D. D. Lee and W. D. Arnold. This included washing the resin twice with ten volumes of 2.0 M formic acid, followed by washing with the same amount of distilled water. Next, five additions of 0.25 M NaOH, each six times the solid volume, and three additions of distilled water, each ten times the solid volume, were used to wash the resin. Then the resin was air dried.

In the batch tests, 10 mL of the simulant solution was added to 50 mg of sorbent. Samples were run in triplicate with batch contact times of 4 and 17 h. The results from these tests are summarized in Table 2.5 and illustrated in Figs. 2.5 to 2.8. The average values are shown, along with the relative standard deviation. In some cases, the values are reported as minimum or maximum values because of difficulty in accurately counting very low level tracer concentrations.

Cesium sorption by the SRR was lower than anticipated. The reasons for the lower sorption are not yet known. Two of the NaT materials removed >99% of the strontium within 4 h. The third sample of NaT was less effective, removing 71% of the strontium in 4 h and 85% of the strontium in 17 h.

Table 2.5. Sorption of cesium and strontium from REDC caustic dissolver solution

	Sorbent			
Parameter	SRR	NaT-A[a]	NaT-B[b]	NaT-C[c]
Cesium distribution, mL/g in 4 h	110 ± 9	<11	<5	<10
Cesium distribution, mL/g in 17 h	144 ± 8	<9	<7	<13
Cesium removed, % in 4 h	36 ± 2	<6	<2	<5
Cesium removed, % in 17 h	42 ± 1	<4	<4	<6
Strontium distribution, mL/g in 4 h	280 ± 20	$>10^4$	43900 ± 4000	500 ± 30
Strontium distribution, mL/g in 17 h	399 ± 4	$>10^4$	$>5 \times 10^4$	1200 ± 200
Strontium removed, % in 4 h	59 ± 2	>99	>99	71 ± 1
Strontium removed, % in 17 h	66.5 ± 0.3	>99	>99	85 ± 2

[a] Produced by Cerac, Inc.
[b] Produced by R. Dosch.
[c] Produced by Tam Ceramics, Inc.

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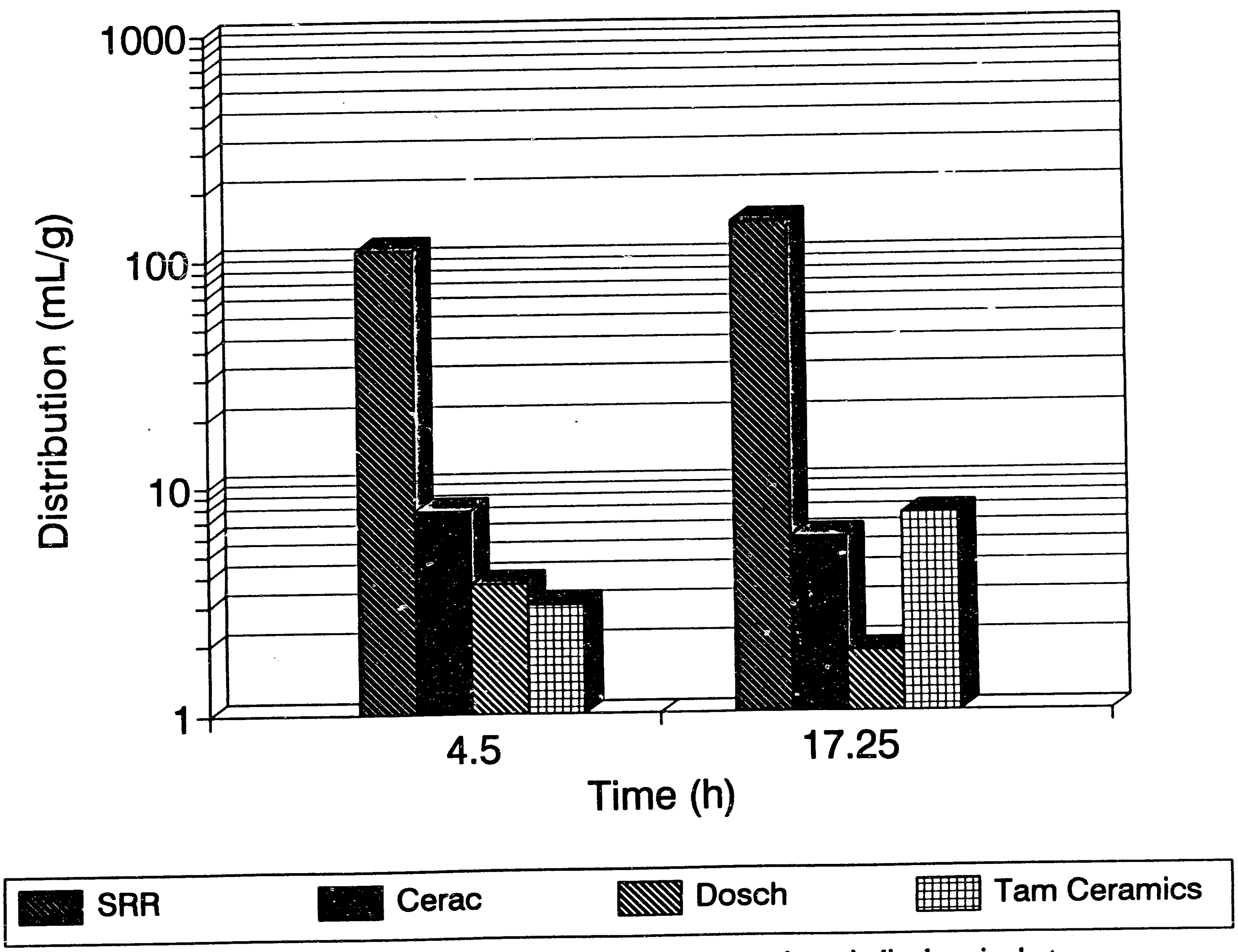

Fig. 2.5. Cesium distribution between various sorbents and caustic dissolver simulant.

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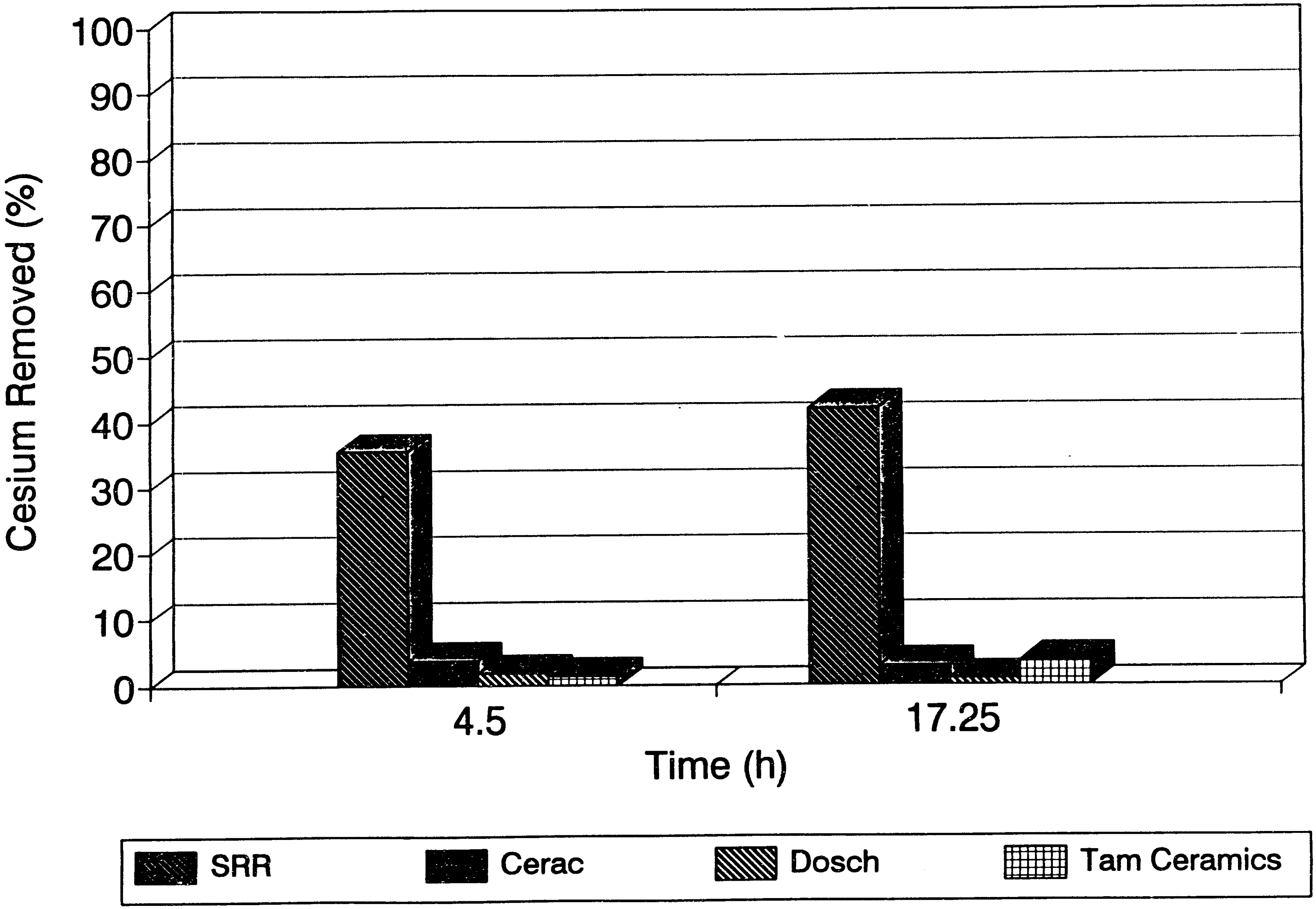

Fig. 2.6. Percent cesium removal various sorbents from caustic dissolver simulant.

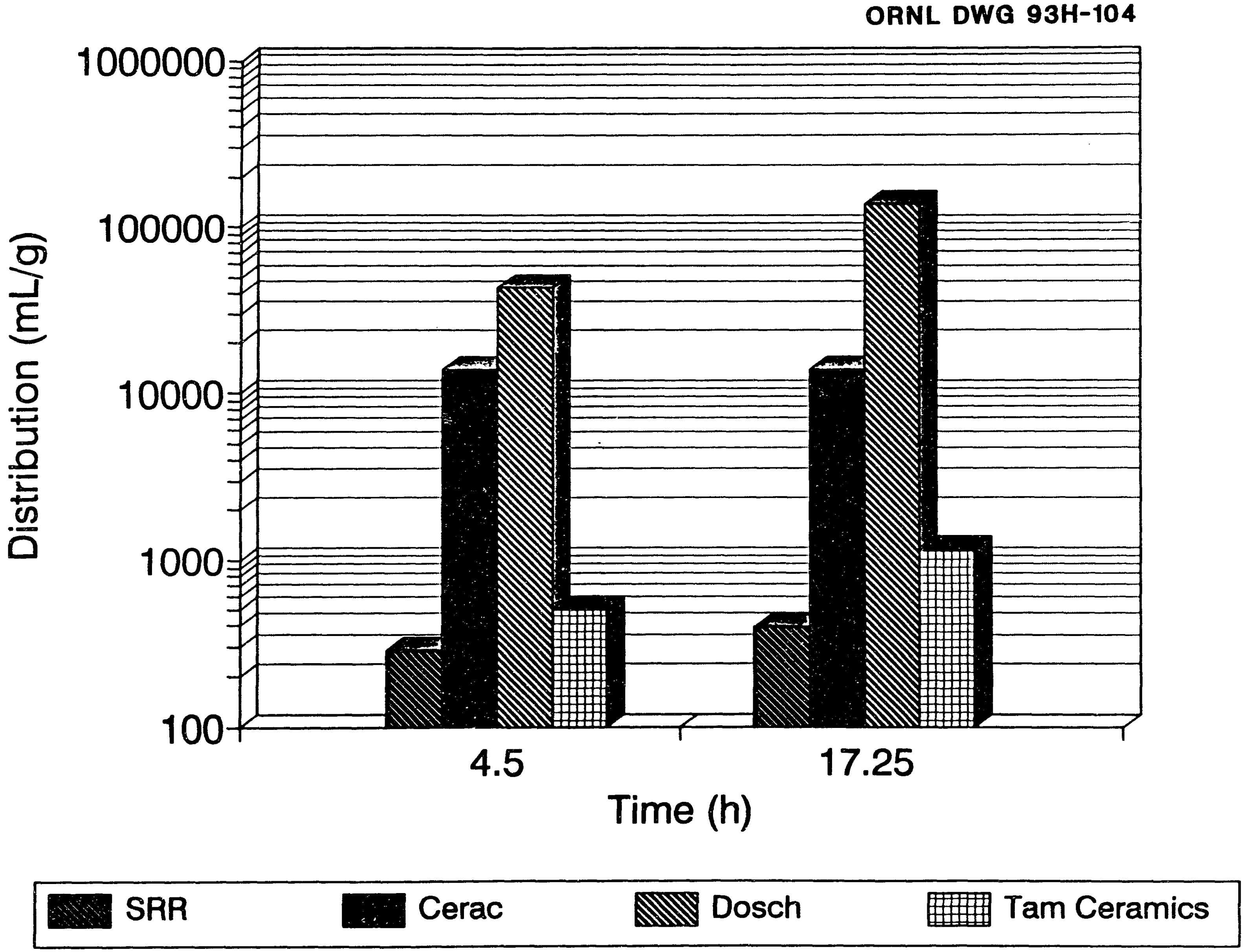

Fig. 2.7. Strontium distribution between various sorbents and caustic dissolver simulant.

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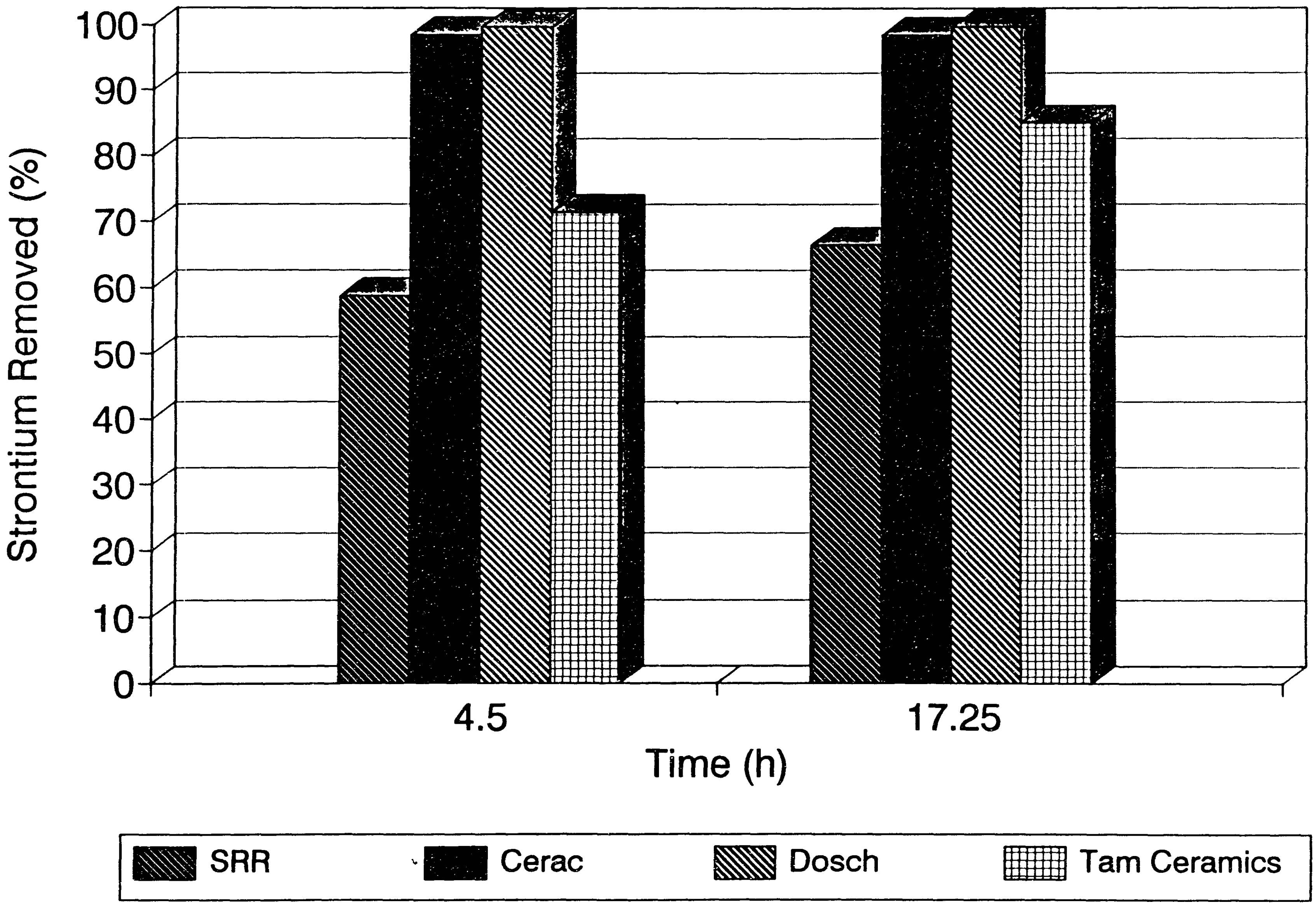

Fig. 2.8. Percent strontium removal by various sorbents from caustic dissolver simulant.

Additional studies are needed to further evaluate the SRR for cesium removal from the caustic dissolver solution. Preliminary tests at REDC indicate that the behavior of the SRR may be related to storage or treatment conditions. When a reliable, stable batch of resin is identified, then further column studies are needed to determine optimum parameters for operating a column in a hot cell with actual waste solutions.

3. REMOVAL OF RADIONUCLIDES FROM ORGANICS

3.1 INTRODUCTION

Solvent extraction separation processes at REDC generate mixed-waste streams consisting of organic solvents containing light actinides, lanthanides, and fission products. Technologies are needed to remove the radionuclides from the organic solutions so that they are no longer classified as mixed wastes and possibly could be recycled. Experimental studies have been used to evaluate several inorganic ion exchangers for removing radionuclides, especially trivalent elements, from organic solutions that simulate organic process streams from processes at REDC. Studies included (1) measuring the stability of selected inorganic ion exchangers in organic solutions; (2) measuring the sorption of europium from organic solutions onto selected sorbents; (3) determining the effect of organic composition and extractant concentration on sorption properties; and (4) determining the effect of various sorbent pretreatments on sorption properties.

The sorption measurements were made using various organic solutions containing $^{152\text{-}154}Eu^{3+}$, which was previously extracted into the organic phase. In most studies, the organic consisted of different concentrations of di-2-ethylhexyl phosphoric acid (HDEHP) in dodecane as the diluent. In addition, the waste organics from the Cleanex and Pubex processes were simulated by the solutions shown in Table 3.1.

The simulants are modeled after the actual process mixed waste from the Pubex and Cleanex processes. The actual waste organics are normally stripped with acid to remove most of the radioactivity. However, the radioactivity level remains >100 nCi/g, and, consequently, the wastes are considered TRU wastes.

Table 3.1. **Composition of simulated organic waste solutions**

Pubex waste	Cleanex waste
0.5003 M HDEHP	1.001 M HDEHP
0.04993 M DBHQ[a]	0.2016 M Adogen 364[b]
in	in
90% DEB,[c] 10% 2-EH[d]	88% Dodecane, 12% DIPB[e]

[a]DBHQ = 2,5 di-tert-butylhydroquinone.
[b]Adogen 364 = n(C_8-C_{10})-trialkylamine.
[c]DEB = diethylbenzene.
[d]2-EH = 2-ethylhexanol.
[e]DIPB = diisopropylbenzene.

3.2 STABILITY OF INORGANIC ION EXCHANGERS IN ORGANIC SOLUTIONS

The exchangers examined in this study were HTiO, HZrO, TiHP, and ZrHP. In order to determine the applicability of these exchangers to the decontamination of mixed waste, the stability of the exchangers in various organic solvents was examined.

The results of the solvent stability determinations are presented in Tables 3.2 and 3.3. The various color changes refer to the color of the exchangers and not the solvent, unless otherwise noted. The dry exchangers appear to be more stable than the wet exchangers in the various media. The term "wet" exchangers refers to those exchangers that were soaked in distilled, deionized water for 14 h prior to being immersed in the organic solvent. Note that the "wet" hydrous oxides dissolved in the Cleanex simulant, rendering them unusable for those conditions. Also, wet ZrHP microspheres fused together into a glassy mass in 2.44 M Adogen 364. Most of the color changes produced either orange or yellow exchangers, and the changes occurred within 72 h. An exception is the dry HTiO, which turned grayish blue after several weeks of contact with dodecane.

The stability studies were performed with contact times ranging from 1 week to 2 months, and the longer times produced greater effects on the exchangers' appearance. However, neither the cause of the color changes nor the effect on exchanger performance is known. Sorption studies using the discolored exchangers must still be performed to determine the effect of the color changes on the sorption characteristics.

Table 3.2. Stability of dry inorganic ion exchangers in organic solutions

Solvent	Exchanger HTiO	 TiHP	 HZrO	 ZrHP
Dodecane	Grayish blue	NC[a]	NC	NC
2-EH[b]	Bright yellow	Orange	NC	Slightly yellow
MIBK[c]	Bright yellow	Yellow	NC	NC
Adogen 364[d]	Cracked	NC	NC	NC
Pubex waste	NC	NC	NC	NC
Cleanex waste	NC	NC	NC	NC

[a]NC = no change.
[b]2-EH = 2-ethylhexanol.
[c]MIBK = methylisobutyl ketone.
[d]Adogen 364 = n(C_8-C_{10})-trialkylamine.

Table 3.3. Stability of wet inorganic ion exchangers in organic solvents

Solvent	Exchanger HTiO	 TiHP	 HZrO	 ZrHP
Dodecane	Bright yellow	NC[a]	NC	NC
2-EH[b]	Yellow	Orange	NC	Slightly yellow
MIBK[c]	Yellow	Bright yellow	Slightly yellow	NC
Adogen 364[d]	NC	NC	NC	Fused
Pubex waste	Solution lightened	Solution darkened	NC	NC
Cleanex waste	Dissolved	NC	Dissolved	NC

[a]NC = no change.
[b]2-EH = 2-ethylhexanol.
[c]MIBK = methylisobutyl ketone.
[d]Adogen 364 = n (C_8-C_{10})-trialkylamine.

3.3 EFFECTS OF PRETREATMENT OF SORBENT AND ORGANIC COMPOSITION ON Eu SORPTION

The following sorption data are presented according to the method of exchanger pretreatment. Sorption experiments involved the removal of Eu^{3+} ion from various di-2-ethylhexyl phosphoric acid (HDEHP) solutions with toluene or dodecane as the diluent. The equilibration time for the sorption experiments ranged from 2 to 7 d.

In an attempt to increase the sorption of the dry ZrHP, some samples were allowed to swell overnight in distilled, deionized water. After the excess water was removed, sorption experiments with both the wet and dry ZrHP microspheres were performed to examine the effect of the water. Table 3.4 shows the results of the comparison study that was performed using 0.08 M HDEHP in toluene equilibrated for 7 d with duplicate samples of wet and dry ZrHP. The removal of Eu under these conditions is much higher in the case of the wet exchangers. However, the behavior of the wet exchangers was somewhat peculiar in that some of the samples aggregated, or clumped together, and others did not. There was no discernible difference in sorption behavior between those microspheres that clumped and those that did not. There was, likewise, no detectable pattern to the clumping behavior.

Table 3.4. Comparison of wet and dry ZrHP for removing Eu from 0.08 M HDEHP in dodecane toluene*

Sorbent	Distribution ratio, D (mL/g)	Eu Removal (%)
Dry ZrHP	11.9	57.0
Dry ZrHP	11.5	57.2
Wet ZrHP	1130	99.3
Wet ZrHP	1030	99.3

*Equilibration time = 7 d; volume of organic = 3 mL; exchanger = 0.35 to 0.42 g.

Because the use of the water-swelled ZrHP met with a measure of success, all four exchangers were swelled in water, and Eu^{3+} distribution ratios from solutions of HDEHP in dodecane were compared. The results (Figs. 3.1 and 3.2 and Tables 3.5 and 3.6) were compared after the samples were equilibrated for 3 and 7 d. The bar graphs display the data

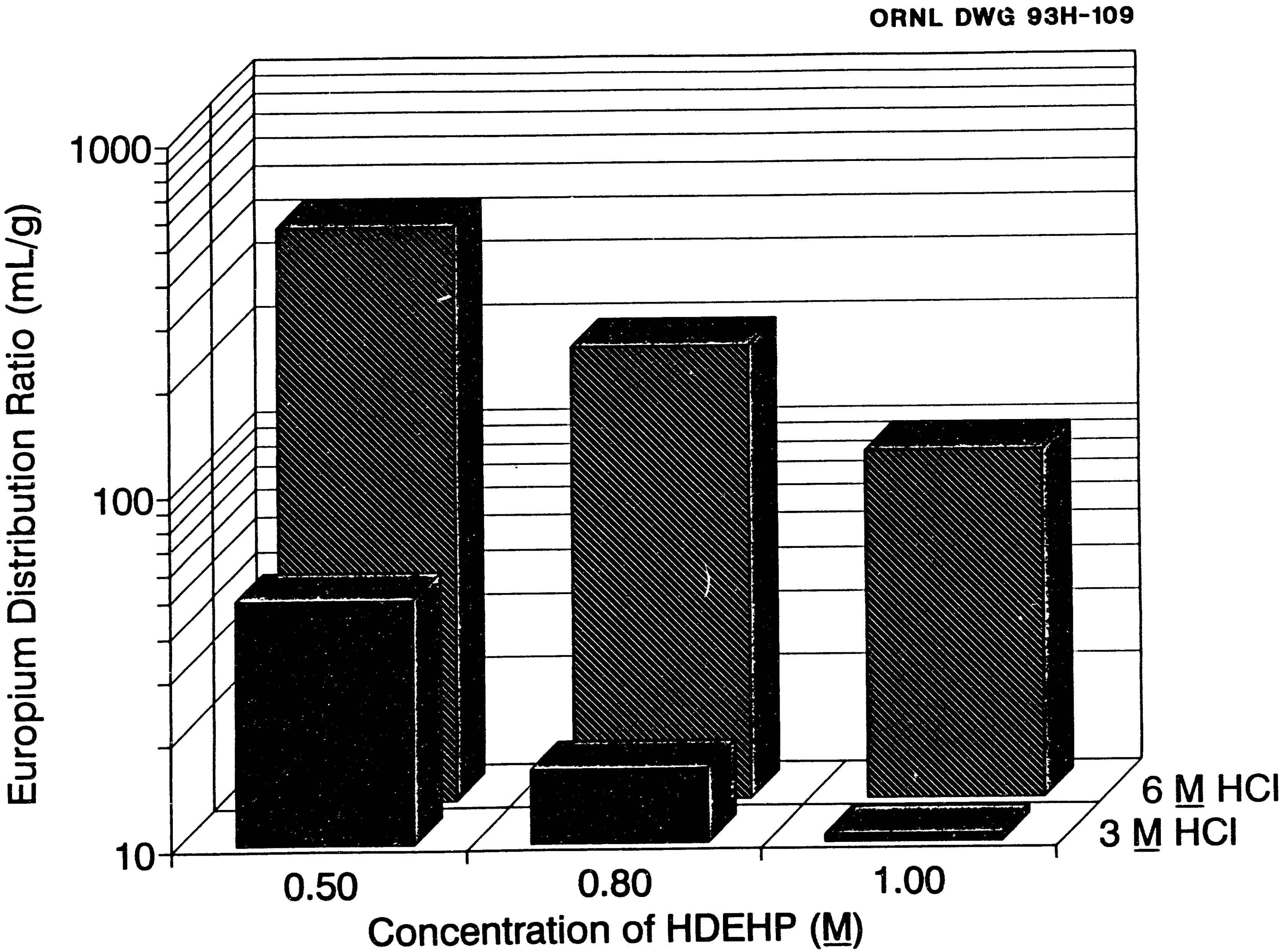

Fig. 3.1. Europium distribution between various sorbents (swelled in water) and solutions of HDEHP in dodecane.

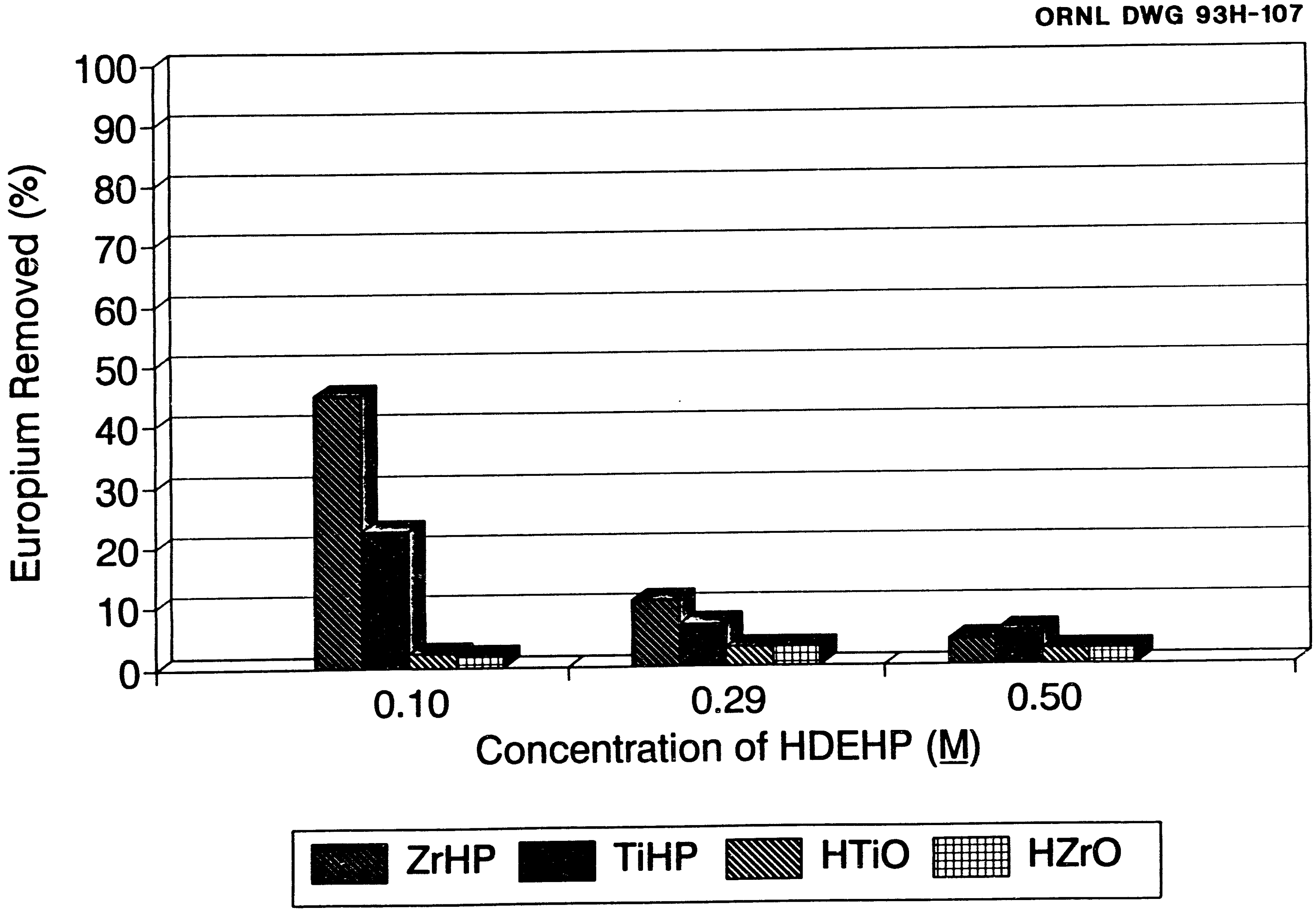

Fig. 3.2. Percent of europium removal by various sorbents (swelled in water) and solutions of HDEHP in dodecane.

Table 3.5. Effect of HDEHP concentration on Eu removal by inorganic ion exchangers swelled in water and equilibrated with the organic for 7 d

	0.10 M HDEHP		0.29 M HDEHP		0.50 M HDEHP	
Exchanger	Distribution ratio	% Eu removal	Distribution ratio	% Eu removal	Distribution ratio	% Eu removal
HZrO	0.16	1.8	0.15	3.0	0.13	2.6
ZrHP	7.34	45.0	0.89	10.8	0.31	4.2
TiHP	2.52	22.7	0.51	6.8	0.39	5.6
HTiO	0.19	2.3	0.18	2.9	0.19	2.4

Table 3.6. Effect of HDEHP concentration on Eu removal by inorganic ion exchangers swelled in water and equilibrated with the organic for 3 d

	0.10 M HDEHP		0.29 M HDEHP		0.50 M HDEHP	
Exchanger	Distribution ratio	% Eu removal	Distribution ratio	% Eu removal	Distribution ratio	% Eu removal
HZrO	0.08	1.0	0.06	1.0	0.09	1.7
ZrHP	6.5	42.0	0.56	7.0	0.28	3.8
TiHP	0.80	8.5	0.22	3.1	0.20	2.9
HTiO	0.11	1.4	0.12	1.9	0.17	2.1

from the 7-d equilibration experiment; Fig. 3.1 shows the distribution data, and Fig. 3.2 shows percent removal. From these data, it was concluded that TiHP and ZrHP were the most promising exchangers. At the higher HDEHP concentrations, all four behaved similarly. But the best exchanger, ZrHP, removed only 45% of the Eu, and even then only from 0.1 M HDEHP. The sorption was much less at 0.5 M HDEHP. Therefore, this pretreatment method was an improvement, but not practical for Eu removal in these systems where the goal would be nearly complete Eu removal in 1.0 M HDEHP. ZrHP and TiHP were chosen for further study, based on their performance relative to the hydrous oxides.

In further attempts to maximize the europium extraction from more concentrated HDEHP, dry ZrHP was allowed to swell overnight in various HCl concentrations ranging from 0.1 to 6.0 M. These "acid-swelled" microspheres were then used in the europium sorption experiments. A plot of distribution (log D) vs HCl concentration (Fig. 3.3) shows a significant effect of the HCl, even at 0.1 M.

In addition to the effect on the europium distribution, the acid pretreatment also produced different swelling characteristics with ZrHP. The swelling percentage varied directly with the HCl concentration (Fig. 3.4).

Zirconium phosphate was allowed to swell in both 3 M and 6 M HCl and then used to remove europium from solutions with HDEHP concentrations shown in Fig. 3.5. The europium removal was quite high, even in 1.0 M HDEHP. These data are useful because the Cleanex process organic waste is 1.0 M in HDEHP. Thus, acid pretreatment of the exchangers may be very useful for the application to actual process mixed wastes.

In a series of experiments, 0.6- to 0.8-g samples of ZrHP and TiHP were mixed with 3-mL samples of 1.0 M HDEHP solutions containing 0.4 to 32 mg of europium. The europium removal ranged from 79 to 98%. From the most concentrated europium solutions, the exchanger loading values reached 49 mg Eu/g of ZrHP and 37 mg Eu/g of TiHP.

3.4 REMOVAL OF Eu FROM SIMULATED ORGANIC PROCESS WASTE

The goal is to reduce the radioactivity in the organic solutions to a level such that the solution can be disposed of as low-level waste or recycled. To this end, europium was sorbed from the waste simulants (see Table 3.1) by ZrHP soaked in 6 M HCl, and, in the case of Cleanex simulant, TiHP and ZrHP. The results, given in Tables 3.7 and 3.8, show high europium removal from both of the waste simulants.

More work is needed to determine the effectiveness of this system with actual process waste and to determine the effect of macro concentrations of competing ions such as Al^{3+}, Mg^{2+}, and Fe^{3+}. Also, more information is needed on the kinetics and loading of the sorbents. Additional radionuclides of interest include Am, Th, and Ru.

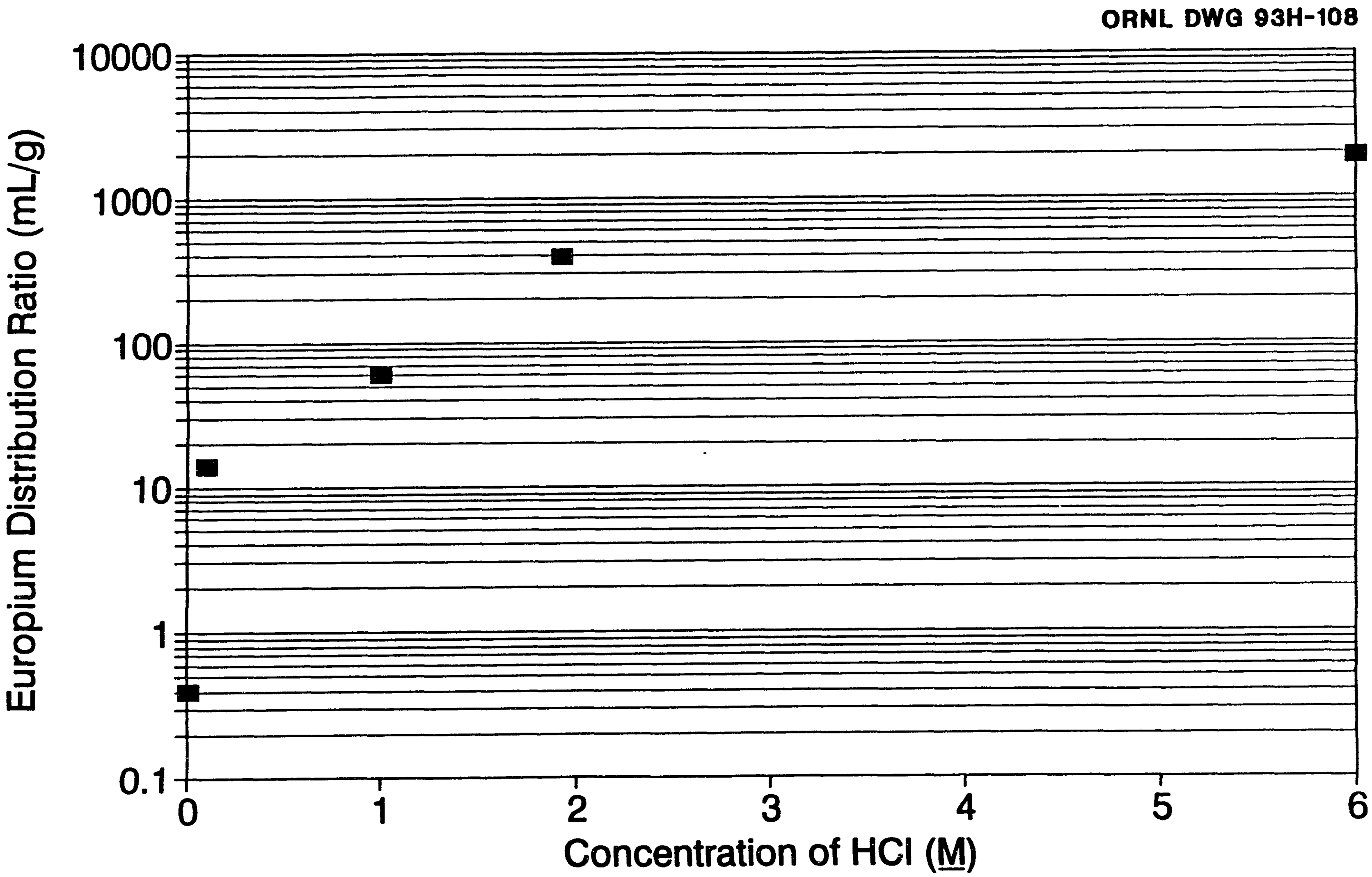

Fig. 3.3. Increase in europium distribution after pretreatment of ZrHP microspheres with HCl.

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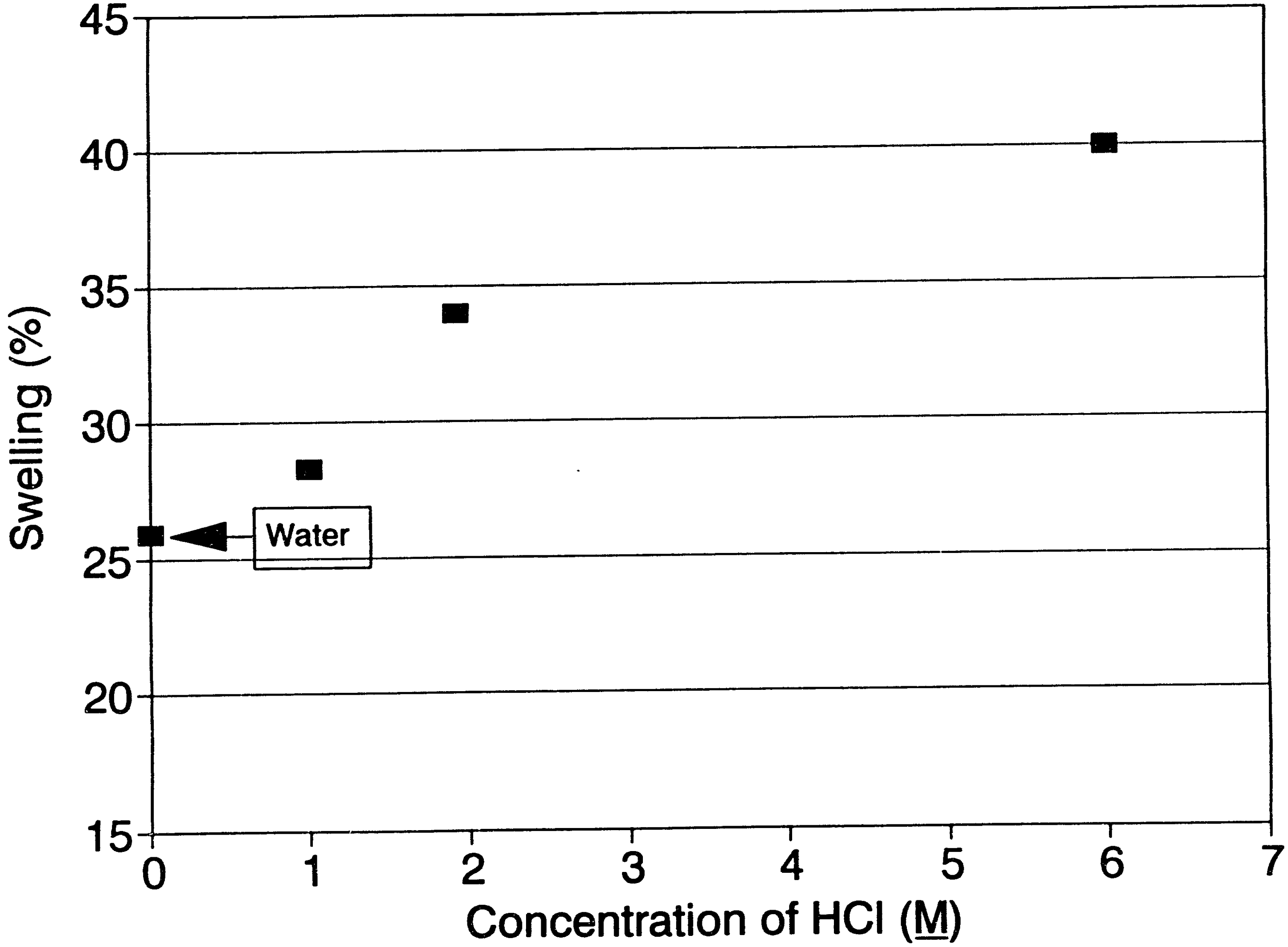

Fig. 3.4. Effect of HCl pretreatment on the swelling of ZrHP microspheres.

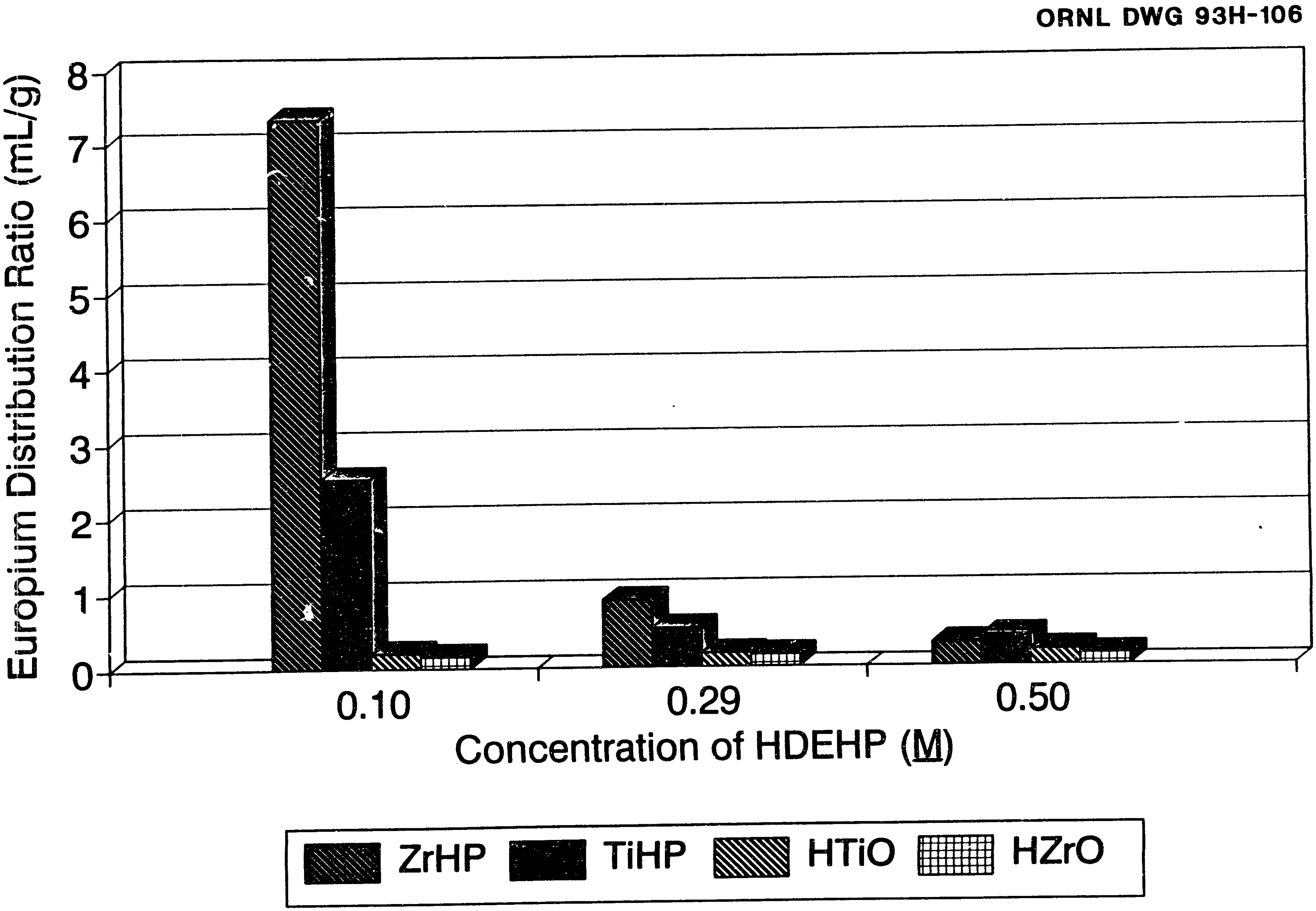

Fig. 3.5. Europium distribution between solutions of HDEHP in dodecane and ZrHP microspheres pretreated with HCl.

Table 3.7. Europium removal from Pubex simulated waste by ZrHP pretreated with HCl*

Pretreatment	Eu^{3+} distribution ratio, D	Log D	% Eu^{3+} removed
3 M HCl	481	2.68	98.9
6 M HCl	887	2.95	99.4

*Equilibration time, 3 d; HDEHP, 0.5 M; 3 mL organic to 0.57—0.58 g of exchanger.

Table 3.8. Europium removal from Cleanex simulated waste by ZrHP and TiHP pretreated with 6 M HCl*

Exchanger	Eu^{3+} distribution ratio, D	Log D	% Eu^{3+} removed
TiHP	2110	3.32	99.7
ZrHP	193	2.29	97.4

*Equilibration time, 3 d; HDEHP, 1 M; 3 mL organic to 0.54—0.58 g of exchanger.

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