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**A PRELIMINARY STUDY OF CESIUM SORPTION
FROM ACID WASTE SOLUTIONS
UTILIZING PHOSPHATE EXCHANGERS**

YVONNE M. JONES

NOVEMBER, 1966

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FROM ACID WASTE SOLUTIONS
UTILIZING PHOSPHATE EXCHANGERS

By

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November 1966

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A PRELIMINARY STUDY OF CESIUM SORPTION FROM ACID WASTE SOLUTIONS UTILIZING PHOSPHATE EXCHANGERS

INTRODUCTION

This report presents preliminary laboratory studies of two cation exchangers to determine their cesium capacities and relative selectivities and capabilities. The results are used in determining the applicability of the exchangers to the cesium recovery and waste management program at Hanford.

In plans developed for fuel element recovery at Hanford, waste streams of various acid content are generated. Schemes for the current waste management program consist of removing heat generating isotopes such as Cs^{137} , Sr^{90} , and rare earths. This process will produce waste streams which can be concentrated and solidified for permanent storage.

Procedures have been developed for removal of these isotopes from both alkaline (1-9) and slightly acid (2, 6, 10-13) wastes by ion exchange techniques. Methods utilizing solvent extraction (14), precipitation (15), and a combination of these techniques (13, 16) have also been developed.

To be considered suitable for isotope recovery, an exchanger should be chemically stable, relatively selective with a moderate-to-high capacity, and stable with respect to high gamma radiation dosages. Sorption and elution rates should be fast. There should also exist practical and efficient

means for isotope removal and exchanger regeneration.

Synthetic and natural zeolites have proven useful in removing cesium from alkaline and neutral solutions. They display, however, low chemical stability at acid concentrations greater than 0.5 to 1M HNO_3 . Thus, either existing acid streams must be partially neutralized resulting in the precipitation of hydrolyzed metallic cations with accompanying cesium occlusion in the resultant sludge or large quantities of complexing agents must be added to the system to keep the cations in solution as the pH was raised. In either case, the volume of the radioactive waste is increased and additional waste material is generated.

Several exchangers have also been developed for removing cesium from highly acidic solutions. These have included the heteropoly acids and acid salts of tungsten and molybdenum, (17-24) as well as the zirconium, titanium, and tin salts of the condensed phosphates. (18, 19 22, 25-33) Studies on the condensed heteropoly acids and their salts, as well as research on the zirconium phosphates, have indicated that they do not fulfill all of the requirements outlined above.

Two phosphate exchangers have recently been introduced by the Société

d'Etudes, de Recherches et s'Applica-
tions pour l'Industrie (SERAI-Brussels,
Belgium) under the registered trade
name ABEDEM TiA (hereafter abbreviated
PhTiA) and ABEDEM Sn (hereafter abbrevi-
ated PhSn). Preliminary studies per-
formed on the PhTiA by the SERAI group
(25,28) and work performed by Inoue,
et al (29-32) on a similar tin phos-
phate exchanger indicated that these
two materials might prove useful here
at Hanford. Since sufficient acid
waste streams are present at Hanford
to warrant an investigation of cesium
removal from waste streams of high
acid content, laboratory studies were
initiated on these two exchangers to
determine their applicability to the
cesium recovery and waste management
program.

SUMMARY

Preliminary studies to determine the
cesium capacities and relative selec-
tivities and capabilities of the two
cation exchangers—PhTiA and PhSn—were
conducted.

Equilibrium cesium capacities
were determined for the H-form ex-
changers in multi-cation systems.
The cesium capacity of the exchangers
in a 1×10^{-3} M CsNO_3 solution at
25 °C was found to be 0.45 meq/g PhTiA
and 0.10 meq/g PhSn. The capacities
of both exchangers increased with in-
crease in solution cesium concentra-
tion. The capacities for cesium were
determined in the presence of the
competing cations--sodium, cerium,
strontium, iron, and hydrogen. Gen-
erally, PhTiA exhibited a higher ce-
sium selectivity than PhSn as reflect-

ed by the change in the measured ca-
pacity. Based on these results, a
relative selectivity scale for the
two exchangers was postulated. The
interfering ions and the concentration
range over which they were studied,
were chosen to correspond to the pos-
tulated composition of typical Hanford
wastes.

A synthetic Purex Acid Waste (PAW)
solution was prepared based on the
proposed composition given in Table I.
The synthetic PAW was prepared at a
concentration factor of two and with-
out the addition of cesium and nitric
acid. The effect of the acid concen-
tration of PAW on cesium sorption at
constant cesium concentration could
then be determined by the addition of
appropriate amounts of cesium and ni-
tric acid to the concentrated feed.
The variation of the cesium capacity

TABLE I. *Composition of Synthetic
Purex Acid Waste (PAW)*

<u>Ionic Component</u>	<u>Concentration, M</u>
Na ⁺¹	1.5
Fe ⁺³	0.067
Al ⁺³	0.034
Cr ⁺³	0.013
Ni ⁺²	0.007
SO ₄ ⁻²	0.104
NO ₃ ⁻¹	1.08
Sr ⁺²	0.56×10^{-4}
Ce ⁺³	0.93×10^{-3}
Rare Earths	1.8×10^{-3}
HNO ₃	2-4
Cs ⁺¹	0.5×10^{-3} - 1×10^{-3}

with increased cesium concentration in PAW at constant acid strength was similarly determined. A decreased capacity with increased acidity and increased capacity with increased cesium concentration was noted for both exchangers. As expected from the relative selectivities, the matrix solution had a more profound effect on the cesium capacity of PhSn than for PhTiA. Both exchangers appeared to be stable up to acid concentrations of $3M$ although analysis indicated a slight dissolution of PhTiA in $3M$ HNO_3 .

Column studies were performed to determine cesium column capacities as a function of PAW acid and cesium concentrations. The same relative dependence as derived from equilibrium data was found in the kinetic studies. PhTiA exhibited a high cesium sorption rate. Essentially no change in the capacity at 50% breakthrough was noted by increasing the effluent flow rate to 16 column volumes per hour (CV/hr). Fifty percent breakthrough capacities were usually about 60% of the equilibrium values.

Elution studies were made on both exchangers using various eluting agents such as NH_4Cl , NH_4NO_3 , NH_4OH , $(NH_4)_2CO_3$ and $NH_4NO_3-HNO_3$. Thermal effects on cesium removal were also investigated. Elution at elevated temperatures ($55^\circ C$) removed cesium more efficiently than elution at room temperature. An acceptable procedure for cesium decontamination would be column loading at room temperature followed by cesium elution using $5M$ NH_4NO_3 at elevated temperatures ($55^\circ C$).

A hot cell run on actual Purex Acid Waste (PAW) was performed in B-Cell of the 325-A High Level Radiochemistry Facility.

Facility using PhTiA. The results of this run indicate that a fast and efficient cesium removal process can be established using this exchanger.

EQUILIBRIUM STUDIES

The cesium sorption capabilities of both PhTiA and PhSn in various aqueous media were ascertained by both static equilibrium and kinetic column methods. Although equilibrium studies were useful in determining the effect of compositional variables on the rate and extent of cesium sorption, column studies more closely approximated actual operating conditions.

The effective cesium capacities, Q , and the distribution coefficients, K_d , were evaluated for both materials by contacting known quantities of the air dried H-form exchangers with appropriate volumes of solutions containing variable amounts of Cs^{137} labeled $0.1M$ $CsNO_3$. The systems were equilibrated for 2 to 3 days in a thermostatically controlled water bath.

The cesium capacity was determined by the relationship

$$Q = (1 - \frac{c}{co}) Co \frac{V}{M}$$

where co is the initial activity in counts per minute of the solution whose concentration is Co (meq/ml), c is the activity of the solution at equilibrium in counts per minute, V represents the volume of the solution in milliliters, and M is the mass of the exchanger in grams.

The distribution coefficients, when calculated, were evaluated by the usual method,

$$K_d = \frac{co-c}{c} \frac{V}{M}$$

where the quantities co , c , V and M are described previously.

To achieve statistically significant changes in count rates, 0.5 g of 50-100 mesh PhSn was contacted with 50 ml of select solutions. For systems utilizing PhTiA, 100 ml of test solution equilibrated with 0.2 g of similarly meshed solid material were needed to attain this same confidence level.

Table II and Figure 1 show the results of studies to determine the cesium sorption capabilities of PhTiA from solutions containing cesium at concentrations up to 5 meq/liter. Corresponding results for PhSn are

also included in Figure 1 and in Table III. The cesium capacity was a more slowly varying function of solution concentration for PhTiA than for PhSn. This direct relationship of cesium capacity to cesium solution concentration was not vitiated by going to a PAW system in which the aggregate concentration of interfering cations was 3 to 4M. The more pronounced influence of foreign cations on the cesium capacity of PhSn indicated a lower cesium selectivity for this exchanger when compared with PhTiA.

FIGURE 1. Effective Cesium Capacity of PhTiA and PhSn as a Function of Cesium Concentration

The effect of acid concentration on the cesium capacity of the two exchangers is shown in Table II and Figure 2 for PhTiA and Table III and Figure 3 for PhSn. Acid ranges were chosen to correspond to those expected in actual reprocessing solutions. Initial cesium concentrations were identical for all systems. The effective cesium capaci-

ty of PhTiA as displayed in the log-log plot of Figure 2 decreased nonlinearly to about 45% of its corresponding acid-free value at a 3M acid concentration. This same general trend was followed in PAW systems where an additional 30% reduction was noted. The nonexistence of a significant alteration in the relative

TABLE II. Effective Cesium Capacity of PhTiA as a Function of Cesium and Acid Concentration at 25.0 ± 0.5 °C

System of Study	HNO ₃ (Mx10 ³)	Co (Mx10 ³)	C (Mx10 ³)	Q (meq/g)	HNO ₃ (Mx10 ³)	Co (Mx10 ³)	Q (meq/g)	K _d
Cs ⁺ - H ⁺	---	0.78	0.12	0.34	0.5	1.0	0.26	554
	---	1.50	0.32	0.59	1.0	1.0	0.27	556
	---	2.99	1.53	0.73	1.5	1.0	0.24	460
	---	4.92	3.06	0.93	2.0	1.0	0.23	423
					3.0	1.0	0.20	319
PAW	2.0	0.74	0.51	0.12	0.5	1.0	0.17	254
	2.0	1.00	0.75	0.12	1.0	1.0	0.15	221
	2.0	1.48	1.14	0.17	1.5	1.0	0.15	208
	2.0	2.92	2.51	0.22	2.0	1.0	0.12	168
	2.0	5.12	4.33	0.39	3.0	1.0	0.11	144
Co the initial cesium concentration								
C the equilibrium cesium concentration								

TABLE III. Effective Cesium Capacity of PhSn as a Function of Cs and Acid Concentration at 25.0 ± 0.5 °C

System of Study	HNO ₃ (Mx10 ³)	Co (Mx10 ³)	C (Mx10 ³)	Q (meq/g)	HNO ₃ (Mx10 ³)	Co (Mx10 ³)	Q (meq/g)	K _d
Cs ⁺ - H ⁺	---	0.78	0.10	0.07	0.5	1.0	0.026	357
	---	1.50	0.20	0.13	1.0	1.0	0.020	244
	---	2.99	0.47	0.25	1.5	1.0	0.013	15
	---	4.92	1.72	0.32	2.0	1.0	0.011	13
					3.0	1.0	0.006	7
PAW	2.0	0.74	0.70	0.004	0.5	1.0	0.013	15
	2.0	1.00	0.95	0.005	1.0	1.0	0.009	10
	2.0	1.48	1.38	0.009	1.5	1.0	0.007	8
	2.0	2.92	2.79	0.013	2.0	1.0	0.005	5
	2.0	5.12	4.70	0.042	3.0	1.0	0.004	4
Co the initial cesium concentration								
C the equilibrium cesium concentration								

FIGURE 2. Effective Cesium Capacity of PhTiA as a Function of Competing Cation Concentration

FIGURE 3. Effective Cesium Capacity of PhSn as a Function of Competing Cation Concentration

ratios of the capacities between the two systems indicate that no substantial change in the nature of successfully competing species was occurring as the acidity of the system was varied. The H-ion concentration exhibited a greater influence on the cesium capacity of PhSn. An increase in the acid concentration produced a reduction in the cesium distribution coefficient of greater than 90% at an acidity of $3M$. The transition to a PAW system had a more pronounced effect on the capacity at lower acid concentrations.

Sodium ions competed more successfully with cesium than did hydrogen cations for PhTiA exchanger sites as

can be seen by examining Figure 2 and Table IV. For PhSn, the reverse was noted as outlined in Table V and Figure 3. The cesium capacity in sodium systems approximated the capacity of corresponding acid systems.

Strontium and cerium are present in reprocessing solutions as fission products at trace concentrations. Tables IV and V and Figure 2 and 3 show the effect of strontium and cerium concentrations on the cesium capacity of the two exchangers. The concentration effects appear to be primarily a colligative property of the system indicating comparable cerium and strontium selectivities for each exchanger.

TABLE IV. Effective Cesium Capacity of PhTiA as a Function of Various Interfering Cation Concentrations at 25.0 ± 0.5 °C

Initial Cs ¹⁺ Concentration = $1 \times 10^{-3} N$ in all Cases								
Y N	Y = Na ¹⁺		Y = Sr ²⁺		Y = Ce ³⁺		Y = Fe ³⁺	
	Q	K _d	Q	K _d	Q	K _d	Q	K _d
0	0.45		0.45		0.45		0.45	
2×10^{-4}			0.437	3751				
3×10^{-4}					0.446	4387		
1×10^{-3}			0.432	3545				
1.5×10^{-3}					0.422	2794		
2×10^{-3}			0.417	2458				
3×10^{-3}					0.410	2517		
1×10^{-2}			0.376	1590				
1.5×10^{-2}					0.346	1130		
3×10^{-2}							0.322	898
9×10^{-2}							0.343	1068
0.18							0.305	771
0.20	0.343	1188						
0.30							0.294	712
0.50	0.3045	777						
1.0	0.242	508						
1.5	0.203	352						
2.0	0.176	276						

TABLE V. Effective Cesium Capacity of PhSn as a Function of Various Interfering Cation Concentrations at 25.0 ± 0.5 °C

Y	Initial Cs ¹⁺ Concentration = 1×10^{-3} N in all Cases							
	Y = Na ¹⁺		Y = Sr ²⁺		Y = Ce ³⁺		Y = Fe ³⁺	
N	Q	K _d	Q	K _d	Q	K _d	Q	K _d
0	0.10		0.10		0.10		0.10	
2×10^{-4}			0.092	1262				
3×10^{-4}					0.094	1851		
1×10^{-3}			0.091	1059				
1.5×10^{-3}					0.092	1308		
2×10^{-3}			0.077	347				
3×10^{-3}					0.090	1140		
1×10^{-2}			0.075	324				
1.5×10^{-2}					0.074	281		
3×10^{-2}							0.071	239
9×10^{-2}							0.074	282
0.18							0.063	168
0.20	0.068	231						
0.30							0.052	107
0.50	0.052	106						
1.0	0.039	68						
1.5	0.028	39						
2.0	0.026	36						

From these same tables and figures, it can be seen that PhTiA possessed a greater affinity for iron than for hydrogen and sodium. Considering the six cations involved, the selectivity scale $\text{Cs} \gg \text{Ce} \approx \text{Sr} > \text{Fe} > \text{Na} > \text{H}$ can be postulated. For the PhSn exchanger, this affinity sequence was permuted to $\text{Cs} \gg \text{Sr} \approx \text{Ce} > \text{H} > \text{Fe} > \text{Na}$.

KINETIC STUDIES

Since cationic exchange in kinetic systems depends on sorption rate as well as selectivity and capacity of the exchanger, information gained from equilibrium studies is useful only when a relationship between static and kinetic data has been eluci-

dated. Column studies using PhTiA and PhSn were performed to establish this relationship.

Column experiments were performed on air dried samples of the H-form exchangers, sieved to a particle size range of 50 to 100 mesh. The columns consisted of double walled glass tubes (1.0 cm ID) connected to a circulating constant temperature bath. Influent solutions were introduced under pressure and consisted, unless otherwise noted, of synthetic PAW solutions in which both the H and Cs concentrations could be varied. The collected effluent was then counted for Cs¹³⁷ activity.

Table VI summarizes the effect of the flow rate expressed as column volumes per hour on the cesium capacity of PhTiA at 50% cesium breakthrough. The corresponding cesium loading curves are plotted using logarithmic probability coordinates in Figure 4. Comparison with equilibrium data indicates that loadings to within 30% of the equilibrium capacity can be attained at flow rates up to 16 CV/hr. This would indicate a relatively fast cesium sorption rate.

Cesium breakthrough curves for PhTiA as a function of the cesium and acid concentrations in PAW systems are presented in Figures 5 and 6. Computed exchanger capacities at

50% breakthrough using these curves are shown in Table VII. Selected corresponding values for PhSn are included in the table for comparison. The over-all effect of cesium and acid concentration on the column loading is what would be expected from equilibrium data. In PhTiA systems values of c/c_0 greater than unity were noted. The cesium capacities were calculated both as grams of adsorption Cs^{137} per liter of swollen exchanger bed, Q' , and as meq cesium per gram exchanger, Q .

ELUTION STUDIES

Some elution characteristics of the two exchangers were investigated. The

TABLE VI. The Effect of Flow Rate on the Cesium Capacity of PhTiA at 25 °C

Particle Size (mesh)	50-100	50-100	50-100
Flow Rate (CV/hr)	1	7	16
CV at 50% BT	41	44	44
Capacity			
Q' , g/liter	27.6	27.4	29.8
Q' , meq/g	0.24	0.26	0.29

TABLE VII. Effective Cesium Capacity of PhTiA and PhSn at 50% Breakthrough in PAW Systems of Varying Cesium and Acid Concentrations

HNO ₃ M	CsNO ₃ Mx10 ³	PhTiA		PhSn	
		Q' , g/liter	Q , meq/g	Q' , g/liter	Q , meq/g
0.5	0.71	11.7	0.100	---	---
1.0	0.71	16.2	0.149	0.74	0.005
2.0	0.71	12.8	0.124	---	---
3.0	0.71	8.2	0.068	---	---
2.0	0.71	12.8	0.124	---	---
2.0	1.5	18.6	0.164	---	---
2.0	3.0	24.9	0.248	1.07	0.007
2.0	5.0	29.8	0.290	1.60	0.011

FIGURE 4. Cesium Loading of PhTiA
 as a Function of Influent Flow Rate

FIGURE 5. Cesium Loading of PhTiA as a Function of Cesium Influent Concentration

FIGURE 6. Cesium Loading of PhTiA
 as a Function of Influent Acid Con-
 centration

elution studies were performed on washed columns loaded with an influent consisting of a $2M$ $NaNO_3$ - $1.5M$ HNO_3 - $5 \times 10^{-3}M$ $CsNO_3$ solution. A material balance calculation determined the amount of cesium loaded. Column loadings were effected at $25^\circ C$ at 15 CV/hr for PhTiA and 5 CV/hr for PhSn. After thermal equilibrium of the column at selected temperatures ($25^\circ C$, $35^\circ C$, $45^\circ C$, or $55^\circ C$), cesium was eluted from the column at a flow rate of 5 CV/hr. The eluate was counted for Cs^{137} activity.

Ammonium nitrate appeared to be a more suitable eluant than ammonium chloride for both exchangers. At $25^\circ C$, less than 70% of the loaded cesium was removed from PhSn by 10 column volumes of $3M$ NH_4Cl while 85% of the loaded cesium was removed by an equal volume of $5M$ NH_4NO_3 . Ammonium chloride was equally effective as ammonium nitrate in removing cesium from PhTiA. However, Beaudet and co-workers ⁽²⁵⁾ have indicated that, although the two reagents elute cesium with comparable efficiency, ammonium chloride effectively elutes iron from the exchanger as well. In their work, this was not noted when ammonium nitrate was the eluant.

Ammonium hydroxide dissolved both exchangers and ammonium carbonate reacted with the acidic exchangers to liberate carbon dioxide. Elutions utilizing ammonium nitrate-nitric acid solutions produced discouraging yields.

The effect of elution temperature on cesium recovery from both exchangers was what would be expected from kinetic considerations. An increased cesium yield was achieved by elevat-

ing the elution temperature. Six column volumes of $5M$ NH_4NO_3 removed 83% cesium at $25^\circ C$ and 90 to 95% of the cesium in the temperature range of 35 to $55^\circ C$ from PhSn. From PhTiA, six column volumes of $5M$ NH_4NO_3 removed 80% cesium at $35^\circ C$, 95% cesium at $45^\circ C$ and greater than 98% cesium at $55^\circ C$.

HOT CELL EXPERIMENT

A hot cell investigation of cesium loading on PhTiA was made in B-cell of the 325-A High Level Radiochemistry Facility using actual Purex Acid Supernatant Waste (PAW) and 50 to 100 mesh H-form exchanger. A glass column was filled to a 10 ml bed volume with an exchanger slurry. The dimensions of the column were comparable to the columns used in the "cold" laboratory studies (i.e., 1.0 cm ID). Since there was no provision for controlled temperature runs, both column loading and column elution were conducted at cell ambient temperatures (circa $26^\circ C$). The influent used was filtered undiluted "green" PAW and was introduced into the column under slight pressure. There was some initial difficulty in establishing and maintaining a steady flow rate but after passage of approximately 15 column volumes of influent, a somewhat steady flow rate of 1 CV/hr was achieved. On two occasions the flow was stopped overnight during the loading cycle. However, the column was run continuously after 20 column volumes.

The cesium breakthrough curve is shown in Figure 7. Fifty percent cesium breakthrough was obtained at 56 column volumes. This value was about 20 column volumes lower than

FIGURE 7. Cesium Breakthrough Using Actual Purex Acid Supernatant Waste (PAW)

the value expected from laboratory studies using synthetic PAW.

The loaded column was washed with tap water. Plugging of the column occurred, presumably, due to hydrolysis and precipitation of the cations present. A 0.5M HNO_3 wash solution was substituted after the passage of 0.5 column volumes with the subsequent resumption of flow rate. Three and a half column volumes of total wash were used although later eluate analyses indicated that a higher degree of sodium and iron decontamination could have been achieved by a longer washing cycle.

Cesium elution was achieved by passing 150 ml of 5.5M NH_4NO_3 through the column. The total cesium eluted was analytically determined, and no attempt was made to construct an elution curve. The composition of the resultant cesium eluate is presented in Table VIII.

The cesium effluent concentration indicated a less than 1% cesium loss in loading the column to essentially 100% breakthrough. Comparison of the eluate and influent data implied that greater than 80% of the cesium was recovered at ambient temperatures.

TABLE VIII. Concentration of Selected Cations in Actual Purex Acid Waste (PAW) Effluent and Eluate

	Total Effluent	Eluate
Cs^{137}	0.2%	82%
Ce^{144}	1.1×10^4 mc/L	11 mc/L
Ru^{106}	3.8×10^3 mc/L	10 mc/L
Zr-Nb^{95}	not detectable	30 mc/L
Na	not determined	0.36 g/L
Fe	<10 g/L	<0.2 g/L
Ti	<5 g/L	<0.1 g/L

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